Fracture Process Zone: Microstructure and Nanomechanics in Quasi-Brittle Materials

by

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Abstract

Cracks begin (and end) at a crack tip; the “Fracture Process Zone” (FPZ) is a region of damage around the crack tip. The context of this research is the FPZ in quasi-brittle materials, which is characterized by cracking at various scales. This study focuses on crack propagation and FPZ development at a fundamental material scale: the scale of the grain. With regard to the FPZ, the study seeks to understand how the FPZ develops and manifests in quasi-brittle material, what the physical and mechanical structure of the FPZ is, and how pre-existing material microstructure influences the developed FPZ.

The attainment of several research objectives marks the course of the investigation: the development of a multi-disciplinary technique to assess both intact and FPZ regions of quasi-brittle material, the assessment of the fundamental properties (microstructure, small-scale mechanical properties) of intact and FPZ quasi-brittle material, and a conceptual model of FPZ development in quasi-brittle material. In pursuit of these objectives, the study uses nanoindentation to probe the nanomechanical properties of the FPZ for two marbles of varying grain size, and microscopy to probe the structure of the FPZ at the grain scale. The marbles are from Carrara, Italy (typical grain size 300 m), and Danby, Vermont (typical grain size 520 m). Grids of nanoindentations and microscopy were placed within the FPZ regions of Danby and Carrara marble specimens. Both marbles exhibited lower nanomechanical properties near the crack tip and/or near the area of future wing-crack formation, i.e. the FPZ. However, the Danby marble exhibited this trend over a larger distance, and thus nanomechanically supports the increase of the FPZ with grain size. The microscopy investigations suggested increased microcracking near FPZ regions, and increased microcrack density with decreased grain size. Ultimately the study provides four contributions to the study of fracture of quasi-brittle materials: an algorithm for the automatic assessment of microcracking from ESEM micrographs, new nanomechanical information on the two marble types, validation of the use of nanomechanics as a tool for identifying damage in quasi-brittle materials, and a quantitative assessment of the role of grain size in the damage of quasi-brittle materials.
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Contents

1 Introduction ........................................... 13
  1.1 Practical Application ........................................... 14
  1.2 Research Question ........................................... 15
  1.3 Research Objectives ........................................... 16
  1.4 Outline of Thesis ........................................... 16

2 Background ............................................ 19
  2.1 Fracture Mechanics ........................................... 19
    2.1.1 Failure of Quasi-Brittle Materials ........................................... 20
    2.1.2 Failure Criteria ........................................... 21
    2.1.3 Stress Distribution around a Crack ........................................... 24
    2.1.4 Fracture Energy (Griffith Energy), $G_f$ ........................................... 27
    2.1.5 Fracture Process Zone (FPZ) ........................................... 30
    2.1.6 Fracture Toughness $K_c$ ........................................... 47
  2.2 Nanomechanics ........................................... 51
    2.2.1 Nanoindentation Procedure ........................................... 51
    2.2.2 Self-Similarity of Indentation Test ........................................... 53
    2.2.3 Indentation Modulus ........................................... 60
    2.2.4 Indentation Hardness ........................................... 65
4.2.1 Algorithm for Microcrack Density Assessment ........................................ 151
4.2.2 Application of Algorithm to FPZ Regions ........................................... 155
4.2.3 Discussion of Imaging Conditions ....................................................... 158
4.2.4 Summary of Trends in BPP ............................................................... 159

5 Small-scale Mechanical Results ................................................................. 161
5.1 Small-Scale Mechanical Properties of Intact Marble ............................... 161
5.1.1 Intact Material and Anisotropy ......................................................... 162
5.1.2 Near Grain Boundaries ........................................................................ 165
5.2 Small-Scale Mechanical Properties of Fracture Process Zone (FPZ) Marble .... 171
5.2.1 Fracture Toughness ............................................................................ 171
5.2.2 Nanoindentation of Carrara Marble .................................................... 173
5.2.3 Nanoindentation of Danby Marble ....................................................... 177
5.2.4 Comparison of Nanoindentation on Carrara and Danby Marbles ............ 180
5.3 Chapter Summary .................................................................................... 181

6 Conceptual Model of the Fracture Process Zone in Quasi-Brittle Materials with Respect to Grain Size ................................................................. 183
6.1 Fracture Toughness from Macro-Scale Strength ........................................ 184
6.1.1 Uniaxial Loading ................................................................................. 184
6.1.2 Lack of Yielding in Uniaxial Loading .................................................. 186
6.2 Density of Microcracking Close to FPZ .................................................... 195
6.2.1 Carrara Marble ................................................................................... 195
6.2.2 Danby Marble .................................................................................... 198
6.2.3 Comparison ......................................................................................... 201
6.3 Nanomechanical Properties Close to FPZ ................................................. 202
6.3.1 Carrara Marble .............................................. 202
6.3.2 Danby Marble ................................................. 209
6.3.3 Comparison ...................................................... 213
6.4 Size of Quasi-Brittle Material FPZ ............................. 213
6.4.1 Size of Nanomechanically-Measured FPZ, \( r_{p,\text{Nanomech}} \) .......................... 213
6.4.2 Microstructure of Nanomechanically-Measured FPZ ......................... 222
6.4.3 Interesting and Important Ratios ................................ 224
6.5 Summary of Quasi-Brittle FPZ Characterization ......................... 230

7 Summary and Perspectives ................................. 233
7.1 Contributions ...................................................... 233
7.1.1 Nanomechanical Properties of Marbles ......................... 234
7.1.2 Experimental Technique ...................................... 234
7.1.3 Role of Microstructure in Fracture of Quasi-Brittle Materials ....... 236
7.2 Limitations .......................................................... 238
7.3 Recommendations for Future Research ............................ 239

A Danby Marble Nanoindentation Parameters .................. 241
A.1 Summary ............................................................. 241
A.2 Specimen Size ...................................................... 242
A.3 Indentation Depth, \( h \) .............................................. 244
A.4 Spacing Between Indentations ................................... 245
A.5 Maximum Load, \( P_{\text{max}} \) ....................................... 245
A.6 Loading Period and Unloading Period ............................ 247
A.7 Hold Period .......................................................... 248

B Edge Detection: Fundamentals, Algorithms, and Microcrack Identification 251
D Boxplots 303

E Statistical Significance 305

F Complete Tensile Test Analyses 307

G Fracture Toughness from Strength: Consideration of Grain Size 337
   G.1 Flat Crack Surface ......................................................... 337
   G.2 Wavy Crack Surface ......................................................... 338
       G.2.1 Spherical Waviness .................................................. 339
       G.2.2 Sinusoidal Waviness .................................................. 341
Chapter 1

Introduction

Two of our most prized senses are sight and touch. Hearing, smell, and taste may come and go, and are used intermittently, but sight and touch are with us from our first moments on earth. The feel of human skin and of a beating heart are key components in the critical first few days of a newborn’s life. The picture of your child or spouse in your wallet or on your desk is proof of the power of sight to comfort us and bring us joy. Sight and touch are continuous and vital components of our interaction with the world around us. They give meaning to our environment, and help us to understand the way our world fits together.

Similarly, two of the most prized tools in the engineer-scientist’s toolbox are sight and touch. Whether using a microscope or a surveyor’s sight, whether doing mechanical testing in a uniaxial machine or sensing vibrations in a structure, engineers and scientists are continually “looking at” and “feeling” structures in order to better understand these structures, and in order to assess the fitness of these structures for service.

This investigation is a scientific and engineering exercise in “looking” and “feeling”. A variety of complex experimental techniques will be used (and described in detail in this chapter and subsequent chapters), but at their cores these techniques simply allow us to look at and feel an important feature in everyone’s life – the crack. In so doing, this investigation simply seeks to better understand a small but prevalent player in our world.
1.1 Practical Application

Cracks can be found at nearly every scale of the known world. At the small end of the scale spectrum, microcracks are generated in our bones every day as we cyclically load our bones by running, jumping, or doing similar activities\(^1\) [Zioupos 2001]. At the macroscale, weathering and mechanical loading can generate cracks in stone monuments [Siegesmund et al. 2010], and even the floor panels of MIT (Figure 1-1). The landslides which threaten hillside homes the word over each year often begin with a crack at their head. At the largest scale, the boundaries of tectonic plates are essentially giant cracks, and these cracks can have lengths upwards of several thousand miles.

An interesting aspect of the multi-scale nature of cracks is that they can inhabit multiple scales \textit{at once}. Moreover, the tiniest cracks of all – those at the micro and nanoscales – are nearly always present. Faults are often surrounded by families of microcracks. Microcracks run rampant through thermally cycled and weathered building veneers. Every crack begins somewhere with a crack tip, and thus begins somewhere at a very small – even micro or nano – scale. This study focuses on the

\(^1\)Barring the adverse effects of ageing or pathophysiological conditions, our bones actually heal themselves by remodelling. Ageing affects the elastic properties of cortical bone tissue, and thus compromises this continual healing process [Zioupos 2001].
1.2 Research Question

Given the importance of the crack to many different industries, the crack is the research focus of this investigation. Specifically, the study focuses on a crucial part of all cracks: their beginning. Cracks begin (and end) at the crack tip. Around the crack tip, there is a region of damage often termed “Fracture Process Zone” or FPZ (for more detail and aliases of this zone, see Section 2.1.5). With regard to the FPZ, the study pursues the answers to three important research questions (Figure 1-2):

1. How does the Fracture Process Zone (FPZ) develop and manifest in a quasi-brittle material?

2. What is the geometric and mechanical structure of the FPZ?

3. How does pre-existing material microstructure influence the developed FPZ?

These questions are pursued at the fundamental scale – the grain scale – of the test material.
1.3 Research Objectives

This thorough investigation of the damage zone around a crack will cross the disciplines of materials science, classical mechanics, rock mechanics, and geology. The attainment of several research objectives marks the course of the investigation:

- **Develop a multi-disciplinary technique to assess both intact and FPZ regions of quasi-brittle material.** A robust and exhaustive technique must be carefully developed in order to compare the relevant properties of different types of quasi-brittle material. This technique will probe both structure and mechanical properties at a fundamental scale of the experimental material.

- **Assess the fundamental properties (microstructure, small-scale mechanical properties) of intact and FPZ quasi-brittle material.** The developed technique must then be applied to the material in order to actually obtain and thereby assess the relevant properties. This assessment will combine visual and mechanical investigative techniques in order to thoroughly understand microproperties of the material within the process zone, in close proximity to the process zone, and far from the process zone.

- **Develop a conceptual model of FPZ development in quasi-brittle material.** In just the way that archaeological findings inform the ways and functions of ancient societies, experimental findings from the developed technique described above will help inform the behavior of the FPZ in quasi-brittle materials. The investigation will help to paint a potential explanation of the development of the FPZ, its structure, and the ways it interacts with existing material microstructure.

1.4 Outline of Thesis

**Chapter 1: Introduction** places this study into the practical and scientific context. **Chapter 2: Background** reviews important fracture mechanics, nanomechanics, and microscopy principles
which inform the chief investigative techniques of the study. Chapter 3: Experimental Approach details the investigative techniques developed and applied within this study. Chapter 4: Microstructural Results presents the study findings on the geometric structure of the FPZ – the “look” of the FPZ. Chapter 5: Small-Scale Mechanical Results presents the study findings on the mechanical response (and trends in mechanical response) of the FPZ. Chapter 6: Conceptual Model of the Fracture Process Zone in Quasi-Brittle Materials with Respect to Grain Size brings together the experimental findings of the study, analyzes their significance and relations, and uses this analysis to describe the likely development of the FPZ, its structure, and its interactions with material. The final chapter, Chapter 7: Summary and Perspectives links this study back to the larger scientific and practical context, and charts out the next steps in this particular research area.
Chapter 2

Background

Every investigation has two elements: a subject of investigation, and a means of investigation. For this investigation, the subject (i.e., process or product which we would like to better understand) is fracture mechanics – specifically, how it plays out at small scales in rock. The means (i.e., the tools used to obtain that understanding) are nanomechanical testing and microscopy.

This chapter presents essential background information on the subject and means of this investigation. Section 2.1 develops the current understanding of quasi-brittle material fracture. Sections 2.2 and 2.3 discuss the key ideas necessary to apply the tools of nanoindentation and microscopy to a material. A full understanding of each of these elements provides a solid foundation for conducting this investigation, and for interpreting its findings in later chapters of this thesis.

2.1 Fracture Mechanics

This section reviews essential and classic macro-scale fracture theories. It begins with basic material behavior under stress, and closes with a review of how cracks influence that behavior\(^1\).

\(^1\)The fracture mechanics discussion of Section 2.1 is motivated by discussion in Anderson [2005] and Ulm [Spring 2009].
2.1.1 Failure of Quasi-Brittle Materials

The load-displacement (or stress-strain) curve of a material under load provides insight into the material type: elastic, or elasto-plastic. (Viscosity introduces another set of material types – viscoelastic, visco-plastic, or visco-elasto-plastic – but such materials are not the focus of this thesis.) Sample curves of both type are shown in Figure 2-1. Linear elastic materials exhibit a linear relationship between stress and strain for the initial portion of the curve, whereas nonlinear-elastic or elasto-plastic materials eventually deviate from this perfectly linear relationship. In the case of elasto-plastic materials, this deviation stems from some damage events in the material, such as the closing or opening of small imperfections and cracks in the material [Jaeger et al. 2007].

![Figure 2-1: Sample load-displacement curve types. From Jaeger et al. [2007].](image)

The material under investigation in this thesis – rock – is an elasto-plastic material. A typical rock load-displacement curve follows an initially linear portion, followed by a non-linear portion, and an eventual sudden failure. This non-linear portion is the reason why rock is often described as a “quasi-brittle” material. This non-linear portion serves as a warning that the rock is nearing its “brittle” (sudden) failure. This warning period prevents the rock from behaving in a completely brittle fashion, and causes the rock to instead behave in a quasi-brittle fashion [Ulm Spring 2009]. The measurement, observation, and effect of these damage events in quasi-brittle materials is the objective of this thesis. (Sections 2.2 and 2.3 discuss the mechanical measurement and visual observation, respectively; Chapter 4 will discuss the effect.)
2.1.2 Failure Criteria

Materials fail when material stresses exceed material capacity. Failure criteria are different rules which predict this failure by predicting at which points in a material this capacity will get exceeded; the criteria differ by their material property inputs and precise formulation. Although no material is a flawless solid, and flaws and imperfections will affect the way in which an engineer or mechanician applies failure criteria to an engineering problem, a basic understanding of failure criteria is an important first step in discussing the mechanics of fractured materials.

Coulomb

Coulomb posited that for rocks and soils, failure would occur along a plane due to shear. The stress along this failure plane is great enough to overcome both the friction coefficient of the material, $\mu$, and the material cohesion, $S_0$. The Coulomb failure criterion thus takes the form:

$$|\tau| = S_0 + \mu \sigma,$$

where $\tau$ is the value of the shear stress along the failure plane. The criterion conversely suggests that failure will not occur along a plane whose shear stress $\tau$ has a magnitude less than that of the right side of Equation 2.1 [Jaeger et al. 2007].

Mohr

Mohr’s circle is a useful engineering tool for determining on which material plane (i.e., orientation) shear stress $\tau$ is exceeded; the tool lends itself to application of the Coulomb failure criterion. The full Mohr’s circle in Figure 2-2 is a visual depiction of the stress state in a material. Mohr’s circle visually relates the orientations and magnitudes of principal stresses $\sigma_I, \sigma_{II}$, and $\sigma_{III}$ to the applied stresses and resulting shear stresses $\tau$ (Figure 2-2). The stresses at all orientations are depicted in Mohr’s circle by plotting the stresses on two axes: normal stress ($\sigma$, horizontal axis), and shear stress ($\tau$, vertical axis). The three principal stresses describe the three surface orientations in a

---

2This failure criteria discussion is based on presentation in Jaeger et al. [2007] and Goodman [1980].
Figure 2-2: Mohr’s circle and Mohr Failure Envelope, adapted from [Jaeger et al. 2007, Nadai 1931].
material where the surface experiences only normal, and no shear stress (i.e., \( \tau = 0 \) on these surfaces). The straight line is a representation of the Coulomb failure criterion (Equation 2.1), and when plotted on the Mohr circle (and paired with the symmetric failure criterion for the material plane at an opposite rotation), can be called the Mohr Failure Envelope. Note the linear relationship in Equation 2.1 between shear stress \( \tau \) and normal stress \( \sigma \). Given the relationship between material friction coefficient \( \mu \) and friction angle \( \phi \):

\[
\mu = \tan \phi,
\]

(2.2)

it can be seen that the straight line represents the point at which the material will just meet the Coulomb failure criterion. Thus, as expressed for Mohr’s circle, the Coulomb failure criterion (Equation 2.1) takes the form:

\[
\tau_m = S_o \cos \phi + s_m \sin \phi,
\]

(2.3)

where \( s_m = \frac{1}{2}(\sigma_I + \sigma_{III}) \), and \( \tau_m = \frac{1}{2}(\sigma_I - \sigma_{III}) \).

Mohr also noticed two problems with the fundamental Coulomb failure criterion. Firstly, the criterion tended to predict a much higher tensile strength than the strength found in the lab. Secondly and also in lab, the value of \( \sigma_I \) at failure did not tend to linearly increase with \( \sigma_{III} \). Thus, rather than consider a linear relation between shear stress \( \tau \) and normal stress \( \sigma \), Mohr considered a non-linear relation:

\[
|\tau| = f(\sigma)
\]

(2.4)

This non-linear relation is depicted in Figure 2-3, for various confinements of a material (i.e., various Mohrs circles; only the large Mohr’s circle between \( \sigma_I \) and \( \sigma_{III} \) is shown). The precise form of \( f \) is found experimentally by loading samples at different confining stresses to failure, and plotting their Mohr’s circles to construct a failure envelope.
2.1.3 Stress Distribution around a Crack

Despite the comprehensive failure criteria described above, very often materials fail at stresses below those predicted by fundamental theories. This reduced capacity is attributed to defects and discontinuities in the material. This section discusses how these material discontinuities—cracks—affect the stress distribution of an otherwise continuous material. The crack universally considered by the four main scholars discussed in this section—Inglis, Westergaard, Irwin, and Dugdale—is shown in Figure 2-4. This figure will be referred to throughout this chapter.

Inglis Stress Distribution

Inglis [1913] first documented and quantified the tendency of stresses to concentrate at material flaws. Inglis began with stress distributions from Love [1906] for two intersecting and deformed bodies, and applied these stress distributions to an elliptical crack (Figure 2-4). He found that the material immediately surrounding the crack experienced a stress greater than the far-field applied stress; this stress was equivalent to the far-field applied stress $R$ (where $R = p \times$ thickness of
Figure 2-4: A composite crack compiled from the fundamental crack shapes considered by Inglis, Westergaard, Irwin, and Dugdale. All four researchers considered an internal slit. Inglis, Westergaard, and Irwin considered the slip to be elliptical at the ends (right side of figure, in gray region), whereas Dugdale considered the slit to be rectangular (left side of figure, in red). Note that $p$ is a line loading (force per length).
specimen) amplified by a factor, such that the stress at the crack tips along the major ellipse axis \((x = a;\) the minor ellipse dimension has a height \(b)\) is:

\[
\sigma = R \left[ 1 + \frac{2a}{b} \right],
\]

(2.5)

and the stress at the top and bottom along the minor axis is:

\[
\sigma = -R.
\]

(2.6)

Note that Inglis found the stress along the minor axis of the elliptical crack to be compressive, and that these stresses decreased in magnitude with distance from the crack. This stress increase at the crack tips would later be termed stress concentration, \(k\). Thus, Inglis pioneered the notion that flaws concentrate stresses in a material.

**Westergaard Stress Distribution**

Westergaard [1939] later refined Inglis’ crack stress distributions by extending the classic Hertz contact problem to various bodies. Westergaard formulated stress distributions between two circular cylinders, non-circular cylinders, wavy surfaces, ridged surfaces, a crack opened by a wedge – and eventually, the classic internal crack initially solved by Inglis (Figure 2-4). Westergaard found that the material at the ends of the crack experienced a tension equal to:

\[
\sigma_y = \frac{p}{\sqrt{1 - \frac{a^2}{z^2}}},
\]

(2.7)

for a crack of length \(2a\), where \(z = x + iy\) (i.e., \(z\) is a complex variable). Thus, the stress intensifying nature of flaws initially pioneered by Inglis was captured in the resulting stress distribution from Westergaard. This stress distribution reaches a maximum at the crack tip, and decreases with distance away from the crack tip.
2.1.4 Fracture Energy (Griffith Energy), $G_f$

Griffith refined the form of the Coulomb criterion (Equation 2.4) in the tensile region of stress states, under the assumption that cracks propagated from existing and randomly oriented small-scale cracks in rocks. (This assumption was based on the Griffith stress criterion, which posits that a structure will fail when material stresses $\sigma$ surpass material strength $\sigma_c$, or $\sigma > \sigma_c$; this criterion also applies in shear $\tau$ and $\tau_c$ [Leguillon 2002].) The Griffith criterion thus suggests that the failure envelope in the tensile region has the form of a parabola.

Griffith [1920; 1924] revolutionized fracture mechanics by considering the fracture of material from an energy perspective. With the help of previous work by Inglis [Inglis 1913], Griffith ultimately formed the concept of energy releasing as new crack surfaces opened. His overarching approach discusses that the potential energy of the cracked body is minimized immediately after rupture. Here, we formulate the classic Griffith Energy, $G_f$, also known as Fracture Energy$^3$.

We begin with the expression of the potential energy, $\varepsilon_{\text{pot}}$ of a system with an existing crack. For a linear elastic material system, the potential energy $\varepsilon_{\text{pot}}$ is the difference between the global free energy of the system, $W$, and the strain energy due to prescribed body and surface forces, $\Phi$:

$$\varepsilon_{\text{pot}} = W - \Phi. \quad (2.8)$$

With the assumption of quasi-static and isothermal evolutions (i.e., assuming $W = 0$), and with the use of Clapeyron's formulas, the potential energy $\varepsilon_{\text{pot}}$ can be expressed in terms of stresses $T$, prescribed stresses $T^{\text{d}}$, displacements $\xi$, and prescribed displacements $\xi^{\text{d}}$:

$$\varepsilon_{\text{pot}} = \frac{1}{2} \int_{\partial_0 \Omega_{\xi d}} T \cdot \xi^{\text{d}} \, da - \frac{1}{2} \int_{\partial_0 \Omega_{T d}} T^{\text{d}} \cdot \xi \, da, \quad (2.9)$$

where $\partial_0$ represents the boundary surface of a body of interest $\Omega$, and $a$ a differential area on that surface.

We can eliminate the factor of $\frac{1}{2}$ by considering a notch of length $l$ rather than a full crack

---

$^3$This presentation of fracture energy is motivated by discussion in Roylance [2001] and Ulm [Spring 2009].
(Figure 2-5; i.e., a flat, homogeneous isotropic plate with uniform thickness, with a notch of length \( l \) at the edge of the plate). The material has Young’s Modulus \( E \). There is an applied far-field tensile stress of \( \sigma \), but no prescribed displacements. For this notch \( l \), the potential energy \( \varepsilon_{\text{pot}} \) may be expressed as:

\[
\varepsilon_{\text{pot}} = \int_{\partial_0 \Omega_d} T^d \cdot \xi \, d\alpha
\]

\[
= \int_{\text{volume}} E \varepsilon \, d\varepsilon
\]

\[
= (\text{volume}) \frac{E \varepsilon^2}{2}
\]

\[
= \frac{\pi l^2 \sigma^2}{2E},
\]

for stresses \( T^d = \sigma = E \varepsilon \) (assumed in tension), for no prescribed displacement \( (\xi^d = 0) \), and for an assumed volume \( \Omega \) with unit width and area \( \pi l^2 \) (see the unloaded triangular region in Figure 2-5).

Differentiating the potential energy \( \varepsilon_{\text{pot}} \) with respect to surface \( \partial \alpha \) yields the change in potential
energy – the energy release $G$ of a material system. $G$ for the notch is:

$$G = \frac{d\epsilon_{pot}}{dl} = \pi \sigma^2 l \frac{E}{E}. \quad (2.11)$$

This investigation is interested in crack initiation; this is the point at which the crack just begins to grow. At this point, the energy release $G$ is equal to the fracture energy $G_F = 2\gamma$, where $\gamma$ is the material surface energy, and the factor 2 accounts for the two opened faces of the crack. Thus, if fracture energy $G_F$ is subtracted from Equation 2.11, 0 remains:

$$G - 2\gamma = 0$$

$$\frac{\pi \sigma^2 l}{E} - 2\gamma = 0 \quad (2.12)$$

Finally, Equation 2.12 is solved for the critical stress $\sigma = \sigma_f$ (in tension) at which fracture will occur:

$$\sigma_f = \sqrt{\frac{2\gamma E}{\pi l}}$$

$$= \sqrt{\frac{E G_F}{\pi l}}, \quad (2.13)$$

for a crack of given length $l$ in a material with Young’s Modulus $E$ and fracture energy $G_F$.

Griffith’s stress criterion and energy approach enhanced study of fracture because of its simplicity. However, the stress criterion and energy approach lacked a vital element, later independently added by Orowan [1949] and Irwin [1948]: a term for plasticity. These researchers found that setting the fracture energy $G_f$ equal only to the material surface energy $2\gamma$ (where the factor 2 accounts for the two faces of the crack) underestimated the value of the energy release $G$ at fracture as formulated from strain energy $\phi$. The plastic work per unit area $p$, Orowan argued, is much greater than surface energy $2\gamma$ (so much so, that the surface energy $2\gamma$ could actually be completely neglected.) This work $p$ goes to plastically deforming the material, such as with small-scale micro-cracks and defects. Thus, the modified Griffith expression for the applied stress at which a crack will begin to propagate is:

$$\sigma_f = \sqrt{\frac{pE}{a}}, \quad (2.14)$$
in a material of Young’s Modulus $E$ and notch length $a$.

**J-Integral**

Although the approach is not the primary focus of this study, no fracture mechanics review would be complete without discussion of the J-Integral. Rice [1968] sought a way to determine the strain field around cracks and notches, for both linear and non-linear materials. The J-Integral is a path-independent way to obtain an averaged value of the localized strain field in the area surrounded by the path. With the selection of either a closed or open path $\Gamma$ surrounding a notch, the J-Integral is formulated as:

$$J = \int_{\Gamma} \left( \phi dy - T \cdot \frac{du}{dx} ds \right) \quad (2.15)$$

where $\Gamma$ is the path around the notch, $\phi$ is the strain energy density ($\phi(x, y) = \phi(\varepsilon) = \int_0^\varepsilon \sigma_{ij} d\varepsilon_{ij}$), $T$ is the traction vector $T_i = \sigma_{ij} n_j$ defined by an outward normal $n_j$ around the path, $u$ is the displacement vector, and $ds$ is an element of arc length along the path $\Gamma$. The J-Integral is equal to 0 for any closed curve. Two different paths surrounding the same notch will yield the same value of the J-Integral. Careful selection of paths will simplify calculation of the J-Integral (for example, choosing a path around the boundary of a material, where stresses and tractions are easily known). For a notch increasing in length (i.e., a growing crack at fracture), the J-Integral corresponds exactly to the negative of the Griffith energy release, $\mathcal{G}$:

$$-\mathcal{G} = -\frac{d\varepsilon_{pot}}{dl}$$

$$= -\frac{d}{dl} (W - \Phi)$$

$$= \int_{\Gamma} \left( \phi dy - T \cdot \frac{du}{dx} ds \right)$$

$$= J \quad (2.16)$$

2.1.5 Fracture Process Zone (FPZ)

The crack tip stress distributions from Inglis and Westergaard were an important first step in understanding the effect of discontinuities on a material, but they presented an incongruity between
model and actual behavior. These distributions predicted an infinite stress in the material immediately surrounding the crack tip. In reality, no material is capable of supporting an infinite stress. In the mid-20th century, three researchers independently caught on to this shortcoming in the existing fracture theory and laid the first foundation stones in Plastic Zone theory. Irwin [1948; 1960], Dugdale [1960], and Barenblatt [1959] postulated that the material nearest the crack tips does not actually contain infinite stresses; this material instead attains yield stress (a material property) and undergoes plastic deformation. This damage zone has many aliases: the Plastic Zone, the Process Zone, the Cohesive Zone, and (especially in this thesis) the Fracture Process Zone (FPZ). The mechanical and structural properties of the FPZ at the micro- and nanoscales in quasi-brittle material is the subject of this thesis.

This section more explicitly presents the FPZ formulations of these forefathers of fracture. Later chapters of this thesis will compare their theoretical predictions and early experiments to precise, small-scale experimental measurements.

Irwin Formulation
The elliptical crack considered by Irwin [1957; 1958; 1960] can be seen on the right side of Figure 2-4. Irwin reformulated Westergaard’s crack tip stress distribution in terms of polar coordinates:

\[ \sigma_y = \sqrt{\frac{EG}{\pi}} \frac{\cos(\theta/2)}{\sqrt{2r}} f(\theta) \]  

(2.17)

where \( r \) is the radial distance from the crack tip, \( \theta \) is the angle from an axis of the crack, and \( f(\theta) \) is some function of that angle \( \theta \). The terms in the front of Equation 2.17 form the Stress Intensity, \( K_I \):

\[ K_I = \frac{EG}{\pi} \]  

(2.18)

The stress intensity \( K_I \) is a constant, and it expresses the increase in the magnitude of stress near the tip of a crack; the term is a descendant of the stress concentration \( k \) presented by Inglis almost 50 years earlier. Irwin presented this stress intensity factor \( K_I \) as a key fracture parameter which summarized the influence of testing geometry, loading, and crack length on the crack tip stress.
distribution.

Solving Equation 2.17 for the radial distance from the crack tip \( r \) (and directly in front of the crack, where \( \theta = 0 \)) at which material stresses \( \sigma_p \) are equal to material yield stress \( \sigma_{\text{yield}} \) formulates the size of the FPZ, \( r_{p, \text{Irwin}} \):

\[
r_{p, \text{Irwin}} = \frac{1}{2\pi} \frac{K_I^2}{\sigma_{\text{yield}}^2}
\]

(2.19)

This formulation of process zone size does not account for the redistribution of stress that occurs as a result of material within \( r_p \) reaching material yield stresses values; thus, \( r_p \) potentially underpredicts the actual size of the process zone. By assuming specimen yielding begins when the stress \( \sigma \) reaches 88 to 115% of material yield stress, Irwin found that actual process zone size could range from 80 to 130% of the \( r_p \) formulated in Equation 2.19 [Irwin 1960]. Thus, \( r_p \) provides a reasonable estimate of process zone size.

**Dugdale/Barenblatt Formulation**

Dugdale [1960] approached the determination of plastic zone size with a similar, but slightly different assumption than Irwin. Dugdale began with the same crack of length \( 2l \) in an elastic-plastic material loaded in tension, but assumed a rectangular slit instead of an elliptical crack. He then considered that material over a distance \( s \) beyond the slit boundaries would have yielded. Dugdale then replaced the initial slit with a hypothetical slit (left side of Figure 2-4), whose length was that of the initial slit, \( 2l \), plus the length of yielded material, \( s \) at each end of the slit. The hypothetical slit thus had a length \( 2a \) such that:

\[
a = s + l
\]

(2.20)

Dugdale used a crack tip stress distribution developed by Muskhelishvili (but found that Westergaard's stress distributions also led to the same result). A scaling factor \( \alpha \) is introduced:

\[
\alpha = \cosh^{-1} \left( \frac{x}{\sqrt{a}} \right)
\]

(2.21)

where \( x \) is a variable measuring distance from the center of the slit (Figure 2-4), and with a limiting
value $\beta$:

$$\beta = \cos^{-1}\left(\frac{1}{a}\right) \quad (2.22)$$

Given these scaling factors, under a remote load of $T$, the remote stress $\sigma_y$ has a value:

$$\sigma_y = \frac{T}{\alpha} \quad (2.23)$$

This stress becomes infinite at the edges of the hypothetical slit ($x = a$). In order to account for this infinite stress, Dugdale postulates that the slit is internally loaded with a stress $Y$ equal to material yield stress $\sigma_{yield}$ (see inside of the slit shown in Figure 2-4); this internal loading yields a material stress field of the form:

$$\sigma_y = \frac{-2\sigma_{yield}\beta}{\pi \alpha} \quad (2.24)$$

Finally, the stress field due to internal loading $Y$ (Equation 2.24) and the stress field due to remote loading $T$ (Equation 2.23) are equated. The factor $\alpha$ drops out, the factor $\beta$ is introduced, taylor series expansion of the trigonometric terms is introduced, and simplification leads to an expression for the size $s$ of the region of yielded material, which may be considered as a size of FPZ $r_{p, Dugdale}$:

$$r_{p, Dugdale} = \frac{\pi^2 T^2 l}{8\sigma_{yield}} \quad (2.25)$$

Barenblatt [1959] proposed a similar problem formulation one year before Dugdale, in which an ideal internal crack contained a "terminal region" at the ends (i.e., in the material outside) the physical crack. In this terminal region, extremely large forces attracted the would-be faces of the crack to each other. Barenblatt then used crack opening displacements developed by Sneddon to develop a similar expression for the size of the crack (i.e., radius of the crack tip) with respect to applied load.

**J-Integral and the Plastic Zone**

Rice’s application of the J-Integral to the plastic zone [Rice 1968] revealed the equivalence of Griffith’s energy approach to the fracture and cohesive zone theory presented by Barenblatt and
Dugdale. Rice first returned to the crack studied by both Dugdale and Barenblatt (Figure 2-6). Note that the crack originally studied by Dugdale and Barenblatt (Figure 2-4) was symmetric about the y-axis. Thus, the crack is shown as a notch in Figure 2-6. A J-Integral for the path around the process zone only (the dashed curve in Figure 2-6) takes the form (from Equation 2.15):

\[
J = - \int_{\Gamma} T \cdot \frac{du}{dx} \, ds \\
= - \int_{\text{Process Zone}} \sigma(\delta) \frac{d\delta}{dx} \, dx
\]  

(2.26)

To understand the equivalence of the first and second integrals in Equation 2.26, note that in the
integral taken with respect to the process zone (the second integral in Equation 2.26), \( \delta \) refers to displacement as the change in spacing between the top and bottom of the process zone (or hypothetical slit). This spacing depends only on \( x \). Simplification of the second integral yields:

\[
- \int_{\text{Process Zone}} \frac{d}{dx} \left( \int_0^{\delta} \sigma(\delta) d\delta \right) dx = \int_0^{\delta_{\text{tip}}} \sigma(\delta) d\delta.
\]

(2.27)

Equation 2.27 expresses the area under a force-separation curve (i.e., force \( \sigma(x) \) and separation \( x \) between two particles), which is by definition equal to twice the surface energy \( (2\gamma) \) of a notch, and therefore its fracture energy \( G_f \) (Equation 2.12). Thus, the equivalence between Equation 2.27 and \( 2\gamma \) expresses the equivalence of the cohesive zone and Griffith energy approaches to fracture.

**FPZ Measurement of Non-Brittle Materials**

There has been extensive experimental investigation of the FPZ in non-brittle materials such as steel and copper. The techniques which have been used to measure the size of the FPZ in these materials may be categorized in major groups [Uguz and Martin 1996]:

- Visual and image-based: optical microscopy, photoelectron microscopy, transmission electron microscopy, interferometry
- Mechanical: microhardness, foil strain gauge
- Chemical: etching

The technique most similar to that employed in this work is the application of microhardness measurements to the crack tip in metals. This technique involves propagating an initial crack in a material by loading the material, and then using a nano- or microindenter to perform a number of small-scale load tests around the tip of a crack. These load tests reveal the trends in mechanical properties around the crack tip (i.e., in the FPZ). A number of studies have found that fatigue cracks in steels [Bathias and Pelloux 1973, Loye et al. 1983, Murase et al. 2007, Nyström et al. 1995], and copper or copper alloys [Purcell and Weertman 1974, Saxena and Antolovich 1975] show a change in hardness at the boundary of the process zone (typically termed “plastic zone” in
metals literature.) These studies are listed in Table 2.1. Loye et al. [1983] conducted microhardness measurements at a variety of orientations (0°, 45°, and 90°) from the crack tip in 316 stainless steel, and found microhardness to be a useful method for determining whether materials strain harden or strain soften (i.e., hardness increases or decreases) within the process zone; Loye then used the hardness measurements to derive strain contours. Nyström et al. [1995] observed fatigue cracking in austenitic and ferritic stainless steel with nanoindentation along a distance perpendicular to crack growth, and defined cyclic plastic zone size (the size of the plastic zone after 2 or more loading-unloading cycles) by the distance at which hardness increased or decreased by 3%. Bathias and Pelloux [1973] also observed the process zone in austenitic and ferritic steel with nanoindentation, and identified distinct cyclic and monotonic hardness plateaus. Murase et al. [2007] observed fatigue cracking under irradiation in SUS304 stainless steel with nanoindentation testing near the crack tip, and found that the size of the process zone increased with fatigue, and exhibited a higher hardness with irradiation. Finally, although Purcell and Weertman [1974] did not find different hardness values for monotonic and cyclic process zones in copper, Saxena and Antolovich [1975] identified an increase in microhardness in copper within the process zone. Given the success of micro- and nanoindentation to measure process zone size in ductile materials, the natural next step is to apply the technique to the process zones of more brittle materials; this application is one objective of this study.

**FPZ Measurement of Quasi-Brittle Materials**

Table 2.1: A compilation of studies of the FPZ in non-brittle materials. The studies utilized both micro- or nanoindentation. Note that although the studies focused on measuring the cyclic plastic zone, the cyclic plastic zone retains FPZ information from the first cycle (i.e., monotonic) plastic zone.

<table>
<thead>
<tr>
<th>Authors and Date</th>
<th>Material</th>
<th>Indentation Test Design</th>
<th>Trends</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bathias and Pelloux [1973]</td>
<td>Steel (Maraging and Austenitic)</td>
<td>Microindentation (25g to 50g), normal to fracture plane</td>
<td>Decrease in hardness close to crack surface for maraging steel; increase in hardness close to crack surface for austenitic steel. Cyclic FPZ is smaller (and contained within) monotonic FPZ.</td>
</tr>
<tr>
<td>Saxena and Antolovich [1975]</td>
<td>Cu-Al Alloys</td>
<td>Microindentation at 0° from crack tip</td>
<td>Increase in hardness near crack tip</td>
</tr>
<tr>
<td>Loye et al. [1983]</td>
<td>Steel (316 Stainless)</td>
<td>Microindentation at 0°, 45°, and 90° from crack tip</td>
<td>Increase in hardness near crack tip. The first cycle (i.e., monotonic FPZ) imposes the most plastic strain (plastic strain is empirically related to change in hardness; 2% plastic strain after 1 cycle, 3% after 50 cycles).</td>
</tr>
<tr>
<td>Nyström et al. [1995]</td>
<td>Steel (Austenitic, Ferritic, and Stainless)</td>
<td>Nanoindentation at 0° from crack tip, in three regions with different stress intensity values</td>
<td>Increase in hardness near crack tip.</td>
</tr>
<tr>
<td>Murase et al. [2007]</td>
<td>Steel (SUS304 Stainless)</td>
<td>Nanoindentation, in grid (5x5) near the notch tip (no crack was generated).</td>
<td>Increase in hardness near notch tip, and increase in hardness with fatigue time.</td>
</tr>
<tr>
<td>All Studies</td>
<td>Metal</td>
<td>Micro or Nanoindentation</td>
<td>Hardness changes between cyclic and monotonic plastic zones, and between monotonic plastic zone and intact material. Monotonic plastic zone is 3-4 times larger than cyclic plastic zone. Hardness increases parabolically in cyclic zone, but linearly/constant in monotonic zone.</td>
</tr>
</tbody>
</table>
non-linear deformation in the FPZ by finding the difference between crack width and the total inelastic deformation of the specimen, measured from the stress-strain curve). In interferometry studies, such as that by Yu and Kobayashi [1994] who observed a mixed-mode fracture in a ceramic composite (SiC\textsubscript{w}/Al\textsubscript{2}O\textsubscript{3}) with Moiré interferometry, a change in the fringe patterns identifies the FPZ just before fracture. The acoustic emission studies often coupled with a second technique, such as microscopy, and found that acoustic emissions identified a larger FPZ than the FPZ identified by microscopy alone [Otsuka and Date 2000, Zang et al. 2000]. Despite the varying techniques, many studies agreed that microcrack density increased exponentially within the FPZ with closeness to the main crack or fault.

In general, these existing quasi-brittle material FPZ studies focus on heterogeneous materials such as granite, concrete, and natural faults in a variety of rock materials. Although such materials are important from an engineering perspective, a study in a comparatively pure geomaterial such as marble removes material heterogeneity as a parameter affecting the FPZ. Study in a pure geomaterial can isolate and illuminate the true effects of the FPZ on material properties.

Moreover, none of the employed techniques discussed above directly measure material properties within the FPZ. Jones et al. [2007] has come close to identifying the mechanical properties of the FPZ of a brittle material. This study monitored a compact tension specimen of a soft lead zirconate titanate ceramic under constant load with high-energy synchotron X-rays, and found in-plane domain switching (a change from one spontaneously polarized state to another) around the crack tip. The domain switching in this ceramic could indicate a change in mechanical properties and thus indicates a good potential for the objective of the current study: to pursue and identify a change in mechanical properties of the material around the crack tip in a quasi-brittle material.
Table 2.2: A compilation of studies of the (monotonic and cyclic) FPZ in quasi-brittle materials.

<table>
<thead>
<tr>
<th>Authors and Date</th>
<th>Material</th>
<th>Technique</th>
<th>Trends</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wong [1982]</td>
<td>Granite (Westerly)</td>
<td>Microscopy</td>
<td>Dependence of microcracking (inter/intragranular, high/low angle) on mineral, deformation. Faulting mechanisms differ from metals: localized to 3-4 grain width zone, no single dominating mechanism.</td>
</tr>
<tr>
<td>Cedolin et al. [1983]</td>
<td>Concrete</td>
<td>Moire Interferometry</td>
<td>FPZ independent of length of notch and mix type. Wider initial crack leads to a shorter FPZ. Interferometry is a good means for determining the FPZ in concrete.</td>
</tr>
<tr>
<td>Labuz et al. [1983]</td>
<td>Granite (less than 10-mm dia.)</td>
<td>Microscopy</td>
<td>The difference between crack width and inelastic deformation (total minus elastic) suggests non-linear deformation (microracking, etc) in the FPZ region</td>
</tr>
<tr>
<td>Knab et al. [1984]</td>
<td>Mortar, Concrete</td>
<td>Microscopy</td>
<td>Fluorescent thin section is a good way to observe the FPZ; can resolve cracks with widths up to 2-3 m.</td>
</tr>
<tr>
<td>Swanson and Spetzler [1984]</td>
<td>Granite (Westerly)</td>
<td>Ultrasonic Pulses</td>
<td>Ultrasonic pulses do not attenuate according to regions predicted by FPZ (microracking) ahead of crack tip, and thus dispute the microcracking-FPZ in rock</td>
</tr>
<tr>
<td>Labuz et al. [1987a]</td>
<td>Granite (less than 10-mm dia.)</td>
<td>Microscopy, Ultrasonic Pulses, Acoustic Emission</td>
<td>The FPZ size measured during crack growth differed from that measured after fracture (on unloading).</td>
</tr>
</tbody>
</table>

Continued on next page
Table 2.2: A compilation of studies of the (monotonic and cyclic) FPZ in quasi-brittle materials.

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<th>Technique</th>
<th>Trends</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chengyong et al. [1990]</td>
<td>Granite, Marble</td>
<td>Laser Speckle Interferometry</td>
<td>The shape of the FPZ inferred from interferometry suggests agreement with Dugdale-Barenblatt and Hillerborg models. The relative size of FPZ is inversely proportional to crack-width/grain-diameter ratio.</td>
</tr>
<tr>
<td>Du et al. [1990]</td>
<td>Concrete</td>
<td>Laser Moire Interferometry</td>
<td>FPZ width tends to be same size as aggregate. Developed expression for crack closure stress as a function of tensile concrete strength, COD.</td>
</tr>
<tr>
<td>Jankowski and Sty [1990]</td>
<td>Concrete</td>
<td>Photoelastic Coating, High Speed Camera</td>
<td>FPZ grows from 70-100% of maximum load; just before maximum load, the FPZ stabilizes.</td>
</tr>
<tr>
<td>Shah [1990]</td>
<td>Concrete</td>
<td>Acoustic Emission, Laser Holography</td>
<td>Microcracking localizes before max load; AE events occur mostly behind the crack tip, which indicates crack closing stress CCS. CTOD sometimes increases without crack propagation.</td>
</tr>
<tr>
<td>Guo et al. [1993]</td>
<td>Concrete</td>
<td>Laser Interferometry</td>
<td>The FPZ is likely responsible for the difference between energy release rates (work to increment crack) and energy dissipation rates (fracture energy, computed from CCS) at large crack extensions. Most energy dissipation is due to FZ.</td>
</tr>
</tbody>
</table>
Table 2.2: A compilation of studies of the (monotonic and cyclic) FPZ in quasi-brittle materials.

<table>
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<tr>
<th>Authors and Date</th>
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<th>Technique</th>
<th>Trends</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scholz et al. [1993]</td>
<td>Natural Faults (shear cracks in natural geomaterial with friction along inner surfaces) with lengths from 10 m to 100 km</td>
<td>Microscopy (observing samples under microscope), Analyzing data from other studies</td>
<td>Dugdale-Barenblatt model fits well (crack density decreases with distance from fault; damaged material left in wake of fault). FPZ is contained in a volume, not a plane. FPZ width scales with breakdown zone length. Maximum crack density in FPZ is scale-independent.</td>
</tr>
<tr>
<td>Anders and Wiltschko [1994]</td>
<td>Natural Faults with lengths of a few km</td>
<td>Microscopy (Universal Stage Microscope)</td>
<td>Dugdale-Barenblatt model fits well (crack density decreases exponentially with distance from fault.) Microcrack density is independent of fault slip, fault type. Fracture zone is independent of fault slip. Most of the FPZ microcracking occurs during initial crack extension – not crack slip.</td>
</tr>
<tr>
<td>Zietlow and Labuz [1998]</td>
<td>Quartzite, Sandstone, Granite</td>
<td>Acoustic Emission</td>
<td>Intrinsic zone and log of grain size are linearly related. Fine-grains yield narrow FPZ; coarse grains yield wide FPZ.</td>
</tr>
</tbody>
</table>

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Table 2.2: A compilation of studies of the (monotonic and cyclic) FPZ in quasi-brittle materials.

<table>
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<th>Authors and Date</th>
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<th>Technique</th>
<th>Trends</th>
</tr>
</thead>
<tbody>
<tr>
<td>Otsuka and Date [2000]</td>
<td>Concrete</td>
<td>Acoustic Emission, X-Rays</td>
<td>AE and X-ray do not agree on shape of FPZ. Fracture core zone (FCZ) is a high energy (AE-derived) region within FPZ, tends to be the crack. Concrete with a smaller aggregate has a longer, thinner FCZ than concrete with a larger aggregate. 95% of energy (AE-derived) defines FPZ. X-ray microcracks at 80% of peak load, max AE activity after peak load. FCZ/FPZ size increases with specimen size.</td>
</tr>
<tr>
<td>Zang et al. [2000]</td>
<td>Granite</td>
<td>Acoustic Emission, Ultrasonic Pulses, Microscopy</td>
<td>AE detects a greater width and length of FPZ than microscopy. Crack spacing is independent of length. FPZ width increases to 10x grain diameter.</td>
</tr>
<tr>
<td>Janssen et al. [2001]</td>
<td>Granite</td>
<td>Acoustic Emission, Microscopy</td>
<td>AE detects a greater width and length of FPZ than microscopy. Crack density decreases with distance from fault plane; variety of crack densities near fault tip. FPZ scales with fault length more than loading conditions.</td>
</tr>
<tr>
<td>Picart et al. [2004]</td>
<td>Concrete (Resin)</td>
<td>Digital Interferometry</td>
<td>&quot;Spatially multiplexed/de-multiplexed (combining many signals into one) digital holograms are a good means of understanding fracture of resin concrete.&quot;</td>
</tr>
<tr>
<td>Pique et al. [2003]</td>
<td>Model Material (steel spheres + epoxy)</td>
<td>Microscopy</td>
<td>The test material was a two-phase material of steel spheres in an epoxy matrix. Fracture would initiate in imperfect connections (i.e., gaps in the epoxy) between spheres. Model material is a good way to study quasibrittle fracture, because one can control the different mechanisms that dissipate energy (such as atypical bonding, etc.). Size of FPZ varied with different stacking of model material.</td>
</tr>
</tbody>
</table>

Continued on next page
Table 2.2: A compilation of studies of the (monotonic and cyclic) FPZ in quasi-brittle materials.

<table>
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<tr>
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<th>Material</th>
<th>Technique</th>
<th>Trends</th>
</tr>
</thead>
<tbody>
<tr>
<td>Denarie et al. [2001]</td>
<td>Concrete</td>
<td>Fiberoptics</td>
<td>Bragg grating is a good way to observe strains near cracks. Confirmed that FPZ width is 3x maximum aggregate size. Nonuniform grating strain suggests microcracking in FPZ.</td>
</tr>
<tr>
<td>Backers et al. [2005]</td>
<td>Sandstone</td>
<td>Acoustic Emission, Microscopy</td>
<td>Increase in intragranular crack density near fracture, in FPZ. AE detects wider FPZ (possibly because microscopy is only a surface measurement). FPZ width independent of loading rate. Elliptical FPZ.</td>
</tr>
<tr>
<td>Nasseri et al. [2006]</td>
<td>Granite</td>
<td>Acoustic Emission, Microscopy</td>
<td>Microcracks in FPZ oriented parallel to fracture; twice the background microcrack density. AE and microcrack density increase exponentially towards fracture, and agree on width of FPZ.</td>
</tr>
<tr>
<td>Lin et al. [2009]</td>
<td>Sandstone</td>
<td>Acoustic Emission, Electronic Speckle Pattern Interferometry</td>
<td>Intrinsic zone initiated at 96-99% of peak stress for unnotched samples, 70-80% of peak stress for notched samples, and 60-80% of peak stress for samples whose notch was off-center. Failure did not always occur at the notch.</td>
</tr>
<tr>
<td>Faulkner et al. [2011]</td>
<td>Natural Fault with length around 1000 km</td>
<td>—</td>
<td>Damage zone increases with fault displacement, and goes to zero at zero displacement. Microcrack density decreases with distance from fault.</td>
</tr>
<tr>
<td>Sowik [2011]</td>
<td>Concrete</td>
<td>FEM</td>
<td>FPZ width is important in simulation of concrete fracture.</td>
</tr>
</tbody>
</table>

*Continued on next page*
Table 2.2: A compilation of studies of the (monotonic and cyclic) FPZ in quasi-brittle materials.

<table>
<thead>
<tr>
<th>Authors and Date</th>
<th>Material</th>
<th>Technique</th>
<th>Trends</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wu et al. [2011]</td>
<td>Concrete</td>
<td>Photography (Digital Image Correlation Method)</td>
<td>FPZ length increases as load increases, increases as specimen height increases, but decreases as notch-depth/specimen-height ratio increases. FPZ length increases until crack-extension/ligament-length 0.91.</td>
</tr>
</tbody>
</table>

Wong [2008], Wong and Einstein [2009c;d] presented microscale information of a unique FPZ phenomenon in marble. The study linked crack coalescence in gypsum and marble specimens with various pre-existing crack (“flaw”) geometries. In this study, it was noted that marble physically brightens, or displays “white patching” at the tips of aws prior to crack coalescence. As determined by scanning electron microscopy, the white patches result from the growth and extension of networks of microcracks, which manifest in one of four qualitative densities: Background (natural density of microcracks in the intact rock), Low, Medium, and High Crack Density. The study thus investigated the scale and structure of this FPZ phenomenon at the microscale. The next step, which is addressed by the current study, is to investigate the accompanying nanomechanical properties.

**FPZ Measurement of Quasi-Brittle Materials – Fault Scale**

Study of the process zone at large scales reveals the potential for driving mechanisms best understood with investigation at a more fundamental scale: the micro- and nanoscales. The Dugdale model (Figure 2-4, Equation 2.25) is a popular fault-scale (faults with lengths from 10 m to 1000 km, see Table 2.2) process zone model. Cowie and Scholz [1992] applied the Dugdale model to data from actual faults, and found very good agreement.

