

**TITANIUM VALENCE IN LUNAR ULTRAMAFIC GLASSES AND OLIVINE-DIOGENITES.** M. J. Krawczynski<sup>1</sup>, S. R. Sutton<sup>2</sup>, J. A. Barr,<sup>1</sup> and T. L. Grove<sup>1</sup>; <sup>1</sup>Massachusetts Institute of Technology, 77 Massachusetts Ave, Bldg 54-1212, Cambridge, MA 02139 (kraw@mit.edu), <sup>2</sup>GSECARS University of Chicago, 9700 South Cass Avenue, Bldg. 434A, Argonne, IL 60439 United States.

**Introduction:** The oxidation state of planetary bodies is a fundamentally important physical characteristic. On Earth we observe a variation in oxidation state in crust and upper mantle rocks. The oxidation states for the Moon and the HED parent body are much lower than Earth, but are not well characterized for their mantles. On the Moon, there are several elements that display a variation in valence state at these more reducing conditions (e.g. V, Cr, Eu, Mn, Ti). We report the first measurements of Ti valence state in olivine/melt pairs from lunar high-titanium (HiTi) ultramafic glasses. These glasses contain sufficient Ti so that the valence state significantly influences the phase equilibria and mineral/melt reactions in these magmas. By comparing the lunar and experimental olivines to those in diogenites we hope to also learn about the variation of silicate melt speciation of Ti species in other reducing planetary magmatic environments.

We have measured the  $Ti^{3+}/Ti^{4+}$  ratios of 4 pristine lunar ultramafic glasses: orange glass (74002,6035), red glass (15426,18), green and yellow glass (15426,72) as well as olivines from the orange glass (74002,6035) and olivine and cpx from MIL03443,9 (classified as a mesosiderite, but actually an olivine-diogenite [1, 2]). In addition to the natural glasses and crystals we have also measured the  $Ti^{3+}/Ti^{4+}$  ratio in high pressure experiments on compositions analogous to the Apollo 15 green glasses.

**Analysis and methods:** *High pressure experiments:* Experiments were carried out in a piston cylinder apparatus using both graphite and spec-pure Fe-metal capsules. The starting material is a mixture of synthetic oxides, combined in correct proportions to recreate the bulk composition of Apollo 15 group A green glasses and conditioned at one atmosphere pressure near the iron-wüstite (IW) buffer. It has previously been shown that experiments in Fe-metal capsules buffer at a lower oxygen fugacity (IW-2) than those performed in graphite capsules (IW+1.2) [3]. Piston cylinder experiments with crystals were prepared as polished thick sections for analysis.

*Synchrotron beam techniques:* We have used the X-ray absorption near-edge spectroscopy (XANES) method to analyze the  $Ti^{3+}/Ti^{4+}$  contents of lunar glasses and natural olivines from the 74002 sample, and the olivines and pyroxenes from olivine-diogenite MIL03443 in conjunction with several synthetic analogues of the green glass.

Titanium K XANES spectra were measured at the Advanced Photon Source using the GSECARS 13-ID-C beamline. A monochromatic X-ray beam from a Si(111) double crystal monochromator was focused onto the sample (3  $\mu$ m spot size). The fluorescent X-ray yield was measured as a function of the incident X-ray energy to obtain information on the oxidation state of Ti (see [4] for details). Previous XANES studies [5] have shown that the intensity and energy of the pre-edge peak in the Ti K XANES spectra of  $Ti^{4+}$  minerals fall into distinct coordination number groups with tetrahedral  $Ti^{4+}$  minerals yielding high intensity and low energy and octahedral  $Ti^{4+}$  minerals yielding low intensity and high energy. Octahedral  $Ti^{3+}$  minerals will exhibit low intensity and low energy. A synthetic forsterite, synthetic acmite, and natural acmite were used as "oxidation state-coordination number" standards in the present work (Fig 1). Oxidation state determinations were made using the lever rule on the resulting " $Ti^{4+}(\text{tet})-Ti^{4+}(\text{oct})-Ti^{3+}(\text{oct})$ " mixing space. High Ti becomes problematic for fluorescence measurements due to strong self-absorption and detector saturation, however by reducing counting times we were able to avoid these problems, and the fluorescence method worked well for all samples.

**Discussion:** *Lunar pristine glasses:* The 4 lunar glass compositions that we measured show complete overlap in their Ti-speciation. All of the glasses plot within error of a valence of pure  $Ti^{4+}$  (~4.05-4.10 +/- 0.1  $2\sigma$ ), although the red glass is slightly more reduced (4.0 +/- 0.1). There is complete overlap of these natural glasses with the experimental glasses examined here and reported previously (green, red and orange).

*Diogenites:* The  $fO_2$  for diogenite genesis is thought to be similar to the conditions in the lunar glasses, due to the presence of Fe-metal in the meteorites and experimental studies [6,7,8]. However for the olivines in MIL03443 there is a significant difference in the substitution site for Ti than for lunar olivines. The Ti is almost completely tetrahedrally coordinated in MIL03443 olivine. Because of the shape of the mixing space for Ti-speciation (Fig 1), it is hard to determine with certainty the oxidation state of the Ti. This is because the mixing trends for samples with >50% tetrahedral Ti are so close it becomes impractical to make a distinction between the oxidation state of the octahedral species.

Cpx is found in this sample as exsolved blebs along olivine-opx boundaries (Fig 2), and our results on the Cpx are consistent with the presence of a significant amount of  $Ti^{3+}$ , with the average valence of Ti being 3.52. This however is a lower limit, because there is also a significant amount of tetrahedral  $Ti^{4+}$ .

