

TITANIUM OXIDATION STATE AND COORDINATION IN THE LUNAR HIGH-TITANIUM GLASS SOURCE MANTLE. M. J. Krawczynski¹, S. R. Sutton², T. L. Grove¹, M. Newville², ¹Massachusetts Institute of Technology, 77 Massachusetts Ave, Cambridge, MA 02139 United States (kraw@mit.edu), ²GSECARS University of Chicago, 9700 South Cass Avenue, Bldg. 434A, Argonne, IL 60439 United States.

Introduction: Lunar high-titanium (HiTi) ultramafic glasses provide us with evidence of the mantle processes that led to the melting of the lunar magma ocean cumulates nearly one billion years after the magma ocean solidified. Constraints on the depth, temperature and melting processes that formed the HiTi glasses are crucial for understanding the melting history of LMO products.

The Apollo 17 orange glass (A17O) and Apollo 15 red glass (A15R) represent two of the HiTi compositions in the spectrum of pristine ultramafic glasses returned from the moon [1]. The difference between these two compositions is that the A15R contains ~40% more TiO₂ than the A17O. The low f_{O2} of the ultramafic glass source regions allows for a certain amount of Ti³⁺ in the source mineralogy; however the amount of Ti³⁺ in the source and the host mineral for this element remain relatively unconstrained.

In addition to the unknown mineralogy of the source region, the high amount of TiO₂* and FeO* in the HiTi magmas makes the phase relations extremely sensitive to changes in the oxidation state of the source region. We have previously investigated the oxidation state effect on the olivine-orthopyroxene multiple saturations points of the A15R and A17O [2,3] and shown that the magnitude of the effect is proportional to the amount of Ti in the system.

X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine-structure (EXAFS) measurements have been made on minerals and glasses in experiments on synthetic analogues to the A17O and A15R. Our results show that Ti³⁺ concentration does indeed affect the multiple saturation points, and is an important constituent in the lunar interior.

Experiments and Analysis: 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 A17O and A15R [1] and conditioned at iron-wüstite (IW) oxygen fugacity conditions. It has previously been shown that experiments in Fe-metal capsules buffer at a lower oxygen fugacity (IW-2) than that of graphite capsules (IW+1.2) [3]. Piston cylinder experiments with crystals were prepared as polished thick sections for analysis.

Titanium K XANES and EXAFS 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 μm spot size). For experiments with crystals, 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 Ti⁴⁺ minerals fall into distinct coordination number groups with tetrahedral Ti⁴⁺ minerals yielding high intensity and low energy and octahedral Ti⁴⁺ minerals yielding low intensity and high energy. Octahedral Ti³⁺ 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 (figure 1). Oxidation state determinations were made using the lever rule on the resulting “Ti⁴⁺(tet)-Ti⁴⁺(oct)-Ti³⁺(oct)” mixing triangle.

The fluorescence method worked well for samples with Ti at concentrations below ~10% (such as olivine, opx, cpx, and garnet) but becomes problematic for the HiTi glasses due to strong self-absorption and detector saturation. Transmission X-ray spectroscopy was used instead for these HiTi samples. Samples were thinned to ~25 μm and doubly-polished for this purpose. Examples of the radial distribution function from transmission EXAFS spectra of two glasses are shown in figure 2.

Results: The pyroxenes and garnets in the Fe-metal capsule contain about 50% Ti³⁺, while the pyroxenes in the graphite capsule contain almost no Ti³⁺ (figure 1). This is consistent with the Fe-metal capsule producing a more reducing environment.

Due to the polarized nature of the incident X-ray beam coming from the synchrotron and the strong crystallographic asymmetry of orthopyroxene, this mineral shows a significant variation in pre-edge peak intensity depending on the orientation of the crystal in the beam. Further X-ray absorption spectroscopy measurements are needed in order to fully quantify this variation, but for the purposes of this initial work, we have used a mean value for the pre-edge peak intensity, based on the notion that such averaging is analogous to averaging over all crystal orientations.

Quenched glass in both capsule types had undetectable amounts of Ti^{3+} . Based on the detection limit of Ti^{3+} and the measurements of the pyroxenes, we estimate that the bulk experiment in Fe-metal has an upper limit at $Ti^{3+}/Ti^{tot} \leq 0.15$, and the graphite experiment has a $Ti^{3+}/Ti^{tot} \sim 0$, however due to the extreme amounts of Ti, even a few percent corresponds to a significant amount of Ti^{3+} in the source.