First, Cowie and Scholz laid the groundwork of the Dugdale theory. They noted that the process zone is larger for low-yield strength materials, and small or infinitesimal in high yield-strength materials. Given the Dugdale theory approach to process zone formation, Cowie and Scholz as-
Figure 2-7: This diagram, from [Cowie and Scholz 1992], shows the Cowie-Scholz model applied to a Mode III fault. Stage 1 contains both the fault tip and fractures which break down the intact rock surrounding the fault. Stage 2 is an intermittent layer consisting of fault gouge. Stage 3 is the well-developed fault center of the fault where residual friction stress is activated.

Assumed a shear remote stress was applied to a Mode III fault. Thus, for large-scale cracks or faults opening in shear, friction is activated in the inelastic zone to lead to the term Frictional Breakdown Zone (FBZ) (Figure 2-7). The FBZ is the major adaptation of the Dugdale theory; Cowie and Scholz consider the FBZ to be a region near the fault tip where the fault surface is in the early stages of formation, but is not yet a through-going sliding surface. The zone begins at a distance \( a - s \) from the center of the fault of length \( 2a \) (i.e., the FBZ is found in the \( s \) region in Figure 2-4). For example, when the Dugdale model is applied to a Mode III fault, the stress within the FBZ is a reduced tip stress \( \sigma_{up} \):

\[
\sigma_{up} = \sigma_0 - \sigma_f
\]

(2.28)

where \( \sigma_0 \) is the shear strength of the rock, and \( \sigma_f \) is the frictional stress on the fault. (Note that a Mode III fault opens in and out of the fault plane, and thus develops frictional stresses on the surface of the fault.) The tip stress and the remote stress are constant with time, which makes sense if friction is a scale-independent phenomenon (i.e., regardless of how the fault grows and increases scale over time, the tip stress and remote stress do not change and remain constant with time).
Then, Cowie and Scholz compared their adapted Dugdale model with data from actual faults. This comparison yielded four major fault properties:

1. The greatest displacement occurs at the center of the fault. Even at large scales, and even in faults that traverse several different material types, the greatest displacement occurs at the center of the fault; displacement significantly decreases at the fault boundaries.

2. There is a constant relationship between the center displacement and the length of the fault. Longer faults tend to displace more.

3. The fault may not be continuously open; the region between the fault tip and the end of the FBZ is often composed of en echelon cracks.

4. Various deformation mechanisms such as fracturing, pressure solution, ductile flow, and frictional wear may occur along the fault. Microfractures also tend to form small angles with the fault plane [Vermilye and Scholz 1998].

These properties, especially property 4, suggest that mechanisms at more fundamental scales – the micro- and nanoscales – ultimately determine cracking behavior.

Cowie and Scholz [1992] further pursued these small-scale mechanisms. Application of the Cowie and Scholz model (a derivative of the Dugdale model) to existing faults reveals a logarithmically decreasing microfracture density within and moving away from the “cohesion zone,” (a low-strength area around a displaced fault, located in the fault-plane region displaced by the fault; Figure 2-7, from [Cowie and Scholz 1992]), and a finite scale-independent limiting microfracture density [Vermilye and Scholz 1998].

The Cowie and Scholz model also considers an FBZ within the cohesion zone, at the very tip of the fault, where intact friction is activated and the stress is the difference between the shear strength and the frictional strength of the rock [Cowie and Scholz 1992]. The documentation by the Vermilye-Scholz study of small scale fractures within the cohesion zone suggests the potential for the as yet unexplored nanomechanical property change within the cohesion zone. The current investigation explores nanomechanical property change within the process zone, an area previously
explored by classic LEFM, Dugdale, and Cowie-Scholz models, including the frictional breakdown zone of the Cowie-Scholz model.

### 2.1.6 Fracture Toughness $K_c$

Fracture toughness $K_c$ is a material property that describes the energy required to fracture a material. If we consider the moment at which an existing crack just begins to crack, and if we then equate the fracture stress from Equation 2.13 with the expression by Irwin [1957] for the stress at a crack tip (adapted from previous solution of crack tip stress distributions by Westergaard [1939]), we find an expression for fracture toughness $K_c$:

$$
\sigma_f = \sqrt{\frac{G_f E}{l\pi}} = \sqrt{\frac{G E}{2\pi r} f(\theta)} = \sqrt{\frac{K_c^2}{2\pi r} f(\theta)}
$$

The final expression of Equation 2.29 reveals the fracture toughness, first known as the intensity factor and first revealed by Irwin [1957]. Thus, fracture toughness $K_c$ relates with material fracture energy $G_f$ by:

$$
G_f = \frac{K_c^2}{E}
$$

The fracture toughness may include a subscript to denote the mode of crack opening relevant to the particular property value; for example, for the mode I crack discussed in this section (Figure 2-5), the fracture toughness may be written as $K_{IC}$. Because fracture toughness $K_c$ scales with fracture energy $G_f$, materials with higher fracture toughness require more energy to fracture. This study measures the fracture toughness of marbles as a quantitative measure of their tendency to fracture.

There are two main recommended techniques for measuring material fracture toughness $K_c$ of rocks [Fowell et al. 1995, Ouchterlony et al. 1988]: a bending technique, and a short rod technique (Figure 2-8). The bending technique propagates an initial crack cut perpendicularly to the cylindrical specimen axis, whereas the short rod technique propagates an initial crack cut parallel to
whereas the bending and short rod techniques are commonly used by the rock mechanics community [Amrollahi et al. 2011, Nasseri et al. 2005], this investigation sought a technique which obtained fracture toughness at the scale of the investigation: the micro- and nanoscales. thus, a recently developed technique of microscratch testing was used. this section describes the theory behind scratch testing, and explains how the desired property of fracture toughness is derived from a scratch test. scratch testing involves driving a probe across a material surface at a specified loading rate, horizontal load, and vertical load. a schematic of the scratch test is shown in figure 2-9.

the scratch testing technique developed by akono et al. [2011; 2012] presents scratching as a fracture-dominated process – especially for wide, shallow scratches. combining two key fracture mechanics theories – the griffith energy and the j-integral for the material in front of the scratch
tester – the key relation of the scratch test is revealed:

\[ K_C = \frac{F_T}{\sqrt{2pA}} \]  \hspace{1cm} (2.31)

where \( F_T \) is horizontal force, \( p \) is the perimeter of the axisymmetric probe, and \( A \) is the projected area of contact of horizontal load. The physical quantities from Equation 2.31 are shown in Figure 2-9a. Equation 2.31 will be returned to in later chapters as the data from scratch testing of materials in this study is presented and analyzed.

Whereas Figure 2-9a shows an idealized schematic of a scratch, Figure 2-10 shows a photograph of and data from an actual scratch. Figure 2-10a shows a photograph of Carrara marble immediately after a scratch test. Figure 2-10b shows the length and depth relationship during a single scratch; note that the depth \( d \) increases as the scratch proceeds along its length. Finally, Figure 2-10c shows the fracture toughness \( K_c \) as the scratch shown in Figure 2-10b increases in depth. The graph in Figure 2-10c is obtained from the continual recording of depth during the scratch test. This continual recording yields many depth points \( d \) for a single scratch. Each depth point can be linked with contact area \( A \) and perimeter \( p \) through probe geometry, and plugged into Equation 2-10c to obtain a fracture toughness \( K_c \) for each depth point \( d \) measured during the scratch. Finally, note that in Figure 2-10c, the depth \( d \) has been normalized by the radius of the probe \( R \) before being plotted on the x-axis. In Figure 2-10c, it is apparent that the fracture toughness \( K_c \) converges towards a constant value near the deepest points (i.e., points with the highest \( d \)
of the scratch.

(a) An optical microscope panoramic image of a scratch in Carrara marble. The length of the scratch is 3 mm.

(b) The length and depth information from the scratch in Figure 2-10a.

(c) $K_c$ values sorted by $\frac{d}{R}$ from the length and depth data in Figure 2-10b.

Figure 2-10: Scratch testing image and data.

A number of studies have explored the relationship of fracture toughness with material microstructure. Studies of alumina (grain size less than 13 $\mu$m) have found that fracture toughness either increases with increased grain size [Tuan et al. 1994] or decreases with increased grain size, but not in a statistically significant way [Yao et al. 2011]. Studies on ceramics and ceramic composites of larger grain size (up to 600 $\mu$m) have found that fracture toughness decreases with increased grain size [Reimanis 1997, Rice 1996]; the same trend was found in a study on zinc sulphide (grain size less than 500 $\mu$m, [Townsend and Field 1990]). A study of primary importance for this work was conducted on marbles with a typical grain size between 1.78 and 8.89 mm$^2$, and agreed that fracture toughness increased with increased grain size (specifically, as grain size decreased ap-
proximately 7 mm², fracture toughness increased approximately 0.3 MPa√m [Amrollahi et al. 2011]).

2.2 Nanomechanics

With the subject of this investigation clearly laid out in Section 2.1, we turn now to laying out the first tool for probing this subject: nanomechanics. Nanoindentation is an ideal method for probing the mechanical response of a material at fundamental scales. This section includes a discussion of nanoindentation, and of the self-similarity of nanoindentation; this property of nanoindentation aids with and streamlines the analysis. The section closes with a brief review of existing applications of nanoindentation to brittle materials.

2.2.1 Nanoindentation Procedure

The Nanoindentation Test
Nanoindentation tests in this investigation were conducted on a CSM Instruments Nano-Hardness Tester (Figures 2-11, 2-12). An indentation test consists of pushing a probe onto a specimen surface at a specified loading rate and peak load (Figure 2-13; [Bobko 2008]). Figure 2-13 depicts the geometry of the surface before and during indentation for a conical probe. Before indentation, the surface is assumed to be infinitely flat. During indentation, the tip of the indenter deforms the surface to an “indentation depth” h at a maximum load P, where h is measured from the surface before indentation to the maximum depth during loading. The actual distance of contact between indenter probe and material is denoted by h_c and is also known as the “contact depth”. The projection of the region of indenter-surface contact at maximum load onto the original undeformed surface is the contact area, A_c.

The particular deformation of the surface during indentation reveals information about the stress-strain behavior and strength of the indented material. This information is contained in two of
The material properties yielded by nanoindentation: indentation modulus, and indentation hardness. The details of these properties are explained throughout this section. Specifically, during each indentation, surface deformation is monitored via a force-depth curve (Figure 2-14). The important physical quantities which constitute indentation modulus and indentation hardness formulation are obtained from the force-depth curve.
Figure 2-12: Cross-section of components of CSM Instruments Nano-Hardness Tester\textcopyright Indenter Head (Figure 2-11). The specimen is placed beneath the reference ring; the reference ring contacts the specimen surface prior to each indentation. From Bobko [2008].

Figure 2-13: This diagram of a typical conical probe indentation indicates contact depth $h_c$, indentation depth $h$, contact radius $a$, equivalent cone angle $\theta$. From Bobko [2008].

2.2.2 Self-Similarity of Indentation Test

A key property of indentation is its self-similarity. This property lays a foundation for the analyses which derive mechanical properties from the indentation load-depth curve, and greatly simplifies these analyses. This section discusses the meaning of self-similarity, and the way in which self-similarity links with indentation\textsuperscript{4}.

The self-similarity of any research problem is of value to the researcher. For a time-dependent

\textsuperscript{4}The self-similarity discussion of this section is inspired by those of Constantinides [2006], Vandamme [2008], and Bobko [2008],
process such as indentation (where depth of indentation changes over time), self-similarity means that a similarity transformation can relate the distribution of properties in space at one point in time to that of the properties at another point in time [Barenblatt 1996]. In particular, the displacement fields at a particular load $P_0$ can help determine the displacement fields at any load $P$.

If the indenter and load satisfy three established criteria of self-similarity, then the indentation conducted by that indenter and load may be described as a self-similar process during loading [Borodich et al. 2003]. These three criteria are:

1. the strains and stresses of the indenter material must follow homogeneous constitutive relations,

2. the shape of the indenter must be a homogenous function of degree $d = 1$ or greater, and

3. the load must always increase during the test.

The first condition can be mathematically expressed by the following equation (which is the definition of a homogenous function):

$$F(\lambda \varepsilon) = \lambda^\kappa F(\varepsilon).$$

(2.32)

In Equation 2.32, $\varepsilon$ is the strain tensor. $F$ is an operator on the strains $\varepsilon$ and stresses of the indenter material which can be described by homogenous, degree $\kappa$ functions with respect to the
components of the strain tensor (and with respect to the components of the strain rate tensor, \( \dot{\varepsilon} \)). \( \lambda \) is an arbitrary positive scaling parameter. The second condition will be expressed in more detail in the next subsection on Probe Geometry. Finally, the third condition may be mathematically expressed by the following equation:

\[
z(\lambda x_1, \lambda x_2) = \lambda^d z(x_1, x_2) \text{ with } \lambda > 0,
\]

where \( z \) is the height of the surface of the probe in the indented material. The expression assumes a Cartesian coordinate system \( O x_1 x_2 x_3 \) with the origin at the tip of the probe (and \( x_3 \) into the depth of the probe; \( z \) is measured along \( x_3 \)). Note especially that upon load decrease, the indentation problem no longer meets the conditions of self-similarity, except in the case of elastic material behavior.

As a result of satisfying self-similarity, indentation analysis is simplified: straightforward scaling relations describe contact area or depth as a function of known homogenous functions and initial contact area or depth. This means that the contact area or depth at any point during the indentation loading may be determined as a simple function of a previous known contact area or depth. This section reviews the conditions of self-similarity as they apply to indentation, and presents the resulting scaling relations.

**Probe Geometry**

A variety of indenter tips, or probes, have been successfully employed for indentation: flat punch, Berkovich (Figure 2-15), Vickers (4-sided pyramidal probe with 68° solid angle), sphere, or cone. The flat punch probe maintains a constant area of contact throughout indentation, but is more commonly used in indentation theory than actual testing. The spherical probe realizes only the elastic range of the indented material for low-load indentations, and is challenging to manufacture. The advantage of the Berkovich probe arises from its sharp geometry; this sharpness means the probe can test a smaller volume of material than the volume required by more blunt probes. Additionally, the particular geometry of the Berkovich probe can be manufactured more accurately than other geometries. The Berkovich probe is thus popular in research. However, even at low loads
the Berkovich probe generates high stress concentrations directly beneath the probe, and thereby solicits the material plastically.

For all probe types, the height $z$ of the surface of the probe in the indented material must follow Equation 2.33. The expression assumes a Cartesian coordinate system $Ox_1x_2x_3$ with the origin at the tip of the probe (and $x_3$ into the depth of the probe). Equation 2.33 is simplified for axisymmetric probes (probes such as cones or paraboloids that are symmetric about their axis, and whose geometry may be described by radius $r$):

$$z(r) = B r^d$$

(2.34)

where $B$ is a proportionality factor representing the radius at unit radius, and $d$ is the degree of the homogeneous function (1 for both Berkovich and conical probes) of the probe geometry. The expression simplifies even further for the Berkovich probe:

$$z(r) = r \tan \theta_{eq}$$

(2.35)

where $\theta_{eq}$ is an "equivalent cone angle" (Figure 2-15). A conical probe which subtends $\theta_{eq}$ gives the same projected contact area at a given depth as the Berkovich probe. Given the contact area
expression of the Berkovich probe [Oliver and Pharr 1992]:

\[ A(h) = 24.56h^2 \] (2.36)

and the contact area expression of a conical probe:

\[ A(h) = \pi(htan\theta)^2 \] (2.37)

equating the two contact area expressions reveals the \( \theta_{eq} \) of the Berkovich probe:

\[ \theta_{eq} = \tan\left(\sqrt{\frac{24.56}{\pi}}\right) \approx 70.32^\circ \] (2.38)

Material Behavior

In order for the indentation problem to be self-similar, the indented material must satisfy a particular condition: the constitutive relations of the material should be homogenous with respect to the strains, \( \varepsilon \) (or stresses, \( \sigma(\varepsilon) \); see Equation 2.32). If we adapt Equation 2.32 to materials operating in their elastic range (both linear and non-linear elastic range), the equation takes the form:

\[ C(\lambda \varepsilon) = \lambda^{\kappa-1} C(\varepsilon) \] (2.39)

where \( \kappa = 1 \) in the case of linear elasticity, and \( C(\varepsilon) \), the secant stiffness tensor, defines the stress tensor \( \sigma = C(\varepsilon) : \varepsilon \).5

Note that Equation 2.39 does not apply to linear-elastic perfectly-plastic materials. This is because there exists no unique \( \kappa \) which can apply for all the strains realized during an indentation in such materials: \( \kappa = 1 \) in the elastic range and \( \kappa = 0 \) at the limit of the elastic domain.

Self-Similar Scaling Relations

5Note that the expression also applies to materials operating at the rigid plastic limit behavior; for such materials, the dissipation function \( \sigma : D = \pi(D) \) defines the stress tensor: \( \sigma = \frac{d\pi}{dD}(D) \) [Dormieux et al. 2006].
The self-similarity of the Berkovich probe is used to relate the load \( P \) and depth \( h \) during indentation to mechanical properties of the indented material. This section reviews the self-similar scaling relations, and presents their link with material hardness \( H \).

Borodich [1990] used the solution of the classic Hertzian contact problem to derive a single relation between load and depth \((P \text{ and } h)\) at any time during the indentation loading, to load and depth \((P_0 \text{ and } h_0)\) at some initial point during the loading:

\[
h = h_0 P^{2 + \kappa(d-1)}
\]

where \( \kappa \) is a constant describing the nonlinearity of the indented material (\( \kappa \neq 1 \) for a nonlinear elastic medium), and \( d \) is the degree of the homogenous function describing the shape of the indenter (Figure 2-15; \( d \) approaches \( \infty \) for flat-punch (cylindrical) indenters, 1 for Berkovich, pyramidal and conical indenters, and 2 for spherical indenters [Vandamme 2008]). A rearrangement of Equation 2.40,

\[
\frac{P}{P_0} = \left( \frac{h}{h_0} \right)^{\frac{2 + \kappa(d-1)}{d}},
\]

yields a scaling relation between load \( P \) and depth \( h \). The scaling relation for contact area \( A_c \) has a similar structure:

\[
\frac{h}{h_0} = \left( \frac{A_c}{A_{c0}} \right)^{\frac{d}{4}}
\]

Here, the definition of hardness \( H \) (defined as the load for a given contact area, or average pressure beneath the probe) is recalled:

\[
H = \frac{P}{A_c}
\]

The definition of hardness \( H \) in Equation 2.43 helps to build the hardness scaling relation:

\[
\frac{H}{H_0} = \frac{\frac{P}{A_c}}{\frac{P_0}{A_{c0}}}
\]

At this point, Equation 2.44 can be further simplified by substituting the scaling relations for load
**P** and Area \( A_c \) from Equations 2.41 and 2.42 into the right-hand side of Equation 2.44:

\[
\frac{H}{H_0} = \frac{\frac{P}{P_0}}{\left(\frac{h}{h_0}\right)^{2/d}} \\
= \frac{\frac{P}{P_0}}{\left(\frac{P}{P_0}\right)^{2 + \alpha(d-1)}} \\
= \left(\frac{P}{P_0}\right)^{1 - \frac{2}{2 + \alpha(d-1)}}
\]  

(2.45)

Finally, with a consideration of the load scaling relation in Equation 2.41, 2.45 simplifies to the ultimate scaling relation for hardness \( H \):

\[
\frac{H}{H_0} = \left(\frac{h}{h_0}\right)^{\frac{\alpha(d-1)}{d}}.
\]  

(2.46)

This hardness scaling relation allows the user to determine hardness at any point during the indentation. This important scaling relation is further simplified by including the contact radius of the probe, \( a \) (Figure 2-15). With a reminder that \( A_c = \pi a^2 \), the first scaling relation (Equation 2.42) reduces to:

\[
\frac{a^d}{h} = \frac{a_0^d}{h_0} = \text{constant}
\]  

(2.47)

For axisymmetric probes, the hardness scaling relation is even further simplified by incorporating Equation 2.35 (the relation between depth \( z \) or \( h \), probe radius \( a \), and constant \( B; h_c = B a^d \)):

\[
\frac{h_c}{h} = \frac{B a^d}{h} = \frac{B h a_0^d}{h h_0} = \frac{B a_0^d}{h_0} = \text{constant.}
\]  

(2.48)
2.2.3 Indentation Modulus

Indentation modulus represents material stress-strain behavior. The quantity is related to the elasticity, and coincides for isotropic materials with the plane-stress modulus. Through the use of the Galin-Sneddon solution and its assumptions, this section formally describes the essential links between indentation modulus, physical quantities measured during the indentation test, and fundamental material properties. These links are the foundations of a meaningful nanoindentation analysis\(^6\).

The Galin-Sneddon Solution

The Galin-Sneddon solution [Sneddon 1965] provides expressions for three components of indentation analysis: the indentation load \(P\) as a function of indentation depth \(h\), the displacement field \(u_z\) of the indented material, and the stress field \(\sigma_{zz}\) of the indented material (Figure 2-16).

The solution considers that the probe is a surface of revolution (such as a cone or paraboloid). Galin and Sneddon employ the theory of Hankel transformations (two-dimensional Fourier transforms which apply to circular symmetric functions) in the expression of the elastic equilibrium

\(^6\)The indentation modulus discussion in this section is inspired by those of Constantinides [2006], Vandamme [2008], and Bobko [2008].
equations, and eventually formulate the indentation depth \( h \):

\[
h = a \int_{\rho=0}^{\rho=a} \frac{f'(\rho)}{\sqrt{a^2 - \rho^2}} \, d\rho
\]

(2.49)

where \( \rho \) is contact radius at any time during loading, \( a \) is radius at maximum depth, and \( z \) is the depth at any time during loading. The indentation load \( P \) may be expressed as:

\[
P = 2 \frac{E}{1 - \nu^2} \int_{\rho=0}^{\rho=a} \frac{\rho^2 f'(\rho)}{a^2 - \rho^2} \, d\rho
\]

(2.50)

In the case of the conical indentation, the above formulations of load \( P \) and depth \( h \) are used to form the expression of the displacement field \( u_z \) of the indented material:

\[
u_z(\rho, 0) = \frac{2h}{\pi a} \left( \arcsin\left(\frac{a}{\rho}\right) - \rho + \sqrt{\rho^2 - a^2} \right)
\]

(2.51)

for \( \rho > a \) (material just outside of the indent; the shape of the deformed surface), and the stress field \( \sigma_{zz} \) of the indented material:

\[
\sigma_{zz}(\rho, 0) = -\frac{Eh}{2(1 - \nu^2)\pi a} \cosh^{-1}\left(\frac{a}{\rho}\right)
\]

(2.52)

for \( \rho < a \) (material inside of the indent; the distribution of pressure under the indenter) [Sneddon 1965]. When applied to an axisymmetric cone of angle \( \theta \), the depth and load expressions reduce to:

\[
h = \frac{\pi}{2} \frac{a}{\tan \theta}
\]

(2.53)

\[
P = \frac{2E\tan \theta}{\pi} \frac{A_c}{1 - \nu^2 \tan \theta}
\]

(2.54)

Finally, differentiation of the load expression with respect to depth yields the Bulychev-Alekhin-Shoroshorov equation (known commonly by its acronym, the BASh equation) [Bulychev et al. 1976] for unloading stiffness \( S \) (see Figure 2-14):

\[
S = \frac{dP}{dh} = \frac{2}{\sqrt{\pi}} M_0 \sqrt{A_c}
\]

(2.55)
where $M_0$, defined both as plane stress modulus and indentation modulus, links with the elastic properties $(E, \nu)$ of the indented material through the expression $M_0 = \frac{E}{1-\nu^2}$. Thus presented, the solution of Galin and Sneddon, in conjunction with the BASH equation, provides an important link between measurable indentation quantities $P, h$ and the sought-after material property, indentation modulus $M$.

**Galin-Sneddon Assumptions**

The Galin-Sneddon solution rests on two assumptions: an assumption of small perturbations, i.e., small displacements and small deformation, and an assumption of a rigid probe. Regarding the first assumption, a correction may be applied to the stiffness to account for the radial displacement of the compressible indented material [Hay et al. 1999]:

$$S = \gamma \frac{2}{\sqrt{\pi}} M_0 \sqrt{A_c}$$

(2.56)

Regarding the second assumption, it may be noted that in practice, the probe deforms elastically. Even diamond probes exhibit a finite Young’s Modulus ($E_i \approx 1141$ GPa) and Poisson’s ratio ($\nu = 0.07$) [Instruments 2004]; ultimately, the elasticity of the probe corresponds to a displacement of both the probe and the indented material. This additional displacement affects measured indentation quantities. Thus, based on Hertz’s contact solution [Hertz 1896], the indentation modulus $M$ is corrected by a consideration of the elasticity of both the probe and the indented material in series [Oliver and Pharr 1992]:

$$\frac{1}{M_0} = \frac{1 - \nu^2}{E} + \frac{1 - \nu_i^2}{E_i}$$

(2.57)

**Dimensional Analysis**

Dimensional analysis is of importance to the researcher and scientist because it allows one to reduce a complex problem with many variables into a system of a finite number of dimensionless quantities. The method, pioneered by Buckingham [1914], is employed here as a means of better
understanding indentation hardness.

Consider again the probe (with solid angle \( \theta \)) which indents a material (with cohesion \( c \), Poisson’s ratio \( \nu \), friction coefficient \( \mu \), and plane stress modulus \( M \)) to a depth \( h \) under applied load \( P \). Initially, the two dependent variables of the problem, \( P \) and \( A_c \), are expressed as functions of the remaining independent variables:

\[
P = f(h, \theta, M_0, \nu, c, \mu) \tag{2.58}
\]
\[
A_c = f(h, \theta, M_0, \nu, c, \mu) \tag{2.59}
\]

The application of Buckingham’s \( \Pi \)-Theorem yields the relation between the dependent variables and independent variables as two dimensionless parameters:

\[
\frac{P}{ch^2} = \Pi_{P, \text{load}} \left( \theta, M_0, \nu, c, \mu \right) \tag{2.60}
\]
\[
\frac{A_c}{h^2} = \Pi_{A_c} \left( \theta, M_0, \nu, c, \mu \right) \tag{2.61}
\]

The indentation modulus can also be considered with a dimensional analysis, with the inclusion of an additional quantity activated during unloading: \( h_{\text{max}} \), indentation depth. Reworking Equation 2.60 can also yield plane stress modulus \( M_0 \) as a dependent variable:

\[
\frac{P}{M_0 h^2} = \Pi_{P, \text{load}} \left( \theta, \frac{c}{M_0}, \nu, \mu, \frac{h}{h_{\text{max}}} \right) \tag{2.62}
\]

If we recall the definition of stiffness \( S \) from Equation 2.55, we can take the derivative of Equation 2.62 with respect to indentation depth \( h \) at \( \frac{h}{h_{\text{max}}} = 1 \):

\[
\frac{d}{dh} \left( \frac{P}{M_0 h^2} \right) = -2PM_0 \frac{1}{h^3} + SM_0 \frac{1}{h^2}, \tag{2.63}
\]
rearrange Equation 2.63 (while reintroducing the parameter $\Pi_{P, \text{load}}$):

$$\frac{SM_0}{h^2} = \frac{d}{dh} \Pi_{P, \text{load}} + \frac{2}{h} \Pi_{P, \text{load}},$$  \hspace{1cm} (2.64)

multiply through by $h$, and formulate a dimensionless parameter for stiffness, $\Pi_S$:

$$\frac{S}{M_0 h_{\text{max}}} = \Pi_S \left( \theta, \frac{c}{M_0}, \nu, \mu \right)$$  \hspace{1cm} (2.65)

Note that $\Pi_S$ has been evaluated at maximum load ($h = h_{\text{max}}$). Recall now that the BASH Equation (Equation 2.55) may be rearranged to form a similar expression to Equation 2.65:

$$\frac{S}{M_0 \sqrt{A_c}} = \frac{2}{\sqrt{\pi}} \frac{h_{\text{max}}}{M_0 h_{\text{max}} \sqrt{A_c}}$$  \hspace{1cm} (2.66)

Substitution of the dimensionless parameters $\Pi_S$ and $\Pi_{A_c}$ reveals:

$$\frac{S}{M_0 \sqrt{A_c}} = h_{\text{max}} \frac{\Pi_S \left( \theta, \frac{c}{M_0}, \nu, \mu \right)}{\sqrt{\Pi_{A_c} \left( \theta, \frac{c}{M_0}, \nu, \mu \right)}}$$  \hspace{1cm} (2.67)

which may be associated with a final invariant, $\Pi_M$:

$$\frac{S}{M_0 \sqrt{A_c}} = \Pi_M \left( \theta, \frac{c}{M_0}, \nu, \mu \right)$$  \hspace{1cm} (2.68)

With the assumption based on the work of Stillwell and Tabor [1961] that initial unloading presents a virtually elastic material response, the independent variables relating to material properties may be removed (i.e., $c$, $M_0$, $\mu$, and $\nu$), and $\Pi_M$ may be further simplified:

$$\frac{S}{M_0 \sqrt{A_c(\theta)}} = \Pi_M (\theta)$$  \hspace{1cm} (2.69)

This resulting dimensionless relation corresponds precisely with the definition for indentation mod-
ulus (with respect to unloading stiffness $S$, Equation 2.55), and is thus equal to $\frac{2}{\pi}$ for the indentation conditions in this investigation.

### 2.2.4 Indentation Hardness

Indentation hardness links with material strength. This section opens with a return to dimensional analysis, and formally describes the essential links between indentation hardness, physical quantities measured during the indentation test, and fundamental material properties. These links are the foundations of a meaningful nanoindentation analysis.\(^7\)

**Dimensional Analysis**

Noting that hardness is defined as the ratio between the two independent variables ($H = P/A_c$, Equation 2.43), a relation of the dimensionless parameters yields a third dimensionless relation, the ratio of hardness to cohesion:

$$\frac{\Pi_P}{\Pi_{A_c}} = \frac{H}{c} = \Pi_H \left( \theta, \mu, \nu, \frac{M_0}{c} \right) \quad (2.70)$$

Note that the hardness-cohesion ratio does not depend on the depth of indentation.

**Link with Strength**

The Rockwell test, developed in the late 19th century, first reported a proportional relationship between material hardness $H$ and uniaxial flow stress of the tested material, via a proportionality factor $C$ called the constraint factor. The value of the constraint factor was found to be dependent on the indenter shape. Prandtl explored the constraint factor $C$ by developing the distribution of stress beneath a flat punch at the onset of plastic flow. Under the assumption of plane strain, and of rigid material surrounding the indenter, Prandtl identified that $C$ had a value of $1 - \frac{\pi}{2}$ [Chandler 1999].

\(^7\) The discussion of this section is inspired by that of Bobko [2008] and Vandamme [2008].
Prandtl [1921] developed the stress beneath a flat punch by assuming three zones (symmetric about the central axis, Figure 2-17) in the material beneath the punch. Prandtl assumed the material followed a Coulomb failure criterion (i.e., linear failure envelope). By applying Mohr's circle to the three zones of material, Prandtl found that the material in the triangle directly beneath the indenter, as well as the material in the triangles to the left and right of the indenter, behaved purely elastically. By applying moment equilibrium to the remaining material in the curved wedges, Prandtl found potential failure surfaces along the boundaries of these wedges. Hill later generalized Prandtl’s work, and the work became the basis of slip-line-field theory. Prandtl’s formulation of the five major zones beneath a flat punch formed the basis of bearing capacity formulations in geomechanics [Nadai 1931, Richards et al. 1993, Taylor 1948].

The experimental work of Tabor [1948] confirmed the $C$ value of Prandtl; he noted experimentally that the average pressure sustained beneath an indentation at the onset of plastic yielding, $H$, tended towards 2.6 to 3 times the material yield strength $Y$, or $H/Y \approx 3$. This empirical relation between hardness and yield strength can specify the previously developed dimensionless relation for hardness $\Pi_H$ (Equation 2.70). Noting first that cohesion $c$ scales with material yield strength $Y$,

$$Y = \sqrt{3c},$$

(2.71)

the incorporation of the cohesion-yield strength relation into the hardness dimensionless relation
\( \Pi_h \) (Equation 2.70):

\[
\frac{H}{c} = \frac{H}{\sqrt{3}} = \Pi_H \left( \theta, \mu, \nu, \frac{M_0}{c} \right)
\]

which may simplify as (for a Von Mises material, with \( \mu = 0 \) and provided that \( \frac{M}{c} \to \infty \)):

\[
\frac{H}{Y} = \frac{1}{\sqrt{3}} \Pi_H = 3.
\]

Thus expressed for the indentation problem in a Von Mises material, hardness fundamentally links with material yield strength.

The hardness of cohesive-frictional materials links also with strength. Ganneau et al [Ganneau et al. 2006] applied yield design theorems to conical probe indentations with varying apex angles to develop cone-angle dependent hardness-cohesion solutions:

\[
\frac{H}{c} = \Pi_c(\mu, \theta)
\]

where \( \mu \) is the friction coefficient of the indented material. Thus expressed for the indentation problem in a cohesive-frictional material, hardness fundamentally connects with material strength. Indentation hardness links with the maximum stress sustained by the material before undergoing plastic deformation, and provides an idea of the material strength behavior.

**Activated Volume of Indented Material**

A question of interest to the researcher is the size \( d \), of the volume of material accessed by the indentation. This volume size may also be formulated as a dimensional analysis problem for the cohesive-frictional material in this investigation:

\[
\frac{d}{h} = \Pi_d \left( \theta, \frac{M}{H}, \nu, \mu, \frac{h}{D} \right)
\]

67
where $D$ is the characteristic size of a particular phase of indented material (See 3.2.1 for more explanation of $D$). For indentations much smaller than the material characteristic size ($\frac{h}{D} \rightarrow 0$), this final material invariant drops out of the analysis; it remains that for the indented phase of size $D$, $d_a$ is proportional to $h$ [Vandamme 2008]:

$$\frac{h}{D} \rightarrow 0 \Rightarrow d_a \propto h$$  \hspace{1cm} (2.76)

Finally, a comparison of the simulated isocontours for Von Mises effective stress and effective plastic strain suggest that the $d_a$ activated elastically by an indentation is greater than the $d_a$ activated plastically (Figure 2-18; [Larsson et al. 1996]). The isocontours show the distribution of Von Mises effective stress (Figure 2-18a) and accumulated plastic strain (Figure 2-18b) under large-strain assumptions, determined using ABAQUS finite-element modeling in aluminum 7075-T6, an elastoplastic material. Note that both stress and strain are highest close to the surface of the indent, and decrease with distance from the indent surface. Von Mises effective stress indicates the material activated elastically during indentation, whereas plastic strain indicates the material activated

---

Figure 2-18: A comparison of the simulated isocontours for a) Von Mises effective stress and b) effective plastic strain suggest that the size $d_a$ of the volume activated elastically by an indentation is greater than the $d_a$ activated plastically. The arrows indicate the isocontours which represent low effective stress and low plastic strain. From Larsson et al. [1996].
plastically during indentation. The isocontour which indicates low effective stress (isocontour “1”, 415 MPa, indicated with arrows in Figure 2-18a) is located much further from the indenter surface than the isocontour which indicates low plastic strain (isocontour “2”, 10% plastic strain, indicated with arrows in Figure 2-18b). Thus, the finite element simulations in Figure 2-18 illustrate that the volume activated plastically by indentation is much smaller than that activated elastically.

2.2.5 Indentation in Heterogeneous Materials

Previous sections of this chapter have explained an important characteristic of the indentation test – its self-similarity – and linked this characteristic with the two main properties measured with indentation in this study (indentation modulus and hardness), and their derivation from indentation test parameters. This section closes the indentation background of this study by commenting on careful test design. Specifically, this section addresses indentation test parameters, and how they should be designed with respect to material properties using the “Scale Separability Condition”.

In order to approach the test analysis with the tools of continuum micromechanics, three scales of the indentation problem must not interfere with each other. The scale separability condition [Constantinides et al. 2006] describes the constituents and relationship of these three scales:

\[ d << L << (h, a, D) \]  \hspace{1cm} (2.77)

where \( d \) is the size of the largest heterogeneity of interest contained within the representative elementary volume (REV), \( L \) is the size of a REV, \( h \) is indentation depth, \( a \) is indentation radius, and \( D \) is a characteristic length scale of the material microstructure. The condition \( L < < (h, a) \) ensures that the mathematical relationships between indentation data and mechanical properties are valid, and the condition \( d < < L \) ensures that the REV contains enough heterogeneities to statistically represent the material. If the scale separability condition (Equation 2.77) is satisfied, indentation to a depth \( h \) will reveal information about the material properties at the scale of the elementary volume \( L \). In order to reveal information about material properties at the characteristic

\[ 8 \text{The scale separability discussion of this section is inspired by that of [Vandamme 2008].} \]
material scale \( D \), an \( h = D \) ratio of 1/10 should be satisfied as well [Constantinides et al. 2006].

2.3 Scanning Electron Microscopy (SEM) and Environmental Scanning Electron Microscopy (ESEM)

Electron microscopy is an ideal technique for obtaining the third element of the current investigation: structural information at fundamental material scales. Many studies have established SEM as an effective means of investigating process zone microstructures. Its ability to sense changes in topography makes the SEM ideally suited for observation of microcracks, spalling, and other process zone microstructures. This section presents the technique, its function, and application.

2.3.1 Operation of the Scanning Electron Microscope (SEM)

There are three basic parts to the operation of the SEM: the electron gun, the lenses, and the evacuated tube (Figure 2-19). The evacuated tube houses all the elements. The electron gun emits an electron beam, and the lenses demagnify and redirect this beam to ultimately focus the beam onto the specimen as a spot with a size of 10 nm (100 Å). The beam is composed of electrons which have been accelerated to a high energy (0.1 - 30 kV) at the gun. The beam interacts with the top few microns of the specimen (“Electron Range” in Figure 2-20, from Gradicek [2010]).

The image is ultimately formed from the detection of electrons that are reflected or re-emitted from the specimen. A scintillator/photomultiplier will amplify the image for display on a cathode-ray tube. Older SEMs, such as the SEM used in work by Wong ([Wong 2008], see Figure 2-21 for an example of an image acquired with an older SEM) also include a slow-scan option for the recording of images onto photography film, and a videoprinter for instant printing of images [Goldstein et al. 2003].

The full image is developed by scanning the beam over the specimen surface in a line-by-line fashion, also known as “rastering.” Rastering occurs due to a mechanism within the evacuated tube: a pair of coils near the electron gun deflects the beam away from the optical axis of the microscope,
and then a second lower pair of coils bends the beam back onto the optical axis. Magnification of a scanned image is achieved by rastering a smaller area of specimen, which is done by deflecting the beam less. Magnification, \( M \), is defined as:

\[
M = \frac{\text{length of raster on viewing screen}}{\text{length of raster on specimen}}. \tag{2.78}
\]

When the signal from one point differs from the signal at another point (due to differences in material, or distance traveled by the electron because of changes in topography), the difference manifests as contrast, or a change of intensity, in the image [Goldstein et al. 2003].

SEM has been used to monitor microcracks in granite with a typical opening of 0.5 \( \mu \text{m} \) and length of 20-30 \( \mu \text{m} \). The visibility of features smaller than this microcrack size such as thin bridges between cracks, as well as scalloping and tiny crystallites at the edges of pores in the rock, suggest that the surface preparation for SEM does not introduce significant damage to the microstructure [Brace et al. 1972]. Because brittle materials that have undergone stressing to induce a process
Figure 2-20: The various signals detected in SEM. PE indicates "primary electrons", i.e. the electron beam. BSE (backscattered electrons) and SE (secondary electrons) are the signals used in the current study. X (X-ray), CL (cathodoluminescence), and AE (Auger electrons) are not used. From Gradicek [2010].

zone have even more such structures visible, it has been suggested that the surface preparation for SEM is even less significant when observing process zone or microcracked materials. However, if used as a final polishing stage, ion thinning may heat the specimen, introduce dimples with diameters ranging from 5 to 50 µm; and some debris may get trapped by larger cavities [Sprunt and Brace 1974]. These consequences may damage the specimen and compromise any image obtained. Additionally, the surface preparation required for SEM may interfere with mechanical properties accessed by nanoindentation (Section 2.2). ESEM, discussed in the next section, is thus an ideal alternative for the assessment of microstructure.

Despite the advantages of SEM, many samples are damaged if placed in a vacuum, and are not conductive to the electron beam. The advent of Environmental SEM (ESEM) and Variable Pressure SEM (VPSEM) had made microscopic imaging of such samples possible, and now over half of the SEM market is devoted to ESEM and VPSEM [Goldstein et al. 2003].
Figure 2-21: (Top) White patching, indicated by the brackets, is visible at the tips of the flaw after loading. (Bottom) Assemblage of SEM images of microcracking and spalling, (a) and (b), from the bottom left corner of the flaw shown at top. The current study investigates mechanical properties at the scale of the bottom image. From [Wong 2008]
2.3.2 Operation of the ESEM

The ESEM operates at pressures ranging from 0 to 3000 Pa (Figure 2-22), and with higher energy electron beams (10-30 keV, as opposed to 1 - 5 keV for standard SEM). The machinery for ESEM

is the same as for standard SEM, with the addition of a few components:

- **High Vacuum Pump.** This component controls pressure. It runs parallel to the evacuated tube containing the electron gun and lenses, and connects to the column in several places. (See the note at the top of Figure 2-22.)

- **Pressure Limiting Aperture (PLA).** The PLA is an aperture with a diameter of a few hundred microns. The purpose of this component is to control the pressures between different sections of the ESEM column (Figure 2-22). One PLA resides at the base of the evacuated
tube, and its tiny diameter allows the chamber pressure to be 100 to 1000 times that of the pressure in the tube, or even higher if two PLAs are connected in series.

• **Gas.** The gas in the chamber is typically water mist. Rather than operating in vacuum conditions as in a standard SEM, the specimen chamber may be operated with a water vapor pressure present (or the vapor pressure of any other gas let through the inlet valve). (See the circled “Gas inlet” pipe in the bottom of Figure 2-22.)

The pressure in the specimen chamber (see “Gas inlet” in the bottom of Figure 2-22) is user-set, and affects the imaging conditions in the specimen chamber by affecting the amount of ionizing gas particles that are present (higher pressures allow for more gas particles to be present). The presence of gas in the ESEM ultimately has competing effects:

• In one respect, gas serves as the limiting feature of the ESEM; electrons from the beam may collide with the gas which affects the ESEM image by reducing image contrast due to beam broadening, or a skirt appearing about a beam in the image. High beam energy and low gas pressure combat beam broadening. Additionally, mounting the PLA even closer to the specimen reduces the Gas Path Length (GPL). Helium, due to its low atomic number, also prevents beam broadening, but it easily ionizes so may allow for sample charging [Danilatos 1993, Goldstein et al. 2003].

• In another respect, gas helps operation of the ESEM. The intent of placing gas in the chamber is to assist the imaging process. If the energy of the beam is four times the ionization energy of the bound outer electron of the gas particles, electrons will ionize the gas as they pass through. The ionized gas particles then adhere to the specimen surface (negative ions to positive regions of the specimen, and positive ions to negative) to prevent a buildup of charge on the specimen. (However, this advantage of having gas in the chamber is very unlikely to occur when the beam energy is much less or much greater than four times the ionization energy of the bound outer electron [Goldstein et al. 2003].) Regardless, it is frequently necessary when focusing an image and setting beam parameters to monitor the image for charging of the specimen.
2.3.3 Imaging Modes

Because the electron beam actually interacts with the topmost micron (depending on imaging mode, discussed below) of the specimen, the image represents not only surface features but also subsurface features such as inclusions, voids, and porosity. This accessibility of the subsurface results in a lower image resolution than the resolution defined by the beam parameters. The volume of the specimen with which the beam interacts is the “interaction volume” [Goldstein et al. 2003].

Electrons interact with the volume in various ways to result in the different imaging modes (Figure 2-20). Both the Backscattered and Secondary Electron imaging modes (BSE and SE, respectively, in Figure 2-20) were used in this study. Once the electrons from the beam (“Primary Electrons”; PE in Figure 2-20) enter the specimen, the positive charges in the nuclei of the specimen atoms attract the electron and redirect their otherwise straight trajectories. This occurrence is called “elastic scattering”. Specimens with a high atomic number induce more elastic scattering events. Once so much elastic scattering has occurred that the electron is deflected back out of the specimen, the electron is referred to as a “backscattered electron”. Additionally, the electron may transfer a lot of energy while traveling within the specimen; these electrons are detected as “secondary electrons”, or electrons with less than 50 eV of energy. Backscattered electrons are particularly well suited for the relatively high morphology of process zone areas imaged in this study because they must travel deep within the specimen compared to secondary electrons (Figure 2-20).

2.4 Definition of Terms

The definition of the following terms varies in the literature; they are here defined for the scope of this study. The main difference between the terms is the material to which they each apply; whereas “Process Zone” is used generally, “White Patching” applies to marble in particular.

**Process Zone:** In various types of brittle materials, the process zone is a zone of inelastic deformation at the tip of a propagating crack. The type of loading determines the nature of deformation. For this study, the white patching near the flaw tip is a process zone region. White patching
contains established process zone microstructural features [Wong 2008], but the nanomechanical properties of the region will provide new information on the process zone.

**White Patching:** In marble specifically, white patching is a zone of inelastic deformation at the tip of a propagating crack. The abundance of microcracks, spalling, and other microfeatures grant the region a white appearance.

### 2.5 Chapter Summary

This chapter has reviewed essential information on the subject and means of this investigation. The most important idea presented about the subject, fracture mechanics and its role in quasi-brittle materials, was shown by Wong [2008], Wong and Einstein [2009c;d]; the white patching which manifests at the tip of a crack prior to propagation shows microstructural evidence of being the manifestation of the FPZ. This white patching is the focus of this investigation. The key process zone ideas presented in this chapter, were the potential of finding a nanomechanical property change in marble similar to that found in a ceramic [Jones et al. 2007], and the tendency of quasi-brittle fracture to show an exponential increase in microcrack density within the process zone with closeness to the main crack or fault. The next chapter will detail the material of choice for this investigation, and discuss the experiments.
Chapter 3

Materials and Method

3.1 Materials

The marbles in this investigation are Carrara marble (quarried from the Carrara mines in northern Italy), and Danby marble (quarried from mines in Vermont, USA). This section reviews the coverage of these marbles in the literature, and covers their geology, deformation, fracture, and engineering applications.

3.1.1 Geology Studies

Regardless of the type of marble (Carrara, Danby, or other,) marble is a metamorphic rock. Metamorphic rocks form under extreme subterranean pressure and/or temperature conditions, which can drive moisture, oxygen, and carbon dioxide out of existing rocks. Marble typically forms from limestone or dolomite, both single-mineral sedimentary rocks. The varied colors of different types of marble are attributed to the parent rock from which they form. Marble is relatively soluble and supports vegetation. These properties complicate the quarrying, or marble extraction, process; the marble is thus often more vulnerable to chemical rather than mechanical weathering processes [Pough 1996]. This section discusses the geology of both Carrara and Danby marbles (Table 3.1).
Table 3.1: A compilation of studies of the geologic history and properties of both Carrara and Vermont marble.

<table>
<thead>
<tr>
<th>Authors and Date</th>
<th>Purpose</th>
<th>Technique</th>
<th>Relevant Findings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bain [1934]</td>
<td>To clarify the geology and structure of Vermont marbles</td>
<td>Observation by eye</td>
<td>Vermont marbles are composed of three structural units: unmetamorphosed sediments in the northern structural unit, fine-textured stone in open folds between thrust faults in the central structural unit, and medium to coarse-grained marble in complex flowage folds in the southern structural unit. The Danby quarry is in the southern unit.</td>
</tr>
<tr>
<td>Burlini and Kunze [2000]</td>
<td>To obtain the relationship between shape fabric and seismic anisotropy of a highly anisotropic mineral</td>
<td>Compressional wave velocity; Seismic wave velocity; Microscopy</td>
<td>Provided information on the anisotropy of Carrara marble protolith with respect to seismicity (in contrast, the current study investigates the anisotropy of Carrara marble with respect to mechanical properties). Carrara marble protolith has very little seismic anisotropy. The mylonite has seismic anisotropy that reduces with increased confining pressure. Thus, the seismic properties of the mylonite cannot be modeled simply as volume averages of the properties of its constituents.</td>
</tr>
<tr>
<td>Molli and Heilbronner [1999]</td>
<td>To understand naturally deformed Carrara marble microstructure (from recently discovered shear zones)</td>
<td>Microscopy</td>
<td>Microstructure study suggests more complete annealing (recovery after heating of deformed material) in Sample A, due to its larger grain size, random grain boundary orientation, and isotropic particle axes. Sample A (the sample used in my study) has an average grain size of 300 m.</td>
</tr>
</tbody>
</table>

Continued on next page
Table 3.1: A compilation of studies of the geologic history and properties of both Carrara and Vermont marble.

<table>
<thead>
<tr>
<th>Authors and Date</th>
<th>Purpose</th>
<th>Technique</th>
<th>Relevant Findings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molli et al. [2000]</td>
<td>To understand the microfabric</td>
<td>Microscopy</td>
<td>Two main microstructures (coarse 150-200 m; fine 40-50 m). Three main microfabrics: annealed with unimodal grain size distribution (my specimen), dynamically recrystallized, and twinned microfabric. The annealed microfabric was created during the static recrystallization phase of the geologic history.</td>
</tr>
<tr>
<td>Leiss and Molli [2003]</td>
<td>To study the (rarely observed) naturally deformed 'High-temperature' texture</td>
<td>Neutron diffraction; Microscopy</td>
<td>The 'High-temperature' texture in naturally deformed Carrara marble is characterized by two maxima on the c-axis, and 3 maxima on the r-axis. Related the texture to antiformal stacking in the geologic history of Carrara marble.</td>
</tr>
<tr>
<td>Molli et al. [2010]</td>
<td>To study a natural fault zone in Carrara marbles</td>
<td>Fracture trace mapping; Digital Imaging; Scan-Line Methods</td>
<td>The fault type is normal-oblique slip fault. The fault has four main regions: hanging wall damage zone, a 3-cm rim, the fault core, and the footwall damage zone. Carbon and oxygen isotopes suggest the role and type of fluids during the fault development. The damage zone microstructure suggests alternating brittle and crystal plastic deformation.</td>
</tr>
</tbody>
</table>

Carrara marble is a popular material used in experimental studies of the fracture behavior of geomaterials. The work of Molli, Leiss, and their colleagues [Leiss and Molli 2003, Molli and Heilbrunner 1999, Molli et al. 2000; 2010] have established the geologic history, and geologic properties of this widely-used material. Carrara Marble originates from the marble quarries near the town of Carrara, in the north-western part of the Alpi Apuane metamorphic complex in Italy (See the circle indicated in Figure 3-1). Typical material properties are displayed in Table 3.2.
Figure 3-1: The Alpi Apuane marble complex in northern Italy. The town of Carrara is circled on the left. Detail of the boxed inset is shown in Figure 3-2. From Molli et al. [2000].
Table 3.2: Typical properties of Carrara marble.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chief Constituents</td>
<td>Calcium Carbonate (CaCO₃)</td>
<td></td>
</tr>
<tr>
<td>Other Constituents</td>
<td>Organic Foliation, Quartz, Albite, White Mica, Opaque Minerals</td>
<td></td>
</tr>
<tr>
<td>Fabric</td>
<td>Homogenous; no preferred grain shape or crystallographic orientation</td>
<td></td>
</tr>
<tr>
<td>Grain Size</td>
<td>40-200μm</td>
<td>Molli et al. [2000]</td>
</tr>
<tr>
<td>Young’s Modulus, $E$</td>
<td>49 GPa</td>
<td>Wong [2008]</td>
</tr>
<tr>
<td>Poisson’s ratio, $\nu$</td>
<td>0.19</td>
<td>Wong [2008]</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.33 - 0.48%</td>
<td>Alber and Hauptfleisch [1999]</td>
</tr>
<tr>
<td>Uniaxial Compressive Strength, $\sigma_c$</td>
<td>84.63 MPa</td>
<td>Wong [2008]</td>
</tr>
<tr>
<td>Flexural Strength</td>
<td>13 MPa</td>
<td>Marini and Bellopede [2009]</td>
</tr>
<tr>
<td>Tensile Strength, $\sigma_{yt}$</td>
<td>3.32 to 5.86 MPa</td>
<td>Butenuth et al. [1993], Zhang [2002]</td>
</tr>
<tr>
<td>Fracture Toughness, $K_{fc}$</td>
<td>0.65 to 1.25MPa/$m$</td>
<td>Alber and Brardt [2003], Atkinson [1979]</td>
</tr>
</tbody>
</table>

Table 3.3: Typical properties of Danby marble.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chief Constituents</td>
<td>Calcium Carbonate (CaCO₃)</td>
<td></td>
</tr>
<tr>
<td>Other Constituents</td>
<td>Mg chlorite, muscovite, sphene, opaques</td>
<td></td>
</tr>
<tr>
<td>Fabric</td>
<td>non-directed</td>
<td>Spectrum Petrographics</td>
</tr>
<tr>
<td>Grain Size</td>
<td>500-1000 μm</td>
<td>Bain [1934]</td>
</tr>
<tr>
<td>Young’s Modulus, $E$</td>
<td>40-50 GPa</td>
<td>Harris [1975] (for Vermont marble)</td>
</tr>
<tr>
<td>Uniaxial Compressive Strength, $\sigma_c$</td>
<td>59 MPa</td>
<td>Corp. [2012]</td>
</tr>
<tr>
<td>Flexural Strength</td>
<td>13 MPa</td>
<td>Corp. [2012]</td>
</tr>
</tbody>
</table>
The constituents of this type of marble are tightly packed grains of calcium carbonate crystals. The grain sizes range from 40-200 \( \mu \text{m} \), and the rock mass is often interspersed with dark ribbons of mineralogical and organic foliation. Despite the relative purity of the marble, other minerals such as quartz, albite, white mica, and opaque minerals may be present. Nevertheless, the microstructure of the rock contributes to its historic popularity as an artistic and structural material. Carrara marble has a homogenous fabric and is composed almost entirely of pure calcite. No preferred grain shape or crystallographic orientation has been identified, contributing further to the homogeneity of the rock [Molli et al. 2000].

