

**EFFECT OF WATER ON THE SURFACE COMPOSITION OF IRRADIATED MINERALS.** Catherine A. Dukes<sup>1</sup> and Raúl A. Baragiola<sup>1</sup>, <sup>1</sup>Labratory for Atomic and Space Physics, Department of Materials Science, University of Virginia, 395 McCormick Road, Charlottesville, VA 22904 (cdukes@virginia.edu).

**Introduction:** Sections of olivine [(Mg,Fe)<sub>2</sub>SiO<sub>4</sub>] and augite [(Ca,Na)(Mg,Fe,Al)(Si,Al)<sub>2</sub>O<sub>6</sub>] exposed to 10<sup>17</sup> Ar cm<sup>-2</sup> ion irradiation and then rinsed in water show up to 60% depletion of surface cations. This change is extraordinarily enhanced compared to non-irradiated surfaces exposed to water [1]. Even more surprisingly, ion bombarded olivine placed for several weeks in a humid atmosphere also undergoes a dramatic ~60% loss of Mg from the surface. This pattern of cation loss is seen in a number of other silicates, including augite (clinopyroxene), anorthoclase and albite (plagioclase feldspars). These results imply that measurements of surface composition of any irradiated mineral must be made *in situ* or by transferring samples which have been stored in an environment that can be assured to be inert.

This finding has important implications for the curation and analysis of returned samples. Planetary samples which have been exposed to solar wind, magnetospheric or ionospheric ion bombardment may be, upon return to Earth, subject to atmospheric humidity during specimen analysis or to liquid water during laboratory processing and/or analysis. With any exposure to water, returned samples will not maintain their intrinsic (extraterrestrial) surface stoichiometry.

**Experiments:** We determined the surface (outermost 30-50 Å) chemical composition and stoichiometry of irradiated-minerals exposed to water, using X-ray photoelectron spectroscopy (XPS). Irradiations were performed *in situ* with 4 keV Ar ions at fluences from 10<sup>14</sup> to 10<sup>19</sup> ion cm<sup>-2</sup> in the ultrahigh vacuum XPS system; samples were subsequently removed from vacuum and exposed to liquid water or humid air (35° C and 70% RH) in a regulated environmental chamber. After exposure, the samples were reintroduced into the analysis chamber. XPS analyses were done before irradiation, after irradiation, and after the irradiated sample had been exposed to water or humidity, allowing identification of changes in composition due solely to ion irradiation and those that required water exposure. We find that the stoichiometry of the minerals did not change significantly under ion irradiation for fluences <10<sup>18</sup> ions cm<sup>-2</sup> for 4 keV Ar<sup>+</sup> [1]. However, even at these low energies, changes in *surface chemistry*, ie. Fe<sup>2+</sup> → Fe<sup>0</sup>, have been observed [2].

**Results:** The surface chemistry of irradiated natural forsterite exposed to humid air for 20.8 days showed 60% Mg loss (Figure 1). For comparison,

unirradiated forsterite, exposed to humidity for 28.2 days showed less than 2% change in the Mg:Si ratio (Figure 2). Measurements using terrestrial augite [pyroxene: (Ca,Na)(Mg,Fe,Al)(Si,Al)<sub>2</sub>O<sub>6</sub>] show cation reductions in surface concentration of approximately 30% Mg, 40% Ca, and 55% Na after 1.9 x 10<sup>17</sup> Ar/cm<sup>2</sup> and five minutes immersion in HPLC water,

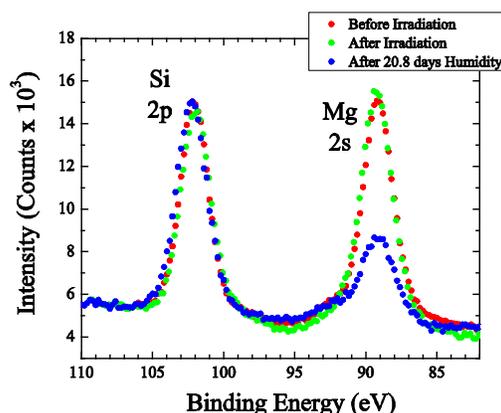


Figure 1. Effect of ion irradiation and ion irradiation plus humidity on irradiated natural forsterite. No Mg loss is observed after 10<sup>17</sup> Ar<sup>+</sup> cm<sup>-2</sup>. Exposure of the irradiated sample to humid air, produces a ~60% loss of Mg relative to Si from the mineral surface.

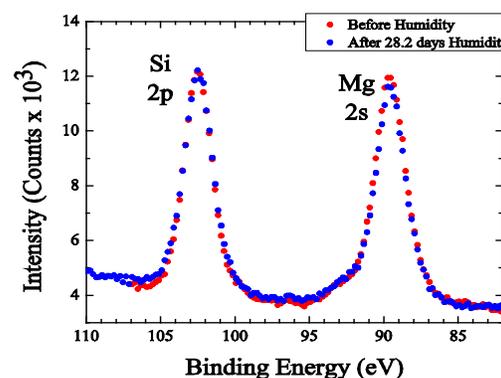


Figure 2. No significant Mg loss relative to Si is observed in unirradiated forsterite exposed to humid air for 28.2 days.

pH: 6.8, (Figure 3). Preliminary results for water-exposed, irradiated albite and anorthoclase show

preferential depletions of  $\text{Na}^+$ , and  $\text{Na}^+$  and  $\text{K}^+$ , respectively, from the mineral surfaces.

