Using Thermochronology to Constrain Exhumation in the Swiss-Italian Alps

by

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ABSTRACT

Twelve bedrock samples were collected from Ticino, Switzerland and Northern Italy for thermochronological studies using the (U-Th)/He technique on zircon and apatite and fission track on subset of zircons. Nine samples were collected from the Lepontine Dome, north of the Insubric Line, six of which were in an approximate vertical, or elevation, transect. Three samples were also taken in a vertical transect from the Southern Alps, south of the Insubric Line. (U-Th)/He Zircon dates from north of the Insubric line ranged from 7 to 14 Ma, and indicate an approximate exhumation rate for the region of 1000 m/Ma. U-Th/He zircon dates from south of the Insubric Line ranged from 100 to 180 Ma, with one reliable apatite date of 23 Ma. These data lead to an approximate exhumation rate of 20 m/Ma in the south with rates increasing to about 150 m/Ma since 23 Ma. Thus very different exhumation histories can be inferred north and south of the Insubric Line, with the north side showing much younger dates and a higher exhumation rate related to continued orogenic activity, whereas to the south, there are lower rates and older dates indicating little to no orogenic activity until ca 23 Ma.
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INTRODUCTION

Many different forces interact to create the landscape that is visible on the earth’s surface. In areas with rugged, mountainous topography, the combination of active tectonics and precipitation work to shape topography. The interaction of climate and tectonics, and the importance of each in a system, is not fully understood, but is a topic of current interest and research (Molnar and England, 1990; Whipple and Meade, 2006). Studying exhumation rates, or the rate at which a rock moves towards the surface of the earth can provide some insight on how mountains evolve. Exhumation is related to climate through erosion, and to tectonics through uplift and normal faulting.

The European Alps are one of the most studied mountain ranges in the world, and provide a natural laboratory for studying exhumation. The mountains were created by a continent-continent collision that began about 65 million years ago. The mountains show strong precipitation gradients from region to region, and high relief. The Lepontine Dome, the specific location for this study, is located on the retro-wedge side of the orogenic wedge of the Alps, close to the Insubric Line, which functions as a back-thrust, and is a window into rocks which are much more deeply exhumed than rocks in the surrounding areas. The dome is located within a precipitation maximum, receiving around three times as much rain as elsewhere in the Alps (Fig. 1) (*Frei and Scär, 1998*). The Southern Alps, in comparison with the Lepontine Dome, fall outside the precipitation maximum, and are south of the Insubric Line away from the center of the mountain belt.
Exhumation rates can be estimated by using low-temperature thermochronology, a technique of dating rocks that yields the time since a rock has been at a specific temperature. By looking at how these ages vary over an elevation profile, or vertical transect, exhumation rates can be estimated. The high relief in the Alps makes it an ideal location for this type of study (Fig. 2).

Figure 1. Precipitation map of the Alps, scales from 500 to 3000 mm per yr. Study area is beneath the central, purple, high precipitation area. Created by Allison Anders from the Hydrologic Atlas of Switzerland (2001)
Figure 2. Looking northward up the Blenio Valley from the location from the BN transect.
GEOLOGICAL BACKGROUND

Alps Geology

The European Alps are the product of the collision of the European Plate in the north with the Adriatic Plate (a sub-plate of Africa) in the south. In the Swiss Alps, the Adriatic Plate overrides the European plate, and compression creates the mountain belt. Figure 3 shows an overview of the major geologic units of the Swiss Alps, and Figure 4 shows an approximately north-south cross section, perpendicular to the strike of the mountain belt. It is apparent that the Alps are a large scale fold and thrust belt that record several episodes of extension and subsequent compression.

The Jura Mountains are the northernmost tectonic unit in the Alps. At it's base is a Triassic aged evaporite deposit which is in turn overlain by Jurassic aged carbonate rocks. The evaporites act as the major décollment on which the thin-skinned deformation takes place and detaches from the European crust, which subducts beneath Adria. Moving south, the next rocks encountered are the mollasse and flyche belts, and Tertiary sedimentary deposits of the of the Swiss Basin, a foreland basin. The next unit south is referred to as the Prealps. This is actually a section of the Penninic Nappes which were thrust over the top of the Helvetic zone, and then eroded such that only an isolated patch remains.
Figure 3. Tectonic Map of the Alps. Box outlines the study area, and line indicates the cross section shown in fig 4. The intrusion to just to the east of the study area is the Bergell Intrusion. Figure from Stampfli et al. (2002).
Figure 4. Simplified cross section of the Alps. This is taken to the west of the study area, star indicates lateral equivalent to the nappes from which the samples for this study were taken, and arrow indicates where they are exposed at the surface today. The Periadriatic Line is the lateral equivalent of the Insubric Line. From Stampfli et al. (2002)
The Helvetic units are essentially the European margin. They consist of sedimentary rocks that range in age from Triassic to Tertiary, and are deformed in a nappe stack, such that the southernmost units are now the highest structurally, as is visible in cross section (Fig. 4).

The Massifs found in the central Alps are crystalline basement rocks, which are typically exposed in high terrain from uplift and erosion from the Tertiary orogeny; they include the Aar and Gotthard. In addition there are Pre-Triassic sedimentary rocks exposed in the troughs between the basement rocks.

The Pennine Nappes are the distal part of the European Margin, intensely deformed Mesozoic sedimentary cover of two ocean basins, pre-Triassic basement, and the Brainçonnais carbonate platform. They are intensely folded and sections show medium to high grade metamorphism. There are local sections of ophiolites, which are interpreted as remnants of the Tethys Ocean (Schmid, 1996). The samples for the northern transect were taken along a stack of amphibolite facies nappes, the Lucomagno, Simano, Leventina, and Maggia, within the Lepontine Dome, and considered to be part of the European basement.

To the east are the Austroalpine units, which represent pieces of Adriatic crust which have been detached and thrust over the Penninic units. Moving south, the Insubric Line is crossed, a deep penetrating fault structure which connects to the Periadriatic lineament system, which functions as the backthrust for the Alps. It is often viewed as the border between Europe and Adria. The units to the south are the Southern Alps, pieces of the Adriatic crust which have not been detached from
the basement. The Southern Alps contain the Ivrea and Strona-Ceneri Zones, sections of deep crust. The southern transect for this project was taken from the Southern Alps from the Strona Zone, which represents middle Adriatic crust. The final unit south is the Po basin, another sedimentary foreland basin on the southern side of the Alps.

There are considered to be two major orogenies in the tectonic history of the Alps, one during the Cretaceous and the other during the Tertiary, separated by a late Cretaceous period of extension. Development and evolution of the Tertiary orogen is shown schematically in Figure 5, from Schmid et al. 1996.

A late Cretaceous period of extension was followed by the beginning of the Tertiary orogeny with subduction of the Valais ocean and its cover, the North Penninic Bündnerschiefer, and the Brainçonnais Carbonate Platform. By 50 Ma the European basement, represented by the Adula Nappe in Figure 5, began to be subducted. Peak pressures were reached in the Eocene, approximately 40 Ma (Heinrich 1986, Schmid et al. 1996). Exhumation was rapid, and moderate pressures of 6-8 kbar were reached by about 35 Ma, when the temperature dominated, Lepontine, metamorphism began (Frey et al. 1980).

At the end of the Eocene, 35-30 Ma the orogenic wedge thickened enough that the European lithosphere delaminated, and only the lower crust continued to be subducted. Around this time it has been hypothesized that the subducting European lithosphere broke off (von Blanckenburg and Davies 1995), which caused upwelling asthenosphere and produced the melt for the Bergell Intrusion. Between 32 and 19
a) Early Paleocene  65 Ma

N of Insubric line:

- Upper crust of Apulian margin
- Aa: Austroalpine nappes
- Pl: Platten-Archaen ophiolites
- Ab: Avera Bundnerschieter
- B: Briogemiales upper crust
- Su: Surtsey
- Te: Tertiary nappes
- Sch: Schams
- Vol: Voltaic ophiolite
- V: Valais ophiolite
- North Pannonian Bundnerschieter (NPB)

b) Early Eocene  50 Ma

c) Late Eocene  40 Ma

d) Earliest Oligocene  35 Ma

- Upper crust of European margin
  - Aa & Gr: Adula Grief
  - St: St. Gotthard
  - L: Lutetmagena
  - Gr: Gerlitzzig
- Ae: external nappe
- Ha: Helvetic nappes
- Lower crust of European margin

- S: Sargi intrusion

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Figure 5. Illustration of the tectonic evolution during the Tertiary Orogeny. From Schmid et al. (1996), their Fig. 8.
Ma back thrusting of the central Alps began along a mylonite belt associated with the Insubric Line (Schmid et al. 1989). The southern part of the Lepontine Dome is the location of much of the back-folding and back-thrusting (Milnes 1974, Heitzmann 1987). The Bergell area was exhumed very quickly at a rate of about 5 mm/yr from a combination of back thrusting and erosion (Geiger and Hurford 1989).

After 19 Ma, the majority of deformation was concentrated in the Southern Alps.