Molli and Heilbronner [1999] determined the grain sizes of Carrara marble by preparing thin sections of marble from various locations, hand tracing and digitally scanning the grain boundaries, then analyzing grain size distribution using NIH Image Software for pixel areas and grain perimeters, and StripStar for area correction. Grain shape and grain boundary smoothness were also analyzed. The three chief microfabrics of Carrara marble provide insight into the two geologic events that were involved in its creation.

Molli and Heilbronner [1999] studied the microstructure near and around the Carrara quarry to deduce the geologic events responsible for the formation of the quarry. (An additional study by Molli et al. [2010] details a normal-oblique slip fault in the region.) Type A microfabric, the type used in this investigation, is located in the normal limb of a northeast-facing isoclinal fold. The precise location of the marble used in this study is displayed in Figure 3-2. The grain shape of the Type A microfabric is equant polygonal with straight or slightly curved boundaries. The location
of the microfabric, the isoclinals fold, characterizes the first geologic event: nappe emplacement to develop isoclinal folds. Besides the Type A microfabric, two other microfabrics were identified nearby. Type B microfabric consists of a dynamically recrystallized microfabric, and references the end of the first geologic event: stacking after the nappe emplacement. Type C microfabric is a twinned microfabric, and suggests the second geologic event: deformation, in conjunction with folding and the development of shear zones.

To summarize the likely geologic history which created the three described microfabrics, after an early folding stage, thermal relaxation occurred, and then heating to statically recrystallize the rock and produce the annealed Type A microfabric. The change in grain size within the Type A microfabric, in conjunction with the random grain boundary orientation and isotropic particle axes, suggests that a portion of the fabric underwent more complete annealing (i.e., recovery after heating of deformed rock material) in the portion of the Type A microfabric with larger grains [Molli and Heilbronner 1999]. Stacking eventually re-worked the Type A microfabric into the dynamically recrystallized Type B microfabric. Finally, late deformation produced the twinned Type C microfabric [Molli et al. 2000].

Whereas microfabric describes the shape, arrangement and orientation of the grains, microstructure describes the size of the grains. Two main microstructures dominate the three microfabrics just described (A, B, and C): fine grains with a size of 40 to 50 μm (Figure 3-3), and coarse grains with a typical size of 150 to 200 μm (this microstructure corresponds with the material used in this investigation). The typical grain size of the Type A microfabric (used in this study) is large, 300 μm (D in the scale separability condition, Equation (2.37)). There is an increase in the grain
size from east (80 to 100 \( \mu \text{m} \)) to west (250 to 300 \( \mu \text{m} \)). Thus, the relatively pure and homogenous microstructure of Carrara marble makes the rock an interesting material for scientific research, especially in the area of rock mechanics [Molli et al. 2000].

Recent studies of Carrara marble have provided new insights on some unique aspects of the marble: the naturally deformed “High-Temperature” texture of Carrara marble, the fabric and seismic properties of Carrara marble mylonite and its protolith, and the geologic context of a fault through Carrara marble in the Alpi-Apuane complex. The “High-Temperature” texture [Leiss and Molli 2003] was studied with neutron diffraction, and its elongated grains mimic a texture developed in a pure-shear regime. Thus, it is posited that the high temperature texture has a weak simple shear component. The texture ultimately suggests antiformal stacking at a point in the geologic history (likely during the time the Type A microfabric was being reworked into Type B.)

Danby marble (typical properties displayed in Table 3.3) is quarried in Vermont, U.S.A., and available in ten different macroscopic texture classifications [Corp. 2012]. Most marbles in North America were formed by thermal metamorphism, when hot solutions of limestone flowed along bedding planes. Historically, during the creation of the Vermont marbles, noncalcareous elastic sediments buried pure limestones. Under the high pressure and temperature, the limestones became plastic and flowed towards the center of a deepening basin. These flows cracked beds of dolomite, and became solution channels for recrystallization, decolorization, and silication. Given this geologic history, Vermont marbles can be divided into three main structural units:

- The Northern zone, consisting of bituminous limestone and unmetamorphosed sediments.

- The Central zone, consisting of mixed white and gray marble. The marble in this region is fine-textured, and exists in open folds between thrust faults.

- The Southern zone, consisting of white calcite. The marble in this region is medium to coarse grained; the Danby quarry is in this zone.

Large flowage folds in the southern unit became beds thick enough to quarry. The Danby quarry (Figure 3-4) is in a Columbian deposit in the Southern unit which wraps from the east to the north slope of Dorset Mountain. The deposit has a roof composed of a dolomite bed, and has a typical
Figure 3-4: The geological layout of the quarry at Danby. The Brook marble deposit (at the top of the diagram) forms the roof of a dolomite bed. Figure from Bain [1934].

grain size of 1 mm in thick beds to 500 μm in thin beds; the crystal size increases as the beds thicken (see Figure 3-4) [Bain 1934].

3.1.2 Deformation Studies

Quite substantial work has been done to understand the deformation behavior of Danby and Carrara marble (Table 3.4). These experiments involve observing the microstructure of the marbles subjected to high temperatures and pressures, such that plastic deformation mechanisms of the marbles are activated. Brace [1965], Wong and Brace [1979] have explored the linear and volume compressibility of Danby marble, as well as its thermal expansion (slope of temperature-strain curve). They found that for a rock with constituent properties $V_a, V_b, V_c$ and $\beta_a, \beta_b, \beta_c$ (volume percentage and volume compressibilities of minerals $a, b,$ and $c$, respectively), the average of the
Voigt bound of compressibility, $\beta_R$:

$$\beta_R = V_a\beta_a + V_b\beta_b + V_c\beta_c + ...$$  

(3.1)

and Reuss bound of compressibility, $\beta_V$:

$$\frac{1}{\beta_V} = \frac{V_a}{\beta_a} + \frac{V_b}{\beta_b} + \frac{V_c}{\beta_c} + ...$$  

(3.2)

provides a good approximation of the compressibility measured in lab for the bulk rock. Danby marble exhibited a volume compressibility of $8.7 \text{ mb}^{-1}$ when measured at low pressure, and substantially lower volume compressibility (between 1 and 2 mb$^{-1}$) when measured at higher pressure [Brace 1965]. Wong and Brace [1979] found that unlike compressibility, especially for Danby marble, thermal expansion measured in the laboratory differed substantially from thermal expansions calculated from the thermal expansions, stiffnesses, and volume fractions of the constituents of a rock. They postulated that this difference arose from the highly anisotropic nature of Danby marble, and also the hypothesis that thermal cycling changes the geometry of existing cracks in a rock, and thus changes the response of the rock to further thermal cycling.
Table 3.4: A compilation of studies of deformation of marble.

<table>
<thead>
<tr>
<th>Authors and Date</th>
<th>Purpose</th>
<th>Material</th>
<th>Technique</th>
<th>Relevant Findings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brace [1965]</td>
<td>To understand the link between the compressibility of mineral constituents and bulk compressibility of a rock</td>
<td>10 rocks (including Danby marble)</td>
<td>Triaxial apparatus</td>
<td>Most rocks exhibited anisotropy at low pressures, more isotropic linear compressibility at high pressures; likely due to closure of cracks and porosity. Most rocks have slight reduction in volume compressibility with increased pressure. Averaging the Voigt and Reuss bounds of compressibility calculated from mineral constituents is a good approximation of volume compressibility for a rock; Danby marble has grain size of 200 μm, and a volume compressibility around 8.7 Mb⁻¹ (with no confinement).</td>
</tr>
<tr>
<td>Wong and Brace [1979]</td>
<td>To understand thermal expansion of rocks at pressures greater than room pressure</td>
<td>6 rocks (including Danby marble)</td>
<td>Triaxial apparatus (heated)</td>
<td>Above a critical pressure, thermal expansion (slope of temperature-strain curve) is reversible and constant (i.e., linear slope). This critical pressure depends heavily on the thermal history of the rock; thermal cycling may widen the cracks that control this behavior. Danby marble is anisotropic (because the thermal expansion of calcite is anisotropic), so its measured thermal expansion (5.5×10⁻⁶/°C) differs from that calculated from the single crystal thermal expansion and stiffness.</td>
</tr>
</tbody>
</table>

Continued on next page
Table 3.4: A compilation of studies of deformation of marble.

<table>
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<tr>
<th>Authors and Date</th>
<th>Purpose</th>
<th>Material</th>
<th>Technique</th>
<th>Relevant Findings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fredrich and Evans [1989]</td>
<td>To monitor deformation mechanisms (especially at the transition to plastic behavior)</td>
<td>Carrara marble</td>
<td>Triaxial apparatus; Microscopy</td>
<td>Localized deformation (microcracking, twinning) for confining pressure $P_c &lt; 30$ MPa. Some plastic deformation mechanisms (microcracking, twinning, dislocation glide) above $30$ MPa. A greater portion of energy is dissipated through frictional sliding in the brittle regime than in the semibrittle regime. Can find evidence of interaction between brittle and plastic deformation mechanisms (i.e., between microcracks and twins/dislocation glide).</td>
</tr>
<tr>
<td>Fredrich et al. [1990]</td>
<td>To obtain relationship between grain size and other mechanical properties</td>
<td>3 marbles (including Carrara marble and Solnhofen limestone)</td>
<td>Triaxial apparatus; Microscopy</td>
<td>The confining pressure $P_c$ at the brittle-ductile transition (when twinning/dislocation glide starts to occur) is inversely proportional to grain size, for a tested $P_c$ range of 5 to 450 MPa. The Ashby/Hallam model predicts a non-linear Hall-Petch relation when the initial crack density is varied, so there must be a relationship between grain size $d$ and some OTHER property besides initial flaw size $c$. Experiments show a relationship between shear yield stress and $d$.</td>
</tr>
</tbody>
</table>

Continued on next page
Table 3.4: A compilation of studies of deformation of marble.

<table>
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<tr>
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<th>Technique</th>
<th>Relevant Findings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barnhoorn et al. [2004]</td>
<td>To understand the influence of high shear strain on Carrara marble at low temperatures and constant strain rates</td>
<td>Carrara marble</td>
<td>Torsion apparatus; microscopy</td>
<td>For a tested temperature range of 500 to 727°C and confining pressure of 300 MPa, the main deformation mechanisms were plastic (slip and climb of dislocations). After a critical shear strain is reached, the marble exhibits weakening and recrystallization. Two main crystallographic preferred orientations (CPO); one at low shear strain, and one at high shear strain due to the interaction of different slip systems.</td>
</tr>
<tr>
<td>Bresser et al. [2005]</td>
<td>To understand the role of water in high-temperature deformation of marble</td>
<td>Carrara marble</td>
<td>Triaxial apparatus (heated); microscopy</td>
<td>Water has a small effect on the mechanical behavior and microstructure of calcite at high temperatures. Does enhance grain boundary mobility (and may affect location or shape of dislocations, and thus also affect recovery processes), and contribute to a slight weakening of calcite at 600°C, and more weakening at 700°C.</td>
</tr>
</tbody>
</table>

Fredrich and Evans [1989] have approached deformation of Carrara marble by studying the brittle to plastic transition in Carrara marble. This work has geological implications, because it is thought that the seismic activity in the Earth is limited by deformation mechanisms beyond a certain depth (and therefore, pressure). They found that below a confining pressure of 30 MPa, the deformation of Carrara marble was localized, and consisted of microcracking and twinning. Above a confining pressure of 30 MPa, the deformation mechanisms included microcracking, twinning, and dislocation glide. Moreover, evidence of interaction between the brittle and duc-
In this image from Fredrich and Evans [1989], a twin (labelled “T”) is slightly wider above and slightly narrower below a microcrack (labelled “C”). The image illustrates the complex nature of marble deformation; deformation mechanisms may interact.

tile deformation mechanisms (i.e., between microcracks and twinning or dislocation glide) was found. Barnhoorn et al. [2004] found similar deformation mechanisms (dislocation slip and climb) in high-strain torsion experiments on Carrara marble (Figure 3-6). The work found two main crystallographic preferred orientations (CPO): one at low shear strains, and one at high shear strain due to the interaction of different slip systems. Yang et al. [2008] found that grain size played a role in the deformation of Chinese marble with pre-existing cracks; although medium-grained marbles showed a relation between flaw geometry and strength, coarse grained marble did not show such a relationship for the confining pressures investigated in their study. Fredrich et al. [1990] considered the effect of grain size on deformation of Carrara marble, and found that the confining pressure at which twinning/dislocation glide started to occur — that is, the confining pressure at the brittle to ductile transition — was inversely proportional to grain size. When attempting to explain this behavior through the use of the Ashby/Hallam model (a relation which determines $K_I$ at the tip of a wing crack, based on initial damage or crack density), they found a non-linear Hall-Petch relation when the initial crack density was varied, and concluded that a factor other than grain size (and thus, initial flaw size) controlled the fracture. Bresser et al. [2005] investigated the role of water in the deformation of Carrara marble, and found that Carrara marble samples containing moisture exhibited slightly weaker behavior at high temperatures. They hypothesized that the presence of water enhances grain boundary mobility, and may affect the location or shape of dislocations, and
Figure 3-6: This image, from Barnhoorn et al. [2004], shows thin section photographs (in cross-polarized transmitted light) from different Carrara marble specimens deformed to varying shear strains $\gamma$ at a temperature of 600°C. The central diagrams above the shear strain $\gamma$ indicate an undeformed circle and the simple shear ellipse. The figure indicates that recrystallization increases with increased shear strain $\gamma$. Note that images E and F show nearly 85% recrystallization, whereas images G and H show nearly 100% recrystallization.
thus makes it easier for deformation to occur.

3.1.3 Fracture Studies

Marble is a popular test material for the study of the fracture of quasi-brittle materials (Table 3.5). One of the most popular techniques is to generate fracture in either a precracked or a flaw-free specimen, and to observe the resulting fracture pattern at either the macroscale, the microscale, or both. The most comprehensive work on the fracture of both pre-cracked and intact marble was conducted by Wong and colleagues [Wong and Einstein 2009a;c;d]; indeed, this work (and one of Wong’s samples) formed the foundation of this current study.

Table 3.5: A compilation of fracture studies on marble.

<table>
<thead>
<tr>
<th>Authors and Date</th>
<th>Type of Marble</th>
<th>Technique</th>
<th>Relevant Findings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Harris [1975]</td>
<td>Vermont</td>
<td>McCartney System (Water Jet)</td>
<td>Cut Vermont marble at traverse speeds from 0.012 to 5.34 ft/sec, pressures ranging from 5000 to 30,000 lbf/in², and both still and rotating Water Jet nozzle. Marble spalls at low penetration. For each speed, there is a single pressure with minimum specific energy. This minimum specific energy is desireable when cutting marble because that means spalling will be minimum. The rotating nozzle has the same specific energy as the still.</td>
</tr>
<tr>
<td>Atkinson [1979]</td>
<td>Carrara (+ Tennessee Sandstone)</td>
<td>Double torsion fracture toughness method (loading a notched specimen on top of and perpendicular to the notch)</td>
<td>The double torsion method easily generates a Mode I crack in a quasi-brittle material. Found $K_{IC}$, Carrara Marble = 0.644 + 0.021 MPa$\sqrt{m}$. Agrees with values from other studies.</td>
</tr>
</tbody>
</table>

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</tr>
</thead>
<tbody>
<tr>
<td>Lu and Jackson [1998]</td>
<td>Carrara</td>
<td>Forced torsional apparatus; optical microscope</td>
<td>Torsion tests conducted at temperatures from room temperature up to 560°C. Thermal cracking during the first thermal cycle likely modified the G (shear modulus) and Q (internal friction) relationship with temperature in later cycles by allowing more plastic deformation in later cycles. In low porosity rocks, elastic modulus is affected by Budiansky/O’Connel crack density parameter, which changes with thermal cycling.</td>
</tr>
<tr>
<td>Alber and Hauptfleisch [1999]</td>
<td>Carrara</td>
<td>Triaxial apparatus; microscopy</td>
<td>Applied various differential stress levels (60-90 MPa) under constant confinement of 2MPa to generate microcracking. Stained, and then scanned samples to obtain fracture pattern, then back-calculated fracture properties (GIC, etc) from the fracture locations and material properties.</td>
</tr>
<tr>
<td>Monteiro et al. [2001]</td>
<td>Vermont, Italian, Chinese, and Georgia</td>
<td>Four-point bending</td>
<td>Four point bend tests conducted with loading rates ranging from $2.14 \times 10^{-3}$ to 21.4 MPa/s, with the highest loads delivered with a 220-kN capacity load cell. Derived both linear and non-linear strength vs loading rate relations for four types of marble. Tightly interlocked (xenoblastic) marble is more sensitive to loading rate – Vermont and Georgia marble. Likely because for such grains, it's harder for fracture to go around grains (i.e., through boundaries), and must instead go through grains.</td>
</tr>
</tbody>
</table>

*Continued on next page*
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<th>Technique</th>
<th>Relevant Findings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wong and Einstein [2009c]</td>
<td>Carrara (+ Molded Gypsum)</td>
<td>Uniaxial machine; high-speed camera</td>
<td>Identified nine crack coalescence categories, distinguished by crack types and trajectories.</td>
</tr>
<tr>
<td>Wong and Einstein [2009d]</td>
<td>Carrara (+ Molded Gypsum)</td>
<td>Uniaxial machine; high-speed camera</td>
<td>Found that the white patching in marble is associated with zones of micro-cracking, and thus process zones. Did not find similar process zone behavior in gypsum.</td>
</tr>
<tr>
<td>Wong and Einstein [2009a]</td>
<td>Carrara</td>
<td>Uniaxial machine; high-speed camera</td>
<td>Tensile wing cracks are always the first cracks to appear. Secondary cracks are tensile or shear cracks. Developed a reclassification of rock crack types; high speed camera allowed definitive determination of whether cracks are opening in tension or shear.</td>
</tr>
<tr>
<td>Yang et al. [2009]</td>
<td>Chinese, from eastern ground (grain size = 1.5-2 mm)</td>
<td>Uniaxial machine (displacement control); digital photography</td>
<td>Tests were conducted with maximum load capacity of 1000 kN and maximum displacement capacity of 5mm, for core specimens with 50mm diameter and 100mm height. Intact marble cores tend to fail axially, by splitting. Flawed samples exhibit lower peak stress, lower modulus, and lower modulus at 50% strain. 8 main crack types found; the rock failure is a combination of one or more crack types. (Types I, II, and III are typically first to appear; Types I and III can support load after peak stress.)</td>
</tr>
</tbody>
</table>

Continued on next page
Table 3.5: A compilation of fracture studies on marble.

<table>
<thead>
<tr>
<th>Authors and Date</th>
<th>Type of Marble</th>
<th>Technique</th>
<th>Relevant Findings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Luque et al. [2011]</td>
<td>White Macael, Tranco Macael, and Yellow Triana Macael from Comarca del Marmol, Almeria, Spain</td>
<td>Ultrasonic pulse velocity; mercury intrusion porosimetry; Arorption; hot-stage environmental scanning electron microscopy (ESEM)</td>
<td>Microcracking was monitored via porosity changes, and ESEM. All marbles exhibited an increase in porosity (by as much as 50% in one marble type, from a porosity of 0.41 to 0.67) after thermal cycling. The marble with the largest grain size had an increase in the number of large pores after thermal cycling. Results suggest that thermal cycling has the greatest porosity effect on marbles with a large grain size, well-developed crystals, straight grain boundaries. It’s hard for equidimensional grains to rearrange (and recover their initial positions) during/after thermal cycling. The marbles recovered differently after thermal cycling.</td>
</tr>
<tr>
<td>Bandini et al. [2012]</td>
<td>San Vincenzo</td>
<td>Continuous stiffness measurements (CSM; nanoindentation with an imposed frequency)</td>
<td>Grains of a calcitic rock will fracture around high-load indents (&gt; 3mN) along their cleavage planes, regardless of the orientation/type of indentation. Indentation modulus varies with rock texture (xenoblastic or granoblastic) for indentation depth h &lt; 200 nm.</td>
</tr>
</tbody>
</table>

A unique aspect of Wong’s work was the use of a high-speed camera to capture the initial nature of rock fracture (i.e., the sequence of crack occurrence, and the motion of the crack faces.) The high-speed camera allowed for a precise understanding of the fracture of the marble and gypsum samples in the investigation. Wong identified nine crack coalescence categories for marble and gypsum in unconfined compression (Table 3-7, from [Wong and Einstein 2009c]. Wong also was the first to identify and intensively investigate “white patching”, or a brightening of the marble at the macroscale just before fracture. Wong investigated white patching with SEM, and found
The nine crack coalescence categories identified by Wong, from [Wong and Einstein 2009c].

<table>
<thead>
<tr>
<th>Category</th>
<th>Coalescence patterns</th>
<th>Crack types involved</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image" alt="No coalescence" /></td>
<td>No coalescence</td>
</tr>
<tr>
<td>2</td>
<td><img src="image" alt="Indirect coalescence by two or multiple cracks" /></td>
<td>Indirect coalescence by two or multiple cracks (crack types vary)</td>
</tr>
<tr>
<td>3</td>
<td><img src="image" alt="Type 2 S crack(s)" /></td>
<td>Type 2 S crack(s)</td>
</tr>
<tr>
<td>4</td>
<td><img src="image" alt="Type 1 S crack(s)" /></td>
<td>Type 1 S crack(s)</td>
</tr>
<tr>
<td>5</td>
<td><img src="image" alt="One or more type 2 S crack(s) and type 2 T crack segments between inner flaw tips" /></td>
<td>One or more type 2 S crack(s) and type 2 T crack segments between inner flaw tips</td>
</tr>
<tr>
<td>6</td>
<td><img src="image" alt="Type 2 T crack(s). There may be occasional short S segments present along the coalescence crack." /></td>
<td>Type 2 T crack(s). There may be occasional short S segments present along the coalescence crack.</td>
</tr>
<tr>
<td>7</td>
<td><img src="image" alt="Type 1 T crack(s)" /></td>
<td>Type 1 T crack(s)</td>
</tr>
<tr>
<td>8</td>
<td><img src="image" alt="Flaw tips at the same side linked up by T crack(s) not displaying wing appearance (crack type not classified). There may be occasional short S segments present along the coalescence crack." /></td>
<td>Flaw tips at the same side linked up by T crack(s) not displaying wing appearance (crack type not classified). There may be occasional short S segments present along the coalescence crack.</td>
</tr>
<tr>
<td>9</td>
<td><img src="image" alt="Type 3 T crack(s) linking right tip of the top flaw and left tip of the bottom flaw. There may be occasional short S segments present along the coalescence crack." /></td>
<td>Type 3 T crack(s) linking right tip of the top flaw and left tip of the bottom flaw. There may be occasional short S segments present along the coalescence crack.</td>
</tr>
</tbody>
</table>

Figure 3-7: The nine crack coalescence categories identified by Wong, from [Wong and Einstein 2009c].
that zones of qualitatively high microcracking were flanked by zones of progressively qualitatively lower microcracking. This investigation builds upon Wong's foundational work by pursuing the mechanical properties of white patching, and by quantitatively describing the crack density of the white patching. Later work by Yang et al. [2009] applied a similar approach as Wong to the fracture of Eastern Chinese marble. The geometry of the samples (cylindrical) and flaws allowed them to investigate rock fracture in three dimensions; Yang developed a similar crack classification scheme, which consisted of eight types of cracks.

Many studies have pursued the fracture toughness of Carrara marble. Atkinson [1979] developed a double-torsion method to obtain fracture toughness, a novel technique for developing a Mode I crack in a very brittle material. He found a fracture toughness of Carrara marble to be near 0.64 MPa√m. Alber and Hauptfleisch [1999] took a unique approach to deriving fracture toughness by fracturing Carrara under a confining pressure, staining the fracture surface, and using the geometry of the stained surface to back-calculate fracture energy $G$ and eventually fracture toughness.

Vermont marble has been used to study fracture to a lesser extent than Carrara marble. Harris [1975] presented an early study of the effectiveness of a water jet in cutting Vermont marble, and found that low penetration depths initiated material spalling and compromised the quality of the jet cut. Harris suggested that cuts with a minimum specific energy would present the best cut, and that for a given traverse speed, there existed a small range of cutting pressures that would yield that ideal cut with minimum specific energy. As explained in Section 3.2.2, water jet cutting was an ideal means of cutting both marbles in this investigation, but it was necessary to experiment to find ideal cutting parameters with minimal spalling. Additionally, Monteiro et al. [2001] conducted four-point bending tests on a variety of marbles, including Vermont marble, and derived a relationship between strength and loading rate. Monteiro found that marbles with tightly interlocked grains, such as Vermont marble, were much more sensitive to loading rate, likely because it was more difficult for microcracks to travel around grain boundaries than through the grains themselves.

Finally, an interesting realm of marble fracture literature is devoted to the microcracks which develop during thermal cycling [Lu and Jackson 1998, Luque et al. 2011]. One of the reasons
thermal fracture arises in calcitic marbles is due to the strong thermal anisotropy of calcite. In a bulk marble block with calcite crystals in all different orientations, thermal cycling will cause the calcite crystals to expand and contract in all different directions, and induce microcracking in the block. Microcracks from thermal cycling are of critical importance to any engineering applications of marble, which are discussed in the next section.

3.1.4 Engineering Applications

Studies indicate three chief engineering applications of Carrara marble: as a structural material [Renwick 1909, Stamper 2005, Ward-Perkins 2003], as monuments such as tomb headstones [Garzonio 1995, Siegesmund et al. 2010], and as building veneers [Logan et al. 1993, Winkler 1996] (Table 3.6).

Table 3.6: A compilation of engineering applications of marble.

<table>
<thead>
<tr>
<th>Authors and Date</th>
<th>Type of Marble</th>
<th>Engineering Application</th>
<th>Relevant Findings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stamper [2005], Ward-Perkins [2003]</td>
<td>Carrara</td>
<td>Structural Material</td>
<td>The Temple of Apollo Palatinus (36 B.C.) was built of Carrara marble (the walls were solid marble.).</td>
</tr>
<tr>
<td>Renwick [1909]</td>
<td>Carrara</td>
<td>Structural Material</td>
<td>The London “Marble Arch” was made of Carrara marble.</td>
</tr>
<tr>
<td>Logan et al. [1993]</td>
<td>Carrara</td>
<td>Building Veneer</td>
<td>Two-step theory of bowing marble slabs: Thermal cycling induced differential expansion, then strain under the marble’s self weight weakened the slabs even further and allowed for the bowing. (The thermal cycling alone could not induce the observed degree of bowing, even under extreme temperature fluctuations.) The role of moisture must be further investigated.</td>
</tr>
</tbody>
</table>

Continued on next page
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<th>Engineering Application</th>
<th>Relevant Findings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Garzonio [1995]</td>
<td>Carrara, Veined Carrara (&quot;Venutino&quot;)</td>
<td>Building Veneer; Headstones</td>
<td>Marble strained approx 3.5% during creep tests. Degree of weathering plays a significant role in creep behavior of marble. Veined marble has weaker mechanical properties (Unconfined Compressive Strength, Young’s Modulus)</td>
</tr>
<tr>
<td>Winkler [1996]</td>
<td>Carrara</td>
<td>Headstones</td>
<td>Some observation on locations of convex/concave bowing with respect to tomb in New Orleans. The granoblastic fabric of Carrara marble allows for easy sliding along grain boundaries to accommodate thermal expansion; rocks with more xenoblastic fabrics dilate less.</td>
</tr>
<tr>
<td>Siegesmund et al. [2010]</td>
<td>Carrara</td>
<td>Headstones</td>
<td>Fission tracking and geochemical analysis suggest that the marble in the cemetery is Carrara marble. Ultrasonic pulse velocity measurements suggest that pulse velocity decreases as the stone dries, and decreases in the interior of the stone. Drilling resistance decreases in the interior of the stone. There is likely higher degradation in the interior of the stone monuments. Dolomite marbles are more resistant to thermal weathering than other marble types.</td>
</tr>
</tbody>
</table>

Due to its great expense, Carrara marble found relatively little use as a chief structural component. Some exceptions of its use as a structural material are columns, capitals, pavements, and entablatures. Additionally, the walls of the Temple of Apollo are solid marble, and the London “Marble Arch” is made of Carrara marble Renwick [1909], Stamper [2005], Ward-Perkins [2003]. However, a major concern with engineering applications of Carrara marble is the behavior of the marble after it has been subject to weathering. A comprehensive damage study by Siegesmund
et al. [2010] of headstones placed four centuries ago in a Jewish cemetery in Germany found that
the stones were weakest in their interior. Both ultrasonic pulse velocity and drilling resistance
measurements confirmed this. The stones even showed concentric cracks initiated during nearby
bombing in the first World War. The study concluded that the thermal anisotropy of calcite con-
tributed greatly to its low weathering resistance, and suggested that dolomite-heavy marbles would
better survive environmental weathering. Garzonio [1995] studied the creep behavior of both mar-
ble which had undergone different degrees of weathering (a 200-year old slab from the face of
an Italian college, and 50 and 62-year old slabs from cemeteries in Florence), and found that the
degree of physical-mechanical-petrographic weathering affected the creep constant of the marble.
Indeed, long-term deformation seemed to be a critical factor in a comprehensive study of the slabs
on the face of Chicago’s Amoco Building by Logan et al. [1993]. These Carrara marble slabs ex-
hibited significant bowing less than two decades after their installation. One slab fell and crashed
into a nearby building, and all the slabs were replaced. Logan found that thermal cycling alone
could not account for the significant bowing identified in the slabs, and proposed a two-step, cyclic
theory of the bowing: the marbles first lost strength due to thermal fluctuations and subsequent
fatigue and failure of grain boundaries, and then the weakened marble released residual strain,
elongated, and weakened even further. Thus, although temperature fluctuations play a great role
in the concerns of marble engineering applications, small-scale cracking is at the heart of those
temperature fluctuations. An understanding of small-scale cracking of marble is at the heart of this
thesis.

3.2 Method

This study seeks to understand the mechanisms which drive the fracture of quasi-brittle materi-
als, and the role that material microstructure plays in that fracture. This understanding rests in
the microstructure and small-scale mechanical and fracture properties of intact and process zone
quasi-brittle materials. Thus, the very core of the experimental investigation is the monitoring of
the microstructure and grain-scale properties of elasticity, strength, and fracture toughness. Five
techniques are used to obtain these microproperties and relate them to macroscale crack initiation:

1. Tensile Strength Testing, to obtain tensile strength as an input to the process zone size relation (Equation 2.19),

2. Digital Photography and High-Speed Videography, to visually assess macrostructure and crack formation,

3. Optical and Environmental Scanning Electron Microscopy (ESEM), to visually assess microstructure,

4. Nanoindentation, to yield grain-scale mechanical properties of indentation modulus and indentation hardness, and

5. Nanoscratching, to understand fracture of quasi-brittle materials at the grain scale.

The techniques collectively assess cracking of a particular brittle material, marble, from the macroscale through the microscale, and link directly with previous work by Wong [Wong and Einstein 2009c;d]. Whereas Wong visually related macroscale cracking behavior with the initiation and propagation of cracks at the microscale, this investigation delves deeper into the microscale by directly accessing material mechanics and fracture properties at this scale.

### 3.2.1 Direct Tensile Test

Tensile testing contributes to the current investigation of the FPZ chiefly by providing an approximation of the yield strength in tension used to determine the size of the FPZ in Equation 2.19. When loaded in tension, quasi-brittle materials exhibit yielding at a stress extremely close to their failure stress in yielding (see Figure 3-8, and note that no yield point is apparent in the tensile testing of gypsum, a quasi-brittle material)); thus the tensile strength of a quasi-brittle material is a good approximation of its strength in tension.

Additionally, the test qualitatively describes the fracture behavior of a quasi-brittle material in tension. The FPZ's formed throughout this investigation are formed for a Mode I-II crack in
compression (discussed in Section 3.2.2), but much of the FPZ theory presented in Chapter 2 is derived for a crack in tension. Tensile testing will reveal any qualitative behavioral differences in the way marble fractures for a Mode I-II crack in compression, and the way marble fractures under direct tension. These differences (or lack thereof) will reveal the appropriateness of applying classic fracture theory to the Mode I-II cracks in this investigation. In other words, understanding the true tensile behavior of the materials in this investigation will reveal any qualitative conflicts between the compressive FPZ in this study and the tensile FPZ in classical FPZ theory.

This section explains how tensile testing was conducted for this investigation. It begins with a review of popular tensile testing techniques, presents the precise specimen and equipment details, and provides the testing protocol.

**Existing Methods of Tensile Testing**

The International Society for Rock Mechanics Commission on Standardization of Laboratory and Field Testing suggests two methods for determining the tensile strength of rock materials: a direct
tensile test, and a Brazil test [for Rock Mechanics Commission on Standardization of Laboratory and Testing 1978]. The direct tensile test proposes pulling on a cylindrical sample cemented between two cylindrical metal caps. (The American Society of Testing Materials suggests a similar method in International [2008].) The Brazil test proposes loading a disc with a central notch to generate a crack that opens in tension from the notch.

Although the specimen used in the Brazil test geometrically mimics the mixed-mode flaw geometry used on specimens throughout the study (see Section 3.2.2), the direct tensile test is the basis for the tensile technique used in this study. The selection of the direct tensile test is due to the fact that this test induces a completely tensile stress state in the specimens. The direct tensile test is typically performed with cylindrical specimens. This technique has the disadvantage that the location of the tensile failure is often close to or at the interface between the caps and the specimen, and does therefore not represent the actual tensile strength. Dogbone-shaped specimens avoid this problem. For this reason, dogbone specimens (Figure 3-9) were used rather than cylindrical specimens; the design made it likely for the specimen to break in the center where the specimen is most narrow. The flat-front dogbone design was based on dogbone specimen designs recommended in ASTM Standard D638-10: Standard Test Method for Tensile Properties of Plastics ASTM [2010] (Figure 3-9a). The details of the specimen design are presented in the next section.

**Specimen Preparation**

Dogbone specimens (Figure 3-9b) were cut on the OMAX©Water Jet (Figure 3-10). The Water Jet operates by emitting a high-pressure stream of water and garnet, an abrasive, at a user-selected rate and trajectory. This cutting method also induces a relatively small amount of stress in the specimen. Danby marble was subject to spalling due to the high pressure of the Water Jet at Jet entry and/or exit sites (Figure 3-11). Harris [1975] experienced a similar problem in his study on using water jets to cut Vermont marble, and attributed the phenomenon to the relationship between pressure and specific energy for a given water jet traverse speed. Harris’ study suggested that water jet parameters should be carefully selected when cutting Vermont marble, thus, in this investigation, it was found that the ideal Water Jet environment for cutting Danby marble consisted
(a) Possible specimen dimensions for plastic tensile specimens, from International [2008].

(b) Final specimen design in OMAX® design software. Each grid square is 1"x1".

(c) 3D sketch of final specimen design in AutoCAD®.

(d) Actual marble specimen, after cutting.

Figure 3-9: Evolution of tensile specimen design.
Figure 3-10: OMAX® Water Jet, with close-up of specimen in tank and on top of rubber matting. The position of the specimen may be fixed with a Quick Clamp between the specimen and the tank walls, as indicated by the thick white arrow.

(a) Image of spalling of Danby marble at both the front and back of the material when cutting parameters are poorly chosen. Flaw is approximately 0.5"; spalling is indicated with arrows.

(b) Image of marble after cutting with ideal cutting conditions. The spalling is significantly reduced.

Figure 3-11: Danby marble was subject to spalling in the Water Jet.
Positioning Danby marble specimens over a thin metal sheet minimized spalling when cutting.

of the following parameters (Figure 3-11b):

- Positioning the specimen over a relatively clean, undamaged portion of the rubber matting of the water jet (Figures 3-10 and 3-12),

- Placing a thin sheet of metal beneath the specimen (Figure 3-12),

- Assuring that the specimen will not move during cutting (this can be achieved by weighting the specimen on the sides with either heavy lead blocks, or quick clamps braced between the specimen and the walls of the Water Jet tank (Figure 3-10),

- Ignoring the OMAX©Software suggestions for cutting brittle material (i.e., do not check the checkboxes labeled “Very Brittle Material” and “Use Drill to Pierce”).

Thus, an ideal cut was obtained by placing the specimen over both an unflawed region of matting in the Water Jet and a thin sheet of metal (Figure 3-12), and cutting with a quality of “Minimum Taper” and a custom machinability of 330. “Quality” is an OMAX©water jet parameter which describes how quickly the jet moves while cutting a part. The higher the quality, the slower the jet moves. 5 is the maximum quality designation; the “Minimum Taper” setting, however, will
often slow the jet motion even more than a quality of 5. “Machinability” is a number from 0 to above 6100 which describes how easy it is to machine, or cut through, a material. The higher the machinability, the easier it is to machine the material.

Other possible OMAX® specimen setups were investigated. These setups had worked well for other, non-marble materials; the setups included covering the pierce site (i.e., the precise location where the jet first cuts through the specimen) with aluminum tape, covering the pierce site with standard adhesive tape, and placing the metal sheet on top of the specimen rather than under the specimen. The setup described in the itemized list above yielded the best results (i.e., minimal spalling) for Danby Marble.

The final Danby marble dogbone specimens had a height of 3”, narrowed by 50% width (from a width of 1.5” to a width of 0.75”) at the dogbone center, and maintained the same thickness of 1.5” (Figure 3-9d). Any irregularities along the specimen boundaries were removed with sanding by either an orbital sander or hand.

**Testing Equipment**

When performing a direct tensile test, it is extremely important to apply the load as close as possible along the central axis of the specimen. Thus, it was necessary to use special equipment – top and bottom specimen plates, metal side plates, and angle blocks – to ensure that the line of the load fell along the central axis of the specimen. The specimen plates were designed and employed by Wang [1989] and Pheeraphan [1993], but the details of application of the dogbone specimens as discussed below were unique to this investigation.

The specimen was epoxied with a 4-hour epoxy (Loctite Hysol E-30CL) between two 4”x4”x0.5” steel plates. Epoxying the specimen between these two plates was actually a detailed, multi-step process; these steps are outlined below, and displayed in Figure 3-13:

1. An acrylic Epoxy Reservoir (simply four walls of acrylic adhered at their ends with cyanoacrylate) was first epoxied to one steel plate and allowed to cure for 24 hours. This reservoir served to inhibit flow of the epoxy away from the specimen (Figure 3-14).
Figure 3-13: The multiple steps involved in epoxying a tensile specimen between two 4”x4”x0.5” steel plates. Step 4 also shows the heavy angle blocks used to align the specimen with the steel plates.
2. Then the specimen was epoxied to the bottom plate and left to cure for 24 hours.

3. Next, an Epoxy Reservoir was epoxied to the top plate and allowed to cure for 24 hours.

4. Finally, the specimen was flipped over and epoxied to the top plate and allowed to cure for 24 hours (Figure 3-15). The alignment of the top and bottom plates in both x-, y-, and z- directions was critical to both fitting the specimen in the machine and to ensuring load application along the desired central axis of the specimen.

In order to achieve the alignment discussed in Step 4, the final curing setup (i.e., the curing of the specimen to the top plate) consisted of resting the bottom plate on two metal walls of the same height with top and bottom parallel, and of squaring both the top and bottom plates with two 10-lb angle blocks at right angles (Figures 3-16)

When the setting specimen was squared against the metal side plates and angle blocks, it was essential that there was virtually no seam between the top and bottom plates and the angle blocks (Figures 3-13 and 3-17.) In order to ensure that there was no seam between the top and bottom plates and the angle blocks, the plates are pushed first against one angle block, and then against the other. When the plates and blocks are not flush, a “ding” will be heard (Figure 3-18) as the plate is pressed against the block. When the plates and blocks are completely flush, no “ding” will be heard. This sound test was used to ensure the plates and blocks were as flush as possible; the seam
Figure 3-15: Schematic (designed in AutoCAD®) after Step 4, from Figure 3-13, before aligning with angle blocks. Alignment with angle blocks shown in Figure 3-16. The epoxy reservoir is not shown in this schematic, but it can be seen in Figures 3-13 (Step 4) and 3-14 as a transparent acrylic wall that wraps around the epoxy at both ends of the specimen.
Figure 3-16: A schematic of a specimen curing between top and bottom metal plates, and set flush against two angle blocks. Note the tight seam between the metal plates and angle blocks. A photograph of an actual specimen in this setup is shown in Step 4 of Figure 3-13.

Figure 3-17: The seams along the right side and bottom of the plate against the angle blocks are very tight, as indicated in Figure 3-18.
Figure 3-18: View of angle blocks and metal plate (expansion of Figure 3-17, as a diagram). When the angle blocks are pushed against the plate in the direction indicated by the thick arrows, if the plates and blocks are not already flush, a “ding” will be heard as they come together, as indicated by the thin arrow.

was very tight. Ultimately, the metal walls ensured alignment in the z-direction, and squaring the plates with the angle blocks ensured alignment in the x- and y- directions. This alignment was a critical aspect of the setup for tensile testing.

Testing Protocol

After the specimen was epoxied between the top and bottom plates, the specimen was installed in an 11-kip MTS load frame with Instron actuator and controller (Figure 3-19a). Both the top and bottom plates were bolted into matching plates above and below the specimen in the MTS (this bolting step is the reason for the importance of obtaining the correct alignment (as discussed in the previous section); without a well-aligned specimen, the top and bottom plates cannot be bolted into place (Figure 3-19b.))

Two signals were recorded during a tensile test: a load signal from a load cell above the specimen, and a displacement signal from the motion of the actuator beneath the specimen. This allowed one to construct a load-displacement graph for each tensile test (Figure 3-8). The specimen was
Figure 3-19: Details of setup for tensile testing.
loaded in displacement control, at a constant displacement rate of 0.025 in/min. This displacement rate was selected because it was the minimum displacement rate performable by the Instron with minimal ringing (i.e., wavering up and down in the displacement signal due to mismatch between the displacement rate and the frequency at which data points are recorded). The specimen was loaded until failure occurred. After specimen failure, the specimen was imaged, and the specimen was removed from the plates by first removing the epoxy reservoir with a hammer and chisel, and then heating the specimen and plates in an oven at a minimum temperature of 150°C for at least 20 minutes. At this point, the epoxy was softened enough to use a hammer and chisel to remove the epoxy (while being careful to not chip the plates).

3.2.2 Generation of Fracture Process Zone (FPZ)

The white patching fracture process zone (FPZ) is a key component of this study. This region represents the earliest interaction between crack and material, because it appears before the crack has fully formed. Most importantly, in marble the FPZ manifests as a brightening of the material (and thus is termed a “white patching FPZ” throughout this investigation). Thus, creation of an FPZ is a vital aspect of this investigation.

This section details the process used to create an FPZ in both Carrara and Danby marble specimens. For both Carrara and Danby specimens, the FPZ creation followed the same four-step process:

1. **Cut Specimens.** Initial cutting of intact specimens from their parent block,

2. **Generate Flaw.** Induction of a pre-existing crack (a “flaw”) in those intact specimens,

3. **Generate White Patching FPZ.** Loading the specimens in a uniaxial machine to generate a white patching FPZ, and

4. **Extract White Patching FPZ.** Extracting the white patching FPZ regions for further investigation with microscopy and nanoindentation.

The rest of this section discusses the detailed application of each step to Carrara and Danby marble.
Figure 3-20: Covington©Heavy Duty Slab Saw, used to trim the large block of marble into slabs.

Cut Specimens

First, 15.2 cm x 7.6 cm x 3.8 cm (6” x 3” x 1.5””) block specimens of each marble type were cut. These dimensions were selected to conform to those of a previous study by Wong [Wong 2008], as a basis of comparison between the current study and previous work. Carrara marble specimens were cut with a Covington Engineering Heavy Duty Slab Saw in the Department of Earth, Atmosphere, and Planetary Sciences at MIT (Figure 3-20) and trimmed with the OMAX©Water Jet in the Hobby Shop at MIT (Figure 3-10). In the Covington Slab Saw, a large disk rotates at a constant speed. The marble slab slides by its own self-weight along a track towards the disk. Abrasives embedded in the sides of the disk abrade the marble to ultimately cut through the marble. The process is slow, and induces a relatively small amount of stress. Danby marble specimens were cut by Vermont Marble Company at the quarry.

Cut Flaw

117
Figure 3-21: An angled flaw and the potential stress conditions for compressive applied stress.

An initial crack, or “flaw” at an angle of 30° (Figure 3-21a), was cut into nearly all specimens (except intact specimens) with the OMAX Water Jet, following the OMAX Water Jet settings and protocol outlined in Section 3.2.1.

The orientation of the flaw causes the the specimen to have a Mixed-Mode loading condition when loaded in a uniaxial testing machine. Whereas Mode I cracks (with force in tension) propagate perpendicular to the in-plane far-field stress, and Mode II cracks (with opposing force directions on either side of the crack) propagate parallel to the in-plane far-field stress, the propagation of a diagonal pre-existing crack has both perpendicular (i.e., Mode I) and parallel (i.e., Mode II) components; the Mode I and Mode II stress intensity factors have formulations (Equations 3.3 and 3.4):

\[ K_I = \sigma \sqrt{a} \cos^2(\alpha) \]  
\[ K_{II} = \sigma \sqrt{a} \cos(\alpha) \sin(\alpha), \]  

so long as \( \alpha \neq 90° \) (which is considered a trivial case in fracture mechanics [Erdogan and Sih 1963]).
For a flaw length of \(2a = 0.0127 \text{ m} \) (0.5 in, such that \(a = 0.0064 \text{ m} \) or 0.25 in), and an inclination \(\alpha = 60^\circ\), the magnitude of the stress intensity factors under a tensile load with equal magnitude to the compressive stress of the current investigation would be \(K_I = 1.7 \text{ MPa} \sqrt{m}\) and \(K_{II} = 2.9 \text{ MPa} \sqrt{m}\). The actual stress state around the inclined crack is simply a superposition of the stress states due to the Mode I and Mode II components of the crack. Expressed mathematically, this superposition resembles:

\[
T = [\sigma^I + \sigma^{II}] \cdot n
\]  

(3.5)

where \(\sigma^I\) and \(\sigma^{II}\) refer to the Mode I and Mode II stress components (that is, the \(\sigma_{rr}, \sigma_{\theta\theta}, \) and \(\sigma_{r\theta}\) due to the Mode I component of the stress field, and the \(\sigma_{rr}, \sigma_{\theta\theta}, \) and \(\sigma_{r\theta}\) due to the Mode II component of the stress field), and \(T\) is the resultant stress (on a plane with unit normal \(n\)). Thus, the propagation is termed Mixed-Mode [Ul'm 2010].

Note that in contrast to the model employed for the above stress intensity calculations (shown in Figure 3-21a), the actual applied stress is compressive. The resulting stress field could resemble Figure 3-21b. Note that such a compressive loading could generate a tensile stress at the tips of the flaw, and thus could generate wing cracks which open in tension [da Silva and Einstein 2012]. Nevertheless, the stress condition shown in Figure 3-21b is somewhat speculative. Despite this uncertainty about the exact stress distribution in the specimens in this investigation, the white patching is more the subject of this investigation (i.e., not their mode of opening).

**Generate White Patching**

White patching was generated in the flawed specimens (i.e., specimens with a flaw induced as described above) by loading in a uniaxial testing machine (Figure 3-22). The samples were loaded through the vertical long axis. Steel brush-platens at the top and bottom of the specimens ensured that far-field stresses were uniformly applied.

Each specimen was loaded at a slow initial rate to eliminate seating effects (0.0017 in/sec to 1000 lb, then 0.003 in/sec to 2500 lb), after which loading continued at a constant rate until failure or the manual stopping of the test. This constant rate was set to be 38.34 lb/sec (170.5 N/sec) for Carrara marble, and 19 lb/sec (85 N/sec) for Danby marble. Danby marble was loaded at a smaller
constant rate because failure occurred so suddenly after seating that the Carrara marble loading rate of 38.4 lb/sec was reduced in order to allow the operator sufficient time to react and stop the machine after white patching development but before complete specimen failure.

The flaw tip of specimens was continuously monitored during loading with a high-resolution Phantom® High-Speed Camera, and high-resolution still pictures were taken as features of interest developed in the specimen, such as the onset of white patching. Note that the observation of the FPZ with the high speed camera is a very unique feature of this investigation and has been discussed in detail by Wong [Wong and Einstein 2009b;c;d]. Once either a significant amount of white patching had developed at the flaw tip or the specimen failed completely, the load was reversed and the specimen was unloaded. The final process zone and flaw were imaged with digital and high speed cameras.

On most specimens white patching emanated as expected from the tips of the preexisting flaw. On some specimens white patching also grew from one of the boundaries towards the flaw. On one Danby Marble specimen, no white patching appeared from the tips of the pre-existing flaw.

**Extract White Patching**
Finally, smaller specimens were removed from the loaded block specimens for microscopy and nanoindentation testing (Figures 3-23 and 3-24). The precise tests performed on each specimen are described in Table 3.7.

Table 3.7: Specimens, the comparisons made on each specimen, and the regions extracted from each specimen. Specimens are shown in Figure 3-23 and 3-24. Specimen d0 is an intact specimen not shown in Figure 3-24.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Comparisons Made on Specimen</th>
<th>Regions Extracted from Specimen</th>
</tr>
</thead>
<tbody>
<tr>
<td>c0</td>
<td>at different orientations</td>
<td>c0-x, c0-y, c0-z</td>
</tr>
<tr>
<td>c1</td>
<td>between grain boundary and grain center; between “intact” and process zone</td>
<td>c1-z1, c1-z2, c1-z3, c1-x, c1-y</td>
</tr>
<tr>
<td>c2</td>
<td>between “intact” and process zone</td>
<td>c2-z</td>
</tr>
<tr>
<td>c3</td>
<td>ESEM only</td>
<td>c3-y</td>
</tr>
<tr>
<td>d0</td>
<td>between grain boundary and grain center</td>
<td>d0-z</td>
</tr>
<tr>
<td>d1</td>
<td>between “intact” and process zone</td>
<td>d1-z1, d1-z2</td>
</tr>
<tr>
<td>d2</td>
<td>between “intact” and process zone</td>
<td>d2-z</td>
</tr>
</tbody>
</table>

The smaller specimens (far right of Figures 3-23 and 3-24) were extracted as follows: the OMAX® Water Jet cut 12 mm cylinders which contained the region of interest. These cylinders correspond to the scale of both the observed white patching and the theoretical process zone predicted by LEFM (Equation 2.19). A diamond drop-saw sliced the cylinder to obtain a disc of the region of interest (Figure 3-25). The final discs had a diameter of 12 mm, and a height of less than 4 mm. The discs were then mounted on stainless steel AFM plates with cyanoacrylate, and prepared for nanoindentation as described in Section 3.2.4: Nanomechanical Assessment. Precise locations of nanoindentation testing are indicated with dark boxes or lines.

