An experimental approach to thermal and solar weathering of Mercury’s crust

by

Stephanie Marie Brown

Submitted to the Department of Earth, Atmospheric, and Planetary Science
in partial fulfillment of the requirements for the degree of Master’s of Science in Earth, Atmospheric, and Planetary Science at the MASSACHUSETTS INSTITUTE OF TECHNOLOGY

June 2011

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Abstract

Mercury MESSENGER aims to map the composition of the Mercurian crust. This composition has direct implications for the formation and evolution of the planet (Solomon, 2003). The instruments that will compositionally map the surface are calibrated and compared with materials in an Earth-like environment. However, minerals on the surface of Mercury are periodically exposed to the solar wind (radiation) while being heated to over 700 K and cooled to below 100 K daily (Madey et al., 1998; Hale and Hapke, 2002). To understand how these effects will change interpretations of spectra taken from MESSENGER and to understand interactions between the space environment and the crust we are simulating the space-weathering environment on minerals we expect to find on the surface of Mercury. We irradiate with fast neutrons and/or heat the low-iron minerals anorthoclase feldspar, enstatite orthopyroxene, and diopside clinopyroxene. Our results indicate that sodium rich feldspars have the potential to contribute sodium to the exosphere, but in order to to produce potassium from the surface, more potassium rich felspars may be necessary. Calcium and magnesium are released from diopside clinopyroxene while enstatite orthopyroxene is relatively unaffected by weathering. This may indicate that there is more clinopyroxene on the surface of Mercury than orthopyroxene in areas correlating to calcium and magnesium source regions. The variable space weathering effects between minerals may have important consequences in the exosphere. In addition, we also observe interactions between these processes which may help explain small scale patterns of exospheric species on Mercury. We stress the need to create spectral libraries that reflect space weathering environments of materials.

Thesis Supervisor: Linda T. Elkins-Tanton
Title: Assistant Professor
Acknowledgments

I would like to thank my advisor Linda T. Elkins-Tanton for all of her encouragement, help, and support during my time at MIT. She has given me invaluable opportunities over the years and I am very grateful. I would like to thank my committee for their time and input, Sang-Heon Shim and Benjamin Weiss. I would like to thank my family and my friends for helping me keep my sanity and provide comments on my papers and presentations.

I would like to thank Lin-wen Hu, Thomas Bork, and Bill McCarthy for their help at the MIT Nuclear Reactor, Carl Francis for supplying our samples from the Harvard Museum of Natural History, Terrence Blackburn for allowing us to use his diffusion code, Nilanjan Chatterjee for help with the MIT Microprobe, Mitchell Galanek and Justin Quinn for their help with safety procedures, and Noah McLean for help with error analysis. This research was supported by a CAREER grant to Elkins-Tanton through NSF Astronomy.
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Chapter 1

Mercury’s extreme environment

Mercury, which at perihelion is only 0.3 AU from the Sun, is exposed to radiation from the solar wind and heat. The maximum and minimum temperatures vary across longitude due to the high eccentricity of Mercury’s orbit; the perihelion maximum surface temperature at equatorial regions is computed to be around 700 K and 580 K at aphelion (Vasavada et al., 1999). The aphelion temperatures fall to around 100 K during the nighttime (Vasavada et al., 1999). The present day mean surface temperature is computed to be around 450 K (Benz et al., 2007).

In addition to high temperatures, Mercury is exposed to radiation. Mercury is largely protected from the solar wind due to its magnetic field; only ~10% of the energetic particles that cross the magnetopause reach around 10% - 25% of the surface, corresponding to an average flux of $4 \times 10^8 \text{ cm}^{-2}\text{s}^{-1}$. This value will change by orders of magnitude due to fluctuations in solar activity, and can increase dramatically during high solar activity. Models indicate the areas most likely to be irradiated correspond to the cusp (areas of open field lines) regions at mid to high latitudes on the dayside (Leblanc, 2003; Massetti et al., 2003; Mura et al., 2005; Killen et al., 2007) and in equatorial regions on the night side (Benna et al., 2010).

This extreme environment may have various effects on the minerals exposed on the Mercurian surface, including creating differences in the spectral signature from that of a mineral taken in an Earth-environment, and provoking processes that form the Mercurian surface-bounded exosphere. These effects are immediately relevant
as Mercury MESSENGER currently aims to map the composition of the Mercurian crust. This composition has direct implications for the formation and evolution of the planet (Solomon, 2003) and the Solar System. For example, knowing the surface composition of the crust may help elucidate the origin of Mercury's large core. To understand how these effects will change interpretations of spectra taken from MESSENGER and to understand interactions between the space environment and the crust we are simulating the high-temperature and radiation space-weathering environment on minerals we expect to find on the surface of Mercury.

1.1 The Mercurian exosphere

The Mercurian exosphere is known to be composed of H, He, O, Na, K, Ca, and Mg from Earth-based observations and data collected from Mariner 10 and MESSENGER (McClintock et al., 2009). The processes thought to be responsible for the species in the exosphere, which need to be continually resupplied, are solar wind sputtering, photon / electron stimulated desorption, thermal desorption, and impact vaporization as shown in Figure 1-1. The ability of each of these processes to create the sustained presence of species in the exosphere has been thoroughly discussed and modeled in the literature (i.e. Madey et al., 1998; Killen et al., 2007), and will not be discussed in detail in this paper. Species cannot be explained by one process (Killen et al., 2007). If each of these processes is at work, we expect that they may interact with each other, i.e. defects generated by ion bombardment may be annealed out by high temperatures. While others have conducted experiments that model some of these processes, our experiments most closely simulate thermal evaporation and solar wind sputtering. Most likely, all these proposed processes work towards creating the exosphere (however, various models prefer specific processes, e.g. Burger et al., 2010). A summary of these processes is presented in Table 1.1.