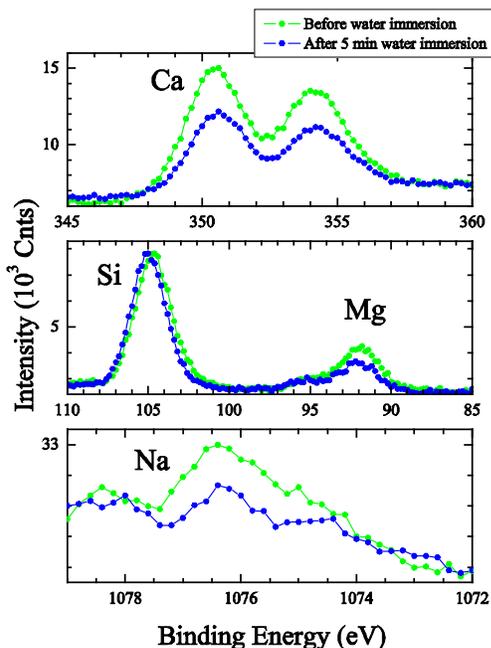


Figure 3. After a five minute water immersion, irradiated ( $2 \times 10^{17} \text{ Ar}^+ \text{ cm}^{-2}$ ) augite shows loss of Ca, Mg, and Na. Only Fe did not show a clear loss with respect to Si. Similar behavior was observed for albite and anorthoclase.

**Discussion:** Previous experiments by a number of investigators have shown contradictory evidence of cation depletion at the surface of irradiated materials [3-6]. Toppani et al see significant cation loss near the surface of IDP minerals. This contrasts with Dukes et al and Jäger et al, who see no stoichiometric change in the surface of their irradiated silicates. We suggest that the difference between these measurements can be explained by water exposure — either atmospheric or perhaps rinsing during sample preparation.

That water may preferentially remove ions from the surface of minerals is well known and has been studied extensively within the geological community [ie.7]. Casey and Bunker have shown that the dissolution rate depends strongly on pH as well as on the  $\text{Mg}^{++}$  linkage to the native silicate bonds at the surface. One likely mechanism for this process is the exchange of protons for surface cations, leached from the exposed layer, as  $2\text{H}^+ \rightarrow \text{Mg}^{2+}$ . We suggest that the radiation damage produced by energetic ion irradiation enhances the penetration of protons into the mineral by breaking the bonds between the  $\text{Mg}^{++}$  and the silicate tetrahedra. To verify this hypothesis, we measure the Mg content of

the rinse water used to dip the forsterite sections with ion chromatography. A distinct correlation between immersion time and Mg content in the HPLC is recorded in Figure 4, supporting the proton-cation exchange mechanism.

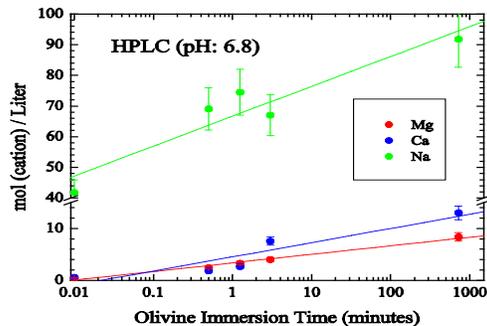


Figure 4. Ion chromatography data gives the ion concentration in a known volume of water. The cation concentration increases with olivine immersion time, supporting the proton exchange hypothesis.

**Conclusion:** The surface stoichiometry of irradiated minerals is compromised by water exposure, both in liquid and gaseous form. Therefore, returned samples exposed to solar wind MUST be stored in vacuum or in an inert (entirely anhydrous) atmosphere to retain intrinsic surface composition. Any leak to air or slow water outgassing may alter the surface chemistry of that particular sample. In addition, laboratory analysis of the surface of lunar material exposed to the solar wind irradiation must be analyzed without exposure to the earth's atmosphere, and sample handling and preparation techniques must NOT include rinsing in water. Likewise, it is important that laboratory simulations of extraterrestrial processes involving irradiation are analyzed without subsequent exposure to air.

**References:** [1] E.D. Cantando et al. (2008) *JGR*, 113, E09011. [2] C.A. Dukes, R.A. Baragiola, and L.A. McFadden. (1999) *JGR*, 104, 1865–1871. [3] A. Toppani et al. (2006) *LPS XXXVII*, Abstract #2056. [4] J. P. Bradley. (1994) *Science*, 265, 925 – 929. [5] K. Demyk et al. *Astron. Astrophys.*, 368, L38–L41. [6] C. Jäger et al. (2003), *Astron. Astrophys.*, 401, 57–65. [7] W.H. Casey and B. Bunker. (1990), *Leaching of mineral and glass surfaces during dissolution*, in *Mineral and Water Interface Geochemistry*, edited by M. F. Hochella and A. F. White, pp. 397–426.

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