As presented in Table 3.7, the specimens were extracted in such a way as to provide contrast in, and therefore a basis of comparison of, the types of quasi-brittle fracture material investigated. These comparisons are discussed in more detail in Chapters 5 and 6, but are discussed generally here. Specimen c0 contained three intact material specimens (c0-x, c0-y, and c0-z) which con-
Figure 3-23: Carrara marble specimens and corresponding regions. Testing details of each region are listed in Table 3.7. Gray squares and straight black lines indicate locations of nanoindentation testing. (Nanoindentation and ESEM data from Specimen c3 is not presented in this thesis, but the specimen is shown here for information.)
Figure 3-24: Danby marble specimens and corresponding regions. Gray squares indicate locations of nanoindentation testing. Testing details of each region are listed in Table 3.7.

Figure 3-25: (a) The diamond drop-saw trimmed marble cylinders cut with the OMAX©Water Jet. (b) Close-up of diamond-drop saw cutting a marble cylinder. (c) Final specimen mounted on stainless steel AFM plate.
trasted in their surface orientation (note that each specimen was removed from a different face of Specimen c0, as can be seen in Figure 5-3a). Specimen c1 contained several process zone material specimens. Nanoindentation testing on these specimens with varying distances from the process zone permitted a comparison of intact and process zone material. Additionally, nanoindentation testing on Specimen c1 both far from and near to the process zone was used to compare grain boundary and grain center material, and how these two materials change close to the process zone. Specimen c2 contained one process zone material specimen, and thus allowed for comparison of material near and with distance from the process zone. Specimen c3 was originally tested and failed by Wong [2008]. Nanoindentation and ESEM data from Specimen c3 is not presented in this thesis, but is discussed by Brooks et al. [2013]. The specimen is shown here for completeness of information. Specimen d0 contained a single intact specimen (not shown in Figure 3-24) which was used to compare grain boundary and grain center material of intact Danby marble. Finally, Specimens d1 and d2 contained three process zone specimens, and allowed for comparison of material near and far from the process zone.

Specimen c0 (Figure 5-3a) was an intact specimen, and was not loaded (and never developed white patching.) During extraction of Specimen c1 with the OMAX©Water Jet, regions c1-z1 and c1-z2 (Figure 3-23b) separated along the white patching. These specimens were mounted, prepared, and tested separately. Specimen c3 (Figure 5-3d) was initially prepared and tested by Wong [2008].

3.2.3 Optical and Environmental Scanning Electron Microscopy

The microstructure of the white patching was assessed with both optical microscopy and Environmental Scanning Electron Microscopy (see Section 2.3: Scanning Electron Microscopy (SEM) and Environmental Scanning Electron Microscopy (ESEM) for a detailed explanation of ESEM.) An Optical Microscope is attached directly to the CSM Instruments Nanoindenter and Nanoscratcher, and enables imaging of specimens immediately before and after nanoindentation and nanoscratching. Optical microscopy images also were used to calculate the grain size distributions of both marble types, as described in Chapter 4. The ESEM, on the other hand, allows for imaging at
Figure 3-26: An estimation of the range electrons travel in a calcite-based material is based on geometric quantities in this diagram, calcite material properties, and Equation 3.6. From [Kanaya and Okayama 1972]

a higher resolution and provides a more detailed understanding of material microstructure. Both techniques collectively contributed to the understanding of microstructure in this investigation.

**Image White Patching**

White patching was visually assessed with the FEI/Philips©XL30 FEG ESEM, in the Center for Materials Science and Engineering Electron Microscopy Shared Experimental Facility at MIT. The ESEM emits electrons at a controlled rate and trajectory onto the surface of a sample. Information about surface topography, material contrast, and other sample properties is derived from the deflection of the electrons off of the sample surface, or absorption and emission of electrons from the sample [Reichelt 2007]. Based on an estimation of electron range from Kanaya and Okayama [1972] for the energies and subsequent range of electrons in calcite-based materials (Figure 3-26 and Equation 3.6):

$$R = \frac{0.0276A}{Z^{0.89}\rho}E_0^{1.67},$$

it is estimated that electrons travel a distance of about 3 to 7 µm in the materials in this investigation, and therefore are returning microstructural information about material within that depth.

Given the calcite-based materials in this investigation, for an atomic weight $A$ of 100.09 g/mol, a density $\rho$ of 2.73 g/cm³, and atomic number $Z$ of 50, and beam energies of 15-25 keV, a range
of 2.9-6.7 μm is expected. This depth represents less than 10% of a typical size of Carrara marble grain. Thus, the ESEM in this investigation may not resolve certain nanoscale features, such as cracks that are less than 3 μm deep, but does essentially return surface topography for the materials in this investigation.

For both Danby and Carrara marble specimens, ESEM was conducted in the same regions as the nanoindentation grids (Section 3.2.4 Nanomechanical Assessment). Several hundred ESEM images were necessary in order to cover the area of a single nanoindentation grid. The ESEM images were post-processed as discussed in Chapter 4 in order to derive a quantity associated with microcrack density: black pixel percentage. Thus, experimentation allowed one to compare the microstructure (observed with ESEM) and the nanomechanical properties (measured by nanoindentation) for the FPZ of the marbles.

3.2.4 Nanomechanical Assessment

This section details the application of nanoindentation and nanoscratching to this investigation. In this study, a nanoindentation “test” consists of several hundred nanoindentations over an area. Although these areas may seem small in comparison to the specimen dimensions, the large number of nanoindentations conducted within the area successfully captures trends and variations in microproperties. These trends and variations ultimately reveal the information sought by this investigation: the difference between process zone and intact brittle materials. Results of nanoscratch testing reveal fracture properties of the test material at the small scale of the investigation.

Surface Preparation for Nanoindentation and Nanoscratching

All specimens required proper surface preparation before nanoindentation and nanoscratch testing. Surface preparation is a vital aspect of any nano- or microscale investigation, and is especially important for micro- and nanomechanical investigations. The ultimate goal is to obtain a smooth surface that best approaches the infinite half-space model of indentation contact models from which Equations 2.55 and 2.43 are derived. Furthermore, minor deformations disrupt the motion of the nanoindenter head, and thereby induce inaccurate data or scatter. In other words, the derived
indentation properties exhibit greater spread for surfaces with a high roughness, but not necessarily an overall decrease in properties [Miller et al. 2008].

Polishing, or rubbing the sample surface with abrasives in stages of decreasing abrasive size, reduces roughness and enhances nanoindentation results. Micro- and nanomechanical investigation of geomaterials is a relatively new field, so a well-established surface preparation procedure for marble did not exist in the literature at the time of this investigation. Ultimately, two surface preparation procedures were combined to develop the marble surface preparation procedure used in this study: the optical microscopy surface preparation procedure for marble, and the nanoindentation surface preparation procedure for cement paste [Austin 2008, Miller et al. 2008]. The abrasive types and sizes came from the optical microscopy surface procedure, while the long duration of the final stage and the type of polishing equipment came from the cement paste surface preparation procedure. The specimen is secured within a cylindrical steel "jig" and beneath a steel "post" (Figure 3-27). The jig and post ensure that the sample rotates about its own axis in addition to the rotation of the table. This double rotation creates an even polish by reducing any tracks or scratches due to polishing. The precise polishing procedures used for the marbles are given in Table 3.8. Possibly due to the difference in microstructure between the marbles, it was necessary to modify the polishing procedure used for Carrara marble when polishing Danby marble in order to obtain a similar quality of polish for both marbles. Specimens were re-polished as necessary.
Table 3.8: The polishing procedures used for Carrara and Danby marbles.

<table>
<thead>
<tr>
<th>Marble</th>
<th>Stage 1</th>
<th>Stage 2</th>
<th>Stage 3</th>
<th>Stage 4</th>
<th>Stage 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carrara</td>
<td>76 μm abrasive, dry, 5 min</td>
<td>22 μm abrasive, dry, 5 min</td>
<td>9 μm diamond, oil, 5 min</td>
<td>3 μm diamond, oil, 5 min</td>
<td>0.25 μm diamond, oil, 9 hr on turntable</td>
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</tr>
<tr>
<td>Danby</td>
<td>15 μm diamond, oil, 70 min on turntable (50 min with weight, 20 min without weight on top of jig)</td>
<td>3 μm diamond, oil, 45 min on turntable</td>
<td>1 μm diamond, oil, 60 min on turntable</td>
<td>None</td>
<td>None</td>
</tr>
</tbody>
</table>

throughout the investigation to expose a smoother surface within the white patching region.

Both the Asylum©Research MFP-3D AFM at the Nanolab in the MIT Department of Material Science and the Nanoscope IV in the MIT Department of Material Science verified the adequacy of the polishing procedures. An Atomic Force Microscope (AFM) is a type of Scanning Probe Microscope (SPM) which traces surfaces with a silicon cantilever to develop high-resolution, microscale interpretations of surface topography (Figure 3-28). The force of the silicon cantilever must be closely monitored to prevent damage to the sample surface, and also to correctly calibrate its height at any given moment. Piezocrystals control this force. The height and displacement of the cantilever is monitored by a laser; an incident laser beam reflects off of the cantilever onto a photodiode. The position of the reflected laser beam on the photodiode reveals cantilever height information [Gradicek 2010].

Following statistical corrections for surface sloping and large scale surface waviness, the final roughness, was determined from (via Mountains SPM Image Analysis Software; Figure 3-29):

\[ R_q = \sqrt{\frac{1}{N^2} \sum_{i=1}^{n} \sum_{j=1}^{n} z_{ij}^2} \]  

(3.7)
where $N$ is the number of pixels along the edge of the AFM scan, and $z_{ij}$ is the height at a position $(i, j)$ above or below a mean reference plane [Miller et al. 2008]. Essentially, the roughness value represents the average distance from a reference point near the sample surface to the highest peaks or the deepest valleys on the surface. Figure 3-29c depicts the topographical information from a single scan; the dark line through the middle represents the reference point. The average distance from this reference point to the actual scan line represents the roughness.

The scans in this investigation had a resolution of 40 pixels by 40 pixels, and a size of 50 $\mu$m by 50 $\mu$m. This yielded a final roughness of $R_q = 9.32$ nm. (Danby marble roughness was verified on the Nanoscope IV with a similar procedure, and slightly different scan parameters; the roughness was found to be near 10 nm.) Existing surface roughness criteria for nanoindentation recommend, dependent on the scanning size, a roughness less than five times the depth of nanoindentation [Miller et al. 2008]. Thus, the above polishing procedure represents an adequate polish for nanoindentation tests conducted to a minimum depth of 50 nm. Nanoindentations in this investigation were conducted to a peak load of 2.85 mN and a typical maximum depth of 250 nm (with a greater load and depth for Danby marble, Appendix A); thus the sample preparation is sufficient for this investigation.
Figure 3-29: An AFM scan yields (a) a color-gradient contour plot of the surface, which may also be displayed as (b) a 3D isometric diagram. (c) depicts height information from a single scan with respect to a reference point, or datum.
Figure 3-30: Force-indentation depth curve of an indentation test into marble. The important physical quantities which determine indentation modulus $M$ and hardness $H$ are obtained from this curve.

**Nanoindentation and Nanoscratching**

An indentation test consists of pushing a diamond-tipped indenter onto a specimen surface at a specified loading rate and peak load $P$. A force-depth $(P - h)$ curve is recorded (Figure 3-30).

The application of continuum-scale contact models to the indentation test condenses the $P - h$ curve into two quantities: the indentation modulus $M$ (Equation 3.8):

$$M = \frac{1}{2} S \sqrt{\frac{\pi}{A_c}},$$

and the indentation hardness $H$ (Equation 3.9):

$$H = \frac{P_{\text{max}}}{A_c},$$

where $S$ is the initial slope of the unloading curve; $P_{\text{max}}$ is the peak load, and $A_c$ is the (projected) contact area at peak load, which can also be determined from the maximum indentation depth upon unloading [Oliver and Pharr 1992]. Nanoindentations whose load-depth relationship deviated from an approximately second-order loading shape (i.e., the load-depth curve shown in Figure 3-30 is shaped like a parabola of power 2 during the loading cycle, as predicted by the classic load-depth relationship derived by Sneddon for conical indentation [Vandamme 2008]) were
Figure 3-31: (a) The CSM Instruments Nano-Hardness Tester. (b) An ESEM image of a grid indentation test. Line indentation tests correspond to a single row from a grid indentation test.

Table 3.9: Nanoindentation Parameters

<table>
<thead>
<tr>
<th></th>
<th>Carrara Marble</th>
<th>Danby Marble</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum Load, $P_{\text{max}}$</td>
<td>2.85 mN</td>
<td>7 mN</td>
</tr>
<tr>
<td>Typical Depth, $h$</td>
<td>$\approx 250$ nm</td>
<td>$\approx 400$ nm</td>
</tr>
<tr>
<td>Load/Unload Period</td>
<td>14 s</td>
<td>30 s</td>
</tr>
<tr>
<td>Hold Period</td>
<td>5 s</td>
<td>5 s</td>
</tr>
<tr>
<td>Space Between Indentations</td>
<td>$\approx 100$ $\mu$m</td>
<td>$\approx 100$ $\mu$m</td>
</tr>
</tbody>
</table>

not included in the analysis, except as noted. Nanoindentations were conducted in a CSM Instruments Nano-Hardness tester (Figure 3-31) with the parameters listed in Table 3.9. For Carrara marble indentation properties were available in the literature [Broz et al. 2006]; the parameters in Table 3.9 were chosen such that derived indentation properties matched the literature-reported indentation properties [Brooks et al. 2010]. However, indentation properties are not available in the literature for Danby marble; parameters were chosen to correspond with continuum mechanics theory [Bobko 2008, Constantinides 2006, Constantinides et al. 2006, Miller et al. 2008, Vandamme 2008] for the scale-separability condition. Appendix A: Nanoindentation Parameters for Danby Marble provides a detailed discussion of the selection of these nanoindentation parameters.

Nanoscratch testing was performed according to procedures in Akono et al. [2012] and Akono et al. [2011]. Fracture toughness $K_c$ was determined from a single scratch test according to Equa-
tion 2.31, repeated here:

\[ K_c = \frac{F_T}{\sqrt{2pA}} \]  

(3.10)

where \( F_T \) is horizontal force, \( p \) is the perimeter of the axisymmetric probe, and \( A \) is the projected area of contact of horizontal load. 20 microscratches with a length of 3 mm and horizontal force ranging from 0.03 to 5 N were then performed on each type of marble (Carrara and Danby).

**Calibrations**

The accuracy of the Nano-Hardness Tester\( ^\circledR \) data relies upon calibration of four components. First, the springs indicated in Figure 2-12 are the key components in determining the force-depth curve. The spring constants of these springs must be determined annually with a spring calibration. Second, the platform which holds the sample must translate the sample from beneath the optical microscope to beneath the indenter head with minimal error. The calibration of this translation distance ensures that the indentation tests are performed in the area selected by the user under the microscope. This user-performed calibration is conducted when the machine undergoes a major change, such as replacement of the probe. Third, knowing the precise area function of the probe is critical to accurate indentation analysis, but the particular probe geometry blunts over time and with extensive use. The probe area function calibration is user-performed several times a year by conducting indents in a material of known properties, such as fused silica. (The area function of the Nanoscratch probe was calibrated by performing scratches in a material of known fracture toughness (fused silica) before each round of nanoscratch testing.) Finally, the compliance of the entire machine is fixed and based on the reference design provided by CSM.

**Nanoindentation Accuracy**

The accuracy of nanoindentation data from the CSM Instruments Nano-Hardness Tester is enhanced by an additional “depth-offset” calibration before the nanoindentation test begins. During the depth-offset calibration, the specimen is raised to make contact with a plastic reference ring which surrounds the indenter head (Figure 2-2). Then the indenter head lowers within the plastic

---

1The discussion of this section inspired by that of [Bobko 2008].
ring to contact the sample and create a single, large indentation. The position of the indenter head relative to the plastic ring at contact serves as the initial depth-offset calibration, and a reference value for all indentations in the test [Bobko 2008]. During the indentation test (which consists of hundreds of individual indentations), each indentation is conducted with respect to this localized system. Before each individual indentation the sample is again raised to contact the plastic ring, and after each indentation, the sample is lowered from the plastic ring. During each indentation, the indenter head lowers to the sample surface, conducts an indentation, and retracts. Moving with respect to the plastic ring minimizes any error associated with thermal drift of the sample or vibrations of the system. If the sample expands or contracts due to vibrations or a slight temperature change in the environment during the test, the indentations will still be conducted and measured with respect to the current sample dimensions [Bobko 2008].

Additionally, the testing parameters were carefully selected to ensure the accuracy of the experimental technique. Nanoindentations conducted to high loads or at high loading rates may fracture the material. Fractures extending from one nanoindentation to the next would influence the mechanical properties derived from nanoindentation testing. For this investigation, it was checked and verified that nanoindentations do not induce significant fracture, if spaced at 8 μm. To investigate this possibility, “exaggerated” nanoindentations were imaged with ESEM (Figure 3-32). These nanoindentations were "exaggerated" because they were conducted at higher loads (by a factor of nearly 100) than typical indentations in the testing campaign. Cracks extending from one indentation to the next would indicate that the nanoindentation process induced significant fracture in the material. However, as shown in Figure 3-32, indentations 80 times the typical load do not induce cracks extending more than 17.2 μm. It is inferred that typical, low-load indentations (Figure 3-31b) would induce cracks of insignificant length. Typical indentations were also imaged with ESEM. Note that inter-indentation cracks are not visible at even high magnifications, and are thus assumed insignificant. A look to the scale separability condition (Equation 2.77) provides a quantitative corollary to the qualitative discussion of indentation spacing. Indentation parameters (spacing between indents s, and depth h) must be carefully selected in order to prevent not only the overlap of indented areas, but also more importantly the overlap of the accessed indentation volumes.
Figure 3-32: An “exaggerated indentation shows little indentation-induced cracking. The greatest observable distance of cracking from the center of the indentation is 17.2 μm (between center of indentation and tip of diagonal crack).

As indicated in Table 3.9, the typical depth of indentation h is 250 nm. Provided that the typical microstructure size D is 2.4 μm or larger, the indentations provide information on the material properties of the microstructure. As discussed in the next section, typical marble grain sizes in this study are upwards of 100 μm; thus, the indentation depth is well within the sought-after scale separability range for this investigation.

A final note of interest is the quality of indentation-induced fracture (in the case of the exaggerated indents, microindentation-induced). Slightly curving cracks emanate from the top and right tips of the impression (see right half of Figure 3-32); they resemble classic tensile wing cracks [Wong 2008]. Additionally, sets of deformation lines parallel to the impression extend outwards from the impression. The regularity and straightness of the lines contrasts with more irregular macro- and microscale crack propagation around grain boundaries. These deformation lines ultimately indicate the regularity of the crystal microstructure of marble within the particular marble grain imaged.
Chapter 4

Microstructure of Fracture Process Zone (FPZ)

This study seeks to understand the role that microstructure plays in the development of the FPZ of marble. Thus, an understanding of the microstructure of both marble types is a critical aspect. This chapter details the microstructure as assessed by both optical microscopy and Environmental Scanning Electron Microscopy (ESEM) in this study, and compares it with microstructural information available in the literature for both marble types.

First, microstructure of both intact marbles obtained via optical microscopy is presented; optical micrographs are then used to obtain a grain size distribution of both marbles. Second, microstructure information of the FPZ of both marbles obtained via ESEM is presented; ESEM micrographs are then used in conjunction with image processing methods to quantitatively assess microcrack density in the FPZ.

4.1 Microstructure of Intact Marble

This section presents the microstructure information of both Carrara and Danby marbles as assessed with optical microscopy. First, some representative optical micrographs are presented and microstructure characteristics are discussed. Then, the methods for obtaining the grain size dis-
Figure 4-1: Typical optical micrographs of Carrara and Danby marbles (desaturated, and brightness/contrast adjusted to show grain boundaries.)

tributions of both Carrara and Danby marbles are presented, and the grain size distributions are discussed and compared with those from the literature.

4.1.1 Microstructural Characteristics

Typical optical micrographs of both Carrara and Danby marble are shown in Figure 4-1. Both micrographs show the microstructure after the surface preparation procedure discussed in Section 3.2.4.

Several shared microstructural qualities of both marbles are apparent. Firstly, both marbles are composed of grains with a polygonal shape. The grain boundaries of both marbles are approximately granoblastic, and thus exhibit no (or very few) interlocking boundaries. Slight variations in the apparent color of grains are also apparent, likely due to both the location of the light source within the optical microscope, and the variations in orientation of the calcite crystals which compose each grain.

One major difference between the marbles is apparent: the typical sizes of grains. A quick comparison of the micrographs in Figure 4-1 suggests that the typical size of a Danby marble grain
is almost twice that of a Carrara marble grain. The grain size distribution of the marbles will more precisely reveal these typical sizes. The next section presents the details of a comprehensive grain size distribution assessment, and compares that assessment with grain size distribution parameters found in the literature for the marbles.

### 4.1.2 Grain Size Distribution of Carrara and Danby Marbles

Two techniques were used to assess the grain size distribution of the marbles in this study: analysis from traced areas, and analysis from line-intercepts. This section details both techniques, compares their results with values found in the literature, and finally presents a grain size distribution of both marbles.

A shared aspect of both techniques is their use of two-dimensional information (i.e., grain sections on optical micrographs) to derive three-dimensional information (i.e., the distribution of particle sizes in a volume.) The next section derives the Saltikov Correction Formula, a popular method for bridging the divide between two-dimensional and three-dimension information in particle analysis.

**Saltikov Correction Formula**

Several important features of using two-dimensional grain sections to derive three-dimensional volume distributions must be discussed. Saltikov laid the foundations of this approach to particle analysis [Saltikov 1967]. Four key assumptions are required to use this approach:

1. the particles are either monodispersed or polydispersed,
2. the particles are similar in shape (although they may be different in size),
3. the particles are shaped such that a plane intersects a particle only once, and
4. the particles are randomly oriented.

The first assumption is easy to fulfill; it means that the particles can be either all the same size, or a variety of sizes. The second assumption means that the particles must have similar shapes, such
Table 4.1: For an experimentally determined maximum particle diameter of 656 µm, a logarithmic scale based on a factor of $10^{-0.1}$ determines the twelve bin boundaries in this table.

<table>
<thead>
<tr>
<th>Class</th>
<th>Max Diameter of Particle in Class, mm</th>
<th>Ratio of Particle Diameter to Global Maximum Diameter</th>
<th>Ratio as Function of Scale Factor, $10^{-0.1}$</th>
<th>Max Area of Particle in Class, mm²</th>
<th>Counts of Particles in Class</th>
<th>Underestimation Probability</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.656</td>
<td>1.000</td>
<td>$10^{-0.1}(0)$</td>
<td>0.338</td>
<td>$N_{A1}$</td>
<td>60.7%</td>
</tr>
<tr>
<td>2</td>
<td>0.521</td>
<td>0.7943</td>
<td>$10^{-0.1}(1)$</td>
<td>0.213</td>
<td>$N_{A2}$</td>
<td>16.8%</td>
</tr>
<tr>
<td>3</td>
<td>0.414</td>
<td>0.6310</td>
<td>$10^{-0.1}(2)$</td>
<td>0.135</td>
<td>$N_{A3}$</td>
<td>8.95%</td>
</tr>
<tr>
<td>4</td>
<td>0.329</td>
<td>0.5012</td>
<td>$10^{-0.1}(3)$</td>
<td>0.085</td>
<td>$N_{A4}$</td>
<td>5.20%</td>
</tr>
<tr>
<td>5</td>
<td>0.261</td>
<td>0.3981</td>
<td>$10^{-0.1}(4)$</td>
<td>0.054</td>
<td>$N_{A5}$</td>
<td>3.13%</td>
</tr>
<tr>
<td>6</td>
<td>0.207</td>
<td>0.3162</td>
<td>$10^{-0.1}(5)$</td>
<td>0.034</td>
<td>$N_{A6}$</td>
<td>1.92%</td>
</tr>
<tr>
<td>7</td>
<td>0.165</td>
<td>0.2512</td>
<td>$10^{-0.1}(6)$</td>
<td>0.021</td>
<td>$N_{A7}$</td>
<td>1.20%</td>
</tr>
<tr>
<td>8</td>
<td>0.131</td>
<td>0.1995</td>
<td>$10^{-0.1}(7)$</td>
<td>0.013</td>
<td>$N_{A8}$</td>
<td>0.75%</td>
</tr>
<tr>
<td>9</td>
<td>0.104</td>
<td>0.1585</td>
<td>$10^{-0.1}(8)$</td>
<td>0.008</td>
<td>$N_{A9}$</td>
<td>0.47%</td>
</tr>
<tr>
<td>10</td>
<td>0.083</td>
<td>0.1259</td>
<td>$10^{-0.1}(9)$</td>
<td>0.005</td>
<td>$N_{A10}$</td>
<td>0.29%</td>
</tr>
<tr>
<td>11</td>
<td>0.066</td>
<td>0.1000</td>
<td>$10^{-0.1}(10)$</td>
<td>0.003</td>
<td>$N_{A11}$</td>
<td>0.19%</td>
</tr>
<tr>
<td>12</td>
<td>0.052</td>
<td>0.0794</td>
<td>$10^{-0.1}(11)$</td>
<td>0.002</td>
<td>$N_{A12}$</td>
<td>0.12%</td>
</tr>
</tbody>
</table>

as being all spherical or all cubic. The third assumption means that no particles are U-shaped, or curve back on themselves in any way to produce several sections in a plane (for example, a sphere with spikes protruding from it would violate this assumption). This assumption ensures that a two-dimensional microscope image does not contain two (or more) sections from one particle. Finally, the fourth assumption assumes there is no dominant directionality to the particle orientations. The assumption thus work together to ensure that a two-dimensional section (such as a microscope image) will capture information about all particle types and orientations, without counting single particles multiple times.

Saltikov began with considering that spherical particle diameters typically follow a log normal distribution. Thus, a given distribution of diameters can be divided into twelve classes using a logarithmic scale which begins with the diameter of the largest particle. Table 4.1 shows the classes of diameters (i.e., maximum diameters of twelve classes) for a set of sections with an experimentally determined maximum particle diameter of 656 µm.
Based on this log normal distribution of particle diameters, the resulting (ideal) log normal distribution of particle areas is determined simply by squaring the maximum particle diameter from each bin (Table 4.1, column 5). The distribution of areas yielded from the two-dimensional sections are plotted into these logarithmic area bins. The number of areas in each bin $A_1$, $A_2$, etc. is denoted as $N_{A1}$, $N_{A2}$, etc (Table 4.1, column 6).

At this point in the process, a key idea arises: a particle of any size will yield areas in the lower size classes. The key complementary idea is that in any given size class, some of the captured sections derive from particles whose diameters actually qualify them for a larger size class. For example, a large 5mm-diameter sphere can be sliced exactly at its equator to yield a 5-mm diameter section, but it has a greater probability of being sliced somewhere above or below its equator to yield a section with diameter less than 5-mm. Thus, the area distribution just created above must be statistically corrected for these “underestimation probabilities.” The “underestimation probability” for each size class is listed in the far right column of Table 4.1.

This correction is achieved by using probability to reduce each $N_{Ai}$ by the number of sections which are likely to actually derive from particles whose diameters qualify them for larger area classes. For example, only 60.7% of particles with an actual size in the first area class ($N_A(1)$) will yield sections with an area in the first area class (and thus show up in the count for the first area class, $N_{A1}$). (The remaining 39.3% of particles with an actual size in the first area class are likely to be sliced either above or below their equator, and thus yield sections with a size smaller than the first area class.) In other words,

$$0.607N_A(1) = N_{A1} \quad (4.1)$$

$$N_A(1) = 1.6461N_{A1} \quad (4.2)$$

Proceeding further, the areas counted in the second area class ($N_{A2}$, between areas $A2$ and $A3$, and thus between diameters $D2$ and $D3$) are obtained from particles with actual areas from the first and second area classes. 16.8% of the $N_A(1)$ particles will show an area in this class, or

$$0.16833 \times N_A(1) = 0.16833 \times 1.6461N_{A1} = 0.2771N_{A1} \quad (4.3)$$
and the remaining count is 60.7\% of particles with an actual size in the second area class, or:

$$0.607N_A(2) = N_{A2} - 0.2771N_{A1}. \quad (4.4)$$

Solving for $N_A(2)$ leads to:

$$N_A(2) = 1.6461N_{A2} - 0.4561N_{A1} \quad (4.5)$$

The application of this logic throughout all twelve classes yields a general formula for correcting the counted areas in each area class:

$$N_{VK} = \frac{1}{DK} \left( 1.6461N_{AK} - 0.4561N_{A(K-1)} ight. $$

$$-0.1162N_{A(K-2)} - 0.0415N_{A(K-3)}$$

$$-0.0173N_{A(K-4)} - 0.0079N_{A(K-5)}$$

$$-0.0038N_{A(K-6)} - 0.0018N_{A(K-7)}$$

$$-0.0010N_{A(K-8)} - 0.0003N_{A(K-9)}$$

$$-0.0002N_{A(K-10)} - 0.0002N_{A(K-11)} \right) \quad (4.6)$$

where $DK$ is the maximum diameter of particles in class $K$, $N_{VK}$ is the number of particles (per volume) whose actual size is in class $K$, and the terms $A_K$ through $A(K-11)$ count backwards through the area classes of larger size. The approach also works for fewer than 12 bins. However, Saltikov found that more than 12 bins is not typically necessary for describing particle distributions in practice. Thus, 12 bins were used for assessing the grain size distributions in this investigation.

Saltikov recommends that this approach works best for spherical particles. Particles of a non-spherical shape may deviate from a typically logarithmic size distribution, and thus the assumption of a logarithmic scale for classifying the area distribution may lead to significant errors. However, particle size distribution methods for non-spherical particles are increasingly mathematically complex, depending on the precise shapes of the particles. Methods exist for particle shapes such as ellipsoids, lamellar shapes, and pentagonal dodecahedrons [Underwood 1970]. The grain shapes
of the marbles in this investigation are not spherical, but neither are they ellipsoids, lamellar, or precise pentagonal dodecahedrons. Thus, given the shortcomings of all methods with regard to assumed particle shape, for this investigation the most common and simple method for particle analysis was used: Saltikov’s method for spherical particles.

The Saltikov correction formula (Equation 4.6) was applied to the distribution of area sections discussed in the next section, and the distribution of line intercepts discussed in the following section.

Area Analysis

The Area Analysis of the grain size distributions of both marbles begins with directly obtaining the distribution of section areas in a set of two-dimensional optical micrographs. In order to do this, each optical micrograph is processed with the ImageJ® image processing software. This software contains an “Analyze Particles” tool which uses various image processing techniques to directly outline the particles in an image, and lists their areas using a user-defined scale. For Danby marble micrographs, the grain boundaries in the processed image set were apparent enough that each image was merely thresholded and then processed with the “Analyze Particles” tool (Figure 4-2). For the Carrara marble micrographs, further image processing was sometimes needed (such as processing with the “Gaussian filter”) in order to accentuate grain boundaries.
27 Carrara marble micrographs and 101 Danby marble micrographs were assessed. Each micrograph yielded a section area distribution, and these section area distributions were combined into a single section area distribution for each marble type. The section area distribution for each marble type was converted into a section diameter distribution (assuming circular section areas) binned into the 12 area classes derived from spherical diameter distributions, as discussed in the previous section. Finally, the section area distribution was corrected with the Saltikov Correction Formula (Equation 4.6) to yield a grain size distribution for each marble type.

As listed in the comparison table (Table 4.2, at the end of Section 4.1.2), the Area Analysis method revealed a maximum Carrara marble grain diameter of 656 μm, and a maximum Danby marble grain diameter of 1269 μm. The average Carrara marble grain diameter was 98.3 μm, the average Danby marble grain diameter was 191 μm, and the ratio of Carrara average grain diameter to Danby average grain diameter was 0.51.

**Line Intercept Analysis**

Although the Area Analysis discussed above yielded useful grain size distribution information, the need to process the Carrara marble images before using the “Analyze Particles” tool suggested that a different approach may be useful in obtaining the size distribution. The Line Intercept approach finds section diameters by directly measuring them with a set of grid lines. This section details the use of the Line Intercept approach in this investigation.

For the Line Intercept approach, two grids at the same size and resolution of the marble micrographs were created: a vertical grid, and a horizontal grid (Figure 4-3, image 1; only vertical grid shown.) The thicknesses of the grid lines were exactly 1 pixel, and the spacing of the grid lines was a constant ≈ 100 or 200 μm (depending on the application, as discussed later.) Then, a set of 100 Carrara marble micrographs and 150 Danby marble micrographs were converted to grayscale images and thresholded in MATLAB® with a user-determined threshold value. Several threshold values were tried on an image from the image set, and the threshold value which best converted grain boundaries to black and the rest of the marble grain (including scratches) to white (Figure 4-3, image 2) was selected. Next, the vertical grid was subtracted from each image (Figure 4-3, image
3.) The resulting Vertical Intercept Image was a set of line segments whose lengths corresponded to particle diameters (Figure 4-3, image 4.) The Vertical Intercept Image was processed using the “Analyze Particles” tool in ImageJ®. Because each line segment had a width of exactly 1 pixel, the area of a line segment determined with the “Analyze Particles” was also a length measurement of particle diameter. Each Vertical Intercept Image yielded a vertical section diameter distribution, and the vertical section diameter distributions from all Vertical Intercept Images for a marble type were combined into a single vertical diameter distribution for each marble type. These steps were repeated with the horizontal grid to yield a single horizontal diameter distribution for each marble type. Both the vertical and horizontal diameter distributions for each marble type were binned into the 12 area classes derived from spherical diameter distributions, as discussed previously. Finally, the area distributions were each corrected with the Saltikov Correction Formula (Equation 4.6.)

Given the larger typical size of Danby marble grains, this Line Intercept analysis was run twice on Danby marble. The second time, both grids and micrographs of double the height and width of the first time were used (Figure 4-4.)

As listed in the comparison table (Table 4.2, at the end of Section 4.1.2), when using the same size micrographs, the Line Intercept Analysis method revealed a maximum Carrara marble grain diameter of 768 \( \mu m \) (horizontal), and a maximum Danby marble grain diameter of 1049 \( \mu m \) (horizontal). The average Carrara marble grain diameter was 116 \( \mu m \) (120 \( \mu m \) vertical, 113 \( \mu m \) horizontal), the average Danby marble grain diameter was 140 \( \mu m \) (141 \( \mu m \) vertical, 139 \( \mu m \) horizontal), and the ratio of Carrara average diameter to Danby average diameter was 0.83 (0.85 vertical, 0.81 horizontal).

However, when using larger micrographs (Figure 4-4) for Danby marble, larger grain sizes are found for Danby marble: a maximum grain size of 1539 \( \mu m \) (horizontal), and an average grain size of 157 \( \mu m \), to yield a ratio of Carrara average diameter to Danby average diameter of 0.74.

Finally it is interesting to note that when only the top 10 area classes are considered, and when also the larger Danby images are considered, the ratio of Carrara average grain diameter to Danby average grain diameter converges with that found by the Area Analysis method. For an average Carrara marble grain size of 145 \( \mu m \), and an average Danby marble grain size of 271 \( \mu m \), the ratio
1. Create a grid to overlay onto images.

2. Convert each image to binary.

3. Subtract grid from binary image.

4. The line lengths that remain correspond to grain diameters.

Figure 4-3: The four main steps in the Line Intercept Analysis, illustrated on an optical micrograph of Danby marble.
Comparison with Literature and Final Distribution
The methods described above precisely determined the grain size distribution for both marbles, as well as distribution parameters such as mean and maximum value. In addition, select distribution parameters are available in the literature for both marble types. The range of grain sizes of the exact Carrara marble sample used in this investigation has an average grain size of 300 μm, and maximum grain size of 480 μm (sample 34, Type A microfabric, from [Molli et al. 2000].) Analysis by Molli was conducted by hand tracing blown-up micrographs, digitizing those tracings, and using image analysis software to analyze the digitized tracings [Molli and Heilbronner 1999]. It should be noted that Carrara marble grain sizes in studies by Molli from other samples range below 100 μm. Danby marble grain size analysis was conducted by Spectrum Petrographics. This analysis was conducted by dimensioning a typical grain on a thin section, as well as dimensioning the largest grain on a thin section. Spectrum Petrographics found a typical grain size of 520 μm, and a
maximum grain size of 3120 μm. The distribution parameters from literature are shown alongside distribution parameters from the Area Analysis and Line Intercept Analysis in Table 4.2.

In Table 4.2, the distribution parameters from the Area Analysis and Line Intercept Analysis suggest a range of typical grain sizes for Carrara and Danby marbles. However, the Line Intercept Analysis (Larger Danby Images, Top 10 Classes) in the final row of Table 4.2 as well as Line Intercept (Top 10 Classes) in the fifth row show Carrara marble typical grain size to Danby marble typical grain size ratios (0.54 and 0.66, respectively) that are close to the ratios from the literature (i.e., Molli [Molli and Heilbronner 1999, Molli et al. 2000] and Spectrum Petrographics, 0.58). These three methods found a variety of grain sizes for the two natural materials, but converged on a ratio of grain sizes. The convergence of the ratios between literature and the methods described and applied above (Area Analysis and Line Intercept Analysis) suggests that although the precise grain size measured may have a strong dependence on the particular sample used (due to the fact that these are natural materials with inherent natural variability), the ratio of typical grain size between the two materials is likely between 0.54 and 0.66. Thus, the Carrara marble microstructure is likely 50 to 60% the size of the Danby marble microstructure. The complete Grain Size Distribution derived from the Line Intercept Analysis using Larger Images for Danby marble is shown in Figure 4-5. The Grain Size Distribution for only the top 10 classes can be seen by ignoring the two smallest Grain Diameter data points for each marble and direction (vertical and horizontal). The microstructure size ratios will be returned to in later chapters which explore the nanomechanical properties and FPZ manifestation in these two materials.

4.2 Microstructure of Fracture Process Zone

This investigation developed an automatic quantitative technique for assessing a parameter correlated with the microcrack density of a particular image: black pixel percentage. This section briefly presents the algorithm used to assess ESEM micrographs for black pixel percentage. Then,
Table 4.2: The various techniques used to assess the grain size distributions of Danby and Carrara marbles, their resulting parameters, and the ratio of Carrara to Danby marble typical grain size.

<table>
<thead>
<tr>
<th>Method</th>
<th>Parameter (μm)</th>
<th>Carrara</th>
<th>Danby</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>From the Literature</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 Molli [1999,2000]</td>
<td>$d_{\text{avg}}$</td>
<td>300</td>
<td>none</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td>$d_{\text{max}}$</td>
<td>480</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 Spectrum Petrographics</td>
<td>$d_{\text{avg}}$</td>
<td>none</td>
<td>520</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td>$d_{\text{max}}$</td>
<td>3120</td>
<td>3120</td>
<td></td>
</tr>
<tr>
<td><strong>Determined in this Study</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 Area Analysis</td>
<td>$d_{\text{avg}}$</td>
<td>98.3</td>
<td>191</td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td>$d_{\text{max}}$</td>
<td>656</td>
<td>1269</td>
<td></td>
</tr>
<tr>
<td>4 Line Intercept</td>
<td>$d_{\text{avg}}$ (Vertical)</td>
<td>120.4</td>
<td>141.1</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>$d_{\text{max}}$</td>
<td>695.3</td>
<td>987.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$d_{\text{avg}}$ (Horizontal)</td>
<td>112.8</td>
<td>138.6</td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td>$d_{\text{max}}$</td>
<td>767.9</td>
<td>1048.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$d_{\text{avg}}$</td>
<td>116.2</td>
<td>140.1</td>
<td>0.83</td>
</tr>
<tr>
<td>5 Line Intercept (Top 10 Classes)</td>
<td>$d_{\text{avg}}$ (Vertical)</td>
<td>141.2</td>
<td>215.5</td>
<td>0.66</td>
</tr>
<tr>
<td></td>
<td>$d_{\text{max}}$</td>
<td>695.3</td>
<td>987.8</td>
<td>0.66</td>
</tr>
<tr>
<td></td>
<td>$d_{\text{avg}}$ (Horizontal)</td>
<td>149.7</td>
<td>226.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$d_{\text{max}}$</td>
<td>767.9</td>
<td>1048.7</td>
<td>0.66</td>
</tr>
<tr>
<td></td>
<td>$d_{\text{avg}}$</td>
<td>145.3</td>
<td>221.4</td>
<td></td>
</tr>
<tr>
<td>6 Line Intercept (Larger Danby Images)</td>
<td>$d_{\text{avg}}$ (Vertical)</td>
<td>149.7</td>
<td>149.7</td>
<td>0.80</td>
</tr>
<tr>
<td></td>
<td>$d_{\text{max}}$</td>
<td>1218.9</td>
<td>1218.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$d_{\text{avg}}$ (Horizontal)</td>
<td>using “Line Intercept” data, Row 4</td>
<td>163.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$d_{\text{max}}$</td>
<td>1539</td>
<td></td>
<td>0.69</td>
</tr>
<tr>
<td></td>
<td>$d_{\text{avg}}$</td>
<td>156.8</td>
<td></td>
<td>0.74</td>
</tr>
<tr>
<td>7 Line Intercept (Larger Danby Images, Top 10 Classes)</td>
<td>$d_{\text{avg}}$ (Vertical)</td>
<td>250.1</td>
<td>250.1</td>
<td>0.56</td>
</tr>
<tr>
<td></td>
<td>$d_{\text{max}}$</td>
<td>1218.9</td>
<td>1218.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$d_{\text{avg}}$ (Horizontal)</td>
<td>using “Line Intercept (Top 10 classes)” data, Row 5</td>
<td>301.8</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>$d_{\text{max}}$</td>
<td>1539</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$d_{\text{avg}}$</td>
<td>270.9</td>
<td></td>
<td>0.54</td>
</tr>
</tbody>
</table>
Figure 4-5: Grain Size Distribution for Danby and Carrara marbles derived with Line Intercept Analysis considering larger images for Danby marble (Rows 7 and 8 in Table 4.2.)
the results of the application of the algorithm to regions on FPZ specimens are presented. Finally, a comparison of the trends is presented.

4.2.1 Algorithm for Microcrack Density Assessment

This investigation used black pixel percentage of processed ESEM micrographs as a quantitative metric to describe the level of microcrack density. Images with higher microcrack density contained a higher percentage of black pixels than images with lower microcrack density. The black pixel percentage of a single ESEM image was obtained with a five-step image processing algorithm (the steps in this algorithm are also illustrated in Figure 4-7, and Appendices B and C fully detail the steps in this algorithm):

1. Create a Spotlight Mask from a sample image with no (or very little) microcracking (Background Image, Figures 4-6 and 4-7, image 1.)
2. Add the Spotlight Mask to a sample image to create an Unspotlighted Image (Figure 4-7, image 2.)
3. Apply a common edge detection algorithm (the “Sobel Edge Detector”, explained in Appendix B.3) to the Unspotlighted Image to obtain a Sobel Image (Figure 4-7, image 3.)
4. Threshold the Sobel Image to obtain the Edge-Detected Image (Figure 4-7, image 4.) Pixels above a user-determined threshold value are replaced with intensity 256 (white), and pixels below a particular value are replaced with intensity 0 (black). The Edge-Detected Image is a binary image, where black pixels should mostly correspond to microcracks.
5. Obtain the ratio of number of black pixels to total number of pixels in the Edge-Detected Image. This ratio is the Black Pixel Percentage (BPP).

The next sections present the results of applying this five-step algorithm to the hundreds of ESEM micrographs obtained from several FPZ specimens in this study. After processing each micrograph, the micrographs from a region were then converted to a BPP-color-coded rectangle,
Figure 4-6: The addition of the Spotlight Mask (middle) to the Background image (top) results in an Unspotlighted Image (bottom). Compare the Unspotlighted and Background Images, and notice that the dark spotlighting rim in the Background Image is completely eliminated in the Unspotlighted Image.
Figure 4-7: The images created after Steps 1-4 of the Edge Detection algorithm used in this investigation.
and these rectangles were then laid out in a map corresponding to their locations within the imaged region (Figure 4-8. Images with 8% BPP were colored totally black, images with 0% BPP were colored totally white, and images with BPP between those values were colored a shade of gray, except as otherwise stated (Regions c1-y and c2-z had minimum BPP greater than 8% high BPP; these image sets were displayed with a higher BPP range). Since each region observed with ESEM consisted of up to over 100 images, this color-code system made regions of high microcracking stand out as being very dark. As a final quantitative step, BPP for each region of ESEM images are presented in boxplot form (see Appendix Chapter D for a discussion of boxplots as presented in this investigation.) Although BPP is to some extent affected by imaging conditions (discussed in Appendix Chapter B), the number provides some idea of the density of microcracking within

Figure 4-8: The construction of the ESEM map for Region d2-z. The ESEM micrographs on the left were processed with the BPP algorithm. Each image was colored according to its BPP as shown on the central scale. Finally, a grid of all of the color-coded micrographs from each region was compiled as shown on the right. The arrows trace first the BPP-coded color, then the corresponding location on the ESEM map.
a region. Colorcoded ESEM-maps and boxplots are presented in the following subsections, and illustrate the development of microcrack density in the FPZ region.

### 4.2.2 Application of Algorithm to FPZ Regions

This section discusses the results of applying the BPP algorithm presented above to two Carrara marble specimens (c1 and c2; Figure 3-23) and two Danby marble specimens (d1 and d2; Figure 3-24). The algorithm was applied to hundreds of micrographs from these specimens, and the average BPP was found in regions of these specimens. The increase and decrease in BPP provided a way to measure the increase and decrease in microcracking across these specimens. This measurement and analysis of microcrack density thus provides a quantitative extension of the qualitative microcrack density exploration by Wong [Wong 2008, Wong and Einstein 2009d].

Three major microcracking trends will be presented in this section:

1. higher BPP near the white patching FPZ, and
2. higher BPP in finer-grained Carrara marble, and
3. increased variety (spread) of BPP with increased BPP.

These trends in BPP confirm the previous hypothesis of increase in microcrack density with closeness to the FPZ, and suggest that a reduction in microstructure size leads to an increase in both microcrack density and variety (spread) of microcrack density.

**Carrara Marble**

*Specimen c1.* Region c1-y from Specimen c1 is located on the white patching surface (y-axis normal) which opened between regions c1-z1 and c1-z2, which separated during specimen preparation. The ESEM map shown in Figure 4-9 is from a portion of this region. The c1-y ESEM map exhibits more than a 5% spread in BPP, with a median BPP of 18%. Additionally, BPP is greatest down the center of the map. (Appendix Chapter C provides more details on the evolution of analysis of ESEM on c1-y.)
Figure 4-9: Carrara Marble, Region c1-y. This region exhibits a spread of more than 5% in BPP, and a median BPP of 18%.

Figure 4-10: Carrara marble, Region c2-z. This region exhibits a spread of more than 3% in BPP, and a median BPP of around 28%, with a slight increase in BPP close to the white patching FPZ.

Specimen c2. Region c2-z from Specimen c2 is located on the specimen surface (z-axis normal) near the white patching and flaw. The location of the ESEM map with respect to the flaw and white patching is shown in the rightmost diagram of Figure 4-10. BPP increases with closeness to the white patching from 27.98% to 28.36%. Note that the typical BPP measured in region c2-z is higher than BPP measured in Region c1-y (18%, Figure 4-9), and that the spread in BPP in both regions is large (above 5%).
Figure 4-11: Danby marble, Regions d1-z1 and d1-z2. These regions exhibited a typical BPP of less than 5%, with an increase in BPP close to the white patching FPZ.

**Danby Marble**

*Specimen d1*. Region d1-z1 is located near the flaw of Specimen d1, and region d1-z2 is located around white patching which emanated from the boundary of Specimen c1. ESEM images were captured from four different locations in these regions (rightmost diagram of Figure 4-11.) In Region d1-z1 (top of Figure 4-11), the typical BPP closest to the flaw, 4.98%, is more than twice the typical BPP furthest from the flaw, 1.23%. It was previously noted that no white patching was visible at the macroscale in Region d1-z1. However, the BPP indicated in Figure 4-11 suggests that microcracking was nevertheless occurring on the specimen. In Region d1-z2, the two regions closest to the white patching exhibit a BPP (3.48% and 2.47%) almost twice that of the ESEM location furthest from the white patching (1.27%). Thus, all four ESEM locations on Specimen d1
Figure 4-12: Danby marble, Region d2-z. This region exhibited a typical BPP of nearly 4%.

exhibit a typical BPP of less than 5%, with an increase in BPP close to the white patching FPZ. These ESEM locations also show a relatively small spread of BPP (less than 5%). In comparison to the ESEM locations on Specimens c1 and c2 (Figures 4-9 and 4-10), the ESEM locations on Specimen d1 show a smaller typical BPP and spread of BPP.

Specimen d2. Region d2-z is located near the flaw and white patching of Specimen d2 (Figure 4-12.) In contrast to the ESEM locations on Specimen c1, c2, and d1, the ESEM location in Region d2-z exhibits an increase in BPP further away from the white patching FPZ (e.g., a decrease in BPP with closeness to the white patching FPZ), from 3.14% to 3.87%. The ESEM locations also exhibit a spread of just under 5%. Note also that Region d2-z exhibits a significantly lower BPP than the Carrara marble regions (all above 27% BPP).

4.2.3 Discussion of Imaging Conditions

Before summarizing the previously established trends, it should be noted that the images in each of the above ESEM images sets were obtained under slightly different imaging conditions. Imaging conditions such as accelerating voltage (the voltage of the ESEM beam), spot size (the size of the spot on the specimen), magnification, working distance (the distance between the specimen surface and the nearest aperture [Danilatos 1993]), and chamber water vapor pressure all affect
Table 4.3: Summary of ESEM Imaging Conditions used on the image sets shown in Figures 4-9 through 4-12. Parameters not recorded are denoted with ‘—’.

<table>
<thead>
<tr>
<th>Region</th>
<th>Acc V (kV)</th>
<th>Spot Size</th>
<th>Magnification</th>
<th>Working Distance</th>
<th>Pressure (Torr)</th>
<th>Avg BPP</th>
</tr>
</thead>
<tbody>
<tr>
<td>c1-y</td>
<td>20.0</td>
<td>3.0</td>
<td>500x</td>
<td>8.4</td>
<td>0.5</td>
<td>18.05%</td>
</tr>
<tr>
<td>c2-z</td>
<td>25.0</td>
<td>3.0</td>
<td>650x</td>
<td>10.0</td>
<td>0.3</td>
<td>27.92%</td>
</tr>
<tr>
<td>d1-z1</td>
<td>15.0</td>
<td>—</td>
<td>350x</td>
<td>9.8</td>
<td>0.4</td>
<td>5.48%</td>
</tr>
<tr>
<td>d1-z1</td>
<td>25.0</td>
<td>4.0</td>
<td>350x</td>
<td>11.6</td>
<td>0.4</td>
<td>1.34%</td>
</tr>
<tr>
<td>d1-z2</td>
<td>15.0</td>
<td>4.0</td>
<td>350x</td>
<td>9.8</td>
<td>0.4</td>
<td>1.37%</td>
</tr>
<tr>
<td>d1-z2</td>
<td>15.0</td>
<td>—</td>
<td>350x</td>
<td>9.8</td>
<td>0.4</td>
<td>2.97%</td>
</tr>
<tr>
<td>d2-z</td>
<td>20.0</td>
<td>4.0</td>
<td>350x</td>
<td>5.3</td>
<td>0.3</td>
<td>3.73%</td>
</tr>
</tbody>
</table>

the final ESEM image. For each image set (which were often obtained from different specimens on different days), the above parameters were fine-tuned to achieve the best image with minimal spotlighting. Table 4.3 presents the image parameters used to image the various regions, as well as the average BPP found in that image set (note that median, not average, BPP are reported in Figures 4-9 through 4-12).