**Ti substitution in Olivine:** The olivine in 74002 and in our experiments on lunar compositions (both on low and HiTi compositions) plot in the same region on the Ti-speciation diagram (Fig 1), leading us to believe that our experiments are appropriately mimicking the natural system. There is a considerable amount of  $Ti^{4+}$  in octahedral coordination in these olivines and experimental Cpx's. This is NOT a high Ti effect however, as we see similar behavior between experimental green glass olivines (<1 wt%  $TiO_2$ ) and experimental HiTi olivines (8-16 wt%  $TiO_2$ ). Also this is in stark contrast to the diogenite sample.

We propose that this difference may be due to the melt compositions in equilibrium with the crystals. Eucrite melts (a possible parent to the cumulate diogenites) have much lower FeO+MgO and much higher  $Al_2O_3$  contents than the lunar ultramafic glasses [9,10]. In this case the  $Al^{3+}$  in the diogenite olivines may be replacing the  $Ti^{4+}$  in the octahedral site.

**Proposed work:** Still left undetermined is how much of the difference in  $Ti^{3+}/Ti^{4+}$  ratios between coexisting crystals and melt is a function of the compatibility of  $Ti^{3+}$  and how much is due to a change in the oxidation state of Ti in the liquid-glass transition during cooling of the magma/experiment (i.e. is the oxidation state of Ti 'quenched'). We will conduct 1-atm crystallization experiments at conditions far more reducing than what is expected for the moon. These experiments will unambiguously be in an  $fO_2$  regime where a significant amount of  $Ti^{3+}$  would be stable.

Measurements of the glasses formed under these conditions should tell us whether we are able to quench some amount of  $Ti^{3+}$ , and if not able to quench the oxidation state, then we will determine what the relevant charge-coupled reactions are. The compatibility of  $Ti^{3+}$  has interesting implications for the evolution of the lunar magma ocean, as well as determination of oxidation state in the early solar systems, and we will explore these implications with the new experimental results.

**References:** [1] Irving et al. (2005) *LPS XXXVI*, #2188. [2] Krawczynski M.J. and Grove T.L. (2008) *LPS XXXIX*, Abstract #1231. [3] Krawczynski M.J. and Grove T.L. (2007) *LPS XXXVIII*, Abstract #1235. [4] Simon S. B. et al. (2007) *GCA*, 71, 3098-3118. [5] Farges F. et al. (1997) *Phys. Rev. B*, 56, 1809-1819. [6] Bartels and Grove (1991) *Proc. Lunar Planet. Sci.*, 21, 351-365. [7] Stolper (1977) *GCA*, 41, 587-611. [8]

Jurewicz et al. (1995) *GCA*, 59, 391-408. [9] Delano J.W. (1986) *JGR*, 91, D201-D213. [10] Planetary Materials (1998) *MSA short course #36*.

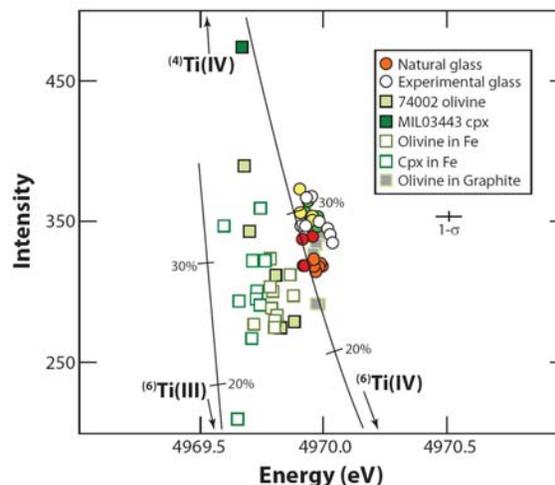


Figure 1: Ti-speciation diagram. The XANES pre-edge peak intensity and energy of the peak centroid are a function of the Ti valence and coordination. Glasses correspond to their color, and all plot in the same vicinity no matter the composition and if they are natural or experimental. Also shown are olivines from 74002 and experimental charges as well as Cpx from MIL03443. Olivines from MIL03443 plot at ~800 intensity and thus are off the scale here.

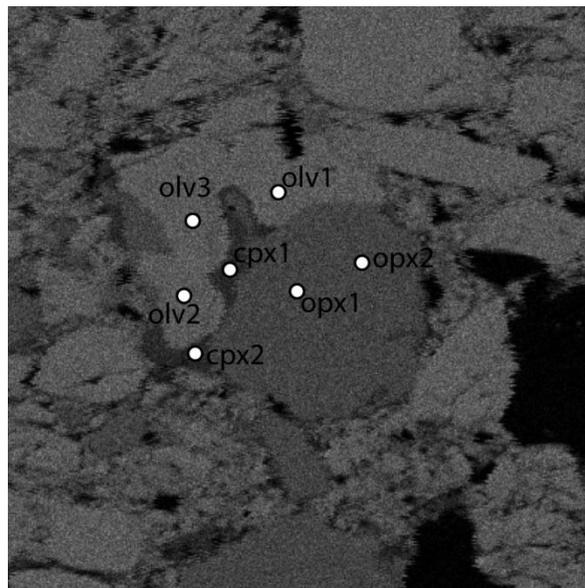


Figure 2: Mg EMP X-ray intensity map of MIL03443 with higher Mg shown in lighter tones, and low Mg as darker. Shown is an intergrowth of olivine and opx with exsolved cpx along the olivine-opx boundary. The intergrowth grain is about 500 microns across. XANES analyses are labeled with white dots.