Solar wind sputtering results from the bombardment of high energy particles (mostly protons) onto the Mercurian surface, and operates by exciting electrons which causes bound elements to be released from the surface as neutrals. This process does
not preferentially release any chemical from a mineral at steady state, thus allowing all types of elements to be released, not just volatiles or trace species. However, prior to steady state, irradiation breaks weaker bonds preferentially. Irradiation also induces defects in the crystal structures of the minerals that make up the planetary surface. Of the elements already found in the exosphere, sputtering has the ability to provide Na, K, Ca, and Mg. Sputtering is limited by diffusion, as it only damages structures near the surface (Killen et al. (2007), and references therein).

The effects of radiation on crystal structures has been investigated in the context of storing nuclear waste and calibrating thermochronology. Studies indicate that radiation does indeed produce more defects, but the relationship between diffusion of species and radiation damage is not simple. For example, in the presence of radiation induced defects in a structure, He\(^+\) is less mobile as it tends to get trapped within the defect sites (Shuster et al., 2006). However, how this relates to the important species on Mercury is unclear. More generally, radiation will increase diffusion rates as a function of temperature, as it allows species more avenues of transport, and will induce amorphization in the crystal structures (Sizmann, 1978; Gu et al., 2000).
Amorphization would also increase the diffusion rate, as diffusion in glass is much faster than in crystals (Killen et al., 2004). It has been also shown that annealing at high temperatures causes radiation defects to be removed from the structures (Dienes and Damask, 1958; Freer et al., 1982; Moreau et al., 1971). Sodium in zeolites has been shown to dramatically decrease in concentration after proton-induced radiation damage, which was attributed to either preferential sputtering and/or diffusion of sodium within the structure (Gu et al., 2000).

Another weathering process that has the ability to produce the elements detected thus far in the atmosphere is micrometeoroid vaporization. The surfaces of planets are constantly being bombarded by micrometeoroids, which vaporize instantly also vaporizing the material around it into the exosphere. Impacts also help to garden the surface, which will affect the efficiency of producing atoms for an exosphere. Of the elements already found in the exosphere, impact vaporization has the ability to provide Na, K, Ca, and Mg, and the vapor it produces most closely resembles the local surface composition. The impactor material will also contribute to the exosphere as it vaporizes along with the regolith and requires determining if species in the exosphere are derived from Mercury or from the impactor. This process is limited by the flux of bombarding particles (Killen et al. (2007), and references therein).

In addition to sputtering and vaporization, the surface of Mercury is also altered by photons and electrons. Photons and electrons may stimulate electronic excitation of individual surface bonds, releasing primarily neutral species. Of the elements already found in the exosphere, photon and electron stimulated desorption has the ability to provide Na and K (Madey et al., 1998) and is also limited by diffusion of the species to the surface (Killen et al., 2007).

The remaining surface weathering process that is thought to influence the Mercurian exosphere is temperature. High temperatures, below the melting point, have various effects on minerals. For surface minerals, heat provides the energy necessary to break surface bonds and vaporize the released elements. The vacancies left by the desorbed atoms can be filled either by resorption (coming from the exosphere) or by diffusion (coming from the interior of mineral grains) (Leblanc et al., 2007). Of
the elements already found in the exosphere, thermal desorption has the ability to provide Na and K, and is limited by diffusion (Killen et al., 2007).

Temperature also affects the number of defects within a crystal (by producing them and eradicating them), and a greater number of defects correlates with more efficient diffusion. The equilibrium number of point defects within a crystal increases with temperature, due to the increase in entropy. When heated, these defects form at dislocations and boundaries, and then diffuse throughout the structure. When cooled down again, the defects must leave the structure by diffusion out of the dislocations and boundaries – if this happens too quickly, then the defects are frozen in at a disequilibrium concentration (Shewmon, 1963; Freer, 1981; Allen and Thomas, 1999).

Radiation produces defects, causing the number of defects to be larger than what the equilibrium concentration would normally be (similar to as if the crystal has frozen in vacancies). Upon heating the defects become mobile and are able to leave the structure, bringing the number of defects back to the equilibrium concentration (Allen and Thomas, 1999). If temperatures are not warm enough to anneal these defects out, diffusion can be accelerated by radiation induced defects. If the structure is damaged enough to have become amorphous, diffusion will be drastically accelerated by several orders of magnitude.

The surface of Mercury is likely negatively charged (Leblanc et al. (2007), and references therein). Cation diffusion would be enhanced towards the surface while anion diffusion would be enhanced towards the interior of the planet, providing another driving force for diffusion of the species found in the Mercurian exosphere (Leblanc et al., 2007).

In order to map the Mercurian crustal and exospheric compositions, MESSENGER is outfitted with a γ-Ray and Neutron Spectrometer (GRNS), an X-Ray Spectrometer (XRS), the Energetic Particle and Plasma Spectrometer (EPPS), and the Mercury Atmospheric and Surface Composition Spectrometer (MASCS) which includes an Ultraviolet-Visible Spectrometer (UVVS) and a Visible-Infrared Spectrograph (VIRS)(Solomon, 2001). The γ-ray spectrometer will measure H, O, Na, Mg, Si, Ca, Ti, Fe, K, and Th. The neutron spectrometer will help calibrate the γ-ray
Table 1.1: Processes that produce Mercurian exospheric elements. Species shown are observed in the exosphere; a mechanism may produce more elements. Table was compiled from Killen et al. (2007) and references therein.