Although the imaging conditions varied from image set to image set, the microcrack density assessment algorithm performed reasonably well on some Carrara and most Danby images (see Appendix B for a full discussion of the application of the algorithm, and sample images of its performance). Nevertheless, the potential influence of imaging conditions should be noted when considering BPP results and trends.

4.2.4 Summary of Trends in BPP

The ESEM locations on Carrara marble Specimens c1 and c2 show a higher typical BPP than the ESEM locations on Danby marble Specimens d1 and d2. This increased BPP of Carrara marble can be seen in the typical values of the BPP boxplots (all above 27% for Carrara marble, Figures 4-9 and 4-10, and below 5% for Danby marble, Figures 4-11 and 4-12). Although the ESEM location on Specimen c1 has a different orientation (y-axis normal) than all the other ESEM locations, it is still notable that the Carrara specimens show a higher BPP, and thus presumably a higher microcracking density, than the Danby specimens.
The ESEM locations on Specimens c1 and c2 also show a greater spread of BPP than the ESEM locations on Specimens d1 and d2. This BPP trend suggests that Carrara marble shows a greater variety in microcracking density than Danby marble. Wong identified a variety of microcracking densities in FPZ regions, with regions of high microcracking surrounded by regions of progressively lower microcracking [Wong 2008, Wong and Einstein 2009d]. This finding may explain the greater spread of the high microcracking marble; the highly microcracked regions of Carrara marble are surrounded by regions with lower microcracking, whereas the lesser microcracked Danby marble does not have regions of lower microcracking.

Finally, on both Carrara and Danby specimens with the exception of specimen d2, there is an increase in BPP with closeness to the white patching FPZ. This trend suggests that microcracking also increases with closeness to the white patching FPZ. It is possible that ESEM images from distance even further from the white patching FPZ than were obtained in Specimen d2 (Figure 4-12) may have revealed a reduction in BPP values (and thus presumably lower microcracking density).
Chapter 5

Small-scale Mechanical Results

This study seeks to understand how microstructure impacts the way the FPZ “looks” and “feels” in marble (i.e., the microstructure and small-scale mechanical properties of the FPZ). The previous chapter presented results on the microstructure of the FPZ; this chapter explores the small-scale mechanical properties of the FPZ. These small-scale mechanical properties are obtained with nanoindentation, a grain-scale tool for accessing mechanical properties. Grain-scale fracture is also studied with nanoscratch testing.

This chapter presents the results of the small-scale mechanical tests used in this investigation. The first section presents the mechanical properties of intact marble as determined by nanoindentation. During the investigation, it was noted that material near grain boundaries exhibited a change in nanomechanical properties; this trend is investigated for both Carrara and Danby marbles at the end of the first section. The second section explores the mechanics of the FPZ in both marble types. First, the results of fracture via nanoscratching are presented. Then, the results of nanoindentation tests conducted in and near the FPZ of both Carrara and Danby marbles are presented.

5.1 Small-Scale Mechanical Properties of Intact Marble

Nanoindentation was used to obtain small-scale mechanical properties in this investigation. As discussed in Chapters 2 and 3, nanoindentations were conducted to depths much smaller than a
typical grain size of Carrara or Danby marble, and thus returned mechanical information at the fundamental grain scale for both marbles.

In this section, the small-scale mechanical information of intact marble is presented. In the first section (Section 5.1.1), both the typical nanomechanical properties, and the anisotropy of these properties at the grain scale in both marble types is presented. These intact values are refined in the next section (Section 5.1.2) by taking a closer look at how these values change near and far from grain boundaries. It is found that indentation modulus tends to be lower near grain boundaries, and higher far from grain boundaries (i.e., near grain centers). This trend holds for both intact and process zone material of both marble types.

5.1.1 Intact Material and Anisotropy

Typical nanomechanical intact properties of both Carrara and Danby marble were desired. Typical indentation hardness values for both marbles range from roughly $2.5$ to $3$ GPa (Figure 5-1 for Carrara marble and Figure 5-2a for Danby marble), and typical indentation modulus values for both marbles range from roughly $65$ to $75$ GPa (Figure 5-1 for Carrara marble and Figure 5-2b for Danby marble).

For Carrara marble, the nanomechanical properties shown in Figure 5-1 were derived from 478 nanoindentations in grid formation conducted on three orthogonal faces of Specimen c0 (Figure 5-3a). For Danby marble, the nanomechanical properties shown in Figure 5-2 were derived from several 20-indentation test series (100 indentations total) at various loads.) Refinement of these very approximate ranges was not pursued, because it was found that nanomechanical properties varied between different marble specimens.

Both marbles are natural materials, and thus exhibit an inherent spread in any property, and especially nanomechanical properties. This inherent spread is visible to some extent in Figure 5-1. Due to this inherent variability of properties, the bulk of the analysis (Section 5.2) focuses on comparing how properties change within a single specimen. This “within-specimen” approach to the analysis is an ideal way to eliminate specimen-to-specimen variability from the investigation.
Figure 5-1: Relation between Indentation Properties and Orientation for Carrara Marble; Specimen c0. See Appendix D for an explanation of boxplots as presented in this investigation.
Figure 5-2: The relationship between prescribed load and indentation hardness, and prescribed load and indentation hardness for various loads in intact Danby marble. Each boxplot represents a 20- indentation test series. Note that regardless of the prescribed load, Danby marble hardness values range from 2.5 to 3 GPa, and modulus values range between 65 and 75 GPa. (Full details of figure in Appendix A. See Appendix D for an explanation of boxplots as presented in this investigation.)

Thus, for this investigation (and throughout Section 5.2), intact marble properties are presented only with respect to corresponding FPZ mechanical properties. As a final note, the intact nanoindentation values presented for Danby marble (Figure 5-2) includes nanoindentations in both the grain centers and grain boundaries (Carrara marble indentations in Figure 5-1 are near, but not on top of, grain boundaries).

Inspection of the nanoindentation results (Figure 5-1) reveals a slight anisotropy of Carrara marble. There is a slightly higher modulus and hardness (73.52 GPa modulus, and 2.98 GPa hardness) on the Z-face (i.e., the face to which the Z-axis is normal) compared to the other two faces (Y-face: 67.3 GPa modulus and 2.78 GPa hardness; X-face: 68.8 GPa modulus and 2.90 GPa hardness). Note also the larger spread of moduli (larger box size) on the Z-face compared to the other two faces (Figure 5-1). The differences in the median modulus and hardness between Region c0-z and the other two Regions (c0-x and c0-y) suggest a slight pre-existing anisotropy of the intact material. However, Region c0-z also exhibits a greater spread of data for modulus values. Thus, the anisotropy may be overshadowed by the existing local variation (i.e., standard deviation) in properties. The anisotropy of the mechanical properties of Danby marble was not investigated.
5.1.2 Near Grain Boundaries

The previous section established the typical ranges of nanomechanical properties in intact Carrara and Danby marble. This section explores how these ranges manifest at the grain scale, by presenting trends in nanomechanical properties near and far from grain boundaries.

Carrara Marble

Grid nanoindentation testing of intact material on Carrara marble (an intact portion of Specimen c1, far from the white patching) reveals lower modulus values near the boundaries of marble grains, but no visible trend in hardness near grain boundaries—only low hardness values directly over grain boundaries. A comparison of a spatial plot of hardness values, a spatial plot of modulus values, and an optical microscopy image illustrates this finding (Figure 5-4a). The color of each square in the pixel plot corresponds to a particular hardness or modulus value; the highest values are white (4.5 GPa hardness, and 90 GPa modulus), and the lowest values are black (1.5 GPa hardness, and 50 GPa modulus). Both the hardness and modulus spatial plots contain a dark line-shaped region in the upper right corner of the plot (Figure 5-4a). This region corresponds to the grain boundary in the upper right corner of the optical image. In the modulus plot, the region corresponding to the center of the marble grain is very light, and the regions closest to the boundaries are darker; thus, a gradient of values exists between grain boundary and center. Both the modulus and hardness plots indicate the grain boundary with a region of low (dark) modulus/hardness values. In contrast to the gradual change of modulus values, there is a more abrupt change in hardness over a relatively small region along the boundary, but otherwise no trend in values near the grain boundary. The nanoindentation grid in process zone material (Figure 5-4b; nanoindentation grid conducted close to the white patching of Specimen c1) reveals a stronger trend in modulus for the indentations near the grain boundary, and the same lack of trend in hardness values near the grain boundary. Thus, in both intact and process zone Carrara

1In this section "Intact material" connotes that the nanoindentation grid was conducted on marble grains in intact material. (For Carrara marble, this nanoindentation grid was actually located on Specimen c1 after the introduction of white patching, but in a region far from the white patching.) "Process zone material" connotes that the nanoindentation grid was conducted in or very near to the white patching on a specimen.
Figure 5-3: Carrara marble specimens and corresponding regions. Gray squares and straight black lines indicate locations of nanoindentation testing. Figure repeated from Chapter 3. (Nanoindentation and ESEM data from Specimen c3 are not presented in this thesis, but the specimen is shown here for information.)
Figure 5-4: Carrara Marble. Comparison of a spatial plot of indentation hardness values, indentation modulus values, and an optical image for two different regions. Note that the modulus and hardness values from all indentations in the grid are shown; thus data displayed includes non-ideal load-depth paths (non-second- order load-depth relationship, Section 3.2.4) which in some cases have been replaced neighboring data.
Grid nanoindentation testing of Danby marble exhibits similar trends to Carrara marble: lower modulus values near the boundaries of marble grains, and a change in hardness only on top of (not near) grain boundaries. A comparison of a spatial plot of hardness values, a spatial plot of modulus values, and an optical microscopy image of an intact region of Danby marble illustrates this finding (Figure 5-6a; an intact specimen not shown in Figure 5-5). The color of each square in the pixel plot corresponds to a particular modulus or hardness value; the highest values are red (4.5 GPa hardness, and 90 GPa modulus), and the lowest values are blue (1.5 GPa hardness, and 50 GPa modulus). The modulus plot of the Danby marble intact image (Figure 5-6a) shows higher modulus values (light blue and green in color) for the grains at the top and bottom of the image near their centers, and lower modulus values (dark blue in color) near the grain boundaries of the image.
Figure 5-6: Danby Marble. Comparison of a spatial plot of indentation modulus values, indentation hardness values, and an optical image for two different regions. Note that the modulus and hardness values from all indentations in the grid are shown; thus data displayed includes non-ideal load-depth paths (non-second-order load-depth relationship, Section 3.2.4)
The nanoindentation grid in process zone material (near the white patching of Region d2-z, Figure 5-6b) shows an even greater contrast between the very red values (high modulus values) at the center of the middle grain, and the lighter values (low modulus values) at the grain boundary. The hardness plots for both intact and process zone Danby marble show no trend in value between grain boundary and grain center, and only an abrupt change in value directly over the grain boundary.

Comparison
A major difference in the grain-scale nanomechanical property trends between the two marbles (Figures 5-4 and 5-6) is that Danby marble exhibits a high variation in the typical properties of a single grain, and Carrara marble exhibits a lower variation. The Danby marble intact image (Figure 5-6a) shows three grains, and the grain in the middle has a vastly different color (and thus, different modulus values) than the grains above and below it. Similarly, the Danby marble process zone image (Figure 5-6b) shows drastically different color between the main grain which takes up most of the center of the modulus plot, and the grain edges shown in the upper left and lower right of the modulus plot. In contrast, neither of the Carrara marble plots show a major difference in typical modulus or hardness values between the grains shown.

The chief similarity in the grain boundary trends of nanomechanical properties for the marble figures shown (Figures 5-4 and 5-6) is that in both marble types, a strong trend in modulus is found between grain boundaries and grain centers. Indentation modulus progressively decreases in locations progressively closer to grain boundaries (and progressively further from grain centers). Another similarity is that, in contrast to indentation modulus, indentation hardness shows no trend between grain boundaries and grain centers, and only an abrupt change directly over grain boundaries. A final similarity is that in process zone material, both marbles exhibit a stronger trend in modulus between grain boundary and grain center material than in intact material. The grain centers of both process zone modulus images are darker, thus suggesting a greater contrast in the modulus between grain center and grain boundary of process zone material. This trend is noteworthy for these two images, but may also be a product of inherent material variability in properties.
Figure 5-7: Data for two scratches from a five-scratch series in Carrara marble. The data has been sorted by increasing $\frac{d}{R}$ (see x-axis), and is plotted against fracture toughness $K_c$. Scratch 4 does not reach a constant $K_C$ as $\frac{d}{R}$ increases, and thus does not converge. Scratch 5 does reach a relatively constant $K_C$ as $\frac{d}{R}$ increases ($K_C = 0.78 MPa\sqrt{m}$), and thus converges.

5.2 Small-Scale Mechanical Properties of Fracture Process Zone (FPZ) Marble

5.2.1 Fracture Toughness

The nanoscratching technique in this study was used on intact marble. The test creates a fracture, and thus creates an FPZ. In this way, the test studies the FPZ of marble. Nanoscratch testing was performed according to procedures in Akono et al. [2012] and Akono et al. [2011]. Fracture toughness $K_c$ was determined from a single scratch test according to Equation 5.1, repeated here from Chapter 2:

$$K_c = \frac{F_T}{\sqrt{2pA}} \quad (5.1)$$

where $F_T$ is horizontal force, $p$ is the perimeter of the axisymmetric probe, and $A$ is the projected area of contact of horizontal load (see Section 2.1.6 for a complete discussion of the scratch test).

20 microscratches with a length of 3 mm and a measured horizontal force ranging from 0.03 to 5 N were then performed on each type of marble (Carrara and Danby). The scratches which converged to a nearly constant $K_c$ for increasing $\frac{d}{R}$ (Figure 5-7) were then used to determine average $K_c$ for the marble types. For each marble type, the data points from the convergent scratches
Figure 5-8: Sorted data from all convergent scratches.

(15 of the 20 scratches on Carrara marble converged, Figure 5-8a, and 10 of the 20 scratches on Danby marble converged, Figure 5-8b) were combined into a single data set (called here a “mega-scratch”), sorted by increasing $\frac{d}{R}$, and plotted (Figures 5-8c and 5-8d). This step essentially converted the 15 convergent Carrara marble scratches into the one “mega-scratch” in Figure 5-8c, and converted the 10 individual Danby scratches into the one “mega-scratch” shown in Figure 5-8d. The data points closest to the convergent end of the mega-scratch were used to determine the average fracture toughness $K_C$ for each marble type. In other words, the second half (with respect to $\frac{d}{R}$) of mega-scratch data for each marble type (i.e., half of $\frac{d}{R_{\text{max}}}$ to $\frac{d}{R_{\text{max}}}$, or from $\frac{d}{R} = 0.045$ to
0.09 for Carrara marble, and similarly for Danby marble) was averaged to determine the characteristic $K_c$ for each marble type. It was found that Carrara marble had a higher fracture toughness ($K_c = 0.95\text{MPa}\sqrt{m}$) than Danby marble ($K_c = 0.67\text{MPa}\sqrt{m}$). Both values are in the range of fracture toughness values for marble found in the literature. Amrollahi et al. [2011] found $K_c$ ranging from 0.7 to 1.5 MPa$\sqrt{m}$ for Iranian marble using the Hollow Centre Cracked Disc (HCCD) technique. Thus, although it is well known that $K_c$ values may vary for a particular material depending on the technique used for measuring $K_c$, the scratch test $K_c$ values derived in this study are within the range of values found in literature, and thus are assumed to lie near the true fracture toughnesses of the material.

5.2.2 Nanoindentation of Carrara Marble

Two to three lines (or grids) of 300+ nanoindentations each were placed progressively closer to the FPZ on Carrara marble specimens (Figure 5-3). This section presents the results of nanoindentation testing on two specimens of Carrara marble: Specimens c1 and c2 (Figures 5-3b and 5-3c). Five regions on these two specimens were investigated: Regions c1-z1, c1-z2, c1-z3, c1-x, and c2-z. Nanoindentation results are presented in boxplot form (for a more extensive discussion of boxplots as they are used in this investigation, see Appendix Chapter D). The main trend of note on the Carrara marble specimens is lower indentation modulus values near and within the white patching FPZ when compared with modulus values of intact material (further from the FPZ).

Specimen c1

Region c1-z1 clearly illustrates a reduction in modulus as well as hardness with distance from the white patching FPZ (Figure 5-9; note that in Figure 5-9, the white patching is located on the right side of the diagram, but on the left side of the boxplot chart). Proceeding closer to the FPZ (white patching) in Region c1-z1 (Figures 5-3b, 5-9), the boxplots drop from a typical indentation hardness of 3.20 GPa farthest from the FPZ, to 2.73 GPa closest to it. Modulus also drops from 71.13 GPa farthest from the FPZ, to 67.71 GPa closest to it.

Proceeding from right to left towards the process zone in Region c1-z2, no significant or
steady decrease in either nanomechanical property is apparent on this surface (Figure 5-10). The hardnesses are relatively steady around 2.87 GPa (Figure 5-10), which is just below the typical hardness value of the Z-face (2.98 GPa, Figure 5-1b). The modulus values peak slightly in the center of the specimen at 72.73 GPa (Figure 5-10). This modulus value is just below the typical modulus of intact material on the Z-face of Carrara marble on Specimen c0 (73.52 GPa, Figure 5-1c).

Similar to Region c1-z2, no significant or steady decrease in either nanomechanical property is apparent in Region c1-z3 (Figure 5-11). The indentation hardnesses are relatively steady around 2.7 GPa (Figure 5-11), which lie below the typical hardness value of the Z-face of Carrara marble on Specimen c0 (2.98 GPa, Figure 5-1b). The typical indentation modulus values (67.5 GPa, Figure 5-11) lie below the typical modulus of intact material on the Z-face of Carrara marble on Specimen c0 (73.52 GPa; Figure 5-1c). It is interesting to note that Region c1-z3 physically lies below Region c1-z2 on Specimen c1 (Figure 5-3b), and that the indentation modulus and hardness values of Region c1-z3 are smaller than those of Region c1-z2 (Figure 5-10).
Figure 5-10: Relation between Indentation Properties and Distance from Fracture Process Zone (FPZ); Region c1-z2

Figure 5-11: Relation between Indentation Properties and Distance from Fracture Process Zone (FPZ); Region c1-z3
Figure 5-12: Relation between Indentation Properties and Distance from Fracture Process Zone (FPZ); Region c1-x

Region c1-x shows a decrease in median indentation modulus values with closeness to the white patching FPZ (Figure 5-12), but the median indentation hardness values show a slight increase. The region shows a typical indentation hardness of 2.65 GPa farthest from the process zone, and 2.75 GPa closest to it (Figure 5-12). The indentation modulus values, however, decrease; the region exhibits a typical indentation modulus of 71.8 GPa farthest from the process zone, and 68.76 GPa closest to it (Figure 5-12).

**Specimen c2**

Region c2-z (Figures 5-3c and 5-13), on a completely different specimen than the other regions just discussed (c1-z1, c1-z2, c1-z3, and c1-x), shows a downward trend of indentation modulus and hardness with closeness to the FPZ. Hardness decreases from 2.53 GPa furthest from the FPZ to 2.43 GPa closest to the FPZ (Figure 5-13). Modulus also decreases from 66.41 GPa furthest from the FPZ to 63.86 GPa closest to the FPZ (Figure 5-13).
5.2.3 Nanoindentation of Danby Marble

This section presents the results of nanoindentation testing on two specimens of Danby marble: Specimens d1 and d2 (Figure 5-5). Three region on these two specimens (d1-z1, d1-z2, and d2-z) are presented. Nanoindentation results are presented in boxplot form.

**Specimen d1**

Region d1-z1 shows a reduction in hardness, but an increase in modulus with closeness to the white patching FPZ (Figure 5-14). Recall that Region d1-z1 does not display visible white patching, but nanomechanical property trends on this specimen suggest that the specimen contains early-stage FPZ development. Wong [2008] has identified microcracking in a region which has undergone an increase in stress, but has not displayed white patching. Region d1-z1 is in a similar state; no white patching is visible, but microcracking has been identified (Section 4.2.2). The nanoindentation grids closest to the flaw tip, which are in the region of expected white patch development, yield lower median hardness values (Figure 5-14) than the grid farthest from the flaw tip. Hardness
Figure 5-14: Relation between Indentation Properties and Distance from Fracture Process Zone (FPZ); Region d1-z1

decreases from 2.69 GPa furthest from the flaw tip, to 2.53 GPa closer to the flaw tip (Figure 5-14). Additionally, the nanoindentation grid closest to the flaw also displays a lower median hardness (2.62 GPa) than the grid furthest from the flaw tip. The nanoindentation grid furthest from the initial crack, and thus furthest from the expected FPZ, displays the highest nanoindentation hardness. The expected hardness trend of decrease in hardness near the FPZ occurs in this early-FPZ region.

In contrast, modulus values for Region d1-z1 (Figure 5-14) do not follow the same trends as hardness. Although the nanoindentation grid with the lowest median hardness also displays the lowest median modulus (67.51 GPa), the nanoindentation grid with the highest median hardness does not display the highest median modulus. In fact, the nanoindentation grid with the second highest median hardness displays the highest median modulus (72.28 GPa). Thus, the region has attained the expected reduction of hardness in the pre-FPZ region, but not the expected reduction of modulus. Although it is noted that one of the grids in this region contained fewer analyzed indentations (70) than other grids, the reduction of hardness but not modulus values in this near-
Figure 5-15: Relation between Indentation Properties and Distance from Fracture Process Zone (FPZ); Region d1-z2. Note that exact distance from FPZ is not indicated in plot, as the first two boxplots lie directly over the white patching and thus would have a measured distance of 0. The third boxplot (furthest right, highest median indentation modulus and hardness values) has a distance of 6 mm from the white patching FPZ.

The crack-tip region remains a notable experimental result.

Region d1-z2 shows a reduction in both modulus and hardness with closeness to the white patching FPZ (Figure 5-15; note that the two boxplots in Figure 5-15 with the lowest median indentation hardness and modulus values lie directly over the white patching in Region d1-z3, and thus have a distance of 0.) For Region d1-z2, the median hardness value nearest the white patching FPZ is 2.54 GPa (Figure 5-15), almost 0.1 GPa lower than the median hardness value of the farthest grid (2.66 GPa). The median modulus value nearest the white patching FPZ is 66.71 GPa (Figure 5-15), almost 7 GPa lower than the median modulus value of the farthest grid (73.28 GPa).

Specimen d2
Region d2z shows a reduction in both indentation modulus and hardness with closeness to the white patching FPZ (Figure 5-16; note that in Figure 5-16, the white patching is located on the right side of the diagram, but on the left side of the boxplot chart). Hardness decreases from 2.57
Figure 5-16: Relation between Indentation Properties and Distance from Fracture Process Zone (FPZ); Region d2-z. Note that the white patching is located on the right side of the diagram, but on the left side of the boxplot chart.

GPa furthest from the white patching FPZ, to 2.47 GPa closest to the white patching FPZ (Figure 5-16). Modulus decreases from 69.42 GPa furthest from the white patching FPZ, to 67.08 GPa closest to the white patching FPZ (Figure 5-16).

5.2.4 Comparison of Nanoindentation on Carrara and Danby Marbles

A majority of the regions tested on Carrara and Danby marbles showed a reduction in indentation modulus and/or indentation hardness with closeness to the white patching FPZ: Region c1-z1, Region c1-x, Region c2-z, Region d1-z1, Region d1-z2, and Region d2-z. The trends found on each region are summarized in Table 5.1.

The distance over which these reductions occurred varied from region to region, and will be explored more fully in the next chapter. The next chapter will also explore the statistical significance of the nanomechanical property trends identified in this chapter.
Table 5.1: A summary of the nanomechanical property trends identified in and near white patching FPZ regions. Trends refer to relationship between test furthest from the white patching FPZ and the test closest to the white patching FPZ (flaw tip, on Specimen d1-z1.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Region</th>
<th>Trends Near White Patching FPZ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Modulus</td>
</tr>
<tr>
<td>c1</td>
<td>c1-z1</td>
<td>Decrease</td>
</tr>
<tr>
<td></td>
<td>c1-z2</td>
<td>Increase</td>
</tr>
<tr>
<td></td>
<td>c1-z3</td>
<td>Increase</td>
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<tr>
<td></td>
<td>c1-x</td>
<td>Increase</td>
</tr>
<tr>
<td>c2</td>
<td>c2-z</td>
<td>Decrease</td>
</tr>
<tr>
<td>d1</td>
<td>d1-z1</td>
<td>Decrease</td>
</tr>
<tr>
<td></td>
<td>d1-z2</td>
<td>Decrease</td>
</tr>
<tr>
<td>d2</td>
<td>d2-z</td>
<td>Decrease</td>
</tr>
</tbody>
</table>

5.3 Chapter Summary

This chapter has presented nanoindentation results for both Carrara and Danby marbles. Both marble types indicated a reduction in indentation modulus near grain boundaries (with respect to grain centers); this reduction was more noticeable around the grain boundaries of process zone material. A reduction in indentation hardness and indentation modulus with closeness to the white patching FPZ was also found in Regions of both marble types.
Experimental results (presented in Chapters 4 and 5) provide clues about the actual mechanisms that govern the FPZ. This section reviews and analyzes those clues, and discusses the possible mechanisms of quasi-brittle fracture that these clues suggest. First, the link between pure fracture (i.e., the formation of microcracks and macrocracks) and the macro-scale loading behavior in this investigation is explored, to understand the complementary (but different) roles of fracture and yielding in quasi-brittle materials. Then, the results of microstructural observation of the FPZ are presented, and used to interpret the small-scale geometric structure of the FPZ in quasi-brittle materials. Finally, the results of nanomechanical measurements of the FPZ are presented, and used to interpret the small-scale mechanical structure of the FPZ in quasi-brittle materials. To close the chapter, all of the presented clues and possible geometric mechanisms are combined to describe the size, structure, and mechanical properties of the quasi-brittle material FPZ based on the work of this investigation.
6.1 Fracture Toughness from Macro-Scale Strength

This section explores the link between fracture toughness $K_C$ measured at a small scale and macro-scale loading behavior. This section theoretically derives fracture toughness $K_C$ for a force-controlled experiment (based on the derivation by Ulm [Spring 2009]), applies this derivation to uniaxial testing from this investigation to reveal expected fracture toughness $K_C$, and then compares this expected $K_C$ with measured $K_C$ from microscratch testing. The discrepancy between expected and measured fracture properties will suggest possible mechanisms of fracture and/or yielding occurring in the quasi-brittle materials in this investigation.

6.1.1 Uniaxial Loading

Figure 6-1 shows the uniaxial loading curves of single-flaw prismatic specimens of Carrara and Danby marble (Carrara marble data from Wong [2008]). Note that most of loading curves in Figure 6-1 (and clarified in Figure 6-2) are from specimens that were loaded to failure, and thus not used for the white patching investigation in this study. These loading curves display the typical behavior of single flaw specimens (Figure 3-22b) of each type of marble. Although the definition of a process zone stated in Section 2.1.5 requires material yielding, the uniaxial loading curves do not clearly show evidence of yielding. Such evidence would be a reduction in the slope of the stress-strain curve, and would clearly indicate material yielding (i.e., a reduction in material stiffness due to either property change or small-scale deformation over time before brittle fracture). The loading portions of the stress-strain curves in Figure 6-1 do not reveal a notable change in slope before the curves plateau at maximum stress. Instead, for most specimens of both marble types, there is a very sudden transition from the initial part of the curve to the plateau of the curve.

The literature reports that white patching develops well before a pre-cracked specimen reaches maximum stress [Wong and Einstein 2009c;d]. (For a specimen with two flaws, white patching may develop as early as 50% of maximum stress.) However, although the specimens in Figure 6-1 are presumed to develop white patching before failure, their uniaxial curves do not show any indication of yielding (i.e., a reduction in the slope of the stress-strain curve). Danby D and Carrara
Figure 6-1: Loading curves of single-flaw prismatic specimens of Carrara and Danby marble. Initial portion of stress-strain data assumed to derive from settling of machine, and removed for each curve. As illustrated in Figure 6-2, final portion of stress-strain data following maximum stress assumed to reflect post-specimen-failure, and removed for each curve.

Figure 6-2: Idealized stress-strain curve from a uniaxial test. Shaded portions indicate the portions removed before plotting the uniaxial test data in Figure 6-1.
F do show a change in the loading curve before the specimen reaches maximum stress. However, Danby D recovers to the initial loading slope, so the slump in the middle of the loading curve may not be yielding. Thus, the quasi-brittle material in this investigation does not seem to show concrete evidence of yielding before fracture. These macro-scale curves suggest a nearly pure brittle behavior. In an attempt to prove the minimal (to nonexistent) yielding of this material, in the next section (Section 6.1.2) these curves will be related to material fracture properties. Although (as will be explained) this derivation is controversial, it may illuminate a complete link between the loading behavior and material fracture properties (and thus, the lack of a link between loading behavior and material yielding).

### 6.1.2 Lack of Yielding in Uniaxial Loading

Existing work has found that the shape of the loading curve can link entirely to fracture properties of the material. This section derives the relationship between uniaxial loading curve and material fracture toughness \( K_c \). There are two chief types of stress-strain behavior: brittle behavior, in which no yielding or damage is apparent in the stress-strain curve and stored elastic energy is released during fracture, and damage behavior, in which some yielding (or damage) is apparent in the stress-strain curve and some stored elastic energy is released during this yield period [Ulm Spring 2009]. In this section, a direct link is drawn between the brittle (i.e., no yielding) stress-strain behavior of the marbles in this investigation and their fracture properties – specifically, fracture toughness \( K_c \). The existence of this link, coupled with their lack of evidence of yielding on the stress-strain curves, could suggest that the crack propagation – and white patch formation – found in this study is derived completely from fracture of the marble, and not from any yielding at the FPZ.

**Theoretical Derivation of Fracture Toughness from Force-Controlled Experiment**

This section derives the material property of fracture toughness, \( K_{fc} \), from the loading behavior (i.e., force-displacement curve) of a force-controlled test, such as a loading test in a uniaxial ma-
Figure 6-3: Force-displacement diagram for any 1-parameter loading. From Ulm [Spring 2009]. Vector 1 is the bottom vector (from the origin to \((u + du, F + dF)\)), Vector 2 is the top vector (from the origin to \((u, F)\)), Component 1 is the \(u\)-component of the vectors, and Component 2 is the \(F\)-component of the vectors. The shaded area corresponds to the energy release \(G\partial l\) at \((u + du, F + dF)\).

First, we apply the energy release expression (derived in Section 2.1.5, Equation 6.1):

\[
\varepsilon_{\text{pot}} = \frac{1}{2} \int_{\partial \Omega_{ld}} T \cdot \xi^d \partial a - \frac{1}{2} \int_{\partial \Omega_{ld}} T^d \cdot \xi \partial a,
\]

(6.1)

to a 1-parameter loading. For such a loading situation, the force \(F\) depends only on the displacement \(u\) (Figure 6-3). Thus, the expression of fracture energy \(G = -\frac{\partial \varepsilon_{\text{pot}}}{\partial l}\) for a 1-parameter loading system first replaces the stress \(T^d\) in Equation 6.2 with force \(F\), and replaces the displacement \(\xi^d\) with displacement \(u\):

\[
\varepsilon_{\text{pot}} = \frac{1}{2} \int_{\partial \Omega_{ld}} F^d \cdot u - F \cdot u^d \partial a
\]

(6.2)

\footnote{Much of the discussion is motivated by the explanation in Ulm [Spring 2009]. It should be noted that the derivation as presented in this section holds only for a test run in force control, i.e. the test system applies a controlled force regardless of the displacement. The uniaxial tests in Figure 6-1 were in fact run in a force-controlled loading frame (after an initial seating load of 2500 lb, equivalent to just under 4 MPa, run in displacement control), so this derivation applies. It should also be noted that this derivation applies for a 1-parameter loading, i.e. loads and displacements are assumed to occur only in one (and the same) direction. Thus, this derivation applies for a test run in a uniaxial machine that ignores any lateral (i.e., Poisson's) effects.}
and thus reads:

$$\mathcal{G} = -\frac{\partial e_{\text{pot}}}{\partial l} = \frac{1}{2} \int_{\partial \Omega_{\text{ext}}} F^d \bullet \frac{\partial u}{\partial l} - \frac{\partial u}{\partial l} \bullet u^d \partial a. \tag{6.3}$$

Finally, considering only unit width of the system $\partial a$ dissolves the integral, and multiplying by change in crack length $\partial l$ yields:

$$\mathcal{G} \partial l = \frac{1}{2} (F \partial u - \partial F u) \tag{6.4}$$

The expression on the right side of Equation 6.4 is the magnitude of the area subtended between two force-displacement vectors (see vectors in Figure 6-3). Given that the area between two vectors is equivalent to one-half of their cross product, Equation 6.4 can be evaluated as:

$$(\text{Vector 1} \times \text{Vector 2}) = \text{Vector 1}_{\text{component 1}} \text{Vector 2}_{\text{component 2}} - \text{Vector 1}_{\text{component 2}} \text{Vector 2}_{\text{component 1}}$$

$$= (u + \partial u)(F) - (F + \partial F)(u)$$

$$= F \partial u - u \partial F \tag{6.5}$$

Thus, the energy release during a 1-parameter loading can be found as the area subtended between two force-displacement vectors.

In the case of a force-controlled experiment, an increase in displacement at constant force allows for the simplification of the energy release from Equation 6.4 (Figure 6-4). This increase in displacement at constant force is here assumed to occur at specimen fracture in the uniaxial tests in Figure 6-1, so we formulate not just energy release $\mathcal{G}$, but fracture energy $\mathcal{G}_F$. With no change in force $F$, $\partial F = 0$ and the second term in Equation 6.4 drops out:

$$\mathcal{G}_F \partial l = \frac{1}{2} F \partial u \tag{6.6}$$

Finally, recall that fracture energy $\mathcal{G}_F$ scales with the square of fracture toughness $K_{\text{IC}}$ over the
Figure 6-4: Force-displacement diagram for a force-controlled 1-parameter loading, at fracture. From Ulm [Spring 2009].

material Young’s modulus $E$ [Irwin 1957]:

$$K_{IC} = \sqrt{EG_F}$$

(6.7)

Thus, fracture toughness $K_{IC}$ can be found from a 1-parameter force-controlled loading:

$$K_{IC} = \sqrt{\frac{1}{2} EF \frac{\partial u}{\partial l}}$$

(6.8)

Application of Fracture Toughness $K_{IC}$ to Uniaxial Testing of Carrara and Danby Marble

In order to apply the fracture toughness expression (Equation 6.8) to a uniaxial test, the variables from a uniaxial test must be introduced. Rather than force $F$, it is more common to report stress $\sigma$ (assumed to act over a uniform cross section $wb$ of material):

$$F = \sigma wb$$

(6.9)

At failure, the stress $\sigma$ corresponds to failure stress $\sigma_F$. Additionally, the displacement of the test relates to change in specimen axial strain, $\partial \varepsilon$, and specimen height, $h$:

$$u = h \partial \varepsilon$$

(6.10)
The area of the assumed flat crack surface, $A_{\text{Flat}}$ (half of this surface is shaded in Figure 6-5), is a simplification of the classic tensile wing crack [Wong and Einstein 2009c], and is approximated by the specimen width $b$ times the specimen height $h$ (for two crack surfaces, each with height $\frac{h}{2}$, Figure 6-5). This crack surface assumption yields an expression for $K_{ic, \text{Flat}}$:

$$K_{ic, \text{Flat}} = \sqrt{\frac{1}{2} E (\sigma_F w b) \frac{h \partial \varepsilon}{bh}} \quad (6.11)$$

Geometric relations simplify Equation 6.11. For the prismatic specimens in this study, the width $w$ is twice the thickness $b$, and the height $h$ is four times the thickness $b$ [Wong 2008]:

$$K_{ic, \text{Flat}} = \sqrt{E b \sigma_F \partial \varepsilon} \quad (6.12)$$

Appendix G details the case in which the specimen is considered to be not a pure solid (as above) but a granular material composed of spherical grains. Under this consideration, the crack surface area will have a size of $A_{\text{Granular}}$ rather than $A_{\text{Flat}}$, as considered above. $A_{\text{Granular}}$ is larger than $A_{\text{Flat}}$ by a factor of $\frac{\pi}{2}$. As shown in the derivation in Appendix G, regardless of the assumed size of the spherical grains, this factor of $\frac{\pi}{2}$ remains constant; the size of the grains does not change.
this factor. Any consideration of material granularity (spherical) will thus yield:

\[ A_{\text{Granular}} = \frac{\pi}{2} A_{\text{Flat}} = \frac{\pi}{2} bh. \]  

(6.13)

Applying the expression for crack surface area in a granular material \( A_{\text{Granular}} \) (Equation 6.13) into the initial expression for fracture toughness from a 1-parameter loading (Equation 6.11) yields:

\[
K_{Ic, \text{Granular}} = \sqrt{\frac{1}{2} E \sigma_F w b \frac{h \partial \varepsilon}{\pi bh}} \\
= \sqrt{\frac{2}{\pi} E \sigma_F b \partial \varepsilon} \\
= \frac{4}{\pi^2} \sqrt{E \sigma_F \partial \varepsilon} \\
= \frac{4}{\pi^2} K_{Ic, \text{Flat}}
\]  

(6.14)

Thus, the above expression demonstrates that the consideration of a granular material reduces the expression of theoretical fracture toughness \( K_{Ic} \) by a factor of \( \frac{\pi^2}{4} \).

Figure 6-1 shows the uniaxial loading curves of single-flaw prismatic specimens of Carrara and Danby marble. Following crack propagation theory [Griffith 1920, Irwin 1957, Saxena 1998], it is assumed that the entire crack surface indicated in Figure 6-5 is opened instantaneously, at peak stress (and thus the plateau) in the loading curves of Figure 6-1 (although unstable crack propagation often starts before peak stress). The \( \partial \varepsilon \) is derived from one typical curve from each marble (Figure 6-6, Carrara A, \( \partial \varepsilon = 0.047\% \), and Danby B, \( \partial \varepsilon = 0.025\% \); see labeled curves in Figure 6-1) as the change in strain between the two circled points on the plots in Figure 6-6, which were selected by hand to encompass the plateau on the stress-strain curve.

For an assumed flat crack surface with area \( A_{\text{Flat}} \), using Equation 6.12 and the Carrara and Danby marble properties listed in Tables 6.1 and 6.2, the fracture toughnesses are found to be \( K_{Ic, \text{Flat}} = 85.8 \text{ MPa} \sqrt{\text{m}} \) for Carrara marble, and 52.4 MPa \( \sqrt{\text{m}} \) for Danby marble.

For an assumed granular crack surface with area \( A_{\text{Granular}} \), using Equation 6.14 and the Carrara and Danby marble properties listed in Tables 6.1 and 6.2, the fracture toughnesses are found to be
Figure 6-6: Selected uniaxial curves from Figure 6-1 used in theoretical derivation of fracture toughness, Equations 6.12 and 6.14. Strain increment \( \partial \varepsilon \) was determined as the difference in strain between the two circled points on each plot.

Table 6.1: Carrara Marble properties used in fracture toughness derivation.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young’s Modulus, ( E )</td>
<td>49 GPa</td>
<td>Wong [2008]</td>
</tr>
<tr>
<td>Tensile Strength, ( \sigma_T )</td>
<td>6.2 MPa</td>
<td>This Investigation</td>
</tr>
<tr>
<td>( \partial \varepsilon )</td>
<td>0.04667</td>
<td>Figures 6-1 and 6-6a, Carrara A</td>
</tr>
<tr>
<td>( b )</td>
<td>1.5 inch = 0.0381 m</td>
<td>Wong [2008]</td>
</tr>
<tr>
<td>( K_{ic, Flat} )</td>
<td>85.8 MPa( \sqrt{m} )</td>
<td>Equation 6.12</td>
</tr>
<tr>
<td>( K_{ic, Granular} )</td>
<td>34.8 MPa( \sqrt{m} )</td>
<td>Equation 6.14</td>
</tr>
<tr>
<td>( K_{c, Scratch Test} )</td>
<td>0.95 MPa( \sqrt{m} )</td>
<td>Scratch Testing</td>
</tr>
</tbody>
</table>

\( K_{ic, Granular} = 34.8 \text{ MPa}\( \sqrt{m} \) for Carrara marble, and 21.3 MPa\( \sqrt{m} \) for Danby marble.

Comparison of Derived Fracture Toughness \( K_{ic} \) with Experimentally Determined Fracture Toughness \( K_{ic} \)

Both the theoretically derived fracture toughness values (\( K_{ic, Flat} \) and \( K_{ic, Granular} \)) are one to two orders of magnitude larger than fracture toughness values experimentally determined from the micro-scratch testing: 0.95 MPa\( \sqrt{m} \) for Carrara marble, and 0.67 MPa\( \sqrt{m} \) for Danby marble (Figures 5-8c and 5-8d). They are also larger than fracture toughness values in the literature for marble experimentally determined from Cracked Chevron-Notches Brazilian Disc and Hollow Center Cracked Disc tests: 1.4 MPa\( \sqrt{m} \) for Neiriz marble, 1.2 MPa\( \sqrt{m} \) for Baghat marble, and 1.3
Table 6.2: Danby Marble properties used in fracture toughness derivation. Carrara and Danby marble have similar indentation moduli, so the Young's Moduli are also assumed to be the same.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young's Modulus, $E$</td>
<td>49 GPa</td>
<td>Assumed same as Carrara</td>
</tr>
<tr>
<td>Tensile Strength, $\sigma_T$</td>
<td>3.7 MPa</td>
<td>This Investigation</td>
</tr>
<tr>
<td>$\partial \varepsilon$</td>
<td>0.02490</td>
<td>Figures 6-1 and 6-6b, Danby B</td>
</tr>
<tr>
<td>$b$</td>
<td>1.5 inch = 0.0381 m</td>
<td>Wong [2008]</td>
</tr>
<tr>
<td>$K_{Ic, Flat}$</td>
<td>52.4 MPa$\sqrt{\text{m}}$</td>
<td>Equation 6.12</td>
</tr>
<tr>
<td>$K_{Ic, Granular}$</td>
<td>21.3 MPa$\sqrt{\text{m}}$</td>
<td>Equation 6.14</td>
</tr>
<tr>
<td>$K_{Ic, Scratch}$</td>
<td>0.67 MPa$\sqrt{\text{m}}$</td>
<td>Scratch Testing</td>
</tr>
</tbody>
</table>

Several factors may explain the difference between the derived and experimental $K_{Ic}$ values. Firstly, a variety of crack events occur during uniaxial loading. Whereas the simplified analysis above assumes that failure occurs by a single wing crack emanating from the flaw tips, in reality a number of cracks may emanate from the flaw and may branch from the wing cracks [Wong and Einstein 2009c;d]. Thus, the failure surface may be greater than the $h$ assumed in Figure 6-5; this possibility would increase the surface term $(bh)$ in the denominator of Equation 6.11, reduce the derived $K_{Ic}$ value, and bring the derived $K_{Ic}$ value closer to the experimental value.

Secondly, fracture toughness varies with respect to the mode of crack opening. Whereas the crack in scratch testing opens in Mode II [Akono et al. 2012], the wing crack assumed in the $K_{Ic}$ derivation (Figure 6-5) branches from a pre-existing crack that tends to open itself in a tensile, or Mode I, fashion [Wong 2008, Wong and Einstein 2009c;d]. Mode II and Mode I fracture may activate different mechanisms in the material; these different mechanisms may explain some of the differences between the derived and experimental $K_{Ic}$ values.

Thirdly, the regime of crack propagation – i.e., stable crack propagation, or unstable crack propagation – differs between the uniaxial test in the derivation of $K_{Ic}$, and the experimental fracture toughness. When the energy release $G$ equals the material fracture energy $G_F$, a crack will propagate in a stable fashion. However, once both the energy release exceeds the fracture energy, and the increase of energy release with respect to crack increment is greater than the increase of fracture energy with respect to crack increment, a crack will propagate in an unstable fashion.
[Saxena 1998]. Thus, the uniaxial test employed in the derivation of \( K_{IC} \) may incorporate unstable growth, and thus activate different mechanisms, than the stable crack used to derive \( K_{IC} \) from the scratch test.

Finally, fracture alone may not be enough to explain the loading behavior of the quasi-brittle materials in this investigation. The theoretically derived fracture toughness values found above were an attempt to link macro-scale loading behavior entirely with fracture. The derived fracture toughness values (\( K_{IC, Flat} \) and \( K_{IC, Granular} \), shown in Tables 6.1 and 6.2) were found to be much larger than fracture toughness values measured with scratch testing (\( K_{IC, Scratch} \), also shown in Tables 6.1 and 6.2). We assume that the \( K_{IC, Scratch} \) values are more accurate (i.e., closer to the true material fracture toughness at the scale of testing in this investigation) than the \( K_{IC, Flat} \) and \( K_{IC, Granular} \) values because the \( K_{IC, Scratch} \) values are very similar to marble fracture toughness values from the literature (found by other means of fracture toughness testing, such as Hollow Centre Cracked Disc (HCCD) [Amrollahi et al. 2011]). Thus, given that the \( K_{IC, Scratch} \) values match the literature, we assume that the \( K_{IC, Flat} \) and \( K_{IC, Granular} \) appear to be inaccurate. The derivation of \( K_{IC, Flat} \) and \( K_{IC, Granular} \) rested on the assumption that only fracture (i.e., the creation of micro- and macrocracks) was responsible for the stress-strain behavior in the investigated materials (Figure 6-6). The apparent inaccuracy of \( K_{IC, Flat} \) and \( K_{IC, Granular} \) suggests the inaccuracy of this assumption, and consequently also suggests that in fact some of the stress-strain behavior (i.e., energy released during loading) must be attributed to material yielding caused by smaller-scale mechanisms.

Nevertheless, it is noted that finer-grained Carrara marble exhibits a higher fracture toughness than coarser-grained Danby marble. Specifically, for the theoretically derived \( K_{IC} \) the ratio of Carrara to Danby marble is 1.6, and 1.4 for the experimentally determined scratch test \( K_{IC} \). The trends in fracture toughness are thus very similar, despite whether the fracture toughness is theoretically derived, or experimentally determined. Thus, the loading behavior reflects the effect of microstructure on fracture toughness: a finer grain size correlates with an increased fracture toughness for marble.

This section has been devoted to theoretically deriving fracture toughness in order to understand the roles of both fracture and yielding in the behavior of the materials in this investigation. There is,
however, a secondary use of deriving fracture toughness: in order to provide a theoretical estimate of the FPZ size, based on Irwin’s energy formulation of FPZ size (Section 2.1.5). The fracture toughness values in this section, in conjunction with the fracture toughness values from scratch testing and tensile strength values will be used to formulate predictions of process zone size based on Irwin’s formulation (Equation 6.15), discussed later in this chapter and following the discussion of nanomechanical study results.

6.2 Density of Microcracking Close to FPZ

The previous section discussed general fracture behavior of the quasi-brittle materials in this investigation. This section returns to the microstructure of fractured quasi-brittle materials by considering the results from Chapter 4. The increased black pixel percentage (BPP) found in white patching FPZ regions suggests that a typical FPZ has formed on the specimens in this investigation. Increased black pixel percentage is related to increased microcrack density, so the median BPP measurements (See Chapter 4) indicate that the characteristic microcracks of an FPZ have formed in these specimens. This section first reviews BPP trends found in testing regions in Carrara marble, and then in Danby marble. These trends are reviewed from the perspective of their statistical significance, and linked with possible indications of FPZ microstructure. The section closes with a comparison of the significant BPP trends in Carrara and Danby marble, and a relation of these trends to the geometric phenomena behind FPZ development.

6.2.1 Carrara Marble

First, Figure 6-7 provides a reminder of orientation for all the specimens in this investigation. The BPP trends on Carrara marble Specimens c1 and c2 (Regions c1-y and c2-z) are shown in Figures 6-8 and 6-9. Specimen c1 exhibits a relatively high median BPP measurement (18.1%). The region measured on Specimen c2 has been divided in half; the left half is very close to the white patching FPZ, and the right half is further away. The half closest to the white patching FPZ exhibits a median BPP measurement higher than that on Specimen c1 (28.36%). The half furthest from the
white patching FPZ exhibits a lower BPP measurement than the half closest to the white patching FPZ (27.98%), but still higher than the measurement on Specimen c1. However, the difference in BPP measurements far from and near to the white patching FPZ on Specimen c2 is statistically significant ($t=1.97$).

Some differences between Specimens c1 and c2 may contribute to the different BPP measurements on these specimens. Region c1-y on Specimen c1 is the inside surface of the white patching which opened as Regions c1-z1 and c1-z2 separated (See Section 4.2.2 for a discussion of this region). In contrast, Region c2-z is from the face of the white patching (on the front of Specimen c2). Region c2-z exhibits a higher BPP than Region c1-y. If BPP is assumed to correlate with microcrack density, and barring any difference in BPP due to differences in ESEM imaging conditions, there are three possible geometric explanations for this difference:

1. Region c2-z initially had more microcracking pre-loading than Region c1-y
Figure 6-9: BPP measurements on Specimen c2, Region c2-z. Statistical significance is indicated with a dashed line and t-value.

2. The face of white patching (represented by Region c2-z) has a higher microcrack density than the within-specimen surface of white patching (represented by Region c1-y)

3. Region c2-z has more damage than Region c1-y, due to receiving increased loading (and higher stress)

The first explanation stems from the differences in grain size (and thus microcrack density) between two specimens of the same marble. The last two explanations relate to the triaxiality of the stress state around a flaw tip, and indicate a possible structure of the FPZ in the marble specimens. If the outer surface of the specimens (represented by Region c2-z) did sustain more loading than the inner part of the specimens (represented by Region c1-y), and thus sustained more stress, then the outer surface of the specimens would exhibit more damage and a higher microcracking density. The triaxial stress state suggested by BPP trends would be high stresses on the outer surfaces of specimens, and low stresses within the specimens likely due to confinement from all of the material within the specimen. This stress state would create an FPZ which has the most damage on the outer surface of specimens, and little to no damage within the body of specimens. With the given experimental results, it is impossible to determine which of the explanations is absolutely correct. However, the BPP trends on Danby marble discussed in the next section may further illuminate the structure of the FPZ in marble.
6.2.2 Danby Marble

The BPP trends on Danby marble Specimens d1 (Regions d1-z1 and d1-z2) and d2 (Region d2-z) are shown in Figures 6-10 and 6-11. Note first that all of the regions exhibit lower median BPP measurements than those on the Carrara marble specimens (Figures 6-8 and 6-9. Of all the Danby marble regions measured, Region d1-z1 has both the highest and lowest median BPP measurements (4.98% and 1.23%), near and far from the flaw tip. Additionally, the difference in BPP measurements near and far from the flaw tip in Region d1-z1 is statistically significant. Region d1-z2 has median BPP values between those found in Region d1-z1 (3.48%, 2.47%, and 1.27%), with the highest two median BPP values closest to the white patching BPP in Region d1-z2. The differences between all median BPP values in Region d1-z2 are statistically significant (note that the t-value for significance for tests in Region d1-z2 is 1.6839, as one of the tests
contains only 40 values; see Appendix E and Ang and Tang [2007]). Region d2-z also has median BPP values (3.87\% and 3.14\%) between those found in Region d1-z1 (4.98\% and 1.23\%), with the lowest BPP values closest to the white patching BPP in Region d2-z.

Again, differences between Specimens d1 and d2 – and amongst the two regions on Specimen d1 – may somewhat explain the different BPP trends between the specimens. Firstly, on Specimen d1, Region d1-z2 showed white patching visible at the macroscale, but Region d1-z1 did not. Because Regions d1-z1 and d1-z2 lie on the same specimen, it is unlikely that pre-existing differences in background crack density are an explanation for the different median BPP values in the regions. However, Region d1-z1 did lie at the flaw tip, which is an area of expected white patch development. It is expected that further loading of Specimen d1 would have developed a macroscale white patch in Region d1-z1. It is assumed that Region d1-z1 represents an early-stage, pre-white patching FPZ with high microcrack density, and that Region d1-z2 represents a late-stage, post-white patching FPZ with lower microcrack density.

The occurrence of microcracking before macroscale white patch development agrees with previous work by Wong and Einstein [2009d]. Wong observed near-flaw-tip regions of specimens loaded to progressively increasing stress levels: 50\%, 70\%, and 90\% of failure stress (Figure 6-12, from [Wong and Einstein 2009c]). Wong’s findings can be summarized in three conceptual steps:
Figure 6-12: Wong identified the qualitative microcrack density in the near-crack tip regions of three specimens loaded to three stress levels: 50%, 70%, and 90% of failure stress. Figure from [Wong and Einstein 2009c].