**Lepontine Dome**

The Lepontine Dome is a part of the Pennine Nappes, and consists of south dipping nappes, which steepen towards the south until they reach vertical to overturned in the Southern Steep Belt, which boarders on the Insubric Line (Burri et al. 2005). The rocks consist mostly of granitic to granitodioritic mica gneisses (Berger et al. 2005). The

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Figure 6. Apatite fission track dates. The latitude and longitude are km in the Swiss coordinate net. From Rahn (2005), “this study” in the legend refers to their data. Approximate location of BN transect for this study is shown.
Insubric Line has vertical movement and is the focus of the backthrusting in the middle crust, but it also has a dextral strike-slip motion (Berger et al., 2005).

Four phases of deformation can be identified within the Lepontine Dome: deformation and metamorphism associated with subduction, high temperature metamorphism during nappe stacking, post nappe folding, and faulting and hydrothermal activity (Berger et al. 2005). High pressure metamorphism from subduction reached conditions of 1 GPa and 450°C in the north and 2-2.5 GPa and 750-800°C in the south part of the region (Dale and Holland 2003, Heinrich 1982). Barrovian, high temperature, metamorphism occurred during nappe stacking (Berger et al. 2005), and conditions at the Simano-Adula nappe boundary reached 625°C and 7 kbar pressure (Rütti 2001). Exhumation in the Lepontine dome has been constrained by several fission track studies. The apatite fission track ages, with a closure temperature of 116°C (Ketcham et al. 1999), range from 3.8 to 16.9 Ma with the youngest being in the Adula nappe and the oldest in the Tambo-Suretta pair (Wagner et al. 1977, Hunziker et al. 1992, Timar-Geng et al. 2004, Rahn 2005). Zircon fission track dates, with a closure temperature of 232°C (Brandon et al 1998), range from 11 to 19 Ma (Wagner and Reimer 1972, Wagner et al. 1977, Steiner 1984, Hurford 1986). Figure 6 shows spatially the apatite fission track data for the region. Both types of fission track ages tend to be young in the north and get older towards the south.
Southern Alps

The Southern Alps are a fold and thrust belt that form the southern orogenic wedge of the Alps. They record deformation from before the Tertiary orogeny, dated to the Early Carboniferous, which is overprinted by later deformation. The Stona-Ceneri zone, from which the southern transect of samples was taken, consists of amphibolite facies granitic gneisses and paragneisses, with some amphibolites and ultramafics (Reinhard 1953). U-Pb dates from the area indicate a heating event 440-460 Ma (Pidgeon et al 1970, Köppel and Grünengelder 1971) which Hunziker and Zingg (1980) interpret to represent the amphibolite grade metamorphic event for the region, whereas Boriani et al (1982/3, 1985) interpret it as magmatism and contact metamorphism.

Rifting and extensional tectonics followed this event until the late Cretaceous and early Tertiary, when the Southern Alps became a fold and thrust belt. In the western portion of the Southern Alps, the deformation is primarily thick-skinned (Schumacher et al 1997). Fission track apatite dates suggest a young uplift (Hunziker et al 1992). Zattin et al (2006) used vitranite reflectance and apatite fission track to estimate the thermal history, and found high heat flows until about 170 to 165 Ma, followed by a long period of thermal relaxation, until an important uplift event in the mid to late Miocene (about 10 Ma).
THERMOCHRONOLOGY BACKGROUND

Thermochronology exploits radioisotopic dating techniques to determine the thermal history of minerals, rocks, and geologic domains. There are a number of different thermochronometers, including U-Pb, (U-Th)/He, $^{40}$Ar/$^{39}$Ar, and fission track, however the general principles are similar for all techniques. A number of different minerals incorporate radioactive elements into their crystal structures when they form, and as those elements decay the mineral accumulates the daughter products. For traditional geochronometers, the ratio of parent to daughter isotopes are measured, and the time since the mineral crystallized can be calculated using the decay constant. For thermochronometers, the quantitative retention of the daughter product in a mineral is dependant on temperature. At higher temperatures, the daughter product diffuses from the mineral, and does not accumulate until the mineral cools through a characteristic temperature, often much lower than the crystallization temperature, when the daughter product begins to be retained. This temperature is termed the bulk closure temperature of the mineral, after Dodson et al (1973). The bulk closure temperature is specific for each mineral and type of daughter product and is a function of many parameters as discussed below. Thermochronology is a powerful technique because if the geothermal gradient from the sample area is known or can be estimated, the closure temperature can be correlated to a depth, and then the age-depth ratio can be interpreted as a first order estimate of the long term erosion rate.
This project focuses primarily on thermochronology using the (U-Th)/He system for the minerals zircon and apatite. Helium dating relies on the $^{238}\text{U}$, $^{235}\text{U}$, $^{232}\text{Th}$, and $^{147}\text{Sm}$ decay schemes, which emit alpha particles, $^4\text{He}$ atoms, during decay. Small amounts of the radioactive parent isotopes are incorporated into a mineral's crystal structure, and they decay at a constant rate over time. The decay equations and constants can be found in Table 1.

Thus the accumulation of $^4\text{He}$ can be written:

$$^4\text{He}=8\left(\frac{137.88}{1+137.88}\right)C_\text{U}(e^{\lambda_{238}t}-1)+7\left(\frac{1}{1+137.88}\right)C_\text{U}(e^{\lambda_{235}t}-1)+6C_\text{Th}(e^{\lambda_{232}t}-1) \quad (1)$$

Where $C_\text{U}$ and $C_\text{Th}$ are the concentrations of uranium and thorium, and $\lambda_{238}$, $\lambda_{235}$, and $\lambda_{232}$ are the decay constants, 137.88 is the present day abundance ratio of $^{238}\text{U}/^{235}\text{U}$, and $t$ is the age (Harrison and Zeitler 2005).

Above the closure temperature, volume diffusion results in the escape of He atoms from the edge of a crystal but below they are quantitatively retained. The bulk closure temperature for a cooling rate of 10°C/Ma and standard spherical radius, for apatite-He is generally taken to be 67°C (Farley 2000) and for zircon-He...
183°C (Reiners et al. 2004). However closure temperature is dependant on many factors and can vary, in a predictable manner, by as much as 10-20%.

The other thermochronological technique used in this project is the fission track (FT) system, which relies on the same decay scheme as (U-Th)/He. When the $^4$He are ejected during decay, the process releases energy and pieces of the nucleus are pushed through the crystal lattice, generally for about 15 μm, which damages the crystal lattice and leaves a visible track. At high temperatures the crystal repairs itself by annealing, but at low temperature the tracks accumulate and can be counted optically. The approximate Closure temperature for FT in apatite is 116°C (Ketcham et al. 1999) and for zircon is 232°C (Brandon et al. 1998) for a cooling rate of 10°C/Ma and average composition.

**Closure Temperature**

The concept of a closure temperature for a mineral is a mathematical simplification of reality. For a given mineral, there is a continuum between temperatures which are so high that virtually all of the daughter product escapes, and temperatures cool enough for which virtually none escapes. Dodson (1973) was the first to define closure temperature, $T_c$, as a mineral’s “temperature at the time corresponding to its apparent age”. He shows that for thermally activated diffusion based on the Arrhenius Equation,

$$T_c = R/[E \ln(AtD_0/a^2)]$$  \hspace{1cm} (2)

where

$$\tau = R/(E dT^{-1}/dt) = -R T^2/(E dT/dt)$$  \hspace{1cm} (3)

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where $R$ is the gas constant, $E$ is the activation energy, $A$ is a constant depending on mineral geometry and the decay constant, $\tau$ is a time for which $D$, the diffusion coefficient diminishes, and $a$ is the characteristic diffusion size (Dodson 1973). This is exact only when $1/T$ increases linearly with time, or monotonic cooling, however it is a good approximation to use the slope of the cooling curve at $T_c$.

Since the cooling curve is often not linear, and a mineral can spend variable amount of time in the region where only part of the daughter product is retained, it is often useful to consider the range of temperatures for which only a portion of the daughter product is retained, the Partial Annealing Zone (PAZ) for fission track (Gleadow and Fitzgerald 1987) or the Partial Retention Zone (PRZ) for argon and helium (Baldwin and Lister 1998, Wolf et al 1998). The amount of time which a mineral spends in the PRZ can significantly affect its cooling age. Baldwin and Lister (1998) define the PRZ as the region in the crust where only part of the daughter product is retained, whereas Wolf et al (1998) define it as the temperature zone where the bulk date ranges from 10% to 90% of the hold time, or time spent in the PRZ. Baldwin and Lister (1998) define PRZ temperatures based on thermal diffusion only, which is useful for understanding how a thermochronometer may record old events (Reiners and Brandon 2006).

Figure 7 shows the loss only PRZ
temperatures for common minerals in the (U-Th)/He system. Wolfe et al (1998) look instead at both loss and production of the daughter product, and how the dates change and eventually reach equilibrium if the rock spends extended time in the PRZ. The length of the hold time can have a significant effect on the cooling date (Fig. 8).