<table>
<thead>
<tr>
<th>Process</th>
<th>Exospheric Elements</th>
<th>Limiting factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>sputtering</td>
<td>Na, K, Ca, Mg</td>
<td>diffusion</td>
</tr>
<tr>
<td>micrometeoroid impacts</td>
<td>Na, K, Ca, Mg</td>
<td>impactor flux</td>
</tr>
<tr>
<td>photon/electron stimulated desorption</td>
<td>Na, K</td>
<td>diffusion</td>
</tr>
<tr>
<td>thermal desorption</td>
<td>Na, K</td>
<td>diffusion</td>
</tr>
</tbody>
</table>

sputtering spectrometer in addition to producing elemental abundances of hydrogen and possibly the group of rare earth elements (Goldsten et al., 2007). The X-ray spectrometer will measure Mg, Al, Si, S, Ca, Ti, and Fe. The UVVS - VIRS spectrometers will measure ferrous bearing minerals, Fe- Ti bearing glasses, and ferrous iron and species in the exosphere (Solomon, 2001). Currently, the spectra produced from these instruments are compared against a spectral library mostly compiled from samples at Earth conditions - at room temperature and pressure and without exposure to the solar wind (Gold, 2001).

1.2 Previous experimental work

Previous space weathering experiments have focused primarily on the spectral effects of weathering on the Moon, Mercury, and asteroids. Micrometeorite impacts are simulated using nanosecond pulsed laser ablation (Yamada and Sasaki, 1999; Sasaki et al., 2001; Brunetto et al., 2006a, 2007). Some of these pulsed laser experiments produce nanophase iron from olivine (Sasaki et al., 2001) and ordinary chondrites (Noble et al., 2011). These previous experiments aim to reproduce and model the expected effects of nanophase iron production on the spectra of these minerals.

Photon and electron stimulated desorption have been simulated by using solar UV photons on sodium deposited SiO₂ films (Yakshinskiy and Madey, 1999, 2000) and on sodium deposited lunar basalts and studied with X-ray photoelectron spectroscopy and low energy ion scattering (Yakshinskiy and Madey, 2004). These experiments
desorb sodium and potassium (Madey et al., 1998), and provide estimates for the Mercurian exosphere. They also indicate a temperate dependent desorption, likely due to increased diffusion at higher temperatures.

Yakshinskiy and Madey (2004) also simulated ion sputtering on the lunar basalts, successfully sputtering sodium. Dukes et al. (2011) simulated sputtering by irradiating sodium bearing feldspars with 4 keV He$^+$ ions, analyzing the samples with X-ray photoelectron spectroscopy and secondary ion mass spectroscopy. Their results indicate that sodium and oxygen are preferentially sputtered, and sputtering produces a large fraction of sodium, aluminum, and silicon ions. Solar wind irradiation has also been simulated on olivine and pyroxene, using H$^+$, He$^+$, Ar$^+$, and Ar$^{++}$ (Yamada and Sasaki, 1999; Strazzulla et al., 2005; Brunetto and Strazzulla, 2005; Brunetto et al., 2006b; Loeffler et al., 2009). These previous experiments are used to characterize and model the space weathering effect of irradiation on the spectra of the minerals.

We simulate thermal desorption and sputtering and study how these processes interact with minerals on the surface of Mercury. The goal of our experiments is to directly measure the compositional, structural, and spectral changes on likely Mercurian crustal minerals due to this weathering using the electron microprobe. We do not deposit any species on our samples and we measure all major elements within our grains.
Chapter 2

Methods

The aim of this study is to simulate space weathering on Mercury by irradiating and heating samples. We analyze weathered samples using the electron microprobe. We attempted to use Raman spectroscopy to characterize the structural damage between the various grains; however, the samples were too translucent to produce a significant difference in the spectra and the results are not reported here.

2.1 Samples

We use natural mineral samples that may reasonably be expected to mimic those on the surface of Mercury. They have low iron contents and have been previously suggested to exist on the surface (Burbine et al., 2002).

We use an anorthoclase feldspar ($\text{Ab}_{73}\text{Or}_{22}\text{An}_{05}$) from Mt. Franklin, Daylesford, Victoria, Australia, a diopside clinopyroxene ($\text{Mg} \# = 63$) from Gilgit-Baltistan, Pakistan, and an enstatite orthopyroxene ($\text{Mg} \# = 99$) from the Chandrika Wewa Reservoir, Sabaragamuwa, Sri Lanka. All of our grains have been reduced to a grain size of 0.85 mm - 1.18 mm. Samples were provided by the Mineralogical Museum at Harvard University.

Sample preparation has proven to be challenging for the heated and/or irradiated samples. The heated grains require epoxy vacuum impregnation, as they are extremely brittle. The irradiated-only grains are generally less brittle than the heated
grains, but are difficult to polish as they contain a large number of pits. For electron microprobe analysis, we mounted the grains in epoxy and polished them using a sequence of Buehler alumina grit with water on Buehler texmet, chemomet, microcloth, and Mark V Laboratory satin polishing cloths. The epoxy mounts were then carbon-coated for analysis.