1. Wong first found medium- and low-density microcracking zones in the 50% loading sample (Figure 6-12a).

2. As loading increased, a dominant high-density microcracking zone became apparent (70% sample, Figure 6-12b). This high-density zone was surrounded by medium- and low-density microcracking zones.

3. As loading increased even further, the medium- and low-density zones widened (90% sample, Figure 6-12b).

If Wong’s model is applied to the current study, then the microcracking on d1-z1 is analogous to the medium- and low-density microcracking zones on the 50% specimen (Step 1); although in the current study, the initial microcrack density lies at a higher density than Wong’s initial density (which is possible given the qualitative nature of Wong’s assessment, and also given that marble is a natural material, and background microcracking may vary from specimen to specimen.)

According to Wong’s model, further loading (Step 2) of Specimen d1 until white patching appeared (such as the white patching of Region d1-z2) could thus increase the microcrack density in Region d1-z1, and flank this region with lower microcrack densities. In our case, no additional loading was applied, but Region d1-z2 encompasses a white patch. Thus, Region d1-z2 is anal-
ogous to Step 2 in Wong’s model. However, Step 2 is the point where observations in this study diverge from Wong’s model: whereas Wong found an increase in microcrack density with further loading, Region d1-z2 exhibits a reduction in microcrack density relative to Region d1-z1. Several factors could contribute to the divergence of the results in this study from Wong’s results: artifacts of the different ESEM imaging conditions used to observed Regions d1-z1 and d1-z2 (discussed in Section 4.2.3), variation in background crack density in Regions d1-z1 and d1-z2 due to the natural variability of the test material, and most importantly the fact that the two regions are at different locations.

A notable similarity in the median BPP values in Regions d1-z1 and d1-z2 is that both regions show increased median BPP values close to the region of macroscale white patching (or expected macroscale white patching). Alternatively, both regions show decreased median BPP values far from the region of macroscale white patching (or expected macroscale white patching). This BPP trend agrees with the increased BPP measurement near the macroscale white patching identified in Region c2-z in Carrara marble. In contrast, in Region d2-z (Figure 6-11, there is a statistically significant drop in BPP measurement closest to the macroscale white patching, from 3.87% to 3.14%. This specimen does not follow the trend of increased BPP measurement near white patching found in Regions d1-z1, d1-z2, and c2-z.

6.2.3 Comparison

Carrara and Danby marble showed similarities and differences in their exhibited BPP trends. The greatest similarities are:

- increased median BPP values near regions of (expected) macroscale white patching, and
- decreased median BPP values far from macroscale white patching.

These similarities were shared by Regions d1-z1, d1-z2, and c2-z.

The greatest difference in BPP between Carrara and Danby marbles is that Danby marble exhibits lower median BPP values both near and far from white patching FPZ than Carrara marble.
The BPP values identified on Carrara marble specimens range from 18-28% (Figures 6-8 and 6-9), whereas the BPP values identified on Danby marble specimens range from 1-5%.

6.3 Nanomechanical Properties Close to FPZ

Following the FPZ microstructure discussion from the previous section, this section returns to the nanomechanical results from Chapter 5. The most notable trend in nanomechanical properties discussed in Chapter 5 was the reduction in nanomechanical properties with closeness to the white patching FPZ. This section reviews nanomechanical property trends found in testing regions first in Carrara, and then in Danby marble. This section reviews those nanomechanical property trends from the perspective of statistical significance, and links the trends with possible aspects of the FPZ structure. The section closes with a comparison of the significant BPP trends in Carrara and Danby marble, and a relation of these trends to the geometric phenomena behind FPZ development.

6.3.1 Carrara Marble

The nanomechanical property trends and their statistical significance on Specimens c1 and c2 (Regions c1-z1, c1-z2, c1-z3, c1-x, and c2-z) are shown in Figures 6-13 through 6-18. Statistical significance is indicated (for select comparisons of boxplots) by a dashed line and the value of the t-statistic.

Specimen c1 indicates a statistically significant reduction in indentation modulus near the white patching FPZ. On Specimen c1, a statistically significant reduction in modulus between the test nearest the white patching FPZ and the test furthest from the white patching FPZ is found in Regions c1-z1 (Figure 6-13; note that in Figure 6-13, the white patching is located on the right side of the diagram, but on the left side of the boxplot chart) and c1-x (Figure 6-16). Region c1-z3 also shows a reduction in modulus near the white patching FPZ, but this reduction is very small and not statistically significant. For these regions, the average distance between the white patching FPZ and the test furthest from the white patching FPZ is approximately 3 mm. If Regions c1-z1, c1-x, and c1-z3 are extrapolated to represent the development of an FPZ, one would assume that in
Figure 6-13:Indentation Hardness and Indentation Modulus trends on Specimen c1, Region c1-z1. Statistical significance of select tests indicated by dashed line and value of $t$-statistic. Note that the white patching FPZ is on the right side of the diagram, but the left side of the boxplot chart.
Figure 6-14: Indentation Hardness and Indentation Modulus trends on Specimen c1, Region c1-z2. Statistical significance of select tests indicated by dashed line and value of t-statistic.

marble, the white patching FPZ in Carrara marble is characterized by a reduction in modulus over a distance of approximately 3 mm around the crack on surfaces with an x- and z- normal (Figure 6-17).

Specimen c1 indicates a change in indentation hardness near the white patching FPZ, but the direction of the change (i.e., increase or decrease with closeness to the white patching FPZ) and its statistical significance varies across the different regions tested from Specimen c1. An increase in indentation hardness can be seen across three of the four Specimen c1 regions: c1-z2, c1-z3, and c1-x (Figures 6-14 through 6-16); the fourth region (c1-z1) shows a statistically significant reduction in hardness (Figure 6-13). Region c1-z2 shows an increase in hardness near the white patching FPZ (albeit statistically insignificant, Figure 6-14), Region c1-z3 also a statistically insignificant increase (Figure 6-15), and Region c1-x a statistically significant increase. The fourth
Figure 6-15: Indentation Hardness and Indentation Modulus trends on Specimen c1, Region c1-z3. The difference between the two tests on c1-z3 was not statistically significant.
Figure 6-16: Indentation Hardness and Indentation Modulus trends on Specimen c1, Region c1-x. Statistical significance of select tests indicated by dashed line and value of $t$-statistic.
Figure 6-17: If Regions c1-z1, c1-x, and c1-z3 are extrapolated to represent the development of an FPZ, one would expect to find modulus reduction in the shaded region, which extends a distance of 3mm from the tensile wing crack (chief white patching FPZ).

region, Region c1-z1 (Figure 6-13), shows a statistically significant reduction in hardness near the white patching FPZ. To summarize, two regions show statistically insignificant changes in hardness (Regions c1-z2 and c1-z3), one region shows a statistically significant increase (Region c1-x), and the final region a statistically significant reduction (Region c1-z1). Thus, no consistent change in hardness can be observed from considering only the regions on Specimen c1. One could conclude either that there is not enough information to decide on the trends in indentation hardness within the FPZ of Carrara marble, or that hardness decreases in the z-direction with closeness to the white patching FPZ and increases in the x-direction with closeness to the white patching FPZ. A look at Specimen c2 may clarify this impasse.

Specimen c2 shows a very clear and statistically significant reduction in both hardness and modulus with closeness to the white patching FPZ in Region c2-z (Figure 6-18). The distance between the white patching FPZ and the test furthest away is just under 3 mm. Thus, Specimen c2-z corroborates the modulus trend on Specimen c1 that indentation modulus reduces over approximately 3mm near the crack in Carrara marble. Specimen c2-z also suggests that indentation hardness similarly reduces in Carrara marble.

Ultimately, looking at the nanoindentation results on the Carrara marble specimens through the lens of statistical analysis suggests that in the white patching FPZ of Carrara marble, indentation
Figure 6-18: Indentation Hardness and Indentation Modulus trends on Specimen c2, Region c2-z. Statistical significance of select tests indicated by dashed line and value of $t$-statistic.
modulus significantly reduces over a distance of approximately 3 mm in the x- and z-directions. The mix of significant and insignificant trends in hardness prevents a definitive conclusion about the nature of indentation hardness within the FPZ of Carrara marble.

6.3.2 Danby Marble

The nanomechanical property trends and their significance in Regions d1-z1, d1-z2, and d2-z are shown in Figures 6-19 through 6-21. Statistical significance is again indicated with a dashed line and the corresponding t-value. Nanoindentation testing on Specimen d1 suggests that both modulus and hardness undergo a statistically significant decrease near the white patching FPZ.

Firstly, Region d1-z1 (Figure 6-19) displays a statistically significant reduction in both hardness and modulus near the white patching FPZ. Before discussing these nanomechanical trends, a review of the micro- and macrostructure of Region d1-z1 is necessary. Recall that Region d1-z1 is located near the pre-existing crack on Specimen d1 and showed evidence suggestive of microcracking (see discussion of significant in increase in BPP in Region d1-z1, Section 6.2.2), but did not show any macroscale white patching, and is thus hypothesized to be in early-FPZ-stage development. Given this micro- and macrostructure, a statistically significant reduction in nanomechanical properties is identified in this region at a “mid-distance” from the flaw tip. In other words, in comparison with the nanoindentation test furthest from the flaw tip, the test in the mid-distance (just over 3mm from the FPZ) does show a statistically significant reduction in both indentation modulus and indentation hardness, but the nanoindentation test nearest the flaw tip (nearly 2mm from the flaw tip) in Region d1-z1 (Figure 6-19) shows no statistically significant reduction (t > 1.6449) in either indentation modulus or indentation hardness. Thus, a statistically significant reduction in nanomechanical properties is found in Region d1-z1, even though it occurs at a mid-distance from the flaw tip rather than closest to the flaw tip.

Region d1-z2 also shows a statistically significant reduction in both modulus and hardness with distance from the white patching FPZ (Figure 6-20). Region d1-z2 is located around white patching which emanated from the boundary of Specimen d1. Both modulus and hardness show a statistically significant drop from the nanoindentation test located furthest from the white patching
Figure 6-19: Indentation Hardness and Indentation Modulus on Specimen d1, Region d1-z1. Statistical significance of select t-tests indicated by dashed line and t-statistic.
Figure 6-20: Indentation Hardness and Indentation Modulus on Specimen d1, Region d1-z2. Statistical significance of select t-tests indicated by dashed line and t-statistic.
Figure 6-21: Indentation Hardness and Indentation Modulus on Specimen d2, Region d2-z. Statistical significance of select t-tests indicated by dashed line and t-statistic.

FPZ, and the test nearest the top of the white patching FPZ (from 2.66 GPa to 2.54 GPa hardness, and from 73.28 GPa to 69.49 GPa modulus). The statistically significant reductions on Specimen d1 reaffirm that the white patching FPZ manifests as a region of reduced indentation hardness and indentation modulus (Region d1-z2). The fact that the reductions on d1-z1 occur at a "mid-distance" suggest that this reduction may begin in a location somewhat removed from the pre-existing crack tip (the mid-distance test in Region d1-z1, Figure 6-19) before spreading closer to the pre-existing crack tip.

Finally, Region d2-z shows a steady and statistically significant reduction in both modulus and hardness near the white patching FPZ (Figure 6-21). If one were to extrapolate the results on Specimen d2 to the general structure of the white patching FPZ, one would assume that both
hardness and modulus are reduced near the white patching FPZ.

6.3.3 Comparison

Collectively, the trends in nanomechanical properties on the Carrara and Danby marble specimens just described show a similarity between the marble types: both marble types show a statistically significant reduction in properties near the white patching FPZ.

A difference in the nanomechanical property trends between the marbles relates to the distance over which a statistically significant reduction is found. This "size of nanomechanically-measured FPZ" will be explored in more detail later in the next section. Another difference in the nanomechanical property trends between the marbles relates to the orientation of the FPZ structure. Specimen c1 showed a significant trend on a surface within the specimen, with an x-axis normal (Specimen c1-x, Figure 6-16) but a similar test was not conducted on a Danby marble specimen. Thus, this investigation does not allow one to draw a definitive conclusion about the within-specimen structure of the FPZ as it relates to grain size.

6.4 Size of Quasi-Brittle Material FPZ

The trends in BPP (Section 6.2) and indentation modulus and hardness (Section 6.3) across the two marbles in this investigation provide insight into the size of the FPZ in quasi-brittle materials. This section explores these trends and discusses FPZ size and the microstructure within that FPZ size. The section closes with presentation of interesting ratios.

6.4.1 Size of Nanomechanically-Measured FPZ, \( r_{p, \text{Nanomech}} \)

One can use the statistically significant trends in nanomechanical properties discussed in Section 6.3 to infer another piece of interesting information about the FPZ in quasi-brittle materials: its size. One can use the locations of nanoindentation test grids conducted at various locations within and near the white patching FPZ as a way to measure the size of the FPZ. Thus, in this section,
Figure 6-22: Nanomechanically-defined FPZ size in Carrara marble. The lines on each microscopy image show the locations of nanoindentation testing. FPZ size was measured on these microscopy images, and is defined here as the distance between the white patching FPZ and the nanoindentation test furthest from the white patching FPZ. Only regions with a statistically significant reduction in indentation hardness (Regions c1-z1 and c1-x) or modulus (Regions c1-z1 and c2-z) are shown.

The “size of nanomechanically-defined FPZ” \( r_{p,\text{Nanomech}} \) will be defined as the distance between the white patching FPZ and the nanoindentation test furthest from the white patching FPZ\(^2\). Figures 6-22 and 6-23 depict the size of nanomechanically-defined FPZ \( r_{p,\text{Nanomech}} \) in regions with a statistically significant reduction in either indentation hardness or indentation modulus.

\( r_{p,\text{Nanomech}} \) was measured on the images shown in Figures 6-22 and 6-23. For Region c1-z1 and Region d2-z, the white patching lay at the very edge of the specimen, so the distance between edge of the specimen and the test furthest from the specimen edge was used to determine FPZ size. Region d1-z1 showed no visible white patching, so the radial distance between the pre-existing flaw tip and the test furthest from the flaw tip was used to determine FPZ size. Region c2-z and Region d1-z2 both showed visible white patching on the specimen, so the distance between the test furthest from this white patching and the white patching was used to determine FPZ size \( r_{p,\text{Nanomech}} \). The different \( r_{p,\text{Nanomech}} \) are tabulated in Table 6.3. Note that with the exception of c1-x, all the

\(^2\)This definition of size of nanomechanically-defined FPZ \( r_{p,\text{Nanomech}} \) is modified slightly for Region d1-z1, which showed no visible white patching but did show a statistically significant reduction in indentation hardness and modulus. In Region d1-z1, \( r_{p,\text{Nanomech}} \) is defined as the distance between the flaw tip and a nanoindentation test grid at a mid-
Figure 6-23: Nanomechanically-defined FPZ size in Danby marble. The lines on each microscopy image show the locations of nanoindentation testing. FPZ size was measured on these microscopy images, and is defined here as the distance between the white patching FPZ (flaw tip, in Region d1-z1, which showed no white patching FPZ) and the nanoindentation test furthest from the white patching FPZ. All regions showed a statistically significant reduction in indentation hardness and indentation modulus.

Table 6.3: Size of Nanomechanically Defined FPZ $r_p, \text{Nanomech.}$

<table>
<thead>
<tr>
<th>Region</th>
<th>Size</th>
<th>Region</th>
<th>Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>c1-z1</td>
<td>4.7 mm</td>
<td>d1-z1</td>
<td>5.1 mm</td>
</tr>
<tr>
<td>c1-x</td>
<td>4.2 mm</td>
<td>d1-z2</td>
<td>6.0 mm</td>
</tr>
<tr>
<td>c2-z</td>
<td>2.9 mm</td>
<td>d2-z</td>
<td>4.2 mm</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>3.9 mm</strong></td>
<td><strong>Average</strong></td>
<td><strong>5.1 mm</strong></td>
</tr>
</tbody>
</table>
specimens in Table 6.3 show a statistically significant decrease in both indentation modulus and indentation hardness between the nanoindentation test furthest and closest to the white patching FPZ. Region c1-x has a statistically significant reduction in hardness (but increase in modulus, Figure 6-16). Statistically significant reduction in nanomechanical properties in the FPZ occurs over an average distance of 5.1 mm in the Danby marble regions considered in this investigation, and 3.9 mm in the Carrara marble regions considered in this investigation. Thus, according to the definition of FPZ size given at the beginning of this section (Section 6.4.1), fine-grained Carrara marble forms a smaller absolute size of FPZ than coarse-grained Danby marble.

Several facts should be noted in consideration of the average FPZ size reported in Table 6.3. Firstly, two regions in Carrara marble (c1-z2 and c1-z3) were not included in the estimation of FPZ size because no statistically significant reduction in nanomechanical properties near the white patching FPZ was identified on these specimens. Both of these regions were located on the “inside” of the tensile wing crack, as indicated in Figures 6-14 and 6-15, with Region c1-z3 located at-depth within the specimen. Any estimation of white patching FPZ size pulled out of the work of this investigation should thus note that this size extends away from the white patching FPZ, on the “outside” of the eventual tensile wing crack. This orientation of FPZ size is the second fact to consider in light of the FPZ size trends reported in this section. The FPZ size measurements were reported as:

- perpendicular to white patching (Regions c1-z1, c1-x, c2-z, and d2-z, Figures 6-22 and 6-23), or
- a radial distance from the tip of white patching (Region d1-z2, Figure 6-23), or
- a radial distance from the tip of a pre-existing crack (Region d1-z1, Figures 6-23).

These three orientations are generally sketched in Figure 6-24. FPZ size may indeed be orientation dependent. A more precise study of the trends in nanomechanical properties along specific directions from the FPZ could paint a more precise picture of the shape and size of the FPZ in quasi-brittle materials.
Figure 6-24: Arrows generally indicate directions in which FPZ size was measured (i.e., direction in which nanomechanical properties reduced significantly) in this investigation. (a) perpendicular to white patching, (b) radiating away from flaw tip (in the absence of white patching), (c) radiating away from tip of white patching.

A final interesting note relates to the volumes sensed by indentation. Three chief facts should be reviewed:

1. The size (diameter) of the spherical volume sensed by an indentation is approximately 3 times the depth of indentation [Constantinides et al. 2006]. This means that for Carrara marble, a single indentation reflects the response of a volume with diameter 0.75 μm, and for Danby marble, a single indentation reflects the response of a volume with diameter 1.2 μm.

2. The volume sensed by indentation modulus is larger than the volume sensed by indentation hardness [Larsson et al. 1996].

3. The distance over which a statistically significant nanomechanical property reduction is found is 3.9 mm for Carrara marble, and 5.1 mm for Danby marble.

These facts are illustrated in Figure 6-25. The first two facts relate to a smaller region (with a size on the order of a few μm) than the region which the third fact relates to (with a size on the order of a few mm). Although Carrara marble indentations sense a smaller volume than Danby marble indentations (due to their smaller indentation depth, see Appendix A) – and although modulus values sense a larger volume than hardness values – the significant nanomechanical property trends
Figure 6-25: (Not to scale). This schematic illustrates that the volume sensed by indentation, shown on the left, is much smaller than the size of nanomechanically measured FPZ.

extend over a distance two orders of magnitude greater than the volume sensed by indentations (or by modulus). The spherical indentation volume shown in Figure 6-25, while not to scale (because if this spherical volume was scaled to the $r_p$, Nanomech scale bar, the spherical volume would not be visible on the page) is much smaller than the distance over which a statistically significant reduction in nanomechanical properties is measured. Thus, the nanomechanical property trends reflect a change in material and material properties, and not just differences in indentation depth. Moreover, statistically significant reductions in both indentation modulus and hardness were found near the white patching FPZ for all specimens in Figures 6-22 and 6-23 (with the exception of Carrara marble specimen c1-x). Thus, despite the slightly larger volume sensed by modulus than hardness, trends were found in both nanoindentation properties.

The most important conclusion to be drawn from the three facts above is that this investigation has identified a trend in the extent of property reduction over a large distance (i.e., on the order of a few mm) from the white patching FPZ quasi-brittle material. This trend suggests that small-scale material changes (such as nanocracks with a size less than the volume sensed by indentation, and reflected in material property changes) lie farther from the FPZ in a large-microstructure material such as Danby marble than in a small-microstructure material such as Carrara marble. A more quantitative understanding of this distance, of this nanomechanically-measured size of FPZ $r_{p, \text{Nano}}$

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3One could argue that the larger volume sensed by Danby marble indents allows them to sense a different type of material change than Carrara marble - for example, nanocracks with a size of 1.2 μm or less, whereas Carrara marble indents could sense nanocracks only with a size of 0.75 μm or less - and that material change could act over a larger distance. A reasonable counterargument would be that those larger nanocracks should only be sensed close to the white patching FPZ, not farther from the white patching FPZ (and thus not contribute to the nanomechanical definition of FPZ size in Table 6.3).
Table 6.4: Comparison between $r_p$ predicted by Irwin’s expression (and various theoretical assumptions, Equation 6.15 and Section 6.1.2), and $r_p_{\text{Nano}}$ nanomechanically-measured (Table 6.3).

<table>
<thead>
<tr>
<th>$r_p$ Method</th>
<th>$K_I$ Value, MPa$\sqrt{m}$</th>
<th>$\sigma_T$ Value, MPa</th>
<th>$r_p$ Size, mm</th>
<th>Ratio (Carrara:Danby)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Carrara</td>
<td>Danby</td>
<td>Carrara</td>
<td>Danby</td>
</tr>
<tr>
<td>$r_p$, Flat</td>
<td>85.8</td>
<td>52.4</td>
<td>6.2</td>
<td>3.7</td>
</tr>
<tr>
<td>$r_p$, Granular</td>
<td>34.8</td>
<td>21.3</td>
<td>6.2</td>
<td>3.7</td>
</tr>
<tr>
<td>$r_p$, Scratch</td>
<td>0.95</td>
<td>0.67</td>
<td>6.2</td>
<td>3.7</td>
</tr>
<tr>
<td>$r_p$, Nano</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

is explored in the next section.

**Comparison of Predicted and Nanomechanically-Measured FPZ**

Comparison of the above nanomechanically-measured size of FPZ $r_p_{\text{Nano}}$ (Table 6.3) with predicted FPZ size based on material properties and fracture mechanics theory can illuminate underlying phenomena of the white patching in marble (Table 6.4). Irwin’s formulation is the basis for the predicted FPZ size (first three rows of Table 6.4):

$$r_{p,\text{Irwin}} = \frac{1}{2\pi \sigma_{\text{yield}}} K_I^2$$ (6.15)

There are three predictions of FPZ size $r_p$ highlighted in this investigation (and shown in the first three rows of Table 6.4); they all depend on Irwin’s formulation:

1. $r_p$, flat, where theoretical fracture toughness values derived from uniaxial compression experiments are used and a flat crack surface is assumed ($K_I = K_{C,\text{Flat}}$);

2. $r_p$, Granular, where theoretical fracture toughness values derived from uniaxial compression experiments are used and a granular crack surface is assumed ($K_I = K_{C,\text{Granular}}$).

3. $r_p$, scratch, where experimental fracture toughness values from scratch testing are used for fracture toughness ($K_I = K_{C,\text{scratch}}$, Section 5.2), and no crack surface is assumed (because the fracture toughness value is fully obtained from scratch testing.)
Figure 6-26: Results of direct tensile testing on dogbone specimens of Carrara and Danby marbles.

Recall that at fracture, fracture toughness $K_C$ is equivalent to stress intensity $K_I$, and thus fracture toughness $K_C$ is a permissible substitute for $K_I$ in Equation 6.15. The values for $K_C, \text{Flat}$ and $K_C, \text{Granular}$ were derived earlier in this chapter (Section 6.1.2). Recall that the yield strength $\sigma_y$ of quasi-brittle materials in tension often lies close to their tensile strength $\sigma_T$, and thus $\sigma_T$ is a permissible substitute for $\sigma_y$ in Equation 6.15. The values for the tensile strength of both marbles were found with direct tensile tests on three dogbone specimens, and are presented in Figure 6-26. With two predictions of $K_C$, one measurement of $K_C$, and the tensile strength $\sigma_T$ of both marbles in hand, we can proceed with a comparison of predicted $r_p$ and measured $r_p$ (Table 6.4).

The most striking fact highlighted by Table 6.4 is the extremely high similarity between the size of FPZ predicted with scratch testing fracture toughness values ($r_p, \text{Scratch}$) and the nanomechanically-measured size of FPZ ($r_p, \text{Nano}$). Both the scratch-testing prediction and the nanomechanical measurement predict that Carrara marble will develop a smaller FPZ than Danby marble by a factor
of \(\approx 0.7\), and that the size of both FPZ will be on the order of 3 to 5 mm. This similarity between a theoretical formulation (admittedly based on the experimental mechanical measurement of scratch testing) and the FPZ size measured in the lab suggests that the laboratory measurement of nanoindentation has the potential to access the true size of the FPZ in quasi-brittle materials.

A few other notes must be made on the trends in Table 6.4. Firstly, note that the \(r_p\) ratio for the theoretically predicted \(r_p\) (\(r_p\), Flat or Granular, final column in Table 6.4, first two rows) is larger than the ratio for the nanomechanically measured \(r_p\) (\(r_p\), Nanomech final row of Table 6.4). Specifically, the ratio of FPZ size for Carrara to Danby marble is 0.95 to 0.96 when theoretically derived from the stress-strain curve and tensile strength values (\(r_p\), Flat or Granular), but 0.76 when measured using statistically significant reductions in nanomechanical properties (\(r_p\), Nanomech). Although both \(r_p\), Flat or Granular and \(r_p\), Nanomech predict that Carrara marble will develop a smaller FPZ than Danby marble, the theoretical predictions overestimate the relative size of the FPZ in smaller-grained Carrara marble.

Irwin’s expression for FPZ was used to formulate the theoretical predictions (see Equation 6.15), and therefore this expression may shed some light on why the theoretical predictions overestimate the relative size of the FPZ in Carrara marble. The size of FPZ predicted by Irwin depends on two parameters – stress intensity \(K_I\) and yield strength \(\sigma_y\). As formulated in Equation 6.15, these parameters lie in both the numerator and the denominator of a rational expression, and thus neither parameter is more important than the other in its relationship to size of FPZ \(r_p\), Irwin. What is important is their relationship to each other, i.e., the precise relationship between stress intensity \(K_I\) and yield strength \(\sigma_y\). According to Irwin’s expression (Equation 6.15), FPZ size is directly proportional to the square of the ratio of stress intensity \(K_I\) to yield strength \(\sigma_y\). Thus, the relation between \(K_I\) and \(\sigma_y\) is critical to the predicted FPZ size.

Given that the precise relation between \(K_I\) and \(\sigma_y\) determines Irwin’s prediction of FPZ size \(r_p\), if inaccurate quantities are used for \(K_I\) or \(\sigma_y\), that inaccuracy will become squared (see the power of 2 in both the numerator and denominator of Equation 6.15). Hence, an inaccurate derivation of \(K_C\) from the stress-strain curve (as discussed at the end of Section 6.1.2) and the consequent value for \(K_I\), amplified by the power 2 in the numerator of Equation 6.15, strongly affected the
prediction of FPZ size \( r_p \) from Equation 6.15. This poor prediction ultimately manifests itself in the first two rows of Table 6.4.

Given this general discussion of a possible inaccuracy (i.e., using different \( K_I \) and \( \sigma_y \) values than the true material values) in using Irwin’s expression (Equation 6.15), a deeper discussion of the nature of that inaccuracy (i.e., obtaining larger values from Irwin’s expression) is here pursued. The theoretical \( r_p \) values are much larger than those identified in the lab, by an order of magnitude of four or less. This provides a further illustration of the suggestion that the direct link made between fracture properties and stress-strain behavior – the underlying assumption in the theoretical \( K_C \) derivation (Section 6.1.2) – overlooks some other energy pathway in the stress-strain behavior of these quasi-brittle materials. In addition, the fact that small-scale testing (scratch testing, row 3 in Table 6.4) was used to obtain an experimental result in great agreement with fracture mechanics theory highlights the importance of small-scale mechanical testing, which is testing at the scale of the phenomena of interest, the white patching.

6.4.2 Microstructure of Nanomechanically-Measured FPZ

A look at the microstructure of the regions discussed above will illuminate the geometric structure of the nanomechanically-measured FPZ in quasi-brittle material (Figure 6-27). The overarching trend is an increased microcrack density (BPP value) within this nanomechanically-measured FPZ region. Region c2-z was explored with ESEM in nearly the same region as it was explored with nanoindentation (Figures 6-27 and 6-9), and a statistically significant increase in BPP was found in nearly the same location as the statistically significant reduction in both indentation modulus and hardness. Region d1-z1 (Figures 6-27 and 6-10) shows a statistically significant increase in BPP near the flaw tip, but BPP was not obtained in the precise region that showed a statistically significant reduction in indentation modulus and hardness. Region d1-z1 (Figures 6-27 and 6-10) does show a statistically significant increase in BPP in the same region as the statistically significant reduction in nanomechanical properties. Finally, Region d2-z breaks with the trend and shows a decreased BPP value (Figures 6-27 and 6-11) in the same region as the statistically significant reduction in nanomechanical properties. Ultimately, Regions c2-z and d1-z1 suggest
Figure 6-27: A summary of the testing regions which showed a statistically significant reduction in nanomechanical properties (top row) in the same region where BPP values were obtained (bottom row).
that microcrack density increases in precisely the same location as nanomechanical properties decrease for the quasi-brittle materials considered in this investigation.

As discussed earlier, an interesting difference between Carrara and Danby marble with respect to BPP is that Carrara marble exhibits higher BPP values, and a smaller increase in BPP within the nanomechanically-measured FPZ regions (only 1% in Region c2-z, Figure 6-9), and Danby marble exhibits lower BPP values, and a greater increase in BPP (up to 3% in Region d1-z1, Figure 6-10).

### 6.4.3 Interesting and Important Ratios

This study has spanned several chief aspects of the fracture of quasi-brittle materials. The investigation measured both material properties:

- nanomechanical properties (indentation modulus and hardness),
- fracture toughness (both theoretical, $K_C$, Flat and $K_C$, Granular), and
- tensile strength $\sigma_T$,

and critical dimensions:

- typical grain size $d$,
- Black Pixel Percentage (BPP) as measure of microcrack density, and
- size of (nanomechanically-measured) FPZ.

These numbers can be combined in different ways to suggest geometric aspects and phenomena about the FPZ in quasi-brittle materials. Table 6.5 displays the most illustrative combinations of these numbers.

### Nanomechanical Property Reduction

The first and second ratio in Table 6.5 illustrate a commonality of the FPZ in quasi-brittle materials regardless of grain size. The average reduction of indentation hardness ($\approx 5\%$) and the average
Table 6.5: The most important relations between various fracture quantities for the quasi-brittle materials in this investigation.

<table>
<thead>
<tr>
<th>Row</th>
<th>Description</th>
<th>Carrara</th>
<th>Danby</th>
<th>Ratio (Carrara : Danby)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Average Indentation Hardness Reduction in FPZ</td>
<td>≈ 5%</td>
<td>≈ 5%</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>Average Indentation Modulus Reduction in FPZ</td>
<td>≈ 4%</td>
<td>≈ 4%</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>Average BPP Near FPZ</td>
<td>27%</td>
<td>3.5%</td>
<td>7.8</td>
</tr>
<tr>
<td>4</td>
<td>Average BPP Increase in FPZ</td>
<td>≈ 1% (4% when normalized with avg)</td>
<td>≈ 3% (86% when normalized with avg)</td>
<td>0.34</td>
</tr>
<tr>
<td>5</td>
<td>Grain Size</td>
<td>0.145 mm</td>
<td>0.271 mm</td>
<td>0.54</td>
</tr>
<tr>
<td>6</td>
<td>Nanomechanically-Measured FPZ Size</td>
<td>3.9 mm</td>
<td>5.1 mm</td>
<td>0.76</td>
</tr>
<tr>
<td>7</td>
<td># of Grains within FPZ ($\frac{FPZ \text{ Size}}{\text{Grain Size}}$)</td>
<td>27</td>
<td>19</td>
<td>1.43</td>
</tr>
<tr>
<td>8</td>
<td>Fracture Toughness $K_{C, \text{ Scratch}}$</td>
<td>0.95 MPa√m</td>
<td>0.67 MPa√m</td>
<td>1.42</td>
</tr>
<tr>
<td>9</td>
<td>Tensile Strength $\sigma_T$</td>
<td>6.2 MPa</td>
<td>3.7 MPa</td>
<td>1.67</td>
</tr>
</tbody>
</table>
reduction of indentation modulus (≈ 4%) in the FPZ is the same for both marble types. In other words, the ratio of modulus reduction in Carrara marble to the modulus reduction in Danby marble, as well as the ratio of hardness reduction in Carrara marble to hardness reduction in Danby marble are both 1. These ratios, shown in rows 2 and 3 of Table 6.5, were determined from the regions with a statistically significant reduction of indentation modulus or hardness (Figures 6-22 and 6-23). A ratio of 1 suggests no geometric or phenomenological difference in the two systems (Carrara and Danby marbles) analyzed. This similar ratio suggests that the FPZ may be defined for quasi-brittle materials as a 4-5% reduction in typical nanomechanical properties. Although this reduction is small, it represents a reduction that was both identified on thousands of individual nanoindentations, and statistically significant on many of the regions tested. Thus, the ratio of 1 which represents change in nanomechanical properties for two types of quasi-brittle materials suggests a nanomechanical definition of the FPZ as an area with a 4-5% reduction in nanomechanical properties.

The third row in Table 6.5 presents the average BPP found in Carrara and Danby regions, and the ratio of Carrara average BPP to Danby average BPP. The Carrara regions averaged are c1-y and c2-z (Figures 6-8 and 6-9) to yield an average BPP of 27% on Carrara marble, and the Danby regions averaged are d1-z1, d1-z2, and d2-z (Figures 6-10 and 6-11) to yield an average BPP of 3.5% on Danby marble. As indicated by the ratio in Row 3, Carrara marble FPZ regions exhibit a greater BPP than Danby marble regions by a factor of just under 8. This large difference in BPP measurements could stem from several factors:

- difference in imaging conditions on different regions (magnification, voltage, spot size; see Section 3.2.3),
- difference in grain size between Carrara and Danby marble, or
- difference in microcracking between Carrara and Danby marble.

The first factor should be mostly eliminated by the BPP Algorithm described in Section 4.2.1 and Appendix B. The algorithm is in part designed to be sensitive to the particular imaging conditions of the image set; the first step in processing each image set is to select a "typical" image and use
this image to correct for image spotlighting. Thus, although the algorithm has the potential to
be improved by incorporating some adjustment for the precise imaging conditions (magnification,
voltage, spot size, etc), or by requiring that all surfaces are imaged under the same conditions, the
algorithm as employed in this investigation represents a relatively uniform method of assessing
microstructure despite differing ESEM conditions. The second factor – the difference in grain size
between Carrara and Danby marble – could be partially responsible for the large difference in BPP
measurements. However, the increase of BPP near white patching regions – that is, the increase of
BPP directly over the white patching in a single region (most beautifully illustrated on the bottom
portion of Region d1-z2, Figure 6-10) – demonstrates the ability of the BPP algorithm to capture
increased microcracking. One can conclude with a high degree of certainty that the increased BPP
measurements in Carrara marble (with respect to Danby) are due to increased microcracking in
Carrara marble, and not just due to the smaller grains of Carrara marble.

The fourth row in Table 6.5 takes a closer look at the increase in BPP measurements near
the white patching FPZ regions of Carrara and Danby marble. Carrara marble shows a smaller
increase in BPP (and presumably a smaller increase in microcrack density) within the FPZ than
Danby marble by a factor of nearly 3 – Carrara marble BPP values increase near the FPZ by 1%
(3% when normalized with the average BPP value of 27%), but Danby marble BPP values increase
near the FPZ by 3% (86% when normalized with the average BPP value of 3.5%). Generalized
to all quasi-brittle materials, this ratio suggests that more microcracks are developed in the FPZ
of a quasi-brittle material with increased grain size (i.e., Danby marble) than in a quasi-brittle
with a smaller grain size (i.e., Carrara marble). Alternatively, rather than simply developing more
microcracks, the precise method used to approximate microcrack density in this investigation (BPP
value, see Chapter 4 and Appendix B), could mean that rather than developing more microcracks,
the larger-grain-sized Danby marble simply developed wider microcracks. However, the three
factors which may affect BPP measurements discussed in the previous paragraph should also be
considered when interpreting this trend in BPP increase.

227
Size of Grains and FPZ

The fifth and sixth ratios in Table 6.5 link together to suggest another commonality of the FPZ in quasi-brittle materials: the size of the FPZ is correlated with the typical microstructure size of the quasi-brittle material. The grain size measurements of Carrara and Danby marble to form these ratios are from the “Line-Intercept (Top 10 Classes)” measurements and method described in Section 4.1.2 and Table 4.2. The FPZ size measurements are averaged from the (statistically significant) FPZ size of Figures 6-22 and 6-23. Therefore, from the grain size ratios and the FPZ size measurements for the two marbles, one can draw two important conclusions: Carrara marble has a grain size that is 54% the grain size of Danby marble, and Carrara marble forms a FPZ that is 76% the size of the FPZ of Danby marble. Generalized to all quasi-brittle materials, these ratios suggest that quasi-brittle materials with a larger grain size form a larger FPZ. A more precise relation between FPZ size and grain size (such as whether the relation is linear, quadratic, exponential, or some other form) would require the application of the methods detailed in this investigation to a material of similar composition to Carrara and Danby marbles, but with a different grain size than either.

Phenomenologically, the similar ratios (i.e., increased FPZ size for increased grain size) makes sense. Consider that a material cracks to dissipate energy. For a given amount of energy to dissipate, and within a given an arbitrary area of 1 mm², the smaller grains of Carrara marble provide more pathways (i.e. grain boundaries) for microcracks to open and dissipate energy than the larger grains of Danby marble provide. Thus, smaller-grained Carrara marble would need to develop a smaller absolute size FPZ than larger-grained Danby marble would need to develop in order to dissipate that given amount of energy. It is interesting also to note that, when FPZ size is compared to grain size, Carrara marble develops a relatively larger FPZ. As illustrated by Row 7 in Table 6.5, Carrara marble fits almost 30 grains into its FPZ, whereas Danby marble fits just under 20. Thus, although the absolute size of the FPZ is smaller in the fine-grained marble than in the coarse-grained marble, the relative size of the FPZ is slightly larger (i.e., contains more grains) in the fine-grained marble than in the coarse-grained marble.
This trend of increased absolute FPZ size with increased grain size agrees with the results of works which have used other techniques to monitor FPZ size with respect to grain size [Chengyong et al. 1990, Janssen et al. 2001, Zang et al. 2000]. Moreover, as this work has used a nanomechanical definition of the FPZ, the trend's corresponding to other works confirms that monitoring the nanomechanical properties of quasi-brittle materials does indeed provide a means of measuring the FPZ development. Nevertheless, the ratios of both grain size and FPZ size in Table 6.5 suggest that in quasi-brittle materials, the size of the FPZ increases with increased grain size.

**Tensile Strength and Fracture Toughness**

The final three ratios in Table 6.5 relate one microstructure property and two material fracture properties: number of grains within FPZ, fracture toughness $K_C$ (as determined by scratch testing), and tensile strength $\sigma_T$. The similarity of the ratios of these properties between Carrara and Danby marble suggest that grain-scale processes govern fracture of quasi-brittle materials.

Both fracture toughness $K_C$ and tensile strength $\sigma_T$ increase as grain size decreases. Smaller-grained Carrara marble has a fracture toughness $K_C$ that is 1.4 times larger than Danby marble's, and a tensile strength $\sigma_T$ that is 1.7 times larger than Danby marble's. The previous section discussed the idea that Carrara marble can dissipate a given amount of energy through microcracking over a much smaller absolute area than Danby marble. Thus, the smaller grain size of Carrara marble is linked with its increased fracture properties and tensile strength. This classic Hall-Petch relation of increased strength at decreased grain size is illustrated with the tensile strength and fracture toughness relations in Rows 8 and 9 of Table 6.5.

Note that the increased energy dissipation ability of smaller grains is illustrated further by the ratio in Row 7 of Table 6.5. Within the average FPZ size of both materials, Carrara marble can fit 27 grains, and Danby marble can fit only 19. Carrara marble can fit 1.43 times as many grains within its FPZ as Danby marble can fit. This ratio is almost precisely the same as their fracture toughness ratios in Row 8.
6.5 Summary of Quasi-Brittle FPZ Characterization

A quasi-brittle material FPZ structure based on the analysis of the specimens studied in this investigation and presented in this chapter takes the following form. Regardless of microstructure size (i.e., large grains or small grains), a reduction in nanomechanical properties indicates the location and size of the FPZ. This reduction is noted as a 4-5% drop from the indentation modulus and hardness values found in the surrounding relatively intact material. Even though indentation modulus and indentation hardness reflect the response of slightly different volumes of material, both volumes are contained within three times the depth of indentation, and a reduction in both indentation properties is found. The orientation of this reduction is perpendicular to the white patching front, and found on both the surface normal to the pre-existing crack (front face of specimen) as well as the within-specimen surface normal to the loading direction (note the location of Region c1-x, Figure 6-16).

The role that microstructure plays in the development of this quasi-brittle material FPZ comes into play when microcracking (specifically, the increase in microcracking near the FPZ with regard to microcracking far from the FPZ) is considered. The microstructure of this damage region contains an increased microcrack density. That increase is larger for the large-grained quasi-brittle material (i.e., Danby marble, normalized increase on the order of 86%) than for the small-grained quasi-brittle material (i.e., Carrara marble, normalized increase on the order of 4%). Given this finding, one could say that grain size affects the geometric structure of the developed FPZ more than its mechanical structure. In other words, no significant difference between the marbles with two different microstructures was found in the reduction of nanomechanical properties within the FPZ, but a significant difference between the marbles with two different microstructures was found in the structure (extent, and microcrack density) of the FPZ. The extent of FPZ is larger and the microcrack density increase larger in the larger-microstructured material.

Stepping away from the FPZ, it can be seen that pre-existing microstructure plays a role in the general fracture behavior of quasi-brittle materials. This microstructure affects the size of the FPZ. Specifically, fracture toughness $K_C$ and tensile strength $\sigma_T$ of a quasi-brittle material tend to decrease with the grain size of the material (at least, for the grain sizes studied in this investigation,
which are larger than 100 $\mu$m). These reductions, along with the reduction in the number of grains that can fit within the FPZ, suggest that larger-grained quasi-brittle materials have fewer pathways for energy dissipation than smaller-grained quasi-brittle materials. Because there are fewer pathways for energy dissipation, the energy must spread farther along those pathways.

As an analogy for energy dissipation around a crack, consider six cars on a road at rushhour (Figure 6-28). The road is the material, and the cars are the energy to be dissipated. A six-lane highway (Figure 6-28a) represents the many energy pathways of a fine-grained material. A single-lane highway (Figure 6-28b) represents the few energy pathways of a coarse-grained material. Six cars can cause a long-reaching traffic jam on that single lane-highway – analogously, a large FPZ in the coarse-grain material. However, the same six cars can easily spread over the six lanes of the “fine-grained material highway” – analogously, a small FPZ. Thus, the few energy dissipation pathways of a coarse-grained quasi-brittle material are evidenced in the increased size of nanomechanically-measured FPZ found in this investigation. The number of pathways ultimately plays a role in the inverse relationship between size of FPZ and size of microstructure in the specimens explored in this investigation.
Figure 6-28: Consider a road at rush hour as an analogy for the energy dissipation in coarse- or fine-grained materials. The "traffic jam", or size of FPZ, is much larger in the coarse-grained material, which has only much fewer pathways for energy dissipation.
Chapter 7

Summary and Perspectives

This investigation sought to understand the development and manifestation of the fracture process zone (FPZ) in quasi-brittle materials. The main goal of the investigation was pursuit of the geometrical and mechanical FPZ structure across two different quasi-brittle materials. A multi-disciplinary investigative technique was first developed, and used to assess the fundamental properties of both intact and process zone material. Finally, the results of the assessment were used to build a conceptual model of the FPZ in quasi-brittle material.

This chapter closes this investigation. The chapter presents both immediate contributions and limitations of the work (Sections 7.1 and 7.2), and closes with the next steps in this developing research area (Section 7.3).

7.1 Contributions

This study presents three primary contributions to the study of material fracture: valuable information on the nanomechanical properties of Carrara and Danby marble (Section 7.1.1), a comprehensive experimental technique for understanding the FPZ in quasi-brittle materials (Section 7.1.2), and most importantly, a new understanding of the role that microstructure plays in the fracture of quasi-brittle materials (Section 7.1.3). Each of these three main contributions can be divided into a number of parts or secondary contributions that are also discussed.
7.1.1 Nanomechanical Properties of Marbles

The first primary contribution of this study is the valuable information on the nanomechanical properties of both Carrara and Danby marbles. These properties, indentation modulus and hardness, are important for two reasons. Firstly, they link with more fundamental material properties (elasticity and strength, respectively) at the grain scale, and therefore provide insight into how Carrara and Danby marbles respond to stress and strain at the grain scale. Secondly, these two properties serve as inputs for various models of material behavior. Such models can ultimately provide a means for understanding and predicting material behavior across many scales. This understanding can enhance many areas of the engineering industry.

Beyond providing nanomechanical property values of Carrara and Danby marble at the grain scale, this study also explores how these values decrease near grain boundaries, in both intact and fracture process zone (FPZ) marble. This knowledge can further enhance the material behavior models mentioned above.

7.1.2 Experimental Technique

The second primary contribution of this investigation is its comprehensive, multi-disciplinary experimental technique for understanding the FPZ of quasi-brittle materials. This technique incorporates both small-scale mechanical testing (i.e., nanoindentation) and small-scale observation of geometric structures (i.e., Environmental Scanning Electron Microscopy, ESEM). These components both independently and collectively yield a number of secondary contributions:

- **Specialization of Nanoindentation for Fractured Quasi-Brittle Materials.** Nanoindentation is one of the two key components of the experimental technique used in this investigation. Although nanoindentation has been used for some time as a research technique, the delicacy of the fractured quasi-brittle materials used in this investigation required the specialization of nanoindentation for this study. A method was devised for carefully extracting the desired regions of damaged (and sometimes intact) materials using the Water Jet, and a detailed surface preparation technique was devised in order to yield specimens of ideal
smoothness for nanoindentation investigation. These two specializations of nanoindentation result in a nanoindentation approach that can be used for investigating damage in various types of marbles, and other types of similar quasi-brittle materials.

Another important aspect of the specialized nanoindentation technique used in this study was that nanoindentation was used to investigate damage surfaces at various orientations. This multi-orientation aspect of the nanoindentation technique results in an understanding of the anisotropy of mechanical properties of the materials in this investigation, and also provides a means for future investigations that use this specialized nanoindentation technique to understand the anisotropy of their materials.

- **Black Pixel Percentage (BPP) Algorithm.** Environmental Scanning Electron Microscopy (ESEM) is the second of the two key components of the experimental technique used in this investigation. Although ESEM micrographs have been a popular research tool for understanding microstructure for some time, this investigation was interested in understanding microstructure from many hundreds of ESEM micrographs. The development of the BPP algorithm in this investigation eliminates the need for many man-hours of hand-tracing individual ESEM micrographs, and provides a quantitative metric of microcrack density (the Black Pixel Percentage, or BPP) as an output. This algorithm could be easily modified and extended for various other types of quasi-brittle materials.

Beyond measuring the BPP value trends in just a single ESEM micrograph, the BPP algorithm also tracks BPP trends over a large region covered by hundreds of ESEM micrographs. This aspect of the algorithm provides a measure of microcrack density trends over a large region, and corroborates earlier qualitative microcrack density trend work by Wong [2008]. The two most notable trends obtained in this investigation were that microcracking can precede white patching\(^1\), and that the appearance of white patching can indicate an increase in microcrack density.

- **Link between Geometric and Mechanical Properties at the Grain Scale in the FPZ.** The

\(^1\)In marble specifically, white patching is a zone of inelastic deformation at the tip of a propagating crack. The abundance of microcracks, spalling, and other microfeatures grant the region a white appearance.
most important aspect of the experimental investigation is that it combines information on both the mechanical and geometric structure of the FPZ at the grain scale in two types of marble. This combination of experimental techniques revealed that in and near the white patching FPZ of marbles, regions of increased microcracking tended to align with regions of reduced nanomechanical properties. These observations combine the classic FPZ signature in quasi-brittle materials—increased microcracking—with the classic FPZ signature in metals—reduced mechanical properties. Thus, the results of this investigation are consistent with an interpretation of the FPZ in quasi-brittle materials as a region with reduced mechanical properties, and the specialized nanoindentation technique employed in this investigation provides a way to measure those nanomechanical property reductions.

- **Direct Tensile Testing.** A third component of the experimental technique used in this investigation is direct tensile testing of rock. (Although this technique did not directly contribute to understanding of the FPZ of the marbles studied, this technique did provide a necessary parameter for predicting FPZ size from classic fracture mechanics definitions.) The direct tension tests performed in this investigation were modified compared to existing standards of tensile testing of rock. The resulting direct tension test outlined in this thesis thus provides a new way to test and analyze the behavior of rock under direct tension, and can be extended to various types of quasi-brittle materials.

### 7.1.3 Role of Microstructure in Fracture of Quasi-Brittle Materials

The third primary contribution of this study is an enhanced understanding of the role that microstructure plays in the fracture of quasi-brittle material. This understanding breaks down into four key relationships: the relationship between grain size and fracture toughness/tensile strength, the relationship between grain size and microcrack density, the relationship between grain size and FPZ size, and the relationship between grain size and nanomechanical property reduction. In order to understand the third and final primary contribution of this study, these relationships are discussed:
• **Negative Relationship between Grain Size and Fracture Toughness, Tensile Strength.** This investigation finds a negative relationship between grain size and two mechanical properties: fracture toughness, and tensile strength. In other words, as grain size decreases, fracture toughness and tensile strength both increase. This negative relationship supports the idea that finer-grained materials can dissipate more energy than coarse-grained materials, and thus can attain higher strength properties.

• **Negative Relationship between Grain Size and Microcrack Density.** The investigation finds a negative relationship between grain size and microcrack density. In other words, as grain size decreases, microcrack density (as measured by BPP value) increases. This negative relationship supports the idea that finer-grained materials develop more microcracks in their damage zones than coarse-grained materials.

• **Positive Relationship between Grain Size and FPZ Size.** The investigation finds a positive relationship between grain size and size of FPZ. This relationship holds whether FPZ size is found using either classic fracture mechanics to predict the size of the FPZ, or statistically significant nanomechanical property reduction to measure the size of the FPZ. In both cases, the finer-grained marble exhibits a smaller absolute size of FPZ, and the coarser-grained marble exhibits a larger absolute size of the FPZ. This positive relationship supports the idea that finer-grained materials dissipate energy more efficiently with respect to space, and therefore can develop a smaller damage zone before fracture.

• **New Approach for Defining the FPZ.** For both marble types, there is a 4-5% reduction of nanomechanical properties near the white patching FPZ with respect to nanomechanical properties further from the white patching FPZ. This suggests that the method used for determining the size of the FPZ in this study – essentially measuring the size of the region showing a statistically significant 4-5% reduction in nanomechanical properties – can be considered as a new means of defining the FPZ in quasi-brittle materials. The strong match between FPZ size measured with this method, and FPZ size predicted with classic fracture mechanics suggests a new definition of FPZ in quasi-brittle materials: a region with a statis-
tically significant 4-5% reduction in indentation modulus and indentation hardness. In order to verify this new definition, the current investigation should be extended to quasi-brittle materials with different grain sizes and constituents than the test materials in the current investigation. Nevertheless, the new means of measuring FPZ size suggested in this work can enhance existing models of rock fracture by providing an important input parameter: the mechanical properties and size of the FPZ.