From the closure temperature equation, there are a number of factors that affect the closure temperature for a given mineral. Faster cooling rates and larger grain sizes act to increase the effective bulk closure temperature. This relationship is shown in Figure 9, the quantity $a$ is the diffusion dimension for the grain, usually taken to be half the grain size unless there is evidence for fast diffusion pathways in the grain such as subgrain boundaries (Hodges, 2003). The closure temperature differences from varying grain sizes can be enough such that it can be exploited to recover a significant time-temperature history for a rock using a single thermochronometer (e.g. Hess et al.,

Figure 8. Effect of hold time on cooling ages. The unlabeled curves are 25°C and 40°C. The top graph had no initial He, whereas the lower one had an initial age of 100 Ma. From Wolfe et al. (1998).

Figure 9. Effects of grain size and cooling rate on closure temperature. Top figure is for fast cooling rates, while lower figure is for very slow cooling rates. From Hodges (2003).
Compositional variations can also affect closure temperature.

**Sampling and Data Interpretation**

In this project uses thermochronological data to constrain the long term exhumation rates in and around the Lepontine Dome. Most samples were taken along an elevation transect. An elevation transect is a sequence of samples, usually taken from a ridgeline to a valley floor which spans as much elevation difference as possible, generally 1 to 3 km, over as short a horizontal distance as possible. By minimizing the horizontal distance, it can be safely assumed that the geothermal gradient, the temperature structure within the crust, is approximately the same for all samples, and therefore that all the samples crossed the isotherm corresponding to the bulk closure temperature for a particular mineral at the same depth. The age and elevation of each sample can be plotted, and the slope can be interpreted as the erosion rate. Vertical transects can also be used to infer changes in erosion rate, if there is a distinct break in slope in the age-elevation relationship (AER). Wagner and Reimer (1972) were the first to recognize the utility of age elevation relationships. They notice that samples from higher elevations tend to have older ages, and they suggest that samples from vertical columns can be used for calculating uplift rates, while comparison of samples of similar elevations show regional uplift trends. Elevation transects have been studied for many mountain ranges in the world (e.g. Deeken et al., 2006; Reiners et al., 2003; Lisker et al., 2003), but not in the Lepontine Dome, the location of this study.
To make robust interpretations, it is very important to understand the thermal structure of the area from which the samples are taken and how the isotherms relate to topography, especially for low temperature chronometers such as (U-Th)/He. To calculate an approximate geothermal gradient, it is necessary to solve the diffusion equation for all the heat elements in the crust:

\[
\kappa \nabla^2 T - u \nabla T + \frac{A}{\rho C} = \frac{\partial T}{\partial t}
\]  \hspace{1cm} (4)

where \( \kappa \) is thermal diffusivity (m\(^2\)/s), \( T \) is the temperature (K), \( u \) is the uplift rate (m/s), \( A \) is the constant of radiogenic heat production in the crust (W/m\(^3\)), \( \rho \) is the density of the crust (kg/m\(^3\)) and \( C \) is the specific heat of the crust (J/kgK). The first term, \( \kappa \nabla^2 T \), is the diffusion term. The second term, \( u \nabla T \), is takes account advection of heat from uplift, the \( \frac{A}{\rho C} \) is the term due to crustal heat production from radioactivity of U, Th, and K. Mancktelow and Graseman (1997) develop several analytical solutions for this equation for different situations, many of which based on the analysis by Turcotte and Schubert (1982) and Stüwe et al (1994). These authors model topography as harmonic functions, which the isotherms replicate, but amplitude is damped with depth. For longer wavelengths the amplitude is damped more slowly, thus the perturbation from topography penetrates to deeper isotherms, whereas very short wavelengths are damped out more quickly. In addition, both studies show that isotopic systems with cooling ages above 200°C are not highly influenced by topography. Quantifying the advection of heat is important for interpreting cooling dates; in mountain belts with rugged topography and high exhumation rates, exhumation rates based on cooling dates can be overestimated, and for fast cooling below 100°C it is important to take into
account lateral cooling. Stuwe et al (1994) attempt to estimate the difference in real and apparent uplift using the equations

\[ u_{real} = u_{apparent} \left( \frac{\Delta z}{H} \right) \quad \text{and} \quad \Delta z = a \exp\left( -\frac{u_{real}}{b} \right) \]

(5), (6)

where \( u \) is the uplift rate, \( H \) is the topographic relief, \( \Delta z \) is the depth difference to the \( T_c \) isotherm from ridge to valley such that if \( \Delta z = H \) the isotherm is flat and if \( \Delta z = 0 \) the isotherm is parallel to topography, and \( a \approx 3000 \) and \( b \approx 3000 \) values estimated from graphing modeled \( U \) against the resulting \( \Delta z \).

Braun (2002) expands on the steady state solutions to model the effects of recent relief change, not just on the thermal gradient, but also on the AER. He shows that relief changes can strongly affect the AER for low temperature thermochronometers, even in some cases causing inversion (Fig 10). He finds that the topographic wavelength, geothermal gradient, and rate of relief change all effect the AER.

Thermochronology is a powerful geologic tool for studying cooling histories, exhumation, and even relief changes. However it is important to study the data and the geology carefully as there are many factors which can affect both the age and how the age can be interpreted.
Figure 10. From Braun (2002). Shows the effects of topography and relief change on the slope of the AER. Both rugged topography and decreasing relief cause and overestimate of the exhumation rate.

(a) High $T_c$ thermochronometers

$$\frac{dh}{da} = \frac{h_0}{a_1 - a_2}$$
$$a_1 = a + \frac{h_0}{2v} \quad \text{&} \quad a_2 = a + \frac{h_0}{2v}$$

hence, $\frac{dh}{da} = \frac{v}{a}$

(b) Low $T_c$ thermochronometry

$$\frac{dh}{da} = \frac{h_0}{a_1 - a_2}$$
$$a_1 = a + \frac{h_0(1 - \alpha)}{2v}$$
$$a_2 = a - \frac{h_0(1 - \alpha)}{2v}$$

hence, $\frac{dh}{da} = \frac{v}{1 - \alpha}$

(c) Low $T_c$ thermochronometry + Relief change

$$\frac{dh}{da} = \frac{h_0}{a_1 - a_2}$$
$$a_1 = a + \frac{h_0(\beta - \alpha)}{2v}$$
$$a_2 = a - \frac{h_0(\beta - \alpha)}{2v}$$

hence, $\frac{dh}{da} = \frac{v(\beta - \alpha)}{1 - \alpha}$
METHODS

Sample Collection
Samples were taken from the Blenio and Ticino river valleys in the Ticino Canton of Switzerland. The samples include seven from a vertical transect near the head of the Blenio Valley and three for horizontal reference south in the Ticino Valley (Fig. 11). The seven samples in the Blenio Valley were collected for the purpose of obtaining an age elevation relationship along a transect from 500 meters to 2,300 meters elevation (See Table 2 in Results section for exact locations). Each sample consisted of several kilograms taken from in-situ bedrock.

Sample Preparation
To separate U-bearing accessory minerals, apatite and zircon, the samples were first crushed, and then the non-magnetic properties and the high density of the minerals were used to isolate them. The samples were first broken into walnut sized pieces, and then repeatedly crushed in a Bico Jaw Crusher. The fraction of sample less than 500 microns diameter was run across a Wilfley Table to separate denser minerals and eliminate rock flour. The residue was then processed using a Frantz isodynamic magnetic separator at 0.6 Amps and 20° inclination to isolate the non-magnetic minerals.

The non-magnetic portion was then further purified using the high-density liquid, Bromoform, with a density of 2.89 g/cm³. Zircon and apatite, with densities of 4.36 g/cm³ and 3.19 g/cm³ respectively, sink, whereas most of the common rock
Figure 11. Geologic Map with sample localities. Blues are Lepontine Dome, grey is Bundersifer, and pink is part of the Southern Alps. Scale of main map 1:500,000, inset of BN transect 1:100,000.
forming minerals float. Bromoform was then filtered in to a 500 mL separatory flask, the sample was poured in, and the mixture was stirred. The fraction that sank was isolated in filter paper, and then thoroughly cleaned with acetone.

The “heavy” fraction was put through the Frantz again at incrementally higher current and less side tilt, up to 1.4 Amps, and in some cases to as little as 0° side tilt. The final, least magnetic fraction was viewed under a microscope to hand pick grains for dating. Apatite crystals were chosen to be as perfect as possible. Criteria included: free of zircon or any other inclusions, as euhedral as possible, size greater than 60 microns in all dimensions, and free of cracks and other damage. Zircon crystals were chosen with similar criteria, although the presence of inclusions was not as much of a consideration. Zircon crystals were chosen for moderate size, greater than 60 microns and less than 150 microns. An example of a typical zircon crystal properly measured is shown in Figure 12.