2.2 Accelerated Processes

2.2.1 Irradiation

We use high-energy fast neutrons at the MIT Nuclear Reactor to simulate accelerated solar wind irradiation on Mercury. Samples were placed in silica tubes during radiation where temperatures did not exceed 80°C. The larger flux and higher energy particles of the nuclear reactor allows us to accelerate radiation compared to Mercury surface conditions, simulating longer surface residence times on Mercury. The accelerated radiation in the reactor; however, may have different physical effects than what occurs on Mercury. Considering that the size of a proton (which is 99% of the solar wind (Killen et al. (2007), and references therein)) is comparable to the mass of a neutron, used in the MIT Nuclear Reactor, and that neutron irradiation may create proton irradiation and is also ionizing like proton irradiation, we believe that fast neutron irradiation is a good approximation for solar wind irradiation (Was, 2002). In addition, fast neutron irradiation at 1 MeV will primary produce elastic collisions that will damage the crystal lattice and produce sputtering. It is thought that ion sputtering on planetary surfaces is proportional to elastic collisions (McCracken, 1975; Johnson, 1990; Brunetto and Strazzulla, 2005) even though proton bombardment is mostly ionizing, and spectra alterations have been found to correlate with percent elastic collisions (Brunetto and Strazzulla, 2005). Inelastic sputtering does occur for fast and multiply charged ions (Baranov et al., 1988); however, this is unrelated to the effect of protons on planetary surfaces.

We can determine the relative amount of time on Mercury by using the energy
Figure 2-1: Accelerated Irradiation of Mercurian-like Minerals

density parameter below, using a mean solar wind flux determined by Massetti et al. (2003):

\[ E = \phi tc, \]  

(2.1)

where \( E \) is the energy parameter, \( \phi \) is the flux of the energetic particle, \( t \) is the amount of time exposed to the flux, and \( e \) is the energy of the energetic particle. We equate energy parameters for Mercury and for the nuclear reactor to calculate the residence time on the surface of Mercury of our sample minerals as shown in Figure 2-1. The nuclear reactor uses fast neutrons with an energy of 1 MeV at an average flux \( \phi \) of \( 4 \times 10^{12} \text{ cm}^{-2}\text{s}^{-1} \). The energy \( e \) of a proton is 1.3 keV, with a constant mean solar wind flux \( \phi \) of \( 4 \times 10^8 \text{ cm}^{-2}\text{s}^{-1} \) (Massetti et al., 2003). Twelve hours irradiation in the nuclear reactor simulates about 10,500 Earth-years on the surface of Mercury.

Direct radiation on the surface of Mercury does not occur constantly or efficiently, and is thought to only effect the northern and southern latitudes, about 10% - 25% of the surface (Killen et al. (2007), and references therein). For that reason, our estimate for the simulated irradiated time on Mercury is a minimum, as we assume a constant...
mean flux of solar wind. For example, if the solar wind only reaches the surface half the time (at the mean flux), then a 12 hour irradiation at the MIT Nuclear Reactor would be equivalent to roughly 21,000 Earth-years on the surface of Mercury.

This energy density parameter is also used to estimate the time-scale of laser irradiation experiments to micrometeoroid impacts (Sasaki et al., 2001; Brunetto et al., 2006a). Strazzulla et al. (2005) produces an estimate timescale of heavy ion weathering by comparing the argon flux in their laser to the argon flux at 1 AU, resulting in a $10^4 - 10^6$ year estimate. Brunetto et al. (2006b) uses this estimate to calibrate their exposure timescale to 2.9 AU based upon a correlation of the damage parameter to the parameterized continuum of reflectance spectra, $C_s$, coefficient. The damage parameter (displacements per cm$^2$) was computed using Stopping and Range of Ion in Matter (SRIM) / the Transport of Ions in Matter (TRIM) Monte Carlo simulations (Ziegler, 1985). Others (e.g. Wurz et al., 2010; Dukes et al., 2011) have also used the SRIM/TRIM simulations to calculate sputtering yields.

We also compare radiation damaged based upon a non-dimensional parameter “displacement per atom” (dpa), related to the damage parameter, which represents the fraction of atoms displaced from their original lattice site. The simplest calculation of dpa is:

$$dpa = \bar{\sigma}_d \phi t,$$

where $\bar{\sigma}_d$[barn] is the average energy dependent displacement cross section. This formulation assumes a constant $\bar{\sigma}_d$, implying that all elements have a similar response to irradiation of a particular energetic particle ($\bar{\sigma}_d$ depends on the element being bombarded and the energy of the particle).

To insure that assuming a constant $\bar{\sigma}_d$ is a valid assumption for the minerals we are studying, we can calculate to an order of magnitude the $\bar{\sigma}_d$ from the elastic cross section ($\sigma_{\text{elastic}}$) for each element, taken from the Evaluated Nuclear Data File (ENDF) on the National Nuclear Data Center database (http://www.nndc.bnl.gov/exfor/endf00.jsp), by (Olander, 1976):
Table 2.1: $\bar{\sigma}_d$ calculated from Equation 2.3

<table>
<thead>
<tr>
<th>Element</th>
<th>$\sigma_{elastic}$ [barns]</th>
<th>$\bar{\sigma}_d$ [barns]</th>
</tr>
</thead>
<tbody>
<tr>
<td>silicon</td>
<td>5</td>
<td>7112</td>
</tr>
<tr>
<td>oxygen</td>
<td>8</td>
<td>19923</td>
</tr>
<tr>
<td>magnesium</td>
<td>4</td>
<td>6572</td>
</tr>
<tr>
<td>calcium</td>
<td>10</td>
<td>9974</td>
</tr>
<tr>
<td>sodium</td>
<td>3</td>
<td>5210</td>
</tr>
<tr>
<td>potassium</td>
<td>2</td>
<td>2045</td>
</tr>
</tbody>
</table>

\[
\bar{\sigma}_d = \frac{e}{4E_d(1 + A)^2} \sigma_{elastic},
\] (2.3)

where $E_d$[eV] is the displacement energy and $A$[g mol$^{-1}$] is the atomic mass of the element. We assume an average displacement energy ($E_d$) of 25 eV (Ziegler, 1985) and an average neutron energy ($e$) of 1 MeV. Averages of $\sigma_{elastic}$ and the calculated $\bar{\sigma}_d$ are given in Table 2.1. They are generally within a magnitude of order of each other, with oxygen being significantly larger, and so we assume a constant weighted mean $\bar{\sigma}_d = 15000$ barns. Inputing this into Equation 2.2 for the various minerals produces a $dpa = 0.003$ for a 12 hour 1 MeV fast neutron irradiation and $dpa = 0.02$ for a 4 day 1 MeV fast neutron irradiation.