7.2 Limitations

In this study, the basis for comparison of intact and process zone materials are two different areas of a specimen post-cracking. Ideally, a study should evaluate microproperties of the same area before and after cracking, or during the crack propagation. Such a method would allow one to measure the development of nanomechanical properties before and after cracking, or during crack propagation. However, the main factor which prevents this approach is the requirement for nanoindentation that the indented surface be extremely flat and smooth (i.e., minimal roughness). Obtaining a flat surface on a large prismatic specimen is not possible with the current surface preparation for accurate nanoindentation (Section 3.2.4). The current specimen preparation procedure requires fitting the specimen inside of the polishing equipment for many hours; this setup is not feasible with a large prismatic specimen. Although the possibility exists to physically scale down the research approach (smaller specimens may be prepared, polished, tested with nanoindentation for microproperties at the crack tip, then cracked and re-tested with nanoindentation at the crack tip), there is a secondary problem. Even if the small-scale mechanical properties of a large prismatic specimen are obtained prior to loading, the deformations induced by nanoindentation (or polishing to remove these initial nanoindentation impressions) may influence the resulting stress distribution during loading, and thereby interfere with the idea of testing the same specimen before and after loading.

A technique that may provide even more relevant data is an evaluation of microproperty change during cracking. Nanoindentation during loading in a uniaxial testing machine is currently unfeasible. However, the study may again be scaled down and apparati designed to accommodate such
an experiment. A simple approach may be to design a specialized specimen-holder which fits inside of the nanoindenter and which could “crack the specimen (incrementally) while nanoindentation measurements are taken. Such a specimen-holder may be a box whose walls touch the specimen and are tightened by screws; tightening the screws would apply more force to the specimen, and crack the specimen. Nanoindentation measurements could be taken at various levels of screw-tightening (i.e., at various levels of cracking).

7.3 Recommendations for Future Research

A first recommendation is to repeat and refine this investigation on materials with a different flaw geometry than the single-flaw geometry investigated herein. It is anticipated that marble specimens with different initial crack geometries will exhibit similar trends of indentation modulus and hardness, as well as microstructural features, following process zone generation. Additionally, the microproperty change around process zones of marble specimens with pre-existing cracks loaded fully in tension or dynamically loaded may be explored.

A second recommendation relates to the test materials. The grain size relationships discussed in Section 7.1.3 hold for only the two materials pursued in this investigation. Repeating this investigation on a third material with either a smaller or larger grain size than the materials in this investigation will further refine these relationships. Moreover, nanoindentation in more heterogeneous granular materials, such as granite, as well as materials with a wider variety of grain sizes will help to refine the mechanism at play near grain boundaries and in the process zone.

A final recommendation for the investigation would be the development of a predictive model. A model which predicts reduction in strength and elastic properties based on the characteristic microstructure size and material constituents of a quasi-brittle geomaterial would not only enhance the study of fracture of quasi-brittle materials, but also improve our understanding and control of the quasi-brittle materials all around us – foundations, wall panels, and hillsides, for example – as they develop cracks and damage.
Appendix A

Danby Marble Nanoindentation Parameters

This appendix reviews the important parameters in the design of a nanoindentation test, the reasons why the parameters are important, and the proposed value of each parameter for testing Danby Marble.

For Carrara marble nanoindentation data and derived properties were available in the literature [Broz et al. 2006]. Nanoindentation parameters were scaled to match with literature-reported properties [Brooks et al. 2010]. However, nanoindentation properties are not available in the literature for Danby marble. Thus, as detailed in this chapter, nanoindentation parameters must be carefully aligned with continuum mechanics theory in order to accurately probe this new material.

A.1 Summary

The following summary checklist of nanoindentation test parameters for Danby marble is explained in detail in the following sections. For comparison, the test parameters for Carrara marble are also presented.

Danby Marble
- **Specimen Size**: 12 mm diameter, 5 mm height, or greater
- **Indentation Depth**, $h$: between 100 and 50,000 nm (0.1 and 50 μm) – 400 nm
- **Spacing Between Indentations**: 300 μm
- **Maximum Load**, $P_{\text{max}}$: 7 mN
- **Loading/Unloading Period**: 30 s
- **Hold Period**: 5 s

*Carrara Marble*

- **Specimen Size**: 12 mm diameter, 5 mm height, or greater
- **Indentation Depth**, $h$: $\approx$ 250 nm
- **Spacing Between Indentations**: 8 μm
- **Maximum Load**, $P_{\text{max}}$: 2.85 mN
- **Loading/Unloading Period**: 14.25 s
- **Hold Period**: 5 s

### A.2 Specimen Size

In order to statistically assess mechanical properties of the desired phases (and at the desired scales), the nanoindentation test must obey the scale separability condition [Bobko 2008, Constantinides 2006, Constantinides et al. 2006, Vandamme 2008]. This condition states:

$$d \ll L \ll (a, h) \quad (A.1)$$

where $d$ is the size of the largest heterogeneity of the tested material, $L$ is the size of the Representative Elementary Volume (REV) utilized in the continuum mechanics derivation of mechanical properties from indentations, and $h$ is the depth of indentation, which is determined from the area of contact $a$ between probe and material. The relationship is illustrated in Figure A-1. The scale
seperability condition is a mathematical expression of the idea that any scientific test reveals information about a material at a particular scale. The scale of revealed information ($L$ in Equation A.1) lies somewhere between the scale of the test ($a$ and $h$ in the expression) and the scale of the largest material heterogeneity ($d$). For example, a uniaxial test conducted on a block of concrete taken from a building reveals information about the strength of the concrete block, but does not reveal information about the strength of the material heterogeneities (i.e., the aggregates in the concrete).

In the case of Danby marble, the heterogeneities probed with nanoindentation are the nano/micro-cracks (nanoscale damage) due to the process zone. Although the length scale of these heterogeneities, $d$, is not known for certain, it can be estimated to lie at scales well below indentation scale, ($a$, $h$) because of previous work on Carrara marble. Indentations in Carrara marble identified a trend in indentation properties near the process zone [Brooks et al. 2010]; this trend must be due to a physical phenomenon at scales below indentation scales. Thus, the nano/micro-cracks must have a length scale of less than 250 nm, as this is the indentation depth of Carrara marble in Brooks et al. [2010].

Scale separability also extends to the specimen scale. At this scale, the heterogeneities probed are the Danby marble grains. These grains range in size, $d$, from 520 to 3120 μm. The specimen itself corresponds to the size, $L$, of the REV; this is because the specimen is assumed to statistically represent the macro-material. The specimen size is a diameter of 12 mm, and a height of at least 5 mm. The smallest dimension of the specimen, 5 mm in height, is at least 1.6 times the size of
the largest marble grain. Thus, the specimen size (12 mm diameter, 5 mm height) satisfies the scale separability condition (Equation A.1), and is adequate for this investigation.

### A.3 Indentation Depth, $h$

There are three factors which restrict the depth of indentation, $h$: the root-mean-square surface roughness $R_q$ of the material, the scale separability condition (Equation A.1), and the area function of the indenter probe.

The surface roughness $R_q$ restricts the minimum depth of indentation $h$. The derivation of the mechanical properties from indentation (modulus, $M$, and hardness, $H$) assume a very flat surface. Thus, the roughness must be very minimal with respect to the depth of indentation in order to allow this assumption to hold. When the depth $h$ is at least 5 times greater than surface roughness (i.e., $5R_q < h$), this assumption remains valid [Miller et al. 2008].

The scale separability condition affects the maximum depth of indentation. Phase referse to the material component of interest, such as a grain of marble or a particular C-S-H component, like high density C-S-H, in a cement sample. The current investigation tracks the changes in the properties of marble grains. In order to statistically represent the grain response at the scale of the grain, $D$, the depth of indentation must not be too much larger than the scale of the phase, otherwise a composite response is sampled (Figure A-1). When the phase (or marble grain) is at least 10 times greater than the depth of indentation (i.e., $h < D/10$), the scale separability condition is maintained [Bobko 2008, Constantinides 2006, Constantinides et al. 2006, Vandamme 2008]. Both assumptions are maintained when Equation A.2 remains valid:

$$5R_q < h < D/10$$

(A.2)

In the case of Danby marble, the surface roughness $R_q$ is on the order of 25 nm. The grain sizes $D$ range from 520 to 3120 $\mu$m. The indentations must be much larger than surface roughness in order to be unaffected by surface roughness. The indentations must be much smaller than
marble grains in order to access properties of grains (and not the composite response of multiple grains. Thus, a depth of indentation $h$ between 100 and 50,000 nm (0.1 and 50 $\mu$m) satisfies continuum mechanics assumptions.

A.4 Spacing Between Indentations

The spacing between indentations must also follow the scale separability condition (Equation A.1). In order for the properties of a phase of size $D$ to be statistically represented by a number $N$ of indentations spaced at length $l$, the spacing should follow [Bobko 2008, Constantinides et al. 2006]:

$$D << l\sqrt{N}$$  \hspace{1cm} (A.3)

Thus, for a test of an arbitrarily large number of indentations ($N=100$), a spacing of 300 $\mu$m is approximately sufficient for the assessment of the largest phase size ($D=3120$ $\mu$m).

A.5 Maximum Load, $P_{max}$

The indentation depth is restricted as described in Section A.3. The load required to reach that depth is determined by the indenter shape, and material properties. With a Berkovich indenter as a control in this study, and with material properties controlled by the material choice (Danby marble), the indentation load $P_{max}$ should be experimentally determined.

Loads ranging from 3 mN to 15 mN were tested by running 20 indentations at 3, 5, 7, 10, and 15 mN, with the loading rate and hold period fixed at 30s and 5s, respectively. It was found that a load of 7 mN yielded indentations with a sufficient depth ($\approx 400$ nm) as prescribed in Section A.3 (Figure A-2), as well as a convergence of indentation modulus (Figure A-3). Although indentation modulus converged to a constant value (around 80 GPa) for loads of 7 mN and higher (Figure A-3), indentation hardness did not converge to a constant value, and instead exhibited decreasing hardness with increasing load (Figure A-4).
Figure A-2: The relationship between prescribed load and indentation depth. Each boxplot represents the results of a 20-indentation test series.

Figure A-3: The relationship between prescribed load and indentation modulus. Each boxplot represents the results of a 20-indentation test series.

Figure A-4: The relationship between prescribed load and indentation hardness. Each boxplot represents the results of a 20-indentation test series.
A.6 Loading Period and Unloading Period

A concern of loading rates (i.e., period of loading, and period of unloading) for brittle materials is the development of indentation-induced fracture during the load. This fracture could extend into the locations of neighboring indents, and disrupt properties derived from them, and would also disrupt the access of elastic information from the current indentation. Microscopy provides a means of monitoring indentation-induced fracture [Chen and Bull 2007]. In the case of viscoelastic materials with time-dependent mechanical properties, the loading rate severely impacts the properties derived, and should thus be a control in the experiment [Vandamme 2008].

Danby marble is a brittle material. Previous work in nanoindentation of cementitious materials suggest a loading and unloading period of 10 seconds [Bobko 2008, Constantinides 2006, Constantinides et al. 2006, Vandamme 2008]. To understand the impact of loading period, 100 indentations were performed at loading and unloading rates of both 30s and 15s, with the maximum load and hold period held fixed at 7 mN and 5s, respectively.

![Figure A-5: The relationship between prescribed loading and unloading rate and indentation modulus. Each boxplot represents the results of a 100-indentation test series.](image)

It was found that a loading period of 30s yielded the least amount of spread in both indentation modulus (Figure A-5) and indentation hardness (Figure A-6), with little change in indentation depth (Figure A-7). Thus, a loading period of 30s will be used in this investigation.
A.7 Hold Period

The period of hold, \( \tau \), at maximum load allows the tested material to creep. The depth at the end of this period determines contact area \( A_c \), and thus greatly influences indentation modulus \( M \) and hardness \( H \). Too short of a hold period will capture only viscous effects and overestimate contact area (thereby underestimating \( H \) and \( M \)); too long of a hold period will also overestimate contact area due to the material creep and underestimate \( H \) and \( M \) [Vandamme 2008].

Similar to the setting of the loading/unloading rate, previous work in nanoindentation of cementitious materials suggest a hold period of 5 seconds [Bobko 2008, Constantinides 2006, Constantinides et al. 2006, Vandamme 2008]. To understand the impact of hold period, 100 indentations were performed at periods of both 5s and 30s, with the maximum load and loading period held...
fixed at 7 mN and 30s, respectively (Figures A-8, A-9, and A-10).

Figure A-8: The relationship between hold period and unloading rate and indentation modulus. Each boxplot represents the results of a 100-indentation test series.

Figure A-9: The relationship between hold period and unloading rate and indentation hardness. Each boxplot represents the results of a 100-indentation test series.

It was found that although an increased hold period of 30s had virtually no effect on indentation hardness or depth of indentation, the indentation modulus increased.
Figure A-10: The relationship between hold period and unloading rate and indentation depth. Each boxplot represents the results of a 100-indentation test series.
Appendix B

Edge Detection: Fundamentals, Algorithms, and Microcrack Identification

B.1 Introduction

A variety of image-processing algorithms exist for identifying the edges of objects. These algorithms are called “Edge Detection Algorithms.” This appendix provides an introduction to image processing fundamentals and specific edge detection algorithms. The structure of this appendix is as follows:

- **B.2 Image Processing Background.** This section explains two fundamental concepts of edge detection: the mathematical expression of images, and operations (such as convolution) on a mathematically expressed image. The section closes with a brief explanation of the final step of many edge detection algorithms: thresholding.

- **B.3 Sobel Edge Detector.** This section explains a specific edge detection algorithm.

- **B.4 Kirsch Edge Detector**, another edge detection algorithm.

- **B.5 Marr-Hildreth Edge Detector**, a third edge detection algorithm.
B.6 Edge Detection for Microcrack Identification. This final section assesses the fitness of the three previously introduced edge detection algorithms (Sobel, Kirsch, and Marr-Hildreth), and then details the particular edge detection algorithm employed in this investigation (Chapter 4).

For each of the edge detection algorithms (Sobel, Kirsch, and Marr-Hildreth, sections B.3 through B.5), the section first details the specifics of the mathematic algorithm that defines the edge detector, then applies the algorithm to a micrograph of geomaterial (either marble, granite, or both), and then assesses the effectiveness of the detector in detecting edges in the geomaterial micrograph(s).

B.2 Image Processing Background

The mathematical expression of images and image operations is vital to understanding how any edge detection algorithm works. This section presents this fundamental information. First, the basic expression of a physical image as a mathematical expression is presented. Then, the concept of performing an operation on that mathematical expression (examples of operations include brightening or darkening the image, or even edge-detecting) is presented. A specific operation – convolution – is then presented. Finally, thresholding is discussed.

B.2.1 Mathematical Expression of Images

A single image can be discretized into image fields; for the purposes of explanation, consider the image fields as the image pixels. Each pixel exhibits a certain radiant energy (light intensity), \( C(x, y, t, \lambda) \) and spectral response (color), \( S_i(\lambda) \), where \((x, y)\) denote the spatial location of the image field, \( t \) the position in time of the image field, and \( \lambda \) the particular wavelength of light in the light spectrum. The spectral image field of the \( i \)th sensor is defined by [Pratt 2007]:

\[
F_i(x, y, t) = \int_0^\infty C(x, y, t, \lambda)S_i(\lambda) \, d\lambda
\]  

(B.1)

1Except as noted, the information in this section is motivated by the presentation of the topic in Pratt [2007].
Thus, the spectral image field essentially corresponds to the shade and color at that position in the image. Thus, Equation B.1 presents the mathematical expression of an image.

In a monochromatic imaging system, this image function $F_i(x, y, t)$ is the luminance, or light per area, of the imaged scene [Johnson 1990, Pratt 2007]. Thus, a monochromatic image does not directly report the colors of the scene, but only the lightness and darkness of the scene. For example, grayscale images report the luminance by displaying bright areas as white or light gray, and dark areas as black or dark gray. In a color imaging system, this function corresponds to red, green, or blue. For example, in a color picture, a particular pixel may appear as light red, dark blue, or any of a number of light or dark colors. Higher values of the image function $F(x, y)$ indicate increased light or brightness of the image. For a binary image, which consists of only two colors – black and white – an image value $F(x, y)$ of 1 corresponds to high brightness, or white. An image value $F(x, y)$ of 0 corresponds to low brightness, or black.

### B.2.2 Mathematical Expression of Image Operations

The image function $F_i(x, y, t)$ allows one to express operations performed on images. Operations can be defined as manipulations performed on an image. Examples of such operations are the brightening of the image, darkening of the image, the reduction of the image to a binary image, or the enhancement of edges in the image. An optional final step is to apply another operation which reduces the edge-enhanced image to a binary image [Parker 2011]; this operation is described in Section B.2.4.

A typical operation will map an input set of $N$ two-dimensional functions:

$$F_1(x, y), F_2(x, y), \ldots, F_N(x, y)$$

to a set of $M$ output functions:

$$G_1(x, y), G_2(x, y), \ldots, G_M(x, y)$$
If the mapping is one-to-one (i.e., \( N = M \)), the operation, \( O\{\cdot\} \), may be expressed as [Pratt 2007]:

\[
G(x, y) = O\{F(x, y)\}
\]  

(B.2)

As an example, in Equation B.2, \( F(x, y) \) could represent an array of pixels in an image, \( O\{\cdot\} \) could represent the action of enhancing all the edges, and \( G(x, y) \) could represent the new, edge-enhanced image.

### B.2.3 Convolution Integral and Convolution Operation

Although image operations refer to a wide class of possible manipulations to perform on an image, convolution refers to a special combination of an external function with the image function (Equation B.1). To understand the mathematical expression of convolution, first note that the image function can be expressed as the product of a delta function, \( \delta(x - \xi, y - \eta) \), and weighting factor, \( F(\xi, \eta) \):

\[
F(x, y) = \int_{-\infty}^{\infty} F(\xi, \eta) \delta(x - \xi, y - \eta) \, d\xi d\eta
\]  

(B.3)

The delta function is defined as being equal to zero at all locations except \( x = \xi \) and \( y = \eta \).

If the image operator is one-to-one, it obeys the property of additive superposition. This property, combined with the expression of the image function with the delta function (Equation B.3), allows one to re-express Equation B.2:

\[
G(x, y) = \int_{-\infty}^{\infty} F(\xi, \eta) \delta(x - \xi, y - \eta)O\{\delta(x - \xi, y - \eta)\} \, d\xi d\eta
\]  

(B.4)

The term with the operation and delta function, \( O\{\delta(x - \xi, y - \eta)\} \), is called the Point-Spread Function (or Impulse Response), and is represented with \( H(x, y; \xi, \eta) \).

The form of \( H(x, y; \xi, \eta) \) is the unique characteristic of the Sobel and Kirsch Edge Detectors, and will be explained in the next section (Section B.3.1). If the point-spread function depends only on \( x - \xi \) and \( y - \eta \), then the integral in Equation B.4 is classified as "space invariant." The integral
is termed the Convolution Integral:

\[ G(x, y) = \int_{-\infty}^{\infty} F(\xi, \eta) \delta(x - \xi, y - \eta) H(x - \xi, y - \eta) \]

(B.5)

The convolution integral may be expressed with the Convolution Operation, \( \otimes \):

\[ G(x, y) = F(x, y) \otimes H(x, y) \]

(B.6)

The convolution operation in Equation B.6 succinctly expresses the relation between various edge detectors \( H(x, y) \), images \( F(x, y) \), and edge-enhanced images \( G(x, y) \).

**B.2.4 Thresholding**

Often, the final step of any edge detecting algorithm is **thresholding**. Thresholding is the process of:

1. Selecting a pixel intensity (i.e., brightness) to be the **threshold intensity**,
2. Setting pixels with a higher intensity (or equal) than the threshold intensity to the maximum intensity (white, intensity of 256),
3. Setting pixels with a lower intensity than the threshold intensity to the minimum intensity (black, intensity of 0),

Thresholding thus results in a binary image. The binary image simplifies the original image by clearly denoting regions as either "edge" or "no edge" (i.e., black or white).

**B.3 Sobel Edge Detector**

There are three main classes of edge detection algorithms. Algorithms of the first class are called "Derivative Operators;" these algorithms seek the locations of large intensity changes in the image. These locations are classified as edges. The second class is "Template-Based." Instead of seeking
intensity changes, these algorithms model edges with a simplified template that highlights intensity changes. The template typically takes the form of a matrix which, when filtered with the image as explained in the following sections, produces an image with enhanced edges. In other words, instead of finding the actual partial derivatives of the intensity in the image and associating those derivatives with edges—a template-based model may use a template to discretely approximate the partial derivatives. This, in fact, is precisely what the Sobel and Kirsch algorithms do. The third class models edges with a mathematical model [Parker 2011].

This section details the specific algorithm employed by the (template-based) Sobel edge detector, applies the Sobel edge detector to a micrograph, and assesses its usefulness in detecting edges in the micrograph.

### B.3.1 How the Sobel Edge Detector Works

The Sobel Edge Detector applies two linear operators to the image array. The two operators are defined as [Abdel-Qader et al. 2003, Abdou and Pratt 1979, Parker 2011]:

\[
H_1 = \begin{bmatrix}
1 & 0 & -1 \\
2 & 0 & -2 \\
1 & 0 & -1 \\
\end{bmatrix}
\]

(B.7)

\[
H_2 = \begin{bmatrix}
-1 & -2 & -1 \\
0 & 0 & 0 \\
1 & 2 & 1 \\
\end{bmatrix}
\]

(B.8)

The first operator \(H_1\) operator enhances vertical edges. For a pixel \(F_i(x, y)\) along a vertical edge, if the neighboring pixels are brighter on the left (i.e. larger values of \(F(x, y)\) on the left) than on the right, the operation will yield a positive value for \(G_1(x, y)\). Conversely, if the pixels are brighter on the right than on the left, the operation will yield a negative value.

Here, we apply the first operator \(H_1\) to a simple image \(F(x, y)\) with a prominent vertical edge.
in order to better understand the effect of the first operator. For the image function:

\[
F(x, y) = \begin{bmatrix}
1 & 0 & 0 \\
1 & 0 & 0 \\
1 & 0 & 0 
\end{bmatrix}
\]  

(B.9)

the binary image may resemble: Note that the simple vertical-edge image is composed of only 9

pixels, and is overlain with the image function \(F(x, y)\). The intensity of each pixel is apparent in
the image function \(F(x, y)\), namely that pixels of intensity 0 are black, and pixels of intensity 1 are
white. The first operator, \(H_1\) applied to the central element of image function \(F(x, y)\) (Equation
B.9) yields:

\[
G_1(x, y) = F(x, y) \oplus H_1(x, y) \\
= 1(1) + 0(0) + (-1)(0) + \\
2(1) + 0(0) + (-2)(0) + \\
1(1) + 0(0) + (-1)(0) \\
= 4
\]

(B.10)

This expression begins with the top left element of the image function \(F(x, y)\) (Equation B.9). The
positive number 4 signifies a vertical edge with higher intensity on the left.

Conversely, if edge is vertical with higher intensity on the right (i.e., larger values of \(F(x, y)\)
on the right), the first operator \(H_1\) will yield a negative value for \(G_1(x, y)\). Here, we apply the first
operator \(H_1\) to a simple image \(F(x, y)\) with a prominent vertical edge with higher intensity on the
right. For the image function:

\[
F(x, y) = \begin{bmatrix}
0 & 0 & 1 \\
0 & 0 & 1 \\
0 & 0 & 1 
\end{bmatrix}
\]

(B.11)
the binary image may resemble: Note that this simple vertical-edge image is also composed of only

9 pixels, and is overlain with the image function $F(x, y)$, but (in contrast to the previous image function) has a vertical edge with higher intensity on the right. The first operator, $H_1$ applied to the central element of this image function $F(x, y)$ (Equation B.11) yields:

$$G_1(x, y) = -4 \quad (B.12)$$

The negative number 4 signifies a vertical edge with higher intensity on the left.

The second operator, $H_2$, enhances horizontal edges. For a pixel $F_i(x, y)$ along a horizontal edge, if the neighboring pixels are brighter below the pixel (i.e. larger values of $F(x, y)$ on the bottom) than above the pixel, the operation will yield a positive value for $G_2(x, y)$.

Here, we apply the second operator $H_2$ to a simple image $F(x, y)$ with a prominent horizontal edge in order to better understand the effect of the second operator. For the image function:

$$F(x, y) = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 1 & 1 & 1 \end{bmatrix} \quad (B.13)$$

the binary image may resemble: Note that this simple horizontal-edge image is composed of only

9 pixels, and is overlain with the image function $F(x, y)$. This image also has a horizontal edge with higher intensity on the top. The second operator $H_2$ applied to the central element of this
image function $F(x, y)$ (Equation B.13) yields:

$$G_2(x, y) = 4$$

(B.14)

The positive 4 indicates a horizontal edge with higher intensity below the edge.

Finally, the second operator yields negative values when neighboring pixels are brighter above the pixel. For example, for the image function:

$$F(x, y) = \begin{bmatrix} 1 & 1 & 1 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

(B.15)

the binary image may resemble: Note that this simple horizontal-edge image is composed of only 9 pixels, and is overlain with the image function $F(x, y)$, but (in contrast to the previous image function) has a horizontal edge with higher intensity above the edge. The second operator $H_2$ applied to the central element of this image function $F(x, y)$ (Equation B.15) yields:

$$G_2(x, y) = -4$$

(B.16)

Finally, note that if, at a particular pixel, an image does not contain the image type detected by the operator, the convolution of the operator with the image at that pixel will be 0. In other words, the convolution of the vertical-edge-operator (first operator, $H_1$) with the central element of the two above horizontal-edge images is 0, and the convolution of the horizontal-edge-operator (second operator, $H_2$) with the vertical-edge images in the beginning of this section is 0.

Now, we take a step back from the specific application of the above algorithms to discuss more generally the results of convolving the Sobel operators with an image function, and the possible
operations on the convolved image to yield a fully edge-detected image. Convolving each operator with the entire image function yields two gradient arrays, $G_1$ and $G_2$:

\begin{equation}
G_1(x,y) = F(x,y) \ast H_1(x,y) \tag{B.17}
\end{equation}

\begin{equation}
G_2(x,y) = F(x,y) \ast H_2(x,y). \tag{B.18}
\end{equation}

These arrays are essentially partially edge-enhanced images with, respectively, vertical and horizontal edges enhanced. As an illustration, consider the image in Figure B-1 of a chess board. This

![Chess Board](image)

Figure B-1: This image will be, in the next figures, convolved with two operators from the Sobel Edge Detector. From Bestchess.com.au [2009].

chess board has nicely defined vertical and horizontal edges, so it will clearly illustrate the effects of the Sobel operators on edge detection. When the respective operators are convolved with this image, the $G_1$ gradient array resembles Figure B-2. All of the vertical edges have been enhanced in Figure B-2. Decreases in brightness – from a white square to a dark square – manifest in this gradient array as positive, white regions, and increases in brightness – from black square to a white square – manifest as negative, and therefore dark, low intensity regions. Regions with no change in intensity also manifest as dark regions (convolving either operator yields a zero, no-intensity value). This explains the “negative” look (i.e., dark background, and nearly all dark squares) of the edge-enhanced image (black background of Figure B-2, in comparison to white background of Figure B-1).
Similarly, the $G_2$ gradient array resembles Figure B-3. All of the horizontal edges have been enhanced in Figure B-3.

The final step of the Sobel Edge Detector is the combination of the gradient arrays $G_1$ and $G_2$ to produce an edge-enhanced image $A(x,y)$, with both vertical and horizontal edges enhanced. The Sobel operators $H_1$ and $H_2$ each enhance vertical and horizontal edges, respectively. However, a user often desires the enhancement of both vertical and horizontal edges from an image. Thus, the gradient arrays $G_1$ and $G_2$ produced by convolution of the image with the operators must be combined to produce an image with both vertical and horizontal edges enhanced.

This combination can be conducted in several different ways. The arrays may use an “rms point nonlinearity” to combine in square-root fashion [Abdou and Pratt 1979, Parker 2011]:

$$A(x,y) = \sqrt{G_1(x,y)^2 + G_2(x,y)^2}$$  \hspace{1cm} (B.19)

For the image in Figure B-1, the rms point operator from Equation B.19 will resemble Figure B-4. However, due to the several arithmetic steps involved in Equation B.19, combining Sobel operators in square-root fashion can be computationally taxing for large images [Parker 2011].
Simpler combination methods are the sum of the absolute values of both operators [Abdou and Pratt 1979, Parker 2011]:

\[ A(x, y) = |G_1(x, y)| + |G_2(x, y)| \]  \hspace{1cm} (B.20)

or the maximum of the two operators:

\[ A(x, y) = \max \{ G_1(x, y), G_2(x, y) \} \]  \hspace{1cm} (B.21)

The applications of both of these combinations (Equations B.20 and B.21) to the Sobel Operators on Figure B-1 are displayed in Figure B-5.

An observation of Figures B-4, B-5(a), and B-5(b) shows great similarity between the application of the square-root combination (Equation B.19, Figure B-4), and the sum of absolute values combination (Equation B.20, Figure B-5(a)) in enhancing the edges of this image. For both of these images, the majority of the chess board is mostly white. However, edges of the squares on the chess board appear to be more distinct with the application of the larger array combination (Equation B.21, Figure B-5(b)). Thus, for the chess board image in Figure B-1, the larger array combination seems to be the best way to combine Sobel operators to produce an edge-enhanced
Figure B-4: The combination of Sobel gradient arrays $G_1$ and $G_2$ in square root fashion from Equation B.19 results in the edge-enhanced image shown here.

Figure B-5: Two different combinations of Sobel Operators output slightly different edge detections from Figure B-1. (a) is the sum of the absolute value of both operators (Equation B.20), (b) is the maximum of both operators (Equation B.21).

The final step of edge detection may be thresholding. As an illustration, Figure B-6 shows the result of thresholding applied to edge-enhanced images of Figure B-5. The selection of the threshold intensity has the potential to be subjective if based only on the "visual agreement" of edges between the thresholded image and the original image. A more quantitative means of selecting the threshold intensity could involve processing the same image at all possible thresholds (from intensity 0 to intensity 256), and determining the minimum threshold intensity which captures the majority of edges (i.e., higher threshold intensities detect very few or no more edges).

Especially after the application of thresholding, it is shown that the Sobel operator successfully identifies edges the chessboard. However, images with different edge types than those apparent in the chess image, such as edges that are more tortuous, or less distinct, may benefit from a different combination of Sobel operators. Thus, although Sobel operators provide a consistent way
to enhance the edges of an image, the way in which the operators are combined greatly impacts the final edge-enhanced image. Ultimately, the user must determine the best combination for his or her application. It seems beneficial to try different combinations for a particular image type (such as is displayed in Figures B-4, B-5(a), and B-5(b)) before settling on a particular combination.

### B.3.2 Application of Sobel Edge Detector

The Sobel Edge Detector, with thresholding, was applied to an Environmental Scanning Electron Micrograph of Carrara marble in Figure B-7. A comparison of Figures B-7(a) and B-7(b) illustrates the application of the Sobel Edge Detector to Marble. The grain boundaries and microcracks are clearly evident in Figure B-7(b).

Thus, the Sobel Edge Detector proves to be a useful means of locating microcracks and grain boundaries in marble. However, the image in Figure B-7(b) does show some noise in the center of the marble grain. Some of the fracture surface texture has been identified as edges, even though the features pertain more to ridges on the marble surface than a distinct separation between or
Figure B-7: The Sobel Edge Detector applied to a micrograph of Carrara Marble. (a) Original micrograph. The image displays an intact marble grain surrounded by grain boundaries and microcracks. (b) Image in (a) after application of Sobel Edge Detector. The Sobel Operators were combined with Equation B.21 (the larger of the two Sobel operators) and thresholded at a threshold intensity of 100 (Section B.2.4.)

across marble grains. This “false-positive” may be reduced or eliminated with a different selection of threshold intensity, or with the application of a different edge detection algorithm entirely. Nevertheless, Figure B-7 illustrates that the Sobel Edge Detector is ultimately able to identify microcracks and grain boundaries in micrographs of Carrara Marble.

### B.3.3 Comparison of Sobel to Thresholding

Thresholding is a simple way to identify microcracks, but the Sobel edge detector greatly improves on this simple approach. In very early stages of this investigation, thresholding alone was used to detect microcracks. The percentage of black pixels in the image after thresholding was assumed to correspond to a crack density level. However, variations in the lighting conditions would yield inconsistent crack density levels across images with roughly the same amount of cracking but variations in the lighting conditions. For example, if a large shadow fell across a portion of the image, then the entire shadow would be classified as an edge. Thus, thresholding alone is a simple but insufficient means of identifying microcracks. As reported by [Parker 2011], contrast-based edge detection algorithms provide a more robust means of identifying edges under varying light conditions [Parker 2011]. The Sobel Edge Detector operates on contrast, and thus is less subject to
varying illumination. This property is especially important in the current study of Carrara Marble, because microscopy images are obtained for different samples under different imaging conditions, and thus different illumination. Not only are contrast-based detectors more robust against varying illumination, they are also more robust against variation in the coloration of the original image. This robustness is illustrated in the granite photograph in Figure B-8.

Figure B-8(a) shows an initial image of a multi-colored granite specimen. The various colors of this image derive from the various minerals composing the specimen. Pure thresholding of this image is shown in Figure B-8(b); however, thresholding has identified all dark minerals as edges. Only a few white minerals are not identified as edges. However, the application of the Sobel Edge Detector results in the image displayed in Figure B-8(c); this image has much more reasonably identified grain boundaries – regions of contrast between the color of minerals – as edges.

Thus, the two greatest advantages of the Sobel Edge Detector are

- Ability to detect edges under varying illumination
- Ability to detect edges under varying coloration of original image

These advantages suggest that further study of the Sobel Edge Detector, as well as other contrast-based edge detectors, will enhance the study of the fracture of geomaterials at the micro- and nanoscales.

Figure B-8: (a) An image of a granite specimen. The various colors correspond to the various minerals composing the specimen. From Miller [2008]. (b) Image in (a) after thresholding. All dark minerals have been identified (or misidentified) as edges. (c) Image in (a) after application of Sobel Edge Detector. Grain boundaries are more reasonably identified as edges in this image.
**B.4 Kirsch Edge Detector**

This section details the specific algorithm employed by the (template-based) Kirsch edge detector, applies the Kirsch edge detector to a micrograph, and assesses its usefulness in detecting edges in the micrograph.

**B.4.1 How the Kirsch Edge Detector Works**

The Kirsch Edge Detector is very similar to the Sobel Edge Detector, except that Kirsch utilizes eight operators instead of two. The eight operators are defined as:

\[
K_0 = \begin{bmatrix}
-3 & -3 & 5 \\
-3 & 0 & 5 \\
-3 & -3 & 5 \\
\end{bmatrix}
\]

(B.22)

\[
K_1 = \begin{bmatrix}
-3 & 5 & 5 \\
-3 & 0 & 5 \\
-3 & -3 & -3 \\
\end{bmatrix}
\]

(B.23)

\[
K_2 = \begin{bmatrix}
5 & 5 & 5 \\
-3 & 0 & -3 \\
-3 & -3 & -3 \\
\end{bmatrix}
\]

(B.24)

\[
K_3 = \begin{bmatrix}
5 & 5 & -3 \\
5 & 0 & -3 \\
-3 & -3 & -3 \\
\end{bmatrix}
\]

(B.25)

\[
K_4 = \begin{bmatrix}
5 & -3 & -3 \\
5 & 0 & -3 \\
5 & -3 & -3 \\
\end{bmatrix}
\]

(B.26)
$K_5 = \begin{bmatrix} -3 & -3 & -3 \\ 5 & 0 & -3 \\ 5 & 5 & -3 \end{bmatrix}$ \hfill (B.27)

$K_6 = \begin{bmatrix} -3 & -3 & -3 \\ -3 & 0 & -3 \\ 5 & 5 & 5 \end{bmatrix}$ \hfill (B.28)

$K_7 = \begin{bmatrix} -3 & -3 & -3 \\ -3 & 0 & 5 \\ -3 & 5 & 5 \end{bmatrix}$ \hfill (B.29)

Whereas the two Sobel operators emphasized brightness changes above/below the central element, and to the sides of the central element, the eight Kirsch operators emphasize brightness changes at each of the eight compass directions [Parker 2011]. The corresponding compass directions are:

- K0: East (vertical edge)
- K1: Northeast (diagonal edge)
- K2: North (horizontal edge)
- K3: Northwest (diagonal edge)
- K4: West (vertical edge)
- K5: Southwest (diagonal edge)
- K6: South (horizontal edge)
- K7: Southeast (diagonal edge)

These changes are illustrated in Figure B-9, which shows the convolution of each Kirsch operator with the chess image (Figure B-1). Note that four of the Kirsch operators (K0, K1, K2, and K3) detect the same edges as the other four (K4, K5, K6, and K7, respectively), but in the other
direction. Whereas K0 returns a positive (and thus white) value when the image is brighter on the right side of a vertical edge, K4 returns a negative (black) value when the image is brighter on the right side of a vertical edge (see the application of operator $H_1$ in Section B.3.1), but both K0 and K4 respond to vertical edges. This symmetry is also illustrated by looking at the uppermost left square on the chessboard and the chessboard border in Figure B-1, and in all the edge-detected images in Figure B-9. The uppermost left square is brighter than the border (Figure B-1); thus the image is in actuality brighter on the right. Convolution with K0 returns positive (white) values for the chessboard border, while convolution with K4 returns the reverse (negative, black values).

### B.4.2 Application of Kirsch Edge Detector

The eight operators of the Kirsch Edge Detector were applied to a micrograph of marble, the chessboard image, and a micrograph of granite in Figure B-10. All of the images in Figure B-10(b), (d), and (f) utilize the larger operator combination (Equation B.21). Then, a thresholding at an intensity of 100 (256 for the marble in Figure B-10(d)) was applied.

Figure B-10(b) shows the improvement of the Kirsch edge detector over the Sobel edge detector (Figure B-6) for simple images (specifically, for the Larger Mask combination, Equation B.21). The borders of all the chessboard squares are well-defined with Kirsch edge detection, whereas the chessboard squares in Figure B-6(b) are missing some horizontal and vertical borders.
However, the microracks in the marble micrograph (Figure B-10(d)) are more thickly delineated than in Figure B-7(b), and the Kirsch image also shows more noise due to texture. The image also had to be thresholded at a very high intensity in order to distinctly contrast the edges. Thus, the Kirsch edge detector appears to be very sensitive to image noise, and may not be as effective as the Sobel edge detector when applied to marble micrographs.

Finally, the Kirsch edge detector seems to show improved delineation of the different-colored regions of granite in Figure B-10(f). Especially when compared to the Sobel edge detected image in Figure B-8(c), the minerals seem to be more distinctly defined with Kirsch than with Sobel.

### B.4.3 Comparison of Kirsch Edge Detector to Sobel

The greatest advantages of the Kirsch edge detector are its improved ability over the Sobel edge detector to detect edges under varying coloration of the original image. These advantages are most likely due to the inherent increased sensitivity of the Kirsch detector; the detector applies more operators in more directions, and thus detects more edges. However, in the case of an image with textural noise, the Kirsch detector seems to be too sensitive and to ultimately produce more...
“false-positives” than the Sobel detector.

## B.5 Marr-Hildreth Edge Detector

This section details the specific algorithm employed by the (derivative-based) Kirsch edge detector, applies the Kirsch edge detector to a micrograph, and assesses its usefulness in detecting edges in the micrograph.

The Marr-Hildreth detector is a mathematical model type edge detector. In order to enhance edges, instead of convolving the image with the simple $3 \times 3$ or $5 \times 5$ template of the Sobel and Kirsch algorithms, the Marr-Hildreth detector employs a more complex and global model based on a mathematical expression [Parker 2011]. Additionally, the Marr-Hildreth edge detector is classified as a Second-Order Derivative Edge Detector, because it classifies edges based on the second derivative of the image function. It is also known as the Laplacian Second Order Edge Detector [Pratt 2007].

### B.5.1 How the Marr-Hildreth Edge Detector Works

The basic structure of the Marr-Hildreth detector is [Parker 2011, Pratt 2007]:

1. Convolve image function with a Gaussian function in two dimensions

2. Differentiate convolved image twice

3. Locate zero crossing pixels – pixels where the opposing neighboring pixels have opposite signs. Classify zero crossing pixels as edge pixels

**Convolve with Gaussian**

In any image, edges exist at a variety of resolutions. An edge detector may seek edges on the order of the image resolution; such edges may be as thin as a single pixel. Alternatively, an edge detector may seek edges which exist only at lower resolutions; such edges may be a few or several
pixels thick. The Marr-Hildreth detector allows the user to define the scale – i.e., resolution – at which to detect edges by convolving the image with a two-dimensional Gaussian function [Marr and Hildreth 1980].

The Gaussian function behaves as a smoothing filter; in this respect, the function sets the scale at which to identify edges. The filter locally averages the image function at each pixel. The size of the Gaussian in image space is determined by a user-input value for \( \sigma \), and the Gaussian essentially averages all the image values within a range of \( \sigma \) at each pixel [Marr and Hildreth 1980]:

\[
H_{\text{Gauss}}(x, y) = \frac{\pi \sigma^2}{2} e^{-\frac{x^2+y^2}{2\sigma^2}},
\]

where \( \sigma \) is a user-set value for the width of the Gaussian function (i.e., size of Gaussian, or number of pixels over which the user wants the Gaussian to average), and \( x \) and \( y \) are pixel positions. For the Marr-Hildreth detector, the Gaussian function is chosen as the smoothing filter for its small variance in both the spatial and frequency domains. This property allows one to use the Gaussian to effectively narrow in on the resolution of the convolved image, \( F_1(x, y) \) [Marr and Hildreth 1980]:

\[
F_1(x, y) = H_{\text{Gauss}}(x, y) \otimes F(x, y)
\]

**Differentiate Convolved Image**

For any differentiable function, a change in the value of the function corresponds to both a local minimum or maximum in the first derivative of the function, and a zero in the second derivative of the function. In the case of the image function \( F(x, y) \), a change in intensity (or value) of the image function corresponds to a peak in \( F'(x, y) \), and a zero in \( F''(x, y) \). The Laplacian \( \nabla^2 \) of the image function provides an orientation-independent second-order differential operator [Marr and Hildreth 1980]:

\[
\nabla^2 \{F(x, y)\} = \frac{\partial^2 F(x, y)}{\partial x^2} + \frac{\partial^2 F(x, y)}{\partial y^2}
\]
The second derivative of the convolved image function \( F_1(x, y) \) is desired, and is referred to as \( F_2(x, y) \):

\[
F_2(x, y) = \nabla^2 \{ F_1(x, y) \} = \nabla^2 \{ H_{\text{Gauss}}(x, y) \otimes F(x, y) \}
\]  
(B.33)

**Locate Zero Crossings**

The zeros of \( F''(x, y) \) correspond to intensity changes in \( F(x, y) \), and thus, presumably, edges. Thus, the zero values of the convolved image function \( F_2(x, y) \) are sought as edges. This search is implemented by seeking opposing neighboring pixels in \( F_2(x, y) \) with opposite signs; their opposite signs imply a zero value lies in the pixel between them [Marr and Hildreth 1980, Parker 2011].

Finally, the derivative rule for convolutions allows for the differentiation of the Gaussian operator before the convolution of Equation B.31. The second derivative of a two-dimensional Gaussian function resembles:

\[
\nabla^2 H_{\text{Gauss}}(x, y) = \frac{-1}{\pi \sigma^4} \left[ 1 - \frac{x^2 + y^2}{2\sigma^2} \right] e^{-\frac{x^2+y^2}{2\sigma^2}}
\]  
(B.34)

With Equation B.34 in hand, steps 1 and 2 of the Marr-Hildreth edge detector (Equation B.33) reduce to:

\[
F_2(x, y) = \nabla^2 H_{\text{Gauss}}(x, y) \otimes F(x, y)
\]  
(B.35)

Edges are sought as zero crossings in the convolved image \( F_2(x, y) \).

**B.5.2 Application of Marr-Hildreth Detector**

The application of the Marr-Hildreth detector to the image of the chessboard image of Figure B-1 illustrates the effectiveness of the detector in locating edges, as well as the effect of varying \( \sigma \) in the Gaussian smoothing filter (Equation B.30; Figure B-11.) Regardless of the value of \( \sigma \) utilized in the Gaussian, the detector identifies edges in a crisp and continuous fashion. For all images in Figure B-11, the edges are identified as thin black lines with no discontinuities.
The application of the Marr-Hildreth detector to the chessboard image of Figure B-1. The top row shows the \( F_2(x, y) \) image after convolution with the second derivative of the Gaussian (Equation B.35.) The second row shows the zeros from the \( F_2(x, y) \) image. Gaussians with four different values of \( \sigma \) (3, 10, 20, and 55) were convolved.

The value of \( \sigma \) affects two aspects of edge-detection with the Marr-Hildreth detector:

1. The identification of noise as an edge ("false-positives"); and

2. The failure to identify edges, which results in a seemingly "smeared" image

If \( \sigma \) is too low, there is an increase in the number of false-positives in the image, and the final zero-crossed image seems very noisy. This can be seen in the \( \sigma = 3 \) image in Figure B-11. The bottom row of chess squares contain extra edges within the chess squares. Alternatively, if \( \sigma \) is too high, existing edges are averaged too much with the Gaussian function, and ultimately disappear by smearing in with the image. This can be seen in the \( \sigma = 20 \) and \( \sigma = 55 \) images in Figure B-11. These images somewhat retain the outer edge of the board, but the details of the chess square are lost. This application of the Marr-Hildreth detector to the chessboard image ultimately shows that \( \sigma \) must be carefully selected to balance both false-positives and smearing – i.e., extra edges and edge loss – for a set of images.

The application of the Marr-Hildreth detector to marble and granite images illustrates the usefulness of the detector in microcrack identification (Figures B-12 and B-13). The usefulness of the Marr-Hildreth detector for marble micrographs seems low. High values of \( \sigma \) totally distort the initial marble micrograph (Figure B-12, \( \sigma=20 \) and 55). Alternatively, low values of \( \sigma \) are susceptible to the noise caused by the texture of the marble; this image inaccurately identifies much of the
Figure B-12: The application of the Marr-Hildreth detector to the marble micrograph of Figure B-7(a). The top row shows the $F_2(x, y)$ image after convolution with the second derivative of the Gaussian (Equation B.35.) The second row shows the zeros from the $F_2(x, y)$ image. Gaussians with four different values of $\sigma$ (3, 10, 20, and 55) were convolved.

Figure B-13: The application of the Marr-Hildreth detector to the granite photograph of Figure B-8(a). The top row shows the $F_2(x, y)$ image after convolution with the second derivative of the Gaussian (Equation B.35.) The second row shows the zeros from the $F_2(x, y)$ image. Gaussians with four different values of $\sigma$ (3, 10, 20, and 55) were convolved.
texture as edges (Figure B-12, $\sigma=3$). This result has also been found in the literature [Basu 2002]. The $\sigma = 10$ image (Figure B-12) presents the most accurate alignment of detected edges and actual cracks. However, qualitatively, both the Sobel (Figure B-7(b)) and Kirsch (Figure B-10(d)) detectors present a more accurate final representation of detected edges.

Figure B-14: A close-up of a granite image and various edge detections illustrates the improvement of the Marr-Hildreth detector in edge detection over the Sobel and Kirsch detectors. Note that image is most clearly visible in soft copy. (a) Original digital image of granite (From Miller [2008].) (b) Close-up of lower left corner of (a). (c) Close-up of Sobel edge-detected lower left corner. (d) Close-up of Kirsch edge-detected lower left corner. (e) Close-up of Marr-Hildreth edge-detected lower left corner.

The Marr-Hildreth detector seems again ideally suited for detecting edges under varying coloration of the original image. For low values of $\sigma$ (i.e., $\sigma = 3$ and 10, Figure B-13), the detector has clearly identified and outlined grain boundaries of the various granite minerals in an improved
fashion over both the Sobel and Kirsch detectors (Figure B-14). Whereas both the Sobel and Kirsch have identified entire grains as edges - especially where the natural grain has a dark color - the Marr-Hildreth detector has identified only grain boundaries as edges. This characteristic is illustrated by observing the crescent-shaped white grain near the lower corner of the specimen (lower corner of Figure B-14a, center of Figure B-14a and indicated with arrows). The Sobel detector has seemingly lost all information about this crescent-shaped grain (Figure B-14c), because no crescent shape is visible in the Sobel image. The Kirsch detector has identified the entire crescent region as a much larger, white region, rather than just its boundaries (Figure B-14d, indicated with arrows). Finally, the Marr-Hildreth detector has cleanly drawn the edges of the crescent-shaped region (Figure B-14e, indicated with arrows).

However, the value of $\sigma$ plays a large role in the ability of the Marr-Hildreth detector to identify the boundaries of minerals. If $\sigma$ is significantly larger than the typical width in pixels of a granite mineral, information on the boundary of that mineral is lost. This characteristic is illustrated by the Marr-Hildreth edge-detected images in Figure B-13 for $\sigma=20$ and 55. These images have lost not only the information on the mineral boundaries, but also the information on the central flaw; the result is a meaningless representation of edges after “over-smearing” the image (i.e., applying too large a Gaussian filter). Thus, $\sigma$ must be carefully selected for the particular typical size of granite mineral with respect to resolution for a set of granite images.

The Marr-Hildreth detector also shows potential for automatic identification of white patching in granite images (Figure B-15). The image in Figure B-15(a) shows a granite specimen (from Figure B-8(a)) immediately after the onset of white patching. The white patching is visible in the box in the center of the image.

Figure B-15c shows an initial attempt to identify this white patching by subtracting two subsequent images of the same specimen during loading [Miller 2008]. The second image (Figure B-15b) is subtracted from the first image (Figure B-15a), and the result is displayed in Figure B-15c. Because the white patches (high intensity values) manifest in the same spot where the first image contains relatively darker grains (low intensity values), the subtraction yields a bright spot (high intensity values, or white) wherever a white patch occurs, and a dark spot (low inten-
Figure B-15: The potential of the Marr-Hildreth detector to identify white-patching in granite. Each of the four images is the same granite image after a different stage of the Marr-Hildreth edge detector. A spot of white patching lies in the center of the rectangle in (b) through (d). (a) Intact granite specimen (also in Figure B-8a), from Miller [2008]. (b) Granite specimen in (a) after occurrence of white patching, from Miller [2008]. (c) Subtraction of white patching image in (b) from intact specimen image in (a). (d) Marr-Hildreth $F_2(x, y)$ image of (b). (e) Subtraction of Marr-Hildreth $F_2(x, y)$ image in (d) from Marr-Hildreth $F_2(x, y)$ image of (a), (displayed with black/white reversed in Figure B-16 for clarity).

...density values, or black) wherever no change occurs between the first and second images. Thus, the white patching from the second image (Figure B-15b) clearly manifests as a white patch in the subtracted image (the small white spot inside the dashed box of Figure B-15c), where as all other grains manifest as black. The subtracted image (Figure B-15c) shows more contrast between the white patching and the rest of the specimen than the original white patching image (Figure B-15b) shows between the white patching and the rest of the specimen, so the white patching stands out more in the subtracted image, and is thus easier to see. (Note that the white patching is most clearly visible in Figure B-15c in the soft copy of this document, rather than the print version.) Although subtraction has somewhat identified the white patching, the contrast of the white patching region with the rest of the image is still minimal. Additionally, the white region does not cover the full extent of the white patching apparent in the original white patching image (Figure B-15b). The
final two images in Figure B-15 illustrate how the Marr-Hildreth could potentially improve upon the subtraction technique (Figure B-15c) in identifying white patching in granite.

Figure B-15d is the first of two Marr-Hildreth images of the original white patching image in Figure B-15b. This image is the $F_2(x, y)$ image (Equation B.35, $\sigma = 3$) of the original white patching image (Figure B-15b). In the $F_2(x, y)$ image, the white patching region manifests as an extended dark region within the white box. The dark region of white patching in the Marr-Hildreth $F_2(x, y)$ image (Figure B-15d) shows greater alignment with the white patching than white region of white patching in the subtraction image (Figure B-15c); more of the original white patching is manifested as black patching in this image than as white patching in the subtraction image (Figure B-15c). Thus, according to the comparison between Figures B-15c and B-15d, the use of the Marr-Hildreth edge detector improves automatic identification of white patching in granite images in one main way: the Marr-Hildreth detector $F_2(x, y)$ image (Figure B-15d) captures more of the white patching than mere subtraction alone (Figure B-15c).