Once the individual crystals were selected, the apatite crystals were placed into 1-mm platinum tubes, and the ends of the tubes were clamped down. Zircon crystals were similarly wrapped niobium tubes. Several “blanks” or tubes without crystals inside were created at this time also.
Helium Extraction

Each packet containing a crystal was placed in a hole in a stainless steel planchet. The sapphire planchet window was covered with a potassium bromide sheet to protect it, and the top was sealed with a copper gasket (Fig. 13). The planchet was placed under the Nd-YAG laser, and attached to the Helium extraction line shown in Figure 14. The whole line is evacuated to a pressure of $10^{-9}$ torr using a turbo pump. For each zircon or apatite analyzed, the laser was focused on the packet containing the grain, and then heated with a beam of 22 to 27 Å to de-gas it. For apatite, the sample was heated with the laser for three minutes, whereas zircon was heated for 15 minutes. After
degassing, the valve to the rest of the line was opened, and the gas is reduced to 16 K using the cryogenic trap, to condense the helium on a piece of active charcoal, and freeze out any other gasses besides helium. The gas was then raised to a temperature 37 K, to preferentially release the helium, and spiked with a known amount of $^3$He. The $^4$He/$^3$He ratio was then measured using a quadrupole mass spectrometer. Since measuring the amount of $^4$H in the sample is the key to determining the “age” of the grain, the ratio allows calculation of the amount of $^4$H produced by decay of U and Th since the number of moles of $^3$He is known. For zircon, the process was repeated on each sample at least once, and more if needed, until the measured helium was less than 2% of the original amount from the sample.

Each day before running any samples, a volume standard, line blank, and “hot” blank were run. To run a standard, the valve to the laser was closed, and the $^3$He spike was added to the line, as well as a known amount of $^4$He from a reference tank, and the ratio was measured. This is to make sure that the amount of $^3$He that is added when analyzing a sample is very accurately known. A line blank is similar to a standard, except that no $^4$He is added. This allows determination of the amount of $^4$He background in the line and in the $^3$He tank so that this can be subtracted when the amount of $^4$He in the samples is calculated. A hot blank is procedurally run the same way as a sample, however, the “sample” is an empty tube, platinum for apatite and niobium for zircon. This again allows assessment of the total blank of the system. At the end of an analytical session, another volume standard was run.
For each planchet of samples that was run, a crystal of known age was also included and treated as if it were a sample. For apatites, a fragment of the Durango apatite in a platinum tube was used, and for zircon, a zircon from the Fish Canyon Tuff in a niobium tube was used. Since these have known and internationally agreed upon dates, they allow us to assess the accuracy of the technique and unknowns.

For more information see
http://www.geo.arizona.edu/~reiners/arhdl/procs.htm

**U-Th-Sm Measurement**

The samples were dissolved and measured using techniques described in Reiners and Nicolescu (2006), the relevant portions of which can be found in Appendix A. Generally, the packets are removed from the planchet and placed in individual vials. The vials containing apatites were spiked with the non-naturally occurring isotopes $^{233}$U, $^{239}$Th and $^{147}$Sm, and the grain and the Pt packet were dissolved by heating it in nitric acid. The zircon packets were placed in Teflon vials, and spiked with $^{233}$U and $^{239}$Th. The Sm concentration in zircons is generally low enough, in comparison with U and Th, that it does not significantly contribute to He production. The grain and Nb packet were dissolved in hydrofluoric acid, within a Parr pressure digestion vessels at a temperature of 225 °C. They were then dried on a hotplate, and hydrochloric acid was added and they were again put in the Parr pressure digestion vessel at 200 °C to dissolve the fluoride salts.
The isotope ratios for U, Th and Sm (for apatites) in the resulting solutions was measured using a Thermo Finnigan Element2 ICP-MS. Also measured at this time were acid blanks, containing only the acids used to dissolve the packets, spike blanks, which contained both acid and spike, and bomb blanks, which are prepared in the same way as a zircon sample including time in the Parr pressure digestion vessel. Spike norms were also measured, which are similar in concept to the volume standards used in the Helium extraction line. For spike norms, both the U-Th-Sm spike and a known amount of naturally occurring U, Th, and Sm isotopes were added to spike blanks, which were processed in the same way as the samples. These blanks and norms allow the cleanliness of the Teflon vials and the chemicals to be assessed.
RESULTS

The dates for the individual crystals are shown in Table 2. The dates range from 7 Ma north of the Insubric Line to 182 Ma south of the Insubric Line. The majority of the apatites dated did not yield enough helium to give good results, only 07LM3-1 is reliable. The Fission Track dates for some samples were done by Rosalba Queirolo at Union College. Sample locations are in UTM WGS84, zone 32N.
### NORTH OF INSUBRIC LINE

<table>
<thead>
<tr>
<th>Sample</th>
<th>Easting</th>
<th>Northing</th>
<th>Elevation (m)</th>
<th>Zircon He Date (Ma)</th>
<th>2σ</th>
<th>Apatite He Date (Ma)</th>
<th>2σ</th>
<th>Zircon FT Date (Ma)</th>
<th>2σ</th>
<th>Sample Description</th>
</tr>
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<tbody>
<tr>
<td>07BN1</td>
<td>495537</td>
<td>5143915</td>
<td>511</td>
<td>8.41</td>
<td>0.58</td>
<td>15.7 ± 1.0</td>
<td></td>
<td>11.88</td>
<td>0.72</td>
<td>gneiss, fine sugary, qtz, bt, plg</td>
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<tr>
<td>07BN4</td>
<td>490241</td>
<td>5145220</td>
<td>2085</td>
<td>9.97</td>
<td>0.74</td>
<td>18.2 ± 1.0</td>
<td></td>
<td>10.68</td>
<td>0.66</td>
<td>gneiss, med schistose, qtz, bt, plg, gt, ky</td>
</tr>
<tr>
<td>07BN7</td>
<td>491000</td>
<td>5145485</td>
<td>1528</td>
<td>8.98</td>
<td>0.62</td>
<td>18.4 ± 1.0</td>
<td></td>
<td>10.68</td>
<td>0.66</td>
<td>gneiss, fine schistose, qtz, bt, mus, plg, gt, ky</td>
</tr>
<tr>
<td>07BN8</td>
<td>491549</td>
<td>5146360</td>
<td>1525</td>
<td>7.15</td>
<td>0.84</td>
<td>18.4 ± 0.9</td>
<td></td>
<td>17.06</td>
<td>7.78</td>
<td>clean calcarenite, qtz, mus</td>
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<tr>
<td>07BN9</td>
<td>493482</td>
<td>5145109</td>
<td>1124</td>
<td>11.27</td>
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<td>18.4 ± 0.9</td>
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<td>0.58</td>
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<td>15.1 ± 0.8</td>
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<td>07TC1</td>
<td>498689</td>
<td>5139695</td>
<td>405</td>
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<td>0.44</td>
<td>1.84 ± 3.5</td>
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<td></td>
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<td>0.56</td>
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<tr>
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<td>0.64</td>
<td>9.38 ± 8.12</td>
<td></td>
<td>13.9</td>
<td>0.94</td>
<td>gneiss, med micaceous, plg, bt, mus, qtz</td>
</tr>
</tbody>
</table>

### SOUTH OF INSUBRIC LINE

<table>
<thead>
<tr>
<th>Sample</th>
<th>Easting</th>
<th>Northing</th>
<th>Elevation (m)</th>
<th>Zircon He Date (Ma)</th>
<th>2σ</th>
<th>Apatite He Date (Ma)</th>
<th>2σ</th>
<th>Sample Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>07LM1</td>
<td>471251</td>
<td>5095963</td>
<td>1412</td>
<td>181.87</td>
<td>8.3</td>
<td>23.44 ± 6.56</td>
<td></td>
<td>gneiss, med crystalline, plg, bt, qtz, epd</td>
</tr>
<tr>
<td>07LM3</td>
<td>470522</td>
<td>5093630</td>
<td>949</td>
<td>158.36</td>
<td>7.28</td>
<td>11.25 ± 13.66</td>
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<td>gneiss, coarse crystalline, plg, bt, qtz</td>
</tr>
<tr>
<td>07LM5</td>
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<td>5093215</td>
<td>480</td>
<td>101.75</td>
<td>4.72</td>
<td>11.25 ± 13.66</td>
<td></td>
<td>weathered gneiss, coarse crystalline, plg, bt, qtz</td>
</tr>
</tbody>
</table>

Table 2. Sample locations, dates, and descriptions.
DISCUSSION

Overview and Data Interpretation

The results show is that there are very different exhumation histories across the Insubric Line. The dates from samples north of the Insubric Line are much younger than from the samples south of the Insubric Line. Zircon-He dates from the north range from 7 to 12 Ma, whereas dates from the south range from 100 to 180 Ma. When points from the vertical transects are fit to regression lines, the slopes indicates an exhumation rate of approximately 1000 m/Ma in the north and about 20 m/Ma in the south. This result shows that there is a much faster exhumation in the north, likely indicating more rapid erosion than south of the Insubric Line.

The apatite results are less conclusive because so few samples yielded sufficient quality apatite for analysis, and the best quality apatite often did not have enough helium for precise measurement. A single robust apatite date of 23 Ma comes from south of the Insubric Line. One possible explanation for the lack of helium in many of the samples from north of the Insubric line is that the cooling ages are very young (less than 5 to 10 Ma), which would indicate that the fast exhumation rates have continued into recent times, still with significantly older dates South of the Insubric Line.