For Mercury, it is possible to calculate the $dpa$ of proton irradiation by using the Transport of Ions in Matter (TRIM) Monte Carlo simulations (Ziegler, 1985). The simulation allows layers to be defined by inputing elements that represent the minerals we are irradiating. We use the default displacement energies of the elements as well as the default compound correct of one. Given that ions only penetrate a finite depth within a layer, we use a layer thickness that is greater than the penetration depth. TRIM then simulates collision of one ion with the layer (up to 9999999 ions) and calculates quantities such as the number of vacancies-Å$^{-1}$ion$^{-1}$. The number of displacements-Å$^{-1}$ion$^{-1}$ is calculated by summing the vacancies-Å$^{-1}$ion$^{-1}$ and replacement collisions-Å$^{-1}$ion$^{-1}$. The $dpa$ value is calculated from the maximum displacements-Å$^{-1}$ion$^{-1}$($D$), the flux ($\phi$), and the atomic density ($N$):
Table 2.2: $t_{\text{Mercury}}$ calculated from Equation 2.5

<table>
<thead>
<tr>
<th>mineral</th>
<th>12 hour irradiation [days]</th>
<th>4 day irradiation [days]</th>
</tr>
</thead>
<tbody>
<tr>
<td>anorthoclase</td>
<td>6</td>
<td>44</td>
</tr>
<tr>
<td>diopside</td>
<td>6</td>
<td>46</td>
</tr>
<tr>
<td>enstatite</td>
<td>5</td>
<td>39</td>
</tr>
</tbody>
</table>

$$dpa = \frac{D \phi t}{N}.$$ \hspace{1cm} (2.4)

Equating the $dpa_{NR}$ of the nuclear reactor with the $dpa$ value given from Equation 2.4 allows us to solve for the residence time on Mercury for each mineral:

$$t_{\text{Mercury}} = \frac{dpa_{NR} N}{D \phi}.$$ \hspace{1cm} (2.5)

The TRIM calculations show that $D$ does not change between anorthoclase, enstatite, and diopside given a 1 keV proton irradiation. The result of the $dpa$ analysis, shown in Table 2.2, provides us with average residence estimates of $t_{\text{Mercury}} = 5.4$ days for the 12 hour irradiation and $t_{\text{Mercury}} = 43$ days for the 4 day irradiation. This analysis does not account for annealing, defect diffusion, accumulated damage (Brunetto and Strazzulla, 2005) and contains numerous simplifying assumptions.

2.2.2 Heating

We simulate the high temperatures on the surface of Mercury by heating unirradiated and irradiated grains to temperatures hotter than those on Mercury, allowing us to accelerate thermal damage. We can determine the relative amount of time on Mercury by using the non-dimensional diffusion parameter $\gamma$ and using parameters taken from Freer (1981):

$$\gamma = D_0 e^{-\frac{E_a}{R T} t a^2},$$ \hspace{1cm} (2.6)

where $D_0 [m^2 s]$ is the maximum diffusion coefficient, $E_a [J mol^{-1}]$ is the activation
energy, $R [J/mol\cdot K]$ is the gas constant, $T [K]$ is the temperature, $t [s]$ is the time, and $a [m]$ is the radius of the grain. We equate $\gamma$ for Mercury and for the furnace to calculate the residence time on the surface of Mercury of one of our sample minerals. The Mercurian grain size is unknown, but it has been assumed that it is similar to the lunar regolith. Most of the grains on the lunar surface are around $60 \mu m$, with a median range of 48 - 802 $\mu m$ (Killen et al., 2004).

The furnace used for these experiments was a SentroTech STT-1700-2.5-6 High Temperature Tube Furnace attached to a Varian SH-110 scroll pump, providing a $10^{-2}$ Torr vacuum. Samples were placed in Al$_2$O$_3$ Ozark Technical Ceramics during heating. We heated the samples for either 200 K below their melting temperatures for 4 days or 8 days at 450 K. Enstatite melts at 1557 $^\circ$C, diopside melts at 1391.5 $^\circ$C, and anorthoclase melts at $\sim$ 1062 $^\circ$C (Morse, 1980) at 1 atm.
Figure 2-2 describes the effects of temperature (considering either the aphelion or perihelion maximum temperature) and grain size on our residence times. Considering a coarse grain size on Mercury at perihelion (700 K), our 4 day experiments would correspond to \(\sim 2\) years on Mercury for anorthoclase (held at 1090 K), \(\sim 15\) years for diopside (held at 1430 K), and \(\sim 40\) years for enstatite (held at 1590 K). Finer grain sizes and hotter surface temperatures on Mercury correspond to shorter residence times.