Figure B-15e is the second of two Marr-Hildreth images of the original white patching in Figure B-15b. Whereas the $F_2(x, y)$ image is shown in Figure B-15d (and discussed in the previous paragraph), Figure B-15e shows the subtraction between the $F_2(x, y)$ images of the subsequent granite images (Figures B-15a and B-15b, using a $\sigma = 3$). In other words, both the original intact granite image (Figure B-15a) and the original white patching granite image (Figure B-15b) were edge-detected using the Marr-Hildreth detector (and a $\sigma = 3$). Then, those two resulting edge-detected images were subtracted to result in the $F_2(x, y)$ subtraction image shown in Figure B-15e. Additionally, this image is shown in Figure B-16 with black and white reversed for clarity. In

Figure B-16: Area around white patching from Figure B-15e, with black and white reversed for clarity. White patching appears as a long black “edge” and is indicated with arrows.
contrast to performing edge detection on only an original white patching image (Figure B-15d), the subtraction of Marr-Hildreth edge-enhanced images in Figure B-15e combines information from before and after the onset of white patching. A white patching region is visible within the white rectangle, and this white patching region shows relatively good alignment with the white patching visible in the original white patching image (Figure B-15b). Nevertheless, the extent of the white patching region in this Marr-Hildreth image does not match the extent visible in Figure B-15b. An improvement could be made by localizing the region of Marr-Hildreth analysis (for example, analyzing only the region within the white box), or by incorporating a continuity analysis. A continuity analysis would look for large, continuous white regions (i.e. of size greater than one or a few pixels, and therefore assumed to be actual white patches rather than just the shifting of individual grains), and interpret those large white regions as white patches. Thus, although there remains room for improvement, the Marr-Hildreth detector shows great potential as an aid to the identification of white patching in granite specimens.

B.6 Edge Detection for Microcrack Identification

Based on the above exploration of the Sobel, Kirsch, and Marr-Hildreth edge-detection algorithms, some findings arise regarding the usefulness of edge detectors for microcrack identification.

1. The Sobel edge detector is the best algorithm for the identification of microcracks in marble micrographs.

2. The Marr-Hildreth edge detector is the best algorithm for the identification of granite mineral boundaries in granite images.

3. The Marr-Hildreth edge detector shows the best potential for the identification of white patching in granite images.

This section first gives reasons for these findings, and then relates them to their objective in this investigation: the identification of microcracks from ESEM micrographs. Finally, this section
presents the precise combination of edge detectors used to analyze micrographs in this investigation.

**Assessment of Stand-Alone Edge Detectors**

Based on the application of “stand-alone” edge detectors in this appendix (i.e., the application of a single edge detection algorithm to an image), the Sobel Edge Detector seems better than the Kirsch Edge Detector for the detection of edges in marble micrographs. As shown in Figure B-7b, the Sobel edge detector has identified microcrack edges and grain boundaries from a Carrara marble micrograph. Although there is some noise where the Sobel detector has identified texture as edges, the microcracks are nevertheless apparent in the edge-detected image.

In contrast to the Sobel Edge Detector, the sensitivity of the Kirsch Edge Detector makes the Kirsch algorithm too sensitive to the texture of the naturally fractured marble surface, and thus prone to detecting “false-positives”. This sensitivity is visible in the high number of false-positives (i.e., edges that are not microcracks) in Figure B-10d. Figure B-7b more accurately identifies microcracks than Figure B-10d.

Also in contrast to the Sobel Edge Detector, the Marr-Hildreth detector seems ineffective for the detection of edges in marble micrographs. Although as exhibited in Figure B-12 a variety of Gaussians were applied to marble micrographs with the Marr-Hildreth Detector, in the zero-crossing image, small Gaussians were too sensitive to texture, and large Gaussians were not sensitive enough to microcracks. None of the Marr-Hildreth images in Figure B-12 identify microcracks as accurately as the Sobel image in Figure B-7b.

A key difference between marble and granite in terms of edge detection is the fact that whereas Carrara marble grains are generally the same color, granite grains are different colors, ranging from white to black. This difference in intact material greatly affects the choice of the best edge detector. Despite the ineffectiveness of most of the edge detectors in marble (with the exception of the Sobel detector), these algorithms had success in identifying edges in granite. The Sobel and Kirsch Edge Detectors simply identify all dark grains as edges (Figures B-8b and B-10f), but the Marr-Hildreth detector seems better than the Kirsch and Sobel Edge Detectors for the detection
of grain boundaries in granite micrographs. Although the Kirsch detector has a high sensitivity for the various colors of the natural granite, the Marr-Hildreth detector more clearly and cleanly identifies the boundaries of the various colored grains (Figure B-13), and, with the additional step of subtraction, shows potential for identifying white patching in granite. Edge detection of granite is outside the scope of this study, but this discussion may prove useful for future investigations of microcracking in multi-colored geomaterials.

Thus, the Sobel Edge Detector proves to be the best stand-alone edge detection algorithm to use for the identification of microcracks in marble. The next section presents the precise edge detection scheme used in this investigation; it includes a few additional steps which enhanced the Sobel edge detection of marble micrographs.

**Edge Detection Combination for Marble Microcrack Identification**

This investigation developed an automatic quantitative technique for assessing a parameter correlated with the microcrack density of a particular image: black pixel percentage (BPP). Images with higher microcrack density contained a higher percentage of black pixels than images with lower microcrack density. The black pixel percentage of a single ESEM image was obtained with a five-step processing algorithm:

1. Create a Spotlight Mask from a sample image with no (or very little) microcracking.
2. Add the Spotlight Mask to a sample image to create an Unspotlighted Image.
3. Apply the Sobel Edge Detector to the Unspotlighted Image to obtain a Sobel Image.
4. Threshold the Sobel Image to obtain the Edge-Detected Image. Pixels above a user-determined threshold value are replaced with intensity 256 (white), and pixels below a particular value are replaced with intensity 0 (black). The Edge-Detected Image is a binary image, where black pixels should mostly correspond to microcracks.
5. Obtain the ratio of black pixels to total pixels in the Edge-Detected Image. This is the black pixel percentage (BPP.)
The steps in this algorithm are illustrated in Figure B-17, and explained below.

Steps 1 and 2 (the creation and application of a Spotlight Mask) confront the problem of spotlighting in ESEM images. Throughout this investigation, spotlighting – the brightening of a large spot in the center of an ESEM micrographs, while the corners of the micrograph are relatively darker – was frequently encountered. The problem arises due to a combination of the user-selected magnification, beam parameters (intensity, spot size, voltage), and water vapor pressure within the chamber. At a particular magnification and beam setting, the electrons on the outside edges of the beam have farther to travel, lose more energy before they are detected, and thus appear darker in the final micrograph. Although adjusting the magnification can reduce or eliminate spotlighting, adjusting the magnification also reduces the specimen area captured by a single image. Thus, rather than increase magnification and require more ESEM micrographs to cover a given specimen area, spotlighting was removed.

The dark rim in a spotlighted image is made up of low intensity pixels (Figure B-17, image 1.) Step 1 creates a Spotlight Mask which has replaced these low intensity pixels with a complementary value such that when the Mask is added to an image with spotlighting, the complementary values in the Mask will raise the low intensity value at the dark rim to a more typical (and therefore, brighter) intensity value. To create the Spotlight Mask (Step 1) for a given set of images from a specimen, first an image was chosen by eye with minimal or no microcracking or grain boundaries (see “Background Image” in Figure B-18). Then, the value of the average pixel intensity in this image was determined. Pixels below this average intensity are dark pixels, and thus are likely to belong to the dark rim from spotlighting. Thus, the final step of creating the Spotlight mask is replacing those dark pixels, in order to obtain a lighter, “rimless” image. Through experimentation, it was found that replacing the pixels with the “Complementary Value” (i.e., difference between the initial pixel value and \(1.1 \times \text{average intensity}\)) resulted in the best, “rimless” Unspotlighted Image.

In Step 2, the Spotlight Mask is added to every image in an image set to create a set of Unspotlighted Images. (Although this operation is only shown for the Background Image in Figure B-18, it is actually performed on every image in an image set.) This image addition is performed according to image operations described in Section B.2.2. To understand the effect of this operation,
Figure B-17: The images created after Steps 1-4 of the Edge Detection algorithm used in this investigation.
Figure B-18: The addition of the Spotlight Mask (middle) to the Background image (top) results in an Unspotlighted Image (bottom). Compare the Unspotlighted and Background Images, and notice that the dark spotlighting rim in the Background Image is completely eliminated in the Unspotlighted Image. The dark rim is eliminated by replacing pixels below 1.1× the average image intensity with higher intensity pixels (as indicated in the white squares in the “Background Image” and “Spotlight Mask”).
note that as described in the previous paragraph, the Spotlight Mask consists entirely of zero value pixels and Complementary Value pixels. On the one hand, zero value pixels have no effect on the Unspotlighted Image; at those pixel positions, the pixels are exactly the same as the pixel at the same position on the sample image. In Figure B-18, the black center of the Spotlight Mask is these zero value pixels. When they're added to the center of the Background Image (to create the Unspotlighted Image), no change occurs. On the other hand, Complementary Value pixels brighten the dark spotlighting edges by increasing the low pixel value to nearly an average value (in actuality, to $1.1 \times$ the average intensity). In Figure B-18, the light rim of the Spotlight Mask is these Complementary Value pixels. When they’re added to the dark rim of the Background Image (to create the Unspotlighted Image), the rim of the image disappears because it has been replaced with pixels of a more average intensity value.

In Step 3, Sobel Edge Detection is performed on the now Unspotlighted Image to create the Sobel Image (Figure B-17, image 3.) It was found that the “maximum of two operators” Sobel value (Equation B.21) yielded the ideal Edge-Detected Image (rather than the sum of absolute values, Equation B.20, or square root approach, Equation B.19.)

In Step 4, the Sobel Image was thresholded to better delineate the detected edges (Figure B-17, image 4.) It was found that a threshold value of 40 yielded an Edge Detected Image whose edges tended to align with microcracks. The proficiency of Steps 1 through 4 in detecting microcracks is illustrated by Figures B-19 through B-23. These figures show the Edge-Detected Images of Carrara and Danby marble from a variety of samples under a variety of imaging conditions (i.e., magnification, beam parameters, etc.) Even under this range of imaging conditions, the algorithm consistently identifies microcracks with few false-positive texture identifications.

Finally, in Step 5, the BPP of the Edge Detected Image was determined.

After processing each micrograph, the micrographs from a region were then color-coded according to BPP, and laid out in a map corresponding to their locations within the imaged region (Figure B-24). Images with 8% BPP were colored totally black, images with 1% BPP were colored totally white, and images with BPP between those values were colored a shade of gray, except as otherwise stated (some image sets had images with very high BPP, and thus were displayed with a
Figure B-19: Original ESEM images on left, and Edge-Detected images on right. Carrara marble, specimen c1-y.
Figure B-20: Original ESEM images on left, and Edge-Detected images on right. Carrara marble, specimen c2-z.
Figure B-21: Original ESEM images on left, and Edge-Detected images on right. Danby marble, specimen d2-z.
Figure B-22: Original ESEM images on left, and Edge-Detected images on right. Danby marble, specimen d1-z2.
Figure B-23: Original ESEM images on left, and Edge-Detected images on right. Danby marble, specimen d1-z2.
Figure B-24: The construction of the ESEM map for Region d2-z. The ESEM micrographs on the left were processed with the BPP algorithm. Each image was colored according to its BPP as shown on the central scale. Finally, a grid of all of the color-coded micrographs from each region was compiled as shown on the right. The arrows trace first the BPP-coded color, then the corresponding location on the ESEM map.
shifted BPP range). Since each region observed with ESEM consisted of up to over 100 images, this color-code system made regions of high microcracking stand out as being very dark. As a final quantitative step, BPP for each region of ESEM images are presented in boxplot form (see Appendix Section D for a discussion of boxplots as presented in this investigation.) These color-coded ESEM-maps and boxplots are presented in Section 4.2.2, and illustrate the development of microcrack density in the FPZ region.

B.6.1 Next Steps

There are many edge detectors that were not discussed in this report, but show potential for microcrack detection in geomaterials. The Prewitt and Robinson edge detectors are similar to the Kirsch detector in that they consist of eight operators, one for each of the compass directions. They differ only in the relative values of each of the elements in the operators [Pratt 2007]. The performance of the Prewitt and Robinson edge detectors on marble and granite images may be investigated in future work, but it is assumed to be similar to that of the Kirsch detector.

Only first-order detectors were discussed in this report due to their computational simplicity, but a second-order detector such as the Canny Operator may work well for geomaterials with a range of mineral colors, such as granite. These detectors look at the second derivative of pixel intensity change. Additionally, noise filters may effectively deal with the natural texture of the marble surface visible in micrographs of marble. Noise filters consider an image as being composed of actual object data, and random, signal-independent noise; the filters approximate and subtract out the noise [Parker 2011]. Finally, the Wallis Filter for the enhancement of contrast in grayscale images [Pratt 2007] is a potential initial step in the application of the edge detection algorithms to geomaterials.
Appendix C

Evolution of Microcrack Detection

The identification of microcracks in marble is an important aspect of both this FPZ study and the previous macroscale crack coalescence study which formed the foundation of this work [Wong 2008, Wong and Einstein 2009c;d]. The methods used to identify microcracks and monitor microcrack density have evolved throughout these studies. This appendix reviews the evolution of techniques used to identify microcracks. The evolution of the techniques may be divided into two parts: qualitative identification, and quantitative identification.

C.1 Qualitative Microcrack Identification

Identifying microcracks in a qualitative manner involves identifying features by eye which seem to be microcracks, and then again using the eye to estimate relative microcracking density. This section discusses the two qualitative approaches used to identify microcracks in these studies, and reviews first the initial technique developed by Wong, and then the subsequent hybrid qualitative-quantitative technique (“Hand-Tracing”) first used in the early stages of this investigation [Brooks 2010].
Wong identified cracks at the microscale and at the macroscale with the same technique: identifying cracks by eye, and then hand tracing them. This identification of microcracks led to a qualitative description of microcrack density as one of three densities: Background, Low, Medium, or High. These four qualitative microcracking densities are shown in the boxes in the upper right corner of Figure C-1.

### C.1.2 Hand Tracing of Cracks

The Hand Tracing method used early in this investigation formed a bridge between the qualitative microcrack detection by Wong, and the quantitative microcrack detection discussed in the next section (with full details in Appendix B.) The first step in the development of the Hand Tracing method was the conversion of the existing qualitative crack density levels to quantitative crack density levels. In order to perform this conversion, the actual crack density of the four boxes in the upper right corner of Figure C-1, total crack per area, was calculated. Each calculated density established an upper bound for four quantitative crack density levels. These quantitative levels are shown in Table C.1

<table>
<thead>
<tr>
<th>Qualitative Crack Density Level (CDL)</th>
<th>Qualitative (Hand Tracing) CDL Crack Length in $\mu$m per 100² $\mu$m² of Marble</th>
<th>Corresponding BPP As percentage of 100² $\mu$m² of Marble</th>
</tr>
</thead>
<tbody>
<tr>
<td>Background (B)</td>
<td>62.3</td>
<td>0.9%</td>
</tr>
<tr>
<td>Low (L)</td>
<td>169</td>
<td>2.5%</td>
</tr>
<tr>
<td>Medium (M)</td>
<td>391</td>
<td>5.9%</td>
</tr>
<tr>
<td>High (H)</td>
<td>630</td>
<td>9.4%</td>
</tr>
</tbody>
</table>

Then, the Hand Tracing method was applied to a specimen. The ESEM location on Specimen C1 (located in Region c1-y) was evaluated with the Hand Tracing method (Figure C-2.) Wong used a 100 $\mu$m square to illustrate the different qualitative crack densities (see the scale bar above the crack density boxes, in the upper right corner of Figure C-1.) It was found that a typical...
Figure C-1: Four qualitative crack densities. (With kind permission from Springer Science+Business Media: [Wong and Einstein 2009d], Figure 12(a).)
Carrara marble grain fit in a square of this size, and that microcracking around the grain was also apparent and traceable in a square of this size. Thus, the ESEM location in Region c1-y was divided into 100 μm x 100 μm square regions, the microcracks in each square were traced by hand in Photoshop©(Figure C-2a), and the crack density for each square (total length of microcracking in a single square region) was determined. (This determination was made by converting the traced area in each square to a traced length based on the size of pixel used for tracing and/or measuring, and then converting traced length to an actual crack length per area based on the scale of the image.) Figure C-2a combines all hand-traced ESEM images in the entire ESEM location. As a final step, the quantitative crack density from Table C.1 of each traced image was determined (Figure C-2b).

C.2 Quantitative Microcrack Identification

Identifying microcracks in a quantitative manner involves using image processing techniques (described in Appendix B) to automatically detect microcracks in an ESEM micrograph, and then to quantitatively evaluate microcracking level based on analysis of the processed micrograph. As described in Appendix B, the quantitative microcrack identification technique used in this investigation requires very little user input, and thus is a less subjective and more repeatable method of microcrack identification.

C.2.1 Edge Detection of Cracks

The quantitative method used for identifying microcracks in this investigation is heavily reliant on image processing techniques, and is discussed in detail in Appendix Chapter B. In short, the method uses image processing techniques such as thresholding and the Sobel Edge Detector for converting ESEM micrographs to binary images where the black pixels correspond to microcracking. The black pixel percentage (BPP) of these images is used as an approximate measure of microcracking level. This final step – using black pixel percentage – is the same final step as in the Hand Tracing technique described in Section C.1.2. Although the crack density levels developed in the quantitative approach and described in Table C.1 are not used to evaluate the specimens, the
a Region c1-y, with hand-traced microcracks.  
b Three of Wong's microcracking densities are found on Region c1-y: Background (no color), Low (light gray), and Medium (dark gray).

Figure C-2: Hand-tracing microcrack analysis of the ESEM location of Region c1-y.
The main idea of determining microcrack level within an ESEM micrograph stems from the qualitative approach. The precise relation between the BPP method and the Qualitative/Hand-Tracing methods can be seen in the far right column of Table C.1. To derive the numbers in this column, for each of the four CDL, it was assumed (arbitrarily) that microcracks had a width of 1.5 $\mu$m, and the corresponding Crack Length in the “Qualitative CDL” column. For example, in the final “High” row, 630 $\mu$m of crack per 100$^2$ $\mu$m$^2$ area is equivalent to 9.4% of that 100$^2$ $\mu$m$^2$ area, through the relation:

$$\frac{(630\mu m)(1.5\mu m)}{100^2\mu m^2} = 9.4\%,$$

under the assumption of a 1.5 $\mu$m crack width.

Figure C-3 shows the same ESEM location analyzed in Figures C-2a and C-2b, but here analyzed with the quantitative method (Figure C-3 fits inside the thick outline in Figure C-3). The most notable aspect of Figure C-3 is that, in comparison to the Qualitative (Hand-Tracing) method, this entire region is classified as having a High CDL. The entire BPP scale lies above 12% BPP; this corresponds to lying above the High CDL range, which ends at 9.4% BPP. Note that despite being classified as entirely High CDL (from a qualitative perspective), a variety of high crack densities exist on this region. This aspect of Figure C-3 points out a great advantage of the Quantitative (BPP) method over the Qualitative (Hand Tracing) method. The Quantitative (BPP) method allows a greater resolution of crack density detail, due to the relativistic nature of the method’s outputs. In other words, it all boils down to the scale that accompanies every ESEM map analyzed with the Quantitative (BPP) method. The existence of this scale means that the crack density levels are reported with respect to crack density levels across the whole region (i.e., the entire image set). Thus, even in a very high density region, a variety of crack density levels – levels that differ by a few percentage of black pixels – can still be resolved by the Quantitative BPP method, whereas the more Qualitative method may simply classify the entire region as being High CDL and leave it at that.
Figure C-3: The same ESEM location shown in Figures C-2a and C-2b, here analyzed with the Quantitative Microcrack Identification scheme discussed in Sections B and C.2.
Appendix D

Boxplots

A box plot provides a first-order means of data analysis for this investigation because it presents a concise summary of the spread and typical values of a data set, whether that set contains BPP values or nanoindentation values. Although box plots may assume various forms and present various statistical parameters, for the data in this investigation the bottom and top of the whiskers correspond to the mean value (either BPP, modulus, or hardness), respectively minus and plus one standard deviation. The central value corresponds to the median value, and the bottom and top of the box correspond to the 25th and 75th percentile of the data. Median is used since it expresses the typical value without being susceptible to outlier values, in the way that mean is susceptible. Note that for normally distributed data sets, approximately 25% of the data can be found between the mean and the 25th or 75th percentile. The closeness of the ends of the box (25th/75th percentile) to the ends of the whiskers (average +/- one standard deviation) indicates the spread of the data. Data sets with little spread will have larger boxes, and smaller distances from box to whiskers; data sets with more spread will have larger boxes, and greater distances from box to whiskers. The box plot thus presents a concise summary of the spread and typical values of a data set.
Figure D-1: A box plot succinctly captures the spread and typical value of a test comprised of many individual nanoindentations or ESEM micrographs.
Appendix E

Statistical Significance

This section presents the means of identifying statistically significant differences for this investigation [Mendenhall and Sincich 1995, Ruxton 2006]. In particular, the t-test provides an effective means of classifying the statistical significance of the results of this investigation. This test considers a particular outcome for the purposes of this investigation, this outcome is a difference in the mean value of two populations and determines whether the outcome is attributable to random chance (i.e., the spread of each populations may overlap or lie very close), or to some more important fundamental difference in the populations. The latter option signifies a statistically significant difference between the populations.

The t-test proceeds by forming a null hypothesis and selecting a confidence level $\alpha$ of mistakenly rejecting the null hypothesis. This confidence level is $\alpha = 5\%$ for this investigation; this particular level is common in scientific investigations [Bobko 2008], and provides a reasonable level of confidence (95%) in the results of the statistical analysis. This confidence level also corresponds to a particular t value ($t = 1.6449$ for the large degree of freedom, $N > 100$, of all tests analyzed in this investigation [Ang and Tang 2007]). The t-test then determines the actual t value with a consideration of the parameters of the two populations: count $n_1$ and $n_2$, sample spread (standard deviation) $s_1$ and $s_2$, and sample mean (average) $x_1$ and $x_2$. A test statistic $t$ is calculated as a function of the parameters. In the case when the populations have the same (or very similar) spreads $s_1$ and $s_2$, the Students t-distribution test statistic $t_{\text{student}}$ is determined [Mendenhall and
Sincich 1995):

\[ s_{\text{student}}^2 = \frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2}{n_1 + n_2 - 2} \]  
(E.1)

\[ t_{\text{student}} = \frac{x_1 - x_2}{s\sqrt{\frac{1}{n_1} + \frac{1}{n_2}}} \]  
(E.2)

In addition to having equal variance, the Student's \( t \)-distribution test statistic rests on two other assumptions: that the populations are independent, and that the populations are normally distributed. In the case when the populations have very different spreads \( s_1 \) and \( s_2 \), the Welch-Satterthwaite test statistic \( t_{ws} \) is determined [Ruxton 2006]:

\[ s_{ws}^2 = \left( \frac{s_1}{n_1} \right)^2 + \left( \frac{s_2}{n_2} \right)^2 \]  
(E.3)

\[ t_{ws} = \frac{x_1 - x_2}{s_{ws}} \]  
(E.4)

The null hypothesis is rejected if the magnitude of \( t_{\text{student}} \) or \( t_{ws} \) is much greater than 1.6449. Based on the pre-selected \( \alpha \) value of 5%, the "rejection of the null hypothesis" means that there is only a 5% chance that the difference between the two populations is due to random chance, and a 95% chance that more fundamental, statistically significant difference between the population dominates [Mendenhall and Sincich 1995]. As discussed in the next section, either \( t_{\text{student}} \) and \( t_{ws} \) were used in the tests analyzed in Chapter 6 based on the difference in the spreads of the tests.
Appendix F

Complete Tensile Test Analyses
Complete Tensile Analyses
(Carrara Marble)

Carrara 1
Carrara 2
Carrara 3
Analysis: Carrara 1

Summary

Carrara 1 - 121116

- Maximum Stress (1010.0 psi) t=32.2s
- Primary Crack Initiation (1010.0 psi) t=-32.2s
- Failure - Full Separation (1010.0 psi) t=32.2s

Fracture Analysis Legend

- Crack Label (alphabetically ordered)
- Crack Mode (Shear or Tensile)
- Stress Normalized to Peak Condition

Crack Type Summary

<table>
<thead>
<tr>
<th>Crack Name</th>
<th>Crack Mode</th>
<th>Initiation Normalized Stress</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{CG}$</td>
<td>Tensile</td>
<td>$\sigma^* = 1.00$</td>
</tr>
</tbody>
</table>
### Analysis: Carrara 1

*Note: All high-speed photographs have been adjusted to better show features of interest. Features are best visible on soft copy.*

#### White Patching and Cracks

<table>
<thead>
<tr>
<th>FRAME #1</th>
<th>FRAME #2</th>
<th>FRAME #3</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Frame 1" /></td>
<td><img src="image2.png" alt="Frame 2" /></td>
<td><img src="image3.png" alt="Frame 3" /></td>
</tr>
<tr>
<td><strong>High Speed Frame ID:</strong> 4864</td>
<td><strong>High Speed Frame ID:</strong> 2100</td>
<td><strong>High Speed Frame ID:</strong> -600</td>
</tr>
<tr>
<td><strong>Time:</strong> 30.8s</td>
<td><strong>Time:</strong> 31.7s</td>
<td><strong>Time:</strong> 32.2s</td>
</tr>
<tr>
<td>$\sigma$: 939.2 psi</td>
<td>$\sigma$: 993.6 psi</td>
<td>$\sigma$: 1010.0 psi</td>
</tr>
</tbody>
</table>

First frame in movie, 1.4s before crack initiation (Frame #5). No white patching is apparent.

White patching has appeared and spread to half of thickness of the neck.

Existing white patching has extended to entire thickness of specimen.
Analysis: Carrara 1

White Patching and Cracks*

*Note: All high-speed photographs have been adjusted to better show features of interest. Features are best visible on soft copy.

**FRAME #4**
High Speed Frame ID: -474
Time: 32.2s
σ: 1010.0 psi

White patching has now extended to width of specimen (i.e., visible on specimen front).

The white patching on the thickness of the neck has widened a bit, but intensified in the center most region. This intensified region is indicated by white in the diagram, and this intensified region transforms into a fracture in the next frame (Frame #5).

**FRAME #5**
High Speed Frame ID: -473
Time: 32.2s
σ: 1010.0 psi

Initiation of crack. Intensified region from Frame #4 has disappeared, and been replaced with the newly initiated crack.

**FRAME #6**
High Speed Frame ID: -471
Time: 32.2s
σ: 1010.0 psi

Complete failure of specimen; virtually continuous failure surface apparent.

Separation of specimen halves increases over the next few frames, then decreases.
**Analysis: Carrara 1**

*Note: All high-speed photographs have been adjusted to better show features of interest. Features are best visible on soft copy.*

**White Patching and Cracks***

<table>
<thead>
<tr>
<th>FRAME #7</th>
<th>FRAME #8</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Diagram" /></td>
<td><img src="image2.png" alt="Diagram" /></td>
</tr>
<tr>
<td>High Speed Frame ID: -466</td>
<td>High Speed Frame ID: -453</td>
</tr>
<tr>
<td>Time: 32.2s</td>
<td>Time: 32.2s</td>
</tr>
<tr>
<td>$\sigma$: 1010.0 psi</td>
<td>$\sigma$: 1010.0 psi</td>
</tr>
</tbody>
</table>
Analysis: Carrara 1

*Note: All high-speed photographs have been adjusted to better show features of interest. Features are best visible on soft copy.

**Failure Surfaces**

**Short Piece**

![IMG_0536]

**Tall Piece**

![IMG_0536]
Analysis: Carrara 2

Summary

<table>
<thead>
<tr>
<th>Crack Name</th>
<th>Crack Mode</th>
<th>Initiation Normalized Stress</th>
</tr>
</thead>
<tbody>
<tr>
<td>A_{cr}</td>
<td>Tensile</td>
<td>$\sigma^* = 1.00$</td>
</tr>
</tbody>
</table>

Fracture Analysis Legend

- Crack Label (alphabetically ordered)
- Crack Mode (Shear or Tensile)
- Stress Normalized to Peak Condition
- Crack
- Shearing Condition
- Point of Coalescence
- Spalling
- Crack Opening
- White Patching

Carrara 2 - 121116

- Maximum Stress (935.9 psi) $t=34.2s$
- Primary Crack Initiation (935.9 psi) $t=34.2s$
- Failure - Full Separation (935.9 psi) $t=34.2s$
**Analysis: Carrara 2**

*White Patching and Cracks*

*Note: All high-speed photographs have been adjusted to better show features of interest. Features are best visible on soft copy.*

<table>
<thead>
<tr>
<th>FRAME #1</th>
<th>FRAME #2</th>
<th>FRAME #3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>High Speed Frame ID:</strong> 4864</td>
<td><strong>High Speed Frame ID:</strong> 3300</td>
<td><strong>High Speed Frame ID:</strong> 1000</td>
</tr>
<tr>
<td><strong>Time:</strong> 32.8s</td>
<td><strong>Time:</strong> 33.3s</td>
<td><strong>Time:</strong> 34.1s</td>
</tr>
<tr>
<td><strong>σ:</strong> 859.0 psi</td>
<td><strong>σ:</strong> 898.7 psi</td>
<td><strong>σ:</strong> 935.9 psi</td>
</tr>
</tbody>
</table>

First frame in movie, 1.4s before crack initiation (Frame #5). Some white patching may be apparent near the base of the neck. (Not denoted in diagram.)

Distinct white patching has appeared and extended halfway across the thickness of the specimen.

White patching has fully extended across the thickness of the specimen neck.
Analysis: Carrara 2

*Note: All high-speed photographs have been adjusted to better show features of interest. Features are best visible on soft copy.

White Patching and Cracks*

FRAME #4
High Speed Frame ID: -460
Time: 34.2 s
$\sigma$: 935.9 psi

White patching has extended to the width (i.e., front face) of specimen.

The existing white patching on the thickness of the specimen has intensified in the center. This intensification is denoted with gray in the diagram. In the next frame (Frame #5) this intensification will become the initiated crack.

FRAME #5
High Speed Frame ID: -459
Time: 34.2 s
$\sigma$: 935.9 psi

Crack initiation simultaneously across width and thickness of specimen.

FRAME #6
High Speed Frame ID: -458
Time: 34.2 s
$\sigma$: 935.9 psi

Complete failure indicated by a nearly continuous fracture across the thickness and width of the specimen.

Over the next frames, the separation of the specimen halves will continue to increase, and then decrease.
Analysis: Carrara 2

White Patching and Cracks*

*Note: All high-speed photographs have been adjusted to better show features of interest. Features are best visible on soft copy.

FRAME #7
High Speed Frame ID: -453
Time: 34.2s
\( \sigma: 935.9 \text{ psi} \)
Post-failure. Maximum separation of specimen halves.

FRAME #8
High Speed Frame ID: -441
Time: 34.3s
\( \sigma: 0.48 \text{ psi} \)
Post-failure. Separation of specimen halves returns to minimum.
Analysis: Carrara 2

Failure Surfaces

*Note: All high-speed photographs have been adjusted to better show features of interest. Features are best visible on soft copy.

Short Piece

IMG_0549
IMG_0550
IMG_0552
IMG_0551

Tall Piece

IMG_0545
Analysis: Carrara 3

Summary

Carrara 3 - 121116

- Maximum Stress (740.6 psi) t=27.4s
- Primary Crack Initiation (740.6 psi) t=27.4s
- Failure - Full Separation (740.6 psi) t=27.4s

Fracture Analysis Legend

Crack Label (alphabetically ordered)

Crack Mode (Shear or Tensile)

Stress Normalized to Peak Condition

- Crack
- Shearing Condition
- Point of Coalescence
- Spalling
- Crack Opening
- White Patching

Crack Type Summary

<table>
<thead>
<tr>
<th>Crack Name</th>
<th>Crack Mode</th>
<th>Initiation Normalized Stress</th>
</tr>
</thead>
<tbody>
<tr>
<td>A_{CTM}</td>
<td>Tensile</td>
<td>\sigma* = 1.00</td>
</tr>
</tbody>
</table>

---

319
Analysis: Carrara 3  

*Note: All high-speed photographs have been adjusted to better show features of interest. Features are best visible on soft copy.

**White Patching and Cracks**

<table>
<thead>
<tr>
<th>FRAME #1</th>
<th>FRAME #2</th>
<th>FRAME #3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><img src="image1.png" alt="High Speed Frame ID: 4864" /></td>
<td><img src="image2.png" alt="High Speed Frame ID: 4864" /></td>
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<tr>
<td></td>
<td><img src="image3.png" alt="High Speed Frame ID: 2900" /></td>
<td><img src="image4.png" alt="High Speed Frame ID: 2000" /></td>
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<tr>
<td></td>
<td><img src="image5.png" alt="High Speed Frame ID: 2000" /></td>
<td><img src="image6.png" alt="High Speed Frame ID: 2000" /></td>
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<tr>
<td></td>
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<td><img src="image8.png" alt="High Speed Frame ID: 2000" /></td>
</tr>
<tr>
<td></td>
<td><img src="image9.png" alt="High Speed Frame ID: 2000" /></td>
<td><img src="image10.png" alt="High Speed Frame ID: 2000" /></td>
</tr>
</tbody>
</table>

**FRAME #1**
High Speed Frame ID: 4864  
Time: 26s  
\(\sigma: 686.5 \text{ psi}\)  
First frame recorded on high speed movie; 1.4s before failure (Frame #9).

**FRAME #2**
High Speed Frame ID: 2900  
Time: 26.6s  
\(\sigma: 713.6 \text{ psi}\)  
Initiation of white patching. Very faint and disperse on top right of specimen neck.

**FRAME #3**
High Speed Frame ID: 2000  
Time: 27.0s  
\(\sigma: 731.6 \text{ psi}\)  
White patching has extended.
Analysis: Carrara 3

*Note: All high-speed photographs have been adjusted to better show features of interest. Features are best visible on soft copy.

White Patching and Cracks

**FRAME #4**
High Speed Frame ID: -1000
Time: 27.2s
\( \sigma: 738.9 \) psi

White patching has extended to almost half of specimen width.

**FRAME #5**
High Speed Frame ID: -625
Time: 27.4s
\( \sigma: 740.6 \) psi

White patching is first visible along thickness of specimen.

**FRAME #6**
High Speed Frame ID: -575
Time: 27.4s
\( \sigma: 740.6 \) psi

White patching has extended.
Analysis: Carrara 3

*Note: All high-speed photographs have been adjusted to better show features of interest. Features are best visible on soft copy.

**White Patching and Cracks**

FRAME #7
High Speed Frame ID: -572
Time: 27.4s
\(\sigma: 740.6 \text{ psi} \)
White patch has extended to half of specimen thickness.

FRAME #8
High Speed Frame ID: -571
Time: 27.4s
\(\sigma: 740.6 \text{ psi} \)
White patching has fully extended across visible width and thickness of specimen. White patching appears to have become less disperse (thinner).
Crack initiation has occurred on specimen front.

FRAME #9
High Speed Frame ID: -570
Time: 27.4s
\(\sigma: 740.6 \text{ psi} \)
Complete specimen failure indicated by continuous crack surface.
Analysis: Carrara 3

*Note: All high-speed photographs have been adjusted to better show features of interest. Features are best visible on soft copy.

**Failure Surfaces**

**Short Piece**

![IMG_0559](image1)

![IMG_0560](image2)

![IMG_0562](image3)

**Tall Piece**

![IMG_0554](image4)

![IMG_0555](image5)
Complete Tensile Analyses
(Danby Marble)

Danby 1
Danby 2
Danby 3
Analysis: Danby 1

Summary

Danby 1 - 121207

Maximum Stress (488.4 psi) \( t=24.4s \)
Primary Crack Initiation (56.1 psi) \( t=25.0s \)

Fracture Analysis Legend

Crack Label (alphabetically ordered)

Stress Normalized to Peak Condition

\[ A(T) = 0.998 \]

Crack Type Summary

<table>
<thead>
<tr>
<th>Crack Name</th>
<th>Crack Mode</th>
<th>Initiation Normalized Stress</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A(T) )</td>
<td>Tensile</td>
<td>( \sigma^* = 0.11 )</td>
</tr>
</tbody>
</table>
**Analysis: Danby 1**

*Note: All high-speed photographs have been adjusted to better show features of interest. Features are best visible on soft copy.*

*White Patching and Cracks*

<table>
<thead>
<tr>
<th>FRAME #1</th>
<th>FRAME #2</th>
<th>FRAME #3</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Frame 1" /></td>
<td><img src="image2" alt="Frame 2" /></td>
<td><img src="image3" alt="Frame 3" /></td>
</tr>
</tbody>
</table>

**FRAME #1**
- High Speed Frame ID: - 43673
- Time: 22.9s
- $\sigma$: 445.5 psi

First frame recorded on high speed movie; 2.08s before crack initiation (Frame #4).

**FRAME #2**
- High Speed Frame ID: - 25000
- Time: 23.8s
- $\sigma$: 476.9 psi

White patching initiation. Note that white patching is extremely faint; it is dispersed over a relatively large region (in comparison to the size of white patching regions in Carrara marble).

**FRAME #3**
- High Speed Frame ID: - 10000
- Time: 24.5s
- $\sigma$: 482.2 psi

White patching fully developed across width and thickness of specimen.
Analysis: Danby 1

White Patching and Cracks

*Note: All high-speed photographs have been adjusted to better show features of interest. Features are best visible on soft copy.

**FRAME #4**

High Speed Frame ID: 1781
Time: 24.9s
\[ \sigma = 56.1 \text{ psi} \]

Crack initiation on the lower-right side of the width of the specimen (neck).

*The state of the trigger at this data point is arguable (the signal is halfway between the on-voltage of 5V, and the off-voltage of 0V). Thus, the stress at this point could also be interpreted to be 458.4 psi.

**FRAME #5**

High Speed Frame ID: 1720
Time: 24.9s
\[ \sigma = 56.1 \text{ psi} \]

Pieces of debris are apparent (and continue to move throughout the next frames). Some debris are indicated by boxes.

Besides the debris, no other specimen changes are apparent for the rest of the movie. **Thus, no complete failure surface has manifested in this specimen.** (After removal from the testing equipment, the specimen was easily pulled into two pieces by hand.)

*See the comment on the trigger in Frame #4.
Analysis: Danby 1

*Note: All high-speed photographs have been adjusted to better show features of interest.
Features are best visible on soft copy.

Short Piece

Tall Piece
Analysis: Danby 2

Summary

Danby 2 - 121207

- Maximum Stress (538.5 psi) t=25.6s
- Primary Crack Initiation (240.3 psi) t=26.4s

Fracture Analysis Legend

- Crack Mode (Shear or Tensile)
- Crack Label (alphabetically ordered)
- Stress Normalized to Peak Condition

<table>
<thead>
<tr>
<th>Crack Name</th>
<th>Crack Type</th>
<th>Initiation Normalized Stress</th>
</tr>
</thead>
<tbody>
<tr>
<td>A(\text{T})</td>
<td>Type 1 - Tensile</td>
<td>( \sigma^* = 0.47 )</td>
</tr>
</tbody>
</table>

Crack Type Summary

- Crack
- Shearing Condition
- Point of Coalescence
- Spalling
- Crack Opening
- White Patching
Analysis: Danby 2

*Note: All high-speed photographs have been adjusted to better show features of interest. Features are best visible on soft copy.

White Patching and Cracks*

**FRAME #1**

High Speed Frame ID: 43673
Time: 24.3s
σ: 495.8 psi

First frame in movie, 2s before crack initiation (Frame #4). No white patching is apparent.

**FRAME #2**

High Speed Frame ID: 16226
Time: 25.6s
σ: 538.5 psi

White patching appears. White patching is very faint/diffuse. Rather than a localized beginning on either the front or side of the specimen, the white patching seems to appear simultaneously all around the width and thickness of the neck.

**FRAME #3**

High Speed Frame ID: 2610
Time: 26.3s
σ: 240.4 psi

First spalling/debris appears; indicated by box. (Size of only a few pixels; virtually invisible in a single high-speed photograph.)

White patching intensifies (becomes brighter) in the center of the white patching band; indicated by white regions in diagram.
Analysis: Danby 2

*Note: All high-speed photographs have been adjusted to better show features of interest. Features are best visible on soft copy.

White Patching and Cracks*

<table>
<thead>
<tr>
<th>FRAME #4</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Speed Frame ID: - 2577</td>
</tr>
<tr>
<td>Time: 26.3s</td>
</tr>
<tr>
<td>$\sigma$: 240.4 psi</td>
</tr>
<tr>
<td>Crack initiation on top right of neck width.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>FRAME #5</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Speed Frame ID: - 2428</td>
</tr>
<tr>
<td>Time: 26.3s</td>
</tr>
<tr>
<td>$\sigma$: 240.4 psi</td>
</tr>
<tr>
<td>Crack extends to half-width of neck. No through-going failure surface is apparent in the high-speed video of this specimen.</td>
</tr>
</tbody>
</table>
Analysis: Danby 2

Failure Surfaces

*Note: All high-speed photographs have been adjusted to better show features of interest. Features are best visible on soft copy.

Short Piece

IMG_0481

IMG_0484

IMG_0486

Tall Piece

IMG_0491

IMG_0492

IMG_0495
Analysis: Danby 3

Summary

Danby 3 - 121207

- Maximum Stress (588.4 psi) t=94.6s
- Primary Crack Initiation (584.1 psi) t=94.8s

Crack Type Summary

<table>
<thead>
<tr>
<th>Crack Name</th>
<th>Crack Mode</th>
<th>Initiation Normalized Stress</th>
</tr>
</thead>
<tbody>
<tr>
<td>AXI</td>
<td>Tensile</td>
<td>σ* = 0.99</td>
</tr>
</tbody>
</table>

Fracture Analysis Legend

- Crack Label (alphabetically ordered)
- Crack Mode (Shear or Tensile)
- Stress Normalized to Peak Condition
- Crack
- Shearing Condition
- Point of Coalescence
- Spalling
- Crack Opening
- White Patching
**Analysis: Danby 3**

*Note: All high-speed photographs have been adjusted to better show features of interest. Features are best visible on soft copy.*

**White Patching and Cracks***

<table>
<thead>
<tr>
<th>FRAME #1</th>
<th></th>
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</thead>
<tbody>
<tr>
<td><strong>High Speed Frame ID:</strong> 43673</td>
<td></td>
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<tr>
<td><strong>Time:</strong> 92.9s</td>
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<tr>
<td><strong>σ:</strong> 527.4 psi</td>
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<tr>
<td>First frame in movie, 2s before crack initiation (Frame #4). No white patching is apparent.</td>
<td></td>
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</tbody>
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<table>
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<tr>
<th>FRAME #2</th>
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<tr>
<td><strong>High Speed Frame ID:</strong> 23000</td>
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<tr>
<td><strong>Time:</strong> 93.9s</td>
<td></td>
</tr>
<tr>
<td><strong>σ:</strong> 569.6 psi</td>
<td></td>
</tr>
<tr>
<td>White patching appears along thickness of specimen neck, on top and bottom of neck.</td>
<td></td>
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</table>

<table>
<thead>
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<th>FRAME #3</th>
<th></th>
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<td><strong>High Speed Frame ID:</strong> 5500</td>
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<tr>
<td><strong>Time:</strong> 94.7s</td>
<td></td>
</tr>
<tr>
<td><strong>σ:</strong> 584.1 psi</td>
<td></td>
</tr>
<tr>
<td>White patching delineates and intensifies along width and thickness of neck. This intensification is denoted by white regions in the diagram. Spalling/debris is apparent at this time (but not noted in the diagram).</td>
<td></td>
</tr>
</tbody>
</table>
Analysis: Danby 3

*Note: All high-speed photographs have been adjusted to better show features of interest.
Features are best visible on soft copy.

White Patching and Cracks*

FRAME #4
High Speed Frame ID: - 3190
Time: 94.8s
σ: 584.1 psi
Crack initiation on bottom right of neck thickness.

FRAME #5
High Speed Frame ID: - 3123
Time: 94.9s
σ: 544.9 psi
Crack extends slightly more. Additionally, further white patch intensification is apparent along the thickness of the neck, and is indicated by gray tracing in the diagram.
Analysis: Danby 3

Failure Surfaces

*Note: All high-speed photographs have been adjusted to better show features of interest. Features are best visible on soft copy.
Appendix G

Fracture Toughness from Strength:
Consideration of Grain Size

In the expression for determining fracture toughness, $K_c$, from macroscale strength values, the fracture toughness $K_c$ depends directly on the area of the crack surface. This appendix chapter discusses the influence of considering a granular material on the area of the crack surface, $A$. As will be shown, the consideration of a simple spherical granular material increases the crack surface area $A$ by a factor $\frac{\pi}{2}$ with respect to a perfectly flat surface — but the characteristic size of the spherical grains does not change this $\frac{\pi}{2}$ factor.

G.1 Flat Crack Surface

A typical prismatic specimen with both a pre-existing central flaw and a central crack surface is shown on the far left of Figure G-1 as “Specimen with Crack Surface”. Typically, wing cracks will emanate from the tips of the flaw. Although these wing cracks are typically curved, for simplicity in Figure G-1 only one flat wing crack is shown. Under the assumption that at failure two such wing cracks exist, the total area of the crack surface would be $bh$, or:

$$A_{\text{Flat}} = bh.$$  \hfill (G.1)
This “Flat Crack Surface” is shown on the far right top of Figure G-1.

G.2 Wavy Crack Surface

Consider now that instead of a pure solid material, as shown on the “Specimen with Crack Surface” image of Figure G-1, the material is granular and composed of close-packed spheres, as shown in the “Specimen as Granular Material” image of Figure G-1. These spheres represent the grains of diameter $d$ which comprise the material. If a crack surface opens completely through the granular material (“Specimen as Granular Material with Crack Surface”, Figure G-1), the crack surface can be considered to have a wavy appearance, as shown in the “Wavy Crack Surface” image on the far right of Figure G-1. The dimension of the waviness is $\frac{d}{2}$. The waviness thus directly accounts for the influence of grain size, $d$, on crack surface area. The complete area of the crack surface is...
found by multiplying the length of the wavy line by the depth of the specimen $b$, or:

$$A_{\text{wavy}} = \int_{z=0}^{z=h} f(z) \, dz.$$

As a first-order approximation of the influence of grain size $d$ on crack surface area (and therefore fracture toughness $K_c$), this discussion considers waviness in one dimension only (i.e., waves which travel down the height $h$ of the specimen). Waviness in the second dimension (i.e., along the depth $b$ of the specimen) is not considered in this discussion, but also will influence (and likely increase) the area of the crack surface.

There are two types of waviness that are appropriate for approximating the actual waviness of this crack surface: waviness that perfectly traces the outlines of the spherical grains, and a sinusoidal waviness that only hits the grains at their full diameters (i.e., $f(z) = a$ function of $\sin(z)$). The next two sections determine crack surface area $A$ for both types of waviness.

### G.2.1 Spherical Waviness

Under the assumption of perfectly spherical waviness (i.e., $f(z)$ simply traces each spherical grain), consider that the crack surface has area $A_{\text{wavy sphere}}$, width $b$, and actual length $\chi$ (where $\chi$ is larger than $h$, due to the waviness).

Now we explore how $\chi$ changes for grains of various size $d$. A finite number of grains $n$ fit along the height of the specimen. Thus, the diameter of each grain can be expressed as $d = h/n$. The crack surface height $\chi$ traces along half of the circumference of each grain. This half circumference has a length:

$$\text{Half Circumference} = \frac{1}{2} (2\pi r)$$

$$= \pi r$$

$$= \pi \frac{d}{2}$$

Multiplying the half circumference length from Equation G.3 by the total number of grains $n$, we
Figure G-2: Illustration of various cases of crack surface, for spherical grains sized such that \( n = 1, 4, \) and \( \infty \).

Find the actual length \( \chi \) of the wavy crack surface is:

\[
\chi = n \pi \left( \frac{d}{2} \right),
\tag{G.4}
\]

and that the area of the spherical wavy crack surface \( A_{\text{wavy sphere}} \) is:

\[
A_{\text{wavy sphere}} = n \pi \left( \frac{d}{2} \right) b.
\tag{G.5}
\]

Consider two example cases of spherical waviness, in order to get an idea of how grain size \( d \) affects \( A_{\text{wavy sphere}} \). In the first example, the specimen is composed of one giant grain. For this specimen, there is only 1 grain so \( n = 1 \) (Figure G-2, far left image). The diameter of this grain equals the specimen height, so \( d = h \). Finally, the area of the wavy surface for this giant-grained specimen \( A_{\text{wavy sphere, giant}} \) is:

\[
A_{\text{wavy sphere, giant}} = \frac{\pi}{2} bh.
\tag{G.6}
\]

In the second example, the specimen is composed of four small (arguably not “small”, but rather “relatively smaller”) grains. For this specimen, there are four grains so \( n = 4 \) (Figure G-2, central image). The diameter of these grains are each 1/4th of the specimen height, so \( d = \frac{h}{4} \). Finally, the
area of the wavy surface for this small-grained specimen $A_{\text{wavy sphere, small}}$ is:

$$A_{\text{wavy sphere, giant}} = 4\pi \left( \frac{h/4}{2} \right) b$$

$= \frac{\pi}{2} bh.$ \hspace{1cm} (G.7)

As a brief final proof, consider that $n$ spheres fit along the length of the height of the specimen $h$, and that the diameter of each sphere is indeed $h/n$. For infinitesimally small spheres, $n \to \infty$ (Figure G-2, far right image). The limit of Equation G.5 as $n \to \infty$ is the same expression as for area of the wavy surface of the giant-grained specimen and of the small-grained specimen: $\frac{\pi}{2} bh$. Thus, under the consideration of a spherically-wavy crack surface, grain size does not influence the area of the crack surface $A_{\text{wavy}}$; in all cases, this area is $\frac{\pi}{2} bh$. Ultimately, considering a granular material increases crack surface area by a factor of $\frac{\pi}{2}$, but the size of the considered grains does not matter.

\section*{G.2.2 Sinusoidal Waviness}

Under the assumption of sinusoidal waviness, we can develop an expression for $f(z)$ by filling out the general expression for a sinusoidal function. The amplitude of the waves are the half-diameters of the spherical grains, or $\frac{d}{2}$. The period of a full wave cycle is two grain diameters, or $\frac{2h}{n}$. Thus, the final expression for the waviness function $f(z)$ is:

$$f(z) = \frac{d}{2} \sin \left( 2\pi \frac{n}{2h} z \right).$$ \hspace{1cm} (G.8)

We can follow the standard arclength formula $L = \int \sqrt{1 + f'(z)^2}$ to find the length $\chi$ of the wavy surface:

$$\chi = \int_0^h \sqrt{1 + \left( \frac{\pi}{2} \cos(\pi d/z) \right)^2} \, dz$$ \hspace{1cm} (G.9)

Finally, the area of the wavy surface $A_{\text{wavy sine}}$ is simply $\chi b$.

Let's apply Equation G.9 to the two granular materials in this investigation. As detailed in Chapter 4, Danby marble has a typical grain size $d$ of 0.2710 mm, and Carrara marble a typical
grain size $d$ of 0.1453 mm. Prismatic specimens in this investigation have a height $h$ of 152.4 mm (or 6 inches), and a depth $b$ of 38.1 mm (or 1.5 inches). These dimensions, and the expression for $\chi$ in Equation G.9 yield $\chi_{\text{Danby}} = 223.08$ mm and $\chi_{\text{Carrara}} = 223.06$. These very similar numbers yield $A_{\text{wavy sine, Danby}} = 8499\text{mm}^2$ and $A_{\text{wavy sine, Carrara}} = 8498\text{mm}^2$. (Note that both these areas are extremely close to the limiting value of area from a completely spherical assumption in the previous section: $A_{\text{wavy sphere}} = \frac{\pi}{2}bh = 9120\text{mm}^2$.)

Ultimately, there are two major things to note from this sinusoidal approximation of wavy crack surface:

1. Grain size $d$ has an insignificant effect on the area of the wavy crack surface $A_{\text{wavy sine}}$, and

2. The area of the wavy crack surface is very nearly a factor of $\frac{\pi}{2}$ larger than the area of the flat crack surface $bh$. 

342
Bibliography


Vermont Quarries Corp. Olympian white danby., 2012.