Another notable aspect of the data is that the two aliquots for each rock do not generally overlap within 95% confidence. This makes the data somewhat hard to interpret because since the whole rock must go through the closure temperature
depth at the same time, the dates for all the grains in the rock should be the same. The fact that the grain dates do not agree either means either that the closure temperature is different for each grain or that the diffusion kinetics and corrections made for alpha-ejections are not completely understood, or some combination of both.

Grain morphology can affect the closure temperature for each grain as it determines the effective diffusion radius. Grains with a larger diffusion parameter, usually half the grain size for zircon and apatite crystals, have higher closure temperatures, and thus would be expected to have older dates. In this case, diffusion diameter ranged from 33 μm to 73μm, with only two grains larger than 51 μm, so it is unlikely that the grain size is the only factor causing the difference in dates for a single rock.

The other major issue is possible zoning of the uranium concentration within the crystal. The decay of uranium is energetic, and the helium atoms are ejected away from the nucleus, up to about 30 μm into the crystal. If the decay occurs in the rim of the crystal, the helium atom can be ejected out of the crystal and lost. A correction is made to the age calculation to account for this helium loss (the F\textsubscript{T} correction), however it is made under the assumption that the uranium is equally distributed throughout the crystal. If the crystal is zoned, and the uranium is concentrated either in the rim or in the core of the crystal, the F\textsubscript{T} correction is not correct, and the impact on the date can be significant (Hourigan et al., 2005).
The uranium zoning for the specific grains dated with the helium technique is unknown, but the zoning can be examined in the zircons dated from the same rocks using the Fission Track technique. 15 grains per mount were examined by Rosalba Queirolo at Union College and categorized based on their zoning patterns.

Representative images are shown in Figure 15. Generally the majority of grains from north of the Insubric Line showed no zoning patterns, while those from the Southern Alps showed significant zoning in the rims, core, and both locations. This could be affecting the age calculation, especially south of the Insubric Line. North of the Insubric Line it is unlikely that all of the dates do not agree because of zoning because most of the grains do not show significant zoning, but it can’t be said for sure without examining the specific grains, or dating more grains per rock to get a sense of the range of dates.

Figure 15. U zoning in zircon crystals. Both crystals are from 07BN4, and etched and mounted for fission track dating. The crystal on the left shows no zoning, or evenly distributed tracks. The one on the right shows rim zoning, higher U-concentration in rims shown by many more tracks on the edge of the grain. Images courtesy Rosalba Queirolo.
**North of the Insubric Line**

The samples north of the Insubric Line were taken from within the Lepontine Dome, and included the BN vertical transect and the TC samples. The BN transect is the more complete of the two transects taken, with five samples, and the TC rocks were taken in a horizontal pattern towards the Insubric Line. One common way of interpreting the dates from this transect is to average all the dates from a single sample and plot them on an age-elevation relationship plot (AER), which is shown in Figure 16. The helium dates from samples north of the Insubric Line show a clear exhumation trend related to orogenic activity. The points in blue on Figure 16 are the samples taken in a vertical transect, whereas the three points in green are those taken down valley toward the Insubric Line for a constant elevation perspective. As expected, the transect shows older dates at high elevations and younger dates at low elevations. Two samples in the middle of the transect are clear outliers.

![Age Elevation Relationship North of Insubric line](image)

**Figure 16. Age Elevation Relationship.** Samples in blue are the BN vertical transect while samples in green are the TC samples toward the Insubric Line. 07BN8 and 07BN9 only have one aliquot plotted, and 07BN8 is not included in the regression calculation. Error bars are average inter-grain variance, 16%.
Sample 07BN8 has two dates that are extremely different, and neither lie as expected on the AER. This sample was a calc-arenite that belongs to the Bündershifer unit to the north, where as all other samples were gneisses belonging to the basement nappes; The older date is 177 Ma, which is an order of magnitude older than any of the other samples in this transect, and indicates that the whole grain was probably not reset during metamorphism. The other date is 7 Ma, which is younger than the other samples, and too young to lie on the AER as expected. The amount of abrasion by sedimentary transport of the two zircon crystals dated was different, one showed some crystal structure with pyramidal terminations, while the other was very rounded. The rounded grain was the younger of the two.

The average date from 07BN9 is older than expected. There was nothing particularly remarkable about this rock in the field, and if the older aliquot is ignored, the younger date, 10.08 Ma, lies on the AER as expected although there is no a priori reason to do so. The other possible explanation for both of the unexpected dates on 07BN8 and 07BN9 is that there is some unrecognized structure in the field.

Samples down valley towards the Insubric Line (The 07TC samples, in green on Fig. 16) get older towards the fault. One can imagine a plane connecting all points of equal age; this surface is termed an isochrone. If the dip between 07BN4 and 07TC3, which have almost the same age, is calculated, the isochrone dips south toward the Insubric Line at an angle of about 5 degrees. This angle is low enough
that the deflection could be caused by the isotherms being warped by topography, or it is possible that the isochrones are being deflected by the Insubric Line.

A more rigorous way to approach the data from the BN vertical transect is to plot all dates on a graph with the age as the dependant variable (Fig. 17). Since the two dates are not the same within analytical uncertainty, it does not actually make sense to average them. Graphed in this way the regression line is minimizing differences in age, the source of the uncertainties, rather than elevation. In this case the exhumation rate is the inverse of slope. When 07BN8 is excluded (because of the grain to grain age differences and rock type) the exhumation rate is 1151 m/Ma, slightly faster than the exhumation rate when graphed in the inverse. However when a 95% confidence interval was calculated, the slope was not significant. The 95% confidence interval does give a lower bound for the possible exhumation rate, which with this data set is about 400 m/Ma.

![Figure 17. All dates except those for 07BN8 from the BN vertical transect. Error bars indicate 2σ analytical uncertainty.](image)

\[ y = 0.0006x + 9.1762 \]
\[ R^2 = 0.1566 \]
Not having a statistically significant slope is partially a product of having too few data points. However it can also be interpreted as meaning that exhumation through the partial retention zone was extremely fast and that all samples have virtually the same date independent of elevation. To constrain the exhumation rate better, it would be necessary to date more than two grains per sample.

If all the points are plotted (still neglecting the 177 Ma date for 07BN8) with age as the dependant variable, it appears that there could be a discontinuity in the transect, probably in the form of a fault (Figure 18). As discussed before, sample 07BN8 comes from a different nappe and paleogeographic domain than the rest of the transect. Paleogeographically it comes from the cover to the Valais ocean basin,

![Fault Model](image)

**Fault Model**

- **Below Fault**
- **Above Fault**
- Linear (Below Fault)
- Linear (Above Fault)

\[
\begin{align*}
y &= 0.0035x + 6.9155 \\
R^2 &= 0.4121
\end{align*}
\]

\[
\begin{align*}
y &= 0.0063x - 1.8587 \\
R^2 &= 0.7054
\end{align*}
\]

Figure 18. Ages plotted indicating with possible fault area shown. Such a fault would indicate east side down relative to the west.
whereas the Lepontine basement nappes are from the distal European basement. There must have been a fault or ductile process to produce this juxtaposition, and such an interpretation of the BN transect would indicate that this faulting was active within the last 10 Ma since the rocks went through the closure isotherm. It also would indicate at least a kilometer of offset in this time period, with the western side of the fault moving up relative to the east. There are other north striking normal faults in close proximity to the transect (Fig. 11), so this could be a splay that is not shown on the map. If this is the case, it would indicate slightly slower exhumation, with rate closer to about 200 m/Ma in the region for this time, though the slopes are not statistically significant, so the exhumation rate could range considerably.

Zircon Fission Track (ZFT) dates for some of the samples were available from Rosalba Queirolo at Union College. ZFT has a higher closure temperature (232°C (Brandon et al 1998)) than the Zircon Helium system (183°C (Reiners et al. 2004)) so the dates for ZFT are older from the same rock. The ZFT dates range from 15 to 18 Ma, and the AER for the ZFT dates is shown in Fig 19. There are only four ZFT points, but the slope indicates an exhumation rate of about 300 m/Ma. The difference in closure temperature can be translated into a pseudo-difference in elevation in one system, with the ZFT having a higher elevation. The simple way to achieve this is to assume a 30°C/km geothermal gradient for the region (Hurford, 1986), and then calculate the closure depth for each thermochronologic system based on the closure temperature (Reiners and Brandon, 2006). This depth is then
added to the topographic elevation to create a pseudo-elevation, or essentially the distance.

Figure 19. Zircon Fission Track Ages plotted with the helium ages. Error Bars show average intergrain variance.

Figure 20. The AER for the region with the Fission Track ages translated into higher elevations in the zircon-He system. Created by Devin McPhillips.
traveled since the closure depth. Pseudo-elevations for both systems can then be plotted on one graph against age. Plotted in this manner (Fig. 20), the data show essentially constant exhumation rates over the past 20 Ma, at a rate of about 350 m/Ma.

A final, simplistic, way in which to interpret the zircon helium dates, is to say that the average date for all points north of the Insubric Line is 10.57 Ma, and the closure depth for zircon helium dates is generally 8 to 10 kilometers, so the exhumation rate since about 10 Ma has been somewhere in the range of 800 to 1000 m/Ma, which is fairly consistent with the exhumation rates gained from the vertical transect.