Volume diffusion has been considered too slow to explain the source of sodium and potassium in Mercury’s atmosphere (Sprague, 1990); however, our experimental setup does not allow for grain boundary or regolith diffusion. We assume our results will be minimum values, and may be a mechanism for the origin of species to eventually be lost by grain boundary or regolith diffusion. Also given the large thermal stresses that may crack and fracture the rock by physical weathering (Molaro and Byrne, 2010), all forms of diffusion will be further accelerated.

A \(\mu\text{m}\) - sized grain on the surface of Mercury will remain there for on average 100 years (Killen et al., 2007). Our residence times for the finer grained minerals on Mercury estimates for both irradiation and heating are less than 100 years, with heated finer grain sizes corresponding to between a few days and a year and irradiated times of many days. Our results will be minimums for a single grain on the surface of Mercury, as they are weathered longer on the Mercurian surface.

### 2.2.3 Diffusion Modeling

We model the loss of species from the crystal structure due to temperature-dependent volume diffusion over time as given by Crank (1999). We approximate the mineral grain as spherical, with a homogeneous or inhomogeneous initial concentration. The finite difference code was written by Terrence Blackburn. Diffusion coefficients were taken from Freer (1981). The results of modeling are not included in the results section due to the ideal boundary condition requiring that the surface concentration be zero. This boundary condition is unrealistic for our experiments. However, modeling indicates that we will see measurable diffusion profiles within the weathered grains.
given the high temperatures and long times in the furnace.
Chapter 3

Results and Discussion

3.1 Macroscopic changes

The unweathered anorthoclase feldspar grains samples are clear, competent grains (Figure 3-1a). When irradiated for 12 hours, the anorthoclase grains remained competent but darkened and yellowed (Figure 3-1b). Upon heating of the irradiated samples, the grains returned to their original clear color (Figure 3-1d). All heated samples became brittle and required epoxy vacuum impregnation before polishing for electron microprobe analysis (Figure 3-1c,d).

The unweathered diopside clinopyroxene samples are light to dark green, competent grains (Figure 3-2a). When irradiated for 12 hours, the diopside grains remained competent but darkened and yellowed (Figure 3-2b). All heated samples darkened and browned and became brittle, requiring epoxy vacuum impregnation before polishing for electron microprobe analysis (Figure 3-2c,d).

The enstatite orthopyroxene unweathered samples are clear, competent grains (Figure 3-3a). When irradiated for 12 hours, the enstatite grains remained competent but darkened and yellowed; however, not as dramatically as irradiated anorthoclase (Figure 3-3b). Upon heating of the irradiated samples, the grains lost the yellowing but became opaque white (Figure 3-3c) The heated-only grains also became opaque white and were too brittle to image. All heated samples became extremely brittle and required epoxy vacuum impregnation before polishing for electron microprobe
Figure 3-1: Reflected light images of unweathered and weathered anorthoclase grains

(a) Unweathered  
(b) Irradiated 12 hours  
(c) Heated 4 days at 1090 K  
(d) Irradiated and Heated

Figure 3-2: Reflected light images of unweathered and weathered diopside grains

(a) Unweathered  
(b) Irradiated 12 hours  
(c) Heated 4 days at 1430 K  
(d) Irradiated and Heated
3.2 Compositional changes

We analyzed the compositional changes within the grains using the MIT JEOL-JXA-733 electron microprobe. To track the movement of species within the grains, we measured multiple transects from the rim to the core of each grain. We analyzed multiple points near the rims and cores of the grains to decrease the statistical error. To calibrate the damage of the irradiated grains, we needed to characterize the distribution of species within the unweathered grains (as they are natural samples, not synthesized). To illustrate this, Figure 3-4 compares a typical unirradiated grain that does not have a constant sodium content from rim to core with an irradiated grain of the same mineral.

For each grain we calculate the weighted mean core and rim composition of each element (in weight percent). We choose to use the unnormalized values from the electron microprobe as we do not want to lose any information by normalizing the values.
Figure 3-4: Na$_2$O example transects of an irradiated and an unweathered mineral grain. The electron backscatter image is of the cross section of an irradiated (for 12 hours) anorthoclase grain. The plotted blue transect matches the transect drawn on the image. The unweathered grain shows a near-homogenous concentration profile, while the irradiated grain shows a concentration decrease near the rim.

to 100%; a damaged structure may not have totals of 100% of the undamaged mineral stoichiometry. Table 3.1 represents the difference between the weighted mean core and the weighted mean rim between the weathered mineral grains and unweathered natural samples, given as:

$$(\bar{x}_{core} - \bar{x}_{rim})_{weathered} - (\bar{x}_{core} - \bar{x}_{rim})_{unweathered}, \quad (3.1)$$

where $\bar{x}$ is the weighted mean. Error is taken as the average weighted mean of the 1 sigma uncertainty from the microprobe counting statistics for each element. This table allows us to see the effects of weathering while accounting for the initial concentration profile in the natural samples.

We expect the rims to lose more species as they are exposed to radiation, so a positive number in the table to the left indicates a loss of that element from the rim during weathering, shown schematically in Figure 3-5a. If an element is enriched near the rim compared to the core in an unweathered grain, then weathering would cause the rim percentage to decrease, but it still may not become lower than the core percentage which may initially appear to be retention of that species (Figure 3-5b).
(a) An ideal homogenous unweathered grain that clearly loses species after weathering, resulting in a positive value in Table 3.1

(b) An inhomogeneous unweathered grain that shows enrichment of the rim. After weathering, the concentration of the rim decreases, but does not become lower than the concentration of the core. This still results in a positive value in Table 3.1

(c) A homogeneous unweathered grain that after weathering, shows an enriched rim and a negative value in Table 3.1; however, the concentration profile likely indicates reabsorption, and may not indicate much loss of species.

(d) A homogeneous unweathered grain that after weathering, shows an enriched rim and a negative value in Table 3.1, but has clearly lost species overall; however, the concentration profile likely indicates reabsorption.

Figure 3-5: Schematic concentration profiles from rim to core of unweathered and weathered grains.
Table 3.1: Average Core minus Average Rim (wt %)

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>Al</th>
<th>Fe</th>
<th>Ca</th>
<th>Na</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anorthoclase</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Irradiated</td>
<td>-0.54</td>
<td>-0.15</td>
<td>-0.02</td>
<td>0.00</td>
<td>0.35</td>
<td>0.01</td>
</tr>
<tr>
<td>Heated</td>
<td>-0.88</td>
<td>-0.12</td>
<td>0.03</td>
<td>-0.01</td>
<td>0.66</td>
<td>0.03</td>
</tr>
<tr>
<td>Irradiated and Heated</td>
<td>-0.23</td>
<td>0.09</td>
<td>-0.03</td>
<td>0.03</td>
<td>0.23</td>
<td>0.01</td>
</tr>
<tr>
<td>Average Error</td>
<td>0.072</td>
<td>0.040</td>
<td>0.010</td>
<td>0.007</td>
<td>0.051</td>
<td>0.013</td>
</tr>
<tr>
<td>Diopside</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Irradiated</td>
<td>-0.62</td>
<td>0.00</td>
<td>-0.60</td>
<td>0.52</td>
<td>-0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>Heated</td>
<td>1.14</td>
<td>0.12</td>
<td>0.23</td>
<td>-0.61</td>
<td>0.37</td>
<td>0.12</td>
</tr>
<tr>
<td>Irradiated and Heated</td>
<td>-0.30</td>
<td>0.07</td>
<td>0.10</td>
<td>-0.04</td>
<td>-0.04</td>
<td>0.06</td>
</tr>
<tr>
<td>Average Error</td>
<td>0.063</td>
<td>0.006</td>
<td>0.065</td>
<td>0.026</td>
<td>0.046</td>
<td>0.012</td>
</tr>
<tr>
<td>Enstatite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unweathered</td>
<td>-0.11</td>
<td>0.00</td>
<td>0.01</td>
<td>0.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Irradiated</td>
<td>0.23</td>
<td>0.02</td>
<td>-0.05</td>
<td>0.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average Error</td>
<td>0.081</td>
<td>0.012</td>
<td>0.017</td>
<td>0.082</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

However, by subtracting the weathered core - rim from the unweathered core - rim, we account for such a situation.

A negative number indicates an increase in the concentration in the rim after processing, evidence for resorption from the exterior as shown schematically in Figure 3-5c.d. A number near zero, or within the error, is considered to be unaffected by the weathering as the concentration profile remains the same.

In each case the rim value is compared to the core of the same processed grain. Therefore, if the whole grain loses an element but then resorbs some onto the surface, it will obtain a negative value in Table 3.1 even though it has a lower concentration of that element that it did before weathering (illustrated by Figure 3-5d).

The compositional data can also be plotted as a function of rim percentage against core percentage of an element (Figures 3-6 and 3-7), which allows the data in Table 3.1 to be combined with total weight percent values of an element. This can be particularly useful for cases such as magnesium in diopside during heating. The value in Table 3.1 would suggest that magnesium rim concentration is increasing, producing a negative value; however, the total weight percent value of magnesium is decreasing from the unweathered grain, indicating that the tabulated value may be reabsorption as illustrated by Figure 3-5d.
The histories of the weathered grains (unweathered, irradiated, heated, versus irradiated and heated) show a clear pattern. In diopside, heating produces the largest loss of rim and core percentage, while irradiation causes a drop in rim percentage, but not as much in the core (as is expected since irradiation is a surface process). Irradiation and heating produces grains with rim and core percentages that lie in between the other weathering histories - indicating an interaction between these processes. This works in reverse for the preferentially enriched elements, such as iron (Figure 3-6b).

The sodium in anorthoclase pattern (Figure 3-7a) is not as clean in Figure 3-6. Irradiation causes a large loss from the rim and the combining of irradiation and heating causes a more minor loss from the rim, and a larger loss from the core. Heating causes a large loss from the rim, but appears to be enriching the core. Table 3.1 indicates that the diffusion profile within the heated grain is clearly indicating a loss in sodium, more so than the other processes, likely indicating that the anomaly is due to variability within the natural samples.
Figure 3-6: Elemental weighted mean of analyzed rim and core points of each grain and each process in diopside. The arrows indicate the direction of composition change during heating, irradiation, and heating + irradiation from the unweathered samples.
Figure 3-7: Elemental weighted mean of analyzed rim and core points of each grain and each process in anorthoclase. The arrows indicate the direction of composition change during heating, irradiation, and heating + irradiation from the unweathered samples.
Chapter 4

Implications for Mercury’s exosphere

Our results indicate a loss in magnesium from diopside, and a noticeable loss in calcium only during heating (but not irradiation and heating), shown by Table 3.1 and Figures 3-6 and 3-7. Interestingly, iron content in diopside increases the mobility of calcium, and higher temperatures slow diffusion due to higher activation energies (Dimanov, 1996). Considering we are using high temperatures and low-iron diopside, calcium may be immobile in pyroxene. As pyroxenes contain much of the magnesium and calcium likely in the Mercurian crust, the calcium found in the exosphere may also be influenced by the low iron content of the surface and the high temperatures.