The apatite dates from north of the Insubric Line are not interpretable because the helium levels in the crystals were too low, only slightly above blank level. It was also very challenging to find quality apatite in these rocks, so apatite was not dated in all the samples. There are two possible explanations for the lack of helium, the first is that uranium concentrations were very low, and the other is that the grains are very young, less that about 5 Ma. The uranium concentrations in the dated apatites was on the low end of normal, so it seems likely that these apatite are quite young, indicating a continued trend of rapid exhumation into more recent times.

**South of the Insubric Line**

The dates for the zircons in the Southern Alps are much older, and while the two grains for each rock still do not agree, the pattern overall seems easier to
interpret. Two different plots of the data are shown in Figures 21 and 22. Both yield and exhumation rate of about 20 m/Ma, much slower than the exhumation rates in the Lepontine Dome, though neither slope is significant on a 95%

**Figure 21.** All zircon-He ages plotted for the LM vertical transect. Error bars are 2σ analytical uncertainties.

**Figure 22.** AER for zircon-He ages from the LM transect. Ages are averaged and error bars are average inter-grain variance.
confidence interval. Zattin et al (1996) in their thermal study of the Southern Alps suggest high heat flow until 170 to 165 Ma, followed by a long period of thermal relaxation, so it is possible that the dates from this study show the beginning of this thermal relaxation period rather than an erosion rate.

There average date south of the Insubric Line was 157 Ma, and with a closure depth of 8 to 10 km, this yields an exhumation rate of about 50 to 65 m/Ma since that time, somewhat faster than the erosion rate yielded by the AER slope. There was one reliable apatite date from the Southern Alps, with an date of 23 Ma. The closure depth for apatite is 3 to 4 km, so this 23 Ma date indicates an exhumation rate of about 130 to 175 m/Ma since 23 Ma, much faster than the 20 m/Ma exhumation rate which is indicated by the vertical transect for between 100 to 180 Ma. This apatite date is also powerful because it can be compared with the zircon date from the same rock. The average zircon-He date for this rock is 165 Ma, so between 165 Ma and 23 Ma, this rock was transported vertically about 6 km, which leads to an exhumation rate of about 40 m/Ma for this period. The apatite date indicates that the exhumation rate in the Southern Alps increased after the zircons went through their closure temperature.

*Synthesis and Orogenic Interpretation*

The location of these samples in the retro wedge and foreland of the Alps provides and interesting timing information on the mechanical deformation of the mountain belt. Willet et al (1993) describe three phases of the orogenic wedge during a continent-continent collision, based on numeric modeling, and Malavieille (1984) showed the first two of these stages in the physical sandbox modeling.
Schematic diagrams of the stages are shown in Figure 23. The first stage is block uplift bounded by step-up faults, the second is development of a low taper pro-wedge and a steeply tapered retro-wedge, and the third is propagation of the retro wedge into undeformed crust. If this model is applied to the Alps, the samples from north of the Insubric Line were taken from the retro-wedge, a section which has received significant uplift and through back thrusting and backfolding, while the samples south of the Insubric Line are taken from the foreland, which underwent little uplift related to orogenesis until stage three of the model was reached.

The southward-stepping of the deformation front, essentially the transition to stage three of the model, is captured by the dates and exhumation rates gleaned from this study. Dates from north of the Insubric Line indicate continuous rapid uplift to close to present times, indicating a continued combination of backthrusting and backfolding in the retro-wedge for the past 18 Ma. The zircon-He dates from the LM transect south of the Insubric Line show the regime previous to deformation in the southern foreland, while the 23 Ma apatite-He date, with the much faster exhumation rate afterwards, indicates that such deformation and uplift is now
taking place. With only one apatite date, it is not possible to give an exact timing for this transition, but Schmid et al. (1989) estimate that back thrusting along the Insubric Line began between 32 and 19 Ma, so it is possible that the back thrusting and stepping south of the deformation front occurred somewhat simultaneously. In any case, dates from this study indicate that since about 20 Ma there has been both back thrusting in the retro-wedge and southward propagation of deformation.
CONCLUSION

The European Alps are an active orogen, where both tectonics and climate shape the landscape. The results from this pilot study show that there are very different exhumation histories north and south of the Insubric Line. The dates to the north indicate rapid, continuous exhumation since at least 18 Ma, probably an indication of back thrusting and back folding in the retro-wedge. Dates to the south indicate that there was little or no uplift related to the orogenic activity north of the line, and therefore very slow exhumation rates, until 23 Ma, consistent with southward propagation of the deformation front.

Further research to clarify the results of this preliminary study should include additional grains from samples reported on here as well as new ones to better constrain exhumation rates and better understand intergrain variability. A more complete transect with additional apatite dates south of the Insubric Line could significantly enhance the interpretation and precisely locate the transition between domains of slower and faster exhumation rates. Comparison of rates from a second vertical transect north of the Insubric Line would also test the hypothesis that there is a fault within the BN transect.
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APPENDIX

Sections from:

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Measurement of parent nuclides for (U-Th)/He chronometry by solution sector ICP-MS

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Minor error in Figure 2 caption corrected. First sentence erroneously stated: “Figure 2. Measurements of $^{232}$Th/$^{229}$Th and $^{231}$U/$^{233}$U in “spiked normal” solutions, comprising either 25 or 50 µl of mixed $^{230}$Th-$^{231}$U spike and 50 µl of a mixed Th-U normal with 50 ng/ml U and 100 ng/ml Th.”

Corrected: “Figure 2. Measurements of $^{232}$Th/$^{229}$Th and $^{238}$U/$^{233}$U in “spiked normal” solutions, comprising either 25 or 50 µl of mixed $^{228}$Th-$^{231}$U spike and 25 µl of a mixed Th-U normal with 50 ng/ml U and 100 ng/ml Th.”
Abstract
(U-Th)/He chronometry requires accurate and precise measurement of U, Th, and in some cases, Sm, in analyzed phases. This is typically accomplished by dissolution and isotope dilution of the dated aliquot, and isotope ratio measurements of the resulting solution by inductively-coupled plasma mass spectrometry (ICP-MS). Here we present analytical procedures for these measurements using sector (high-resolution) ICP-MS, and analytical summaries of several thousand apatite and zircon samples and standards from our lab over approximately the last four years. These methods highlight current approaches and technical challenges in this part of (U-Th)/He chronometry, and also characterize U, Th, and Sm concentrations of these important accessory minerals across a wide range of rock types and locations. Analytical precision on U, Th, and Sm measurements is typically 0.1-1.0%, and precision on typical samples with more than ~10 pg of U and Th is usually better than 0.5%. Long-term reproducibility on spike calibrations is about 0.8-1.3% (one standard deviation over ~4.5 yr). Observed reproducibility of (U-Th)/He ages rarely approaches analytical precision (typically 2-3%, 2σ). Two standard deviations on replicate analyses of the commonly used standards Durango apatite and Fish Canyon Tuff (FCT) zircon are about 6% and 10%, respectively. Weighted mean ages and errors for these standards in our lab are 31.94 ± 0.17 Ma (95% confidence interval, with a 2σ required external error of 1.9 Ma or 5.9%, MSWD = 5.4, n = 169) for Durango apatite and 28.29 ± 0.26 Ma (95%; 2σ external error of 2.6 Ma or 9.3%, MSWD = 20, n = 114) for FCT zircon. Of all other samples in our compilation, approximately 50% of apatites have U and Th concentrations between 10 and 50 ppm and Sm concentrations between 100 and 300 ppm. In the vast majority of cases, 147Sm contributions to 4He in apatite will be greater than ~5% only when U concentrations are lower than about 5 ppm. Zircon samples show a broader range of U-Th concentrations, with U between 100 and 600 ppm in about 60% of zircons and Th between 50 and 200 ppm in about 50%.

Introduction
Thermochronology and geochronology based on accumulation and diffusion of radiogenic 4He (e.g., Zeitler et al., 1987; Wolf et al., 1996; 1998; Farley, 2002) has proliferated in the last fifteen years. It is now widely applied in many tectonic and geomorphic studies, though work understanding its phenomenological bases and developing new analytical and interpretational approaches continues (e.g., Shuster and Farley, 2005; Shuster et al., 2006). Relatively high diffusivity of He in most minerals distinguishes (U-Th)/He dating as a low-temperature thermochronometer, useful in studies of shallow crustal exhumation, but it has also been used for estimating formation ages of materials formed at or near the surface (e.g., Shuster et al., 2005;
Blondes et al., 2007). At present, most (U-Th)/He (following historical usage, Sm is typically not included in the name of the technique) age measurements use a two stage analytical process involving first degassing an aliquot by heating it, and measuring its $^4$He content by gas source mass spectrometry. This is followed by recovery and measurement of the parent nuclides in the same aliquot, usually by acid dissolution, spiking with a calibrated solution of parent nuclides with non-natural isotopic composition (isotope dilution), and measurement on an inductively-coupled plasma mass spectrometer (ICP-MS). Development of other analytical techniques for (U-Th)/He dating, including in-situ laser-ablation, is an active area of research. At the time of writing of this manuscript, laser ablation He dating has been shown to work for compositionally uniform monazite with extremely high U-Th concentrations and a very old He age (Boyce et al., 2006), and this general approach is promising for other minerals.

This paper has two general purposes. The first is to provide an overview of techniques and characterize protocols used by our lab over the last few years for measuring U, Th, and Sm contents of minerals commonly dated by the (U-Th)/He system by solution isotope dilution on a sector ICP-MS. In doing so we highlight a few technical issues and challenges associated with these measurements for both routine He dating and experimental developments. Analytical methods for and results of He analyses will be discussed in a forthcoming paper. The second purpose is to summarize typical concentrations and ranges of U, Th, and Sm concentrations in apatite and zircon from large body of data from approximately four years (2002-2006) of analyses in the (U-Th)/He Lab at Yale University, which is now at the University of Arizona. This compilation may be useful for other geochemical or geochronologic applications. Our approaches to measuring U, Th, and Sm have not necessarily emphasized achieving the highest precision or to exhaustively evaluate all potential sources of isotope ratio inaccuracies such as mass bias or isobaric interferences. Rather, we present our methods, accumulated data, and experience with this approach as a relatively efficient and high-sample throughput method for routine (U-Th)/He chronometry, which is adaptable to a wide range of phases. Other phases dated in our lab using techniques discussed here, with at least partial success, include titanite, garnet, magnetite, rutile, epidote, hibbonite, and biogenic apatite.

**Sector ICP-MS**

Sector ICP-MS (a.k.a. single-collector, high-resolution-ICP-MS, or HR-ICP-MS) is the method of choice for a wide range of inorganic trace and ultra-trace level concentration determination applications, but it is not widely used for geochronology. Most geochronology-related sector ICP-MS studies have focused on U-series isotopes (e.g., Hinrichs and Schnetger, 1999; Dorale et al.,
2001; Shen et al., 2002), although there is a growing interest in (U-Th)/Pb zircon dating (Tiepolo, 2003; Tiepolo et al., 2003; Chang et al., 2006). The lack of simultaneous multiple ion-counting in sector ICP-MS limits the precision of the isotope ratio determinations that are the fundamental basis of most geochronologic methods. However, relative to thermal ionization mass spectrometry and multi-collector ICP-MS, single-collector sector ICP-MS is inexpensive, technically straightforward, and capable of higher sample-throughput. For many geochronologic applications the ability to rapidly perform many analyses easily outweighs the disadvantages of lower precision (i.e., like certain types of cuisine, quantity has a quality all its own). Analytical precision also need not be significantly better than the actual reproducibility of replicate analyses, which for some thermochronologic applications is relatively poor (~2-4%, 1σ). Isotope dilution by sector ICP-MS is also capable of extremely low concentration U-Th (and, in some cases, Sm) determinations required for single-crystal apatite He dating, which is can be difficult for less sensitive quadrupole ICP-MS techniques.

Sector ICP-MS has been widely used for quantification of U (and to a lesser degree Th), and U isotope ratios, primarily in studies of anthropogenic contamination and human health (Kerl et al., 1997; Ting et al., 1999; Boulyga et al., 2000; Quétel et al., 2000; Boulyga and Becker, 2001; Pappas et al., 2002; Desideri et al., 2002; Krystek and Ritsma, 2002; Hinrichs et al., 2003; Gwiazda et al., 2004; Tresl et al., 2004). Analytical results and precision of these studies depend strongly on the application, but in general U-isotope ratios (e.g., $^{235}U/^{238}U$) can be measured to about 0.1% RSD, for solutions with about 1-100 ppt concentrations.

**Analytical Methods**

Because parent nuclide concentrations of individual crystals of accessory minerals can vary widely, even in the same centimeter-scale rock sample, parent and daughter measurements must be performed on the same aliquot. Single-crystal or, occasionally, multiple-crystal aliquots are heated *in vacuo* at ~900-1250 °C for several minutes to degas He, which is then spiked with $^3$He, cryogenically (and/or via gettering) concentrated and purified, and quantified by isotope dilution and comparison to manometrically calibrated $^4$He standards on a gas-source quadrupole mass spectrometer. Early analyses used resistance furnace for heating, but House et al. (2000) developed a method for laser heating of ~1 mm² Pt foils containing single apatite crystals, which has the advantage of significantly lower He blanks and greater sample throughput. Another great advantage of this method, at least for apatite, is that Pt foils can then be directly immersed in nitric acid and the grains inside dissolved for U-Th-Sm analysis without the often difficult task of transferring the degassed apatite crystal(s) from the foil to another vial.
For whole-grain (U-Th)/He dating, parent nuclide contents are measured by isotope dilution using solution ICP-MS. General preparation procedures used in our lab involved addition of isotopically distinctive U, Th, and Sm spikes to the crystal recovered and dissolved after degassing. Final solutions run on the ICP-MS were diluted to about 2-4 ml total volume, and are ~5-10% HNO₃, in some cases with ~0.5% HF. Concentrations of spike isotopes in resulting solutions were ~0.1-0.2 ppb, and the vast majority of natural U and Th concentrations were within 0.5-10 times these concentrations. In detail, different minerals require very different dissolution and dilution procedures. Our lab used nominally pure ²³³U, ²²⁹Th, and the enriched ¹⁴⁷Sm spike of Wasserburg et al. (1981), for spiking. Enriched uranium (²³⁵U) and ²³⁰Th can also be used as spikes.

**Apatite**

The simplest analytical procedure for U, Th, and Sm measurement, following the basics described by House et al. (2000), is that for apatite. Apatite can be dissolved directly from the Pt foil by addition of (in addition to the spike) even fairly dilute (~20%) nitric acid. In our experience, incomplete dissolution of apatite by this method is rare, although it has been observed in cases where Pt was heated by resistance furnace instead of by laser, possibly by metal deposition over openings of the Pt foil, and in cases of very large apatite aliquots. Another concern for apatite He dating in general is the potential for incomplete dissolution of U-Th-bearing inclusions in or on the crystals, which can lead to apparently unsupported He and “too-old” He ages. This potential is well-recognized and motivates careful screening processes during initial sample picking to exclude crystals with inclusions visible under plane-polarized and cross-polarized light at 120-160 times magnification. In some cases, small but high-U-Th inclusions may be difficult or impossible to detect by normal picking procedures (Farley and Stockli, 2002). Adoption of more aggressive dissolution procedures designed to attack refractory inclusions may recover U-Th and avoid the unsupported He problem, but in most cases resulting ages would still suffer from α-ejection correction inaccuracies caused by the inclusions (Farley et al., 1996; Hourigan et al., 2005).

In our lab, Pt foils with degassed apatite crystals were spiked with two different spike solutions, each in 5% HNO₃ solution. The first is 25 or 50 µl of a nominally pure ²³³U-²²⁹Th spike with total U and Th concentrations of 7.55 ± 0.10 ng/ml and 12.3 ± 0.10 ng/ml respectively (uncertainties are long-term one standard deviations of all concentrations determined by spiking normal solutions of assumed known U-Th concentrations). The second is 25 or 50 µl of an enriched (97%) ¹⁴⁷Sm spike with a total Sm concentration of 10.8 ± 0.10 ng/ml. Following
spiking, 200 µl of concentrated SeaStar Baseline HNO₃ is then added to each foil, and the mixture is heated at about 90 °C for two hours. After cooling, the solutions are diluted with 2.5 ml of double-distilled 18 MΩ H₂O, for final spike isotope concentrations of ~0.1-0.2 ppb.

Other minerals

Other phases require different dissolution techniques because they generally do not dissolve in nitric acid alone and require addition of HCl and/or HF. This cannot be performed in Pt foil, because HCl and HF dissolve considerable amounts of Pt, forming PtAr⁻ complexes in the ICP-MS with isobaric interferences on U isotopes. In principle, ¹⁹⁵Pt⁴⁰Ar and ¹⁹⁸Pt⁴⁰Ar could be resolved from ²³⁵U and ²³⁸U using the high resolution mode on a sector ICP-MS, but the disadvantages of lower sensitivity, more difficult mass calibration, and triangular peak shape make avoidance of dissolved Pt in the solution a simpler option. House et al. (2000) used Pd foil for wrapping and laser-heating of titanite, and dissolved titanite directly from the foil in a spiked HCl-HF solution. In our experience however, this method dissolved large amounts of Pd that was difficult to keep in solution and appeared to produce unidentified interferences on U and Th. A more severe practical limitation was that the lower melting temperature made Pd foils more prone to melting or other damage during lasing, leading to relatively high probability of compromising quantitative recovery of the sample within it.

A possible solution to this for some minerals is to simply unwrap the Pt foil, transfer the naked grain(s) manually to a separate vial, and then spike and dissolve the sample there. This has several disadvantages however, not the least of which is the time required and risk of grain loss posed by the grain transfer process. Also, grains often fracture into several pieces or “sweat” during heating, leaving a residue inside the host Pt foil, which can be difficult or impossible to recover. Most importantly, it is difficult if not impossible to use this method to recover materials that break down into small fragments, powder, or melt during laser heating, as we have observed with garnet, epidote, fayalite, and other minerals.