Feldspars will also likely contain much of the calcium in addition to pyroxenes but will also contain much of the sodium and potassium found on the surface. We find that sodium is lost from anorthoclase, while potassium and calcium are largely unaffected. The concentration of potassium and calcium within the feldspar grains is low, which may explain the concentrations; however, this may indicate that there needs to be more potassium-rich K-feldspars on the surface to explain the potassium abundances in the exosphere. Previous models indicate that magmas are likely to be silica saturated or silica over-saturated, in which case potassium would be found in feldspars. However, if the magmas are silica under-saturated, potassium would be found in feldspathoids such as nepheline and leucite. An interesting mineral is
davanite, $K_2TiSi_6O_{15}$, a possible carrier of both potassium and titanium. We propose that this mineral, or similar minerals, may be found on the Mercurian surface, based on the composition of the exosphere.

Figure 3-3 and Table 3.1 indicate that enstatite does not show major compositional alterations, but the color may change during heating. The color changes of the various minerals suggest that the spectra of the minerals will also change during weathering (Helbert and Maturilli, 2009), stressing the need for more studies investigating the effects of space weathering on the spectra of minerals.

These results have interesting implications for the mineral assemblage of the surface of Mercury. There may be more clinopyroxene than orthopyroxene, and potassium-rich feldspars may be present. If there is more clinopyroxene and plagioclase at the surface of the planet, then this may support evidence for a Mercurian magma ocean that may not have overturned due to the high viscosity of the opaques layer, or a Mercurian bulk composition resembling a non-chondritic silicon - magnesium ratio Bencubbinite chondrite (Brown and Elkins-Tanton, 2009).

It is often cited that certain elements have a particular concentration on the surface (such as, the sodium concentration is $\sim 0.005$ (Leblanc, 2003; Killen et al., 2004, 2007; Burger et al., 2010). No element will be spread evenly over the planetary surface. Instead, the concentration will depend on distribution of the relevant glass or mineralogy. Given that we have found a noticeable difference in the response of minerals to radiation and heating, this may have important representations in the exosphere which may allow us to better determine the surface composition.

Heating affects the entire grains, while irradiation causes more surface damage. We combined the two weathering processes to see if they would interact; we found that heating after irradiation generally causes less loss of elements as irradiation defects are annealed out. The reversibility of this damage may be expressed as the color of the anorthoclase grains returned to clear after heating of yellowed - irradiated grains as shown in Figure 3-1. Since species ejected from thermal desorption cannot be measured by the Mercury Atmospheric and Surface Composition Spectrometer onboard MESSENGER, the expression of this interaction will only be visible in the
flux from sputtering. Interaction of high temperatures and radiation only occurs in some regions on the surface of Mercury since the areas exposed to the solar wind are near the poles. However, the region exposed to radiation may extend from the poles to near $\sim 45^\circ$ latitude (Burger et al., 2010).

If this is the case, maximum surface temperatures at perihelion are $\sim 640$ K and maximum surface temperatures do not drop below room temperature until $\sim 88^\circ$ latitude (Vasavada et al., 1999). The maximum surface temperatures at aphelion are $\sim 520$ K, and do not drop below room temperature until $\sim 85^\circ$ latitude (Vasavada et al., 1999). We predict that there may be small scale variations in these high temperature regions that correspond to a decreasing flux nearer higher temperatures above annealing temperatures. Equatorial regions on the nightside can be irradiated, but it would still be cold unless radiation occurred prior to significant cooling. It takes $\sim 4.5$ hours for the surface to cool to room temperature (Vasavada et al., 1999) after it reaches the nightside, so radiation bombarding these hot (but still on the nightside) regions are more likely to be less damaging than in colder regions. This could explain a pattern, if found, suggesting a decrease in flux from the surface near the equatorial terminator regions.

Burger et al. (2010) suggest that radiation-enhanced diffusion explains the large concentration of sodium near the Mercurian poles. While irradiation does induce defects, diffusion is extremely dependent on temperature. Very cool temperatures nearest to the poles will severely limit diffusion, even if there are more defects for atoms to move by. However, if it is possible to increase the flux by 5 times due to these defects, this would imply that only the surface can easily explain these fluxes - as radiation only affects the near surface, and diffusion will be limited closer to the surface at the poles than at the equator.
Chapter 5

Conclusion

Our space weathering experiments indicate that (i) sodium is preferentially lost from sodium rich feldspars during irradiation and heating while calcium and potassium are unaffected (ii) orthopyroxene retains its magnesium during irradiation (iii) calcium is released during clinopyroxene heating, while magnesium is released during clinopyroxene irradiation and heating (iv) generally silicon, aluminum and sometimes iron and magnesium are more susceptible to adsorption (v) grains that were only heated show more loss of calcium and sodium than irradiated-only grains and (vi) grains that were irradiated and heated show the smallest amount of loss, and may represent the interactions between irradiation and heating in crystal structures.

While these experiments do not simulate photon-stimulated desorption or micrometeoroid impacts, these conclusions may still apply to the formation of the Mercurian exosphere. Feldspars may provide much of the volatiles in the exosphere, such as sodium and potassium, while clinopyroxene may provide the more refractory species, such as calcium and magnesium. The amount of potassium in the exosphere may indicate that there is a source of potassium-rich feldspars on the Mercurian surface.

Our experiments indicate that the history of weathering and mineralogy are important factors when considering the formation of Mercury’s exosphere as different minerals and crystal structures are more susceptible to different methods of weathering. Color changes and structural changes are likely to cause dramatic changes in the spectra of crustal minerals. Filling the spectral library with space-weathered
materials is crucial to accurately map the surface composition of Mercury.
References