To overcome these problems and insure dissolution of refractory inclusions, we routinely degassed grains of titanite, zircon, epidote, garnet, fayalite, magnetite, and other minerals in small ~1 mm² Nb foil envelopes, and subsequently dissolved the entire Nb foil and contents in Parr pressure digestion vessels (bombs). Foils with crystals were spiked with the same ²³³U-²²⁹Th and ¹⁴⁷Sm spikes used for apatite, except that zircons and other high U-Th phases received larger spike doses. The foil and spike were mixed with 300 µl of HF and 50 µl of HNO₃ (both Seahast Baseline) in 0.35 ml Teflon “microvials,” inside a larger Teflon liner with nine other microvials and samples, 10 ml HF, and 0.42 ml HNO₃ (both Alfa Aesar Environmental Grade). Large Teflon
liners are bombed at 225 °C for 72 hours in 125 ml Parr bombs. After cooling, microvials are heated to dryness on an open hotplate, and then 300 μl of HCl (Seastar Baseline) is added. Microvials were then rebombed in the large Teflon liner containing 9 ml of HCl (Alfa Aesar Environmental Grade), at 200 °C for 24 hours. Rebombing in HCl is necessary to redisolve refractory fluoride salts. After cooling, microvials are again heated to dryness, and 200 μl of HNO₃ and 25 μl of HF (both Seastar Baseline grade) were added; capped microvials were gently heated for ~ 30 minutes, and then each sample was transferred to a larger Teflon vial, where it was diluted with double-distilled 18 MΩ H₂O to 3.225 ml of solution, at ~6% HNO₃ and 0.8% HF. For zircon, spike U-Th isotope concentrations are about 0.1-0.2 ppb, and about 80% of single crystal samples have natural U and Th concentrations within a factor of ~0.5-10.

A disadvantage of the Nb foil dissolution method is that sensitivity on U and Th peaks is decreased by about 35%, due to the large concentration of dissolved Nb in the solution. Also, although Nb is not routinely measured for other applications using our ICP-MS, it is possible that our Nb foil methods would result in high Nb blanks, were we to attempt to quantify this element in other samples using the same sample introduction equipment. For our purposes, the advantage of not needing to recover crystals or their residues following He extraction outweighs these disadvantages. Another note of caution regarding the use of Nb foil comes from using it with apatite. In several cases we have observed anomalous U-Th contents (particularly Th) of low-Thapatites dissolved with Nb foil. The problem is not observed with Durango apatite, possibly because the extremely high Th of Durango make it less susceptible. At this point the origin of this problem is unclear, but we do know that high resolution analyses on U and Th peaks do not indicate any significant amounts of isobaric interferences that may arise from species such as lanthanide-Nb complexes. In any case, at present we do not use or recommend dissolving and analyzing apatite crystals with Nb foil.

ICP-MS measurements

Instrumentation
All of the results shown here were performed on a Thermo Finnigan Element2, and most samples were processed with an all-PFA sample introduction assembly, including 100 μl/min. nebulizer, single-pass spray chamber, sapphire injector, and quartz torch. Nickel cones were used in all cases, to avoid PtAr interferences. All measurements were made in low resolution mode. Typical sensitivities on ²³⁸U for the range of operating conditions were between 1.2-2.0 x 10⁶ cps/ppb. For
each sample, including blanks and standards, the primary method measured $^{229}$Th, $^{232}$Th, $^{233}$U, $^{235}$U, and $^{238}$U. For Sm measurements, a separate method measuring $^{147}$Sm and $^{152}$Sm was used, in order to avoid large mass jumps between measurements. Take-up times and wash times between samples were both 45 seconds. Wash solution was 6% HNO$_3$ between apatites, and 6% HNO$_3$ + 0.8% HF for zircons and other minerals with dissolved Nb.

Apatite samples were run with a method using EScan peak jumping with the magnet parked at mass 229.031, sample time of 2 ms, 100 samples per peak, mass and averaging windows of 5%, and counting mode, 5 runs and 400 passes for a total of 2000 isotope ratio measurements. Zircons were run with a similar method, except for 100% mass window, 15 samples per peak, 30% search window, 40% integration window, both analog and counting modes for $^{229}$Th and $^{233}$U, and 5 runs/150 passes for a total of 750 ratios. Methods employing either analog or counting modes were used on standards with a large range of U-Th concentrations to check the concordance of measured ratios for both detection modes. The Sm method for all samples was essentially the same as for U-Th on apatite, except magnet mass was set to 146.914.

**Blank and calibration solutions**

A typical ICP-MS measurement day for (U-Th)/He analyses processed about 50-100 samples prepared by the above methods. Each batch of analyses was accompanied by three to six sets of routine standards and blanks, used to check cleanliness of reagents and Teflon, spike concentrations and isotope ratios, and procedural blanks.

"Acid blanks" were mixed HNO$_3$ and H$_2$O, from which cps of U, Th, and Sm were used to check Teflon and reagent cleanliness. No spike is added to these blanks so quantitative determination of background U, Th, and Sm was not possible. On our Element2, which averaged 1.2-2.0 x 10$^6$ cps/ppb, we routinely observed about 100-300 cps for $^{232}$Th and $^{238}$U, and 1-10 cps for $^{229}$Th, $^{233}$U, and $^{235}$U.

"Spike blanks" were the same as acid blanks (5% HNO$_3$ solutions) except with a 25 or 50 µl shot of $^{233}$U-$^{229}$Th spike or $^{147}$Sm spike. Besides being an additional check on U-Th-Sm in the reagents and Teflonware, measured $^{238}$U/$^{233}$U, $^{232}$Th/$^{229}$Th, and $^{152}$Sm/$^{147}$Sm of spike blanks were used to define isotopic abundances used in isotope dilution calculations for concentrations of U, Th, and Sm in the spikes and unknowns run on the same day. Spike blanks run between February 2002 through July 2006 (Fig. 1) yield apparent $^{233}$U and $^{229}$Th atomic abundances in the spikes of 0.9955 ± 0.0024, and 0.9973 ± 0.0030 (uncertainties as one standard deviations). Anomalously impure spike isotope ratios measured near analysis number 60 (Fig. 1) were traced to Teflon vials.
with cracks on the interior surfaces, which presumably trapped U-Th from previous analyses that was not removed by normal boiling-acid washing procedures.

“Spiked norms” contain 1.25 ng and 2.50 ng of natural U and Th, respectively, with either 25 or 50 μl of U-233-Th-229-Th spike. A second type of spiked norm contains 1.25 ng of natural Sm, with 25 μl of Sm spike. Measured 238 U/233 U, 232 Th/229 Th, and 152 Sm/147 Sm ratios of these spiked norms, together with ratios measured on spike blanks, are used to calculate the concentration of U, Th, and Sm in the spikes. Average ratios of three to six spiked norm samples run each analytical session over the last several years are shown in Figure 2. Relative standard deviations (RSD) on isotope ratio measurements of individual spiked norms is typically <0.5%. Long-term reproducibility of spiked norms for the period of November 2003 through July 2006, when a single stock solution was being used, are 0.83% for 232 Th/229 Th and 1.3% for 238 U/233 U (Fig. 2b). This reproducibility probably reflects a fundamental limit to manual pipetting precision, as well as periodic evaporative concentration of the spike solution, as described below.

A significant time-systematic variation in spiked norm ratios that reflects changing spike concentration was observed between about June and November of 2003 (Fig. 2a). During this time, measured 238 U/233 U and 232 Th/229 Th both decreased by about 7-9%. No trend was observed in spike blank ratios over this period. This period corresponds to decreasing volume of the U-Th spikes, from about 15 to about 3-5 ml due to consumption. At this time the volumes of stock U-Th normals remained constant at about 1000 ml. The decreasing ratios were likely caused by evaporative concentration of 233 U and 229 Th in the remaining small volumes of spike. This demonstrates the importance of routine calibrations of spike concentration by this method. Suggestions of episodic trends of decreasing spiked norm ratios on the order of 1.5-2.0% are also observed on shorter timescales between November 2003 and July 2006. These trends are also likely due to evaporation of spike solution from the 30 ml spike vial used for routine spiking, because each trend is punctuated by episodes of by restocking of the 30 ml spike vial from a much larger (1 liter) bottle.

“Platinum blanks” and “Nb blanks” are empty Pt or Nb foil packets processed in exactly the same way as normal apatite or zircon (or other phases requiring bomb dissolution) samples, respectively. These same foils are also heated by laser, to determine 4 He blanks during degassing. Platinum blanks average 0.6 ± 0.4 pg U and 1.0 ± 0.2 pg Th (uncertainties as 1σ standard error) (Fig. 3). Niobium blanks are about four to ten times higher than Pt blanks, averaging 2.6 ± 0.5 pg U and 5.5 ± 1.0 pg Th (Fig. 3). Sm blanks are similar to those of Th.
“Bomb blanks” are procedural blanks for dissolutions requiring Parr “bombing.” They are processed the same way as Nb blanks, but without Nb foil. Bomb blanks are indistinguishable from Nb blanks, averaging 2.7 ± 0.5 pg U and 5.7 ± 1.1 pg Th (Fig. 3).