Discussion: Olivine-Opx Phase Relations: HiTi liquids in equilibrium with olivine have been noted to have olivine-melt partition coefficients (K_D^{Mg-Fe}) lower than the usual ~ 0.32 [2,5,6] and thus the olivine tends to be more Mg-rich than a typical equilibrium K_D would predict. The magnitude of the decrease in the K_D is proportional to pressure, f_{O_2} and the amount of Ti in the system. This is a bit surprising because the f_{O_2} range in question is too low for Fe^{3+} to be in high abundance, and thus any noticeable effect on the olivine-opx phase equilibria must be caused by shifts in the Ti^{3+}/Ti^{4+} ratio.

We thus hypothesize that the Ti^{3+} is coordinating preferentially with Fe^{2+} (a compatible element) in the melt, precluding olivine from incorporating the normal equilibrium amount of Fe^{2+} . Indeed we see a difference in the radial distribution function for Ti in the glass as a function of f_{O_2} , and currently we are analyzing these data to see if they are consistent with Ti coordination with Fe in the melt. This effect of Ti coordination with Fe appears to decrease with pressure, so a melt structure transition may also be affecting the equilibrium as well.

HiTi mare basalt source mineralogy: Estimates of f_{O_2} for the A17O source region are about $\Delta IW-0.6$ [8,9]. At these reducing conditions, based on our XANES spectra, Ti^{3+}/Ti^{tot} should be about 0.1. For a liquid with as much Ti as the A15R, this is equivalent to about 1.4 wt% of the lava being Ti^{3+} . Based on the partitioning we observe between pyroxene and melt (figure 1, and electron probe data for experimental pyroxenes) it is possible to sequester this amount of Ti^{3+} in a pyroxene bearing source, and so no special Ti^{3+} bearing phase is required, although a Ti^{4+} -rich phase such as ilmenite is obviously necessary to account for the other 12.5 wt% Ti.

References: [1] Delano J.W. (1986) *JGR*, 91, D201-D213. [2] Krawczynski M.J. and Grove T.L. (2008) *LPS XXXIX*, Abstract #1231. [3] Grove T.L. et al. (2007) *LPS XXXVIII*, Abstract #1236. [4] Simon S. B. et al. (2007) *GCA*, 71, 3098-3118. [5] Farges F. et al. (1997) *Phys. Rev. B*, 56, 1809-1819. [6] Delano J.W. (1980) *PLSC 11*, 251-288. [7] Xirouchakis et al. (2001) *GCA*, 64, 2201-2217. [8] Sato M. (1976) *PLSC 7*, 1323-1344. [9] M. Nicolis pers. comm.

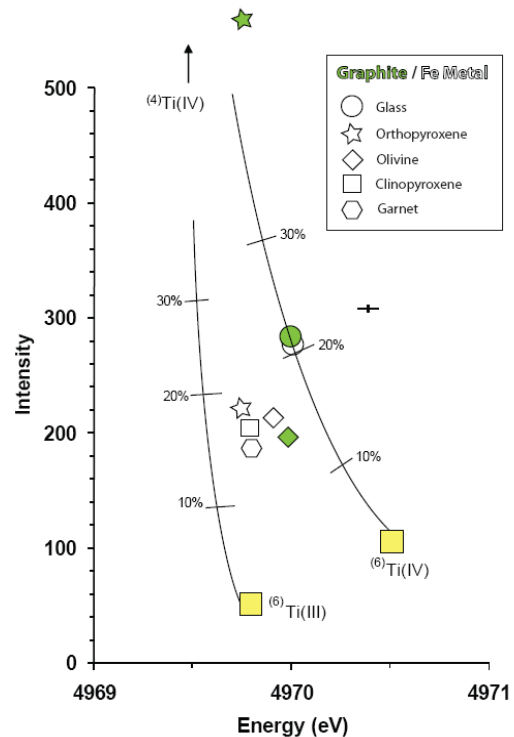


Figure 1: The mean position of the pre-edge peak (in energy and intensity) for the minerals and glass produced in 2 piston cylinder experiments (graphite and Fe-metal). Plotted in a three end-member mixing diagram are the three standards (octahedral Ti^{3+} in synthetic acmite, octahedral Ti^{4+} from natural acmite, and tetrahedral Ti^{4+} from synthetic forsterite(off-scale)). The percentage markers indicate the amount of tetrahedral Ti^{4+} along the mixing trends with the other two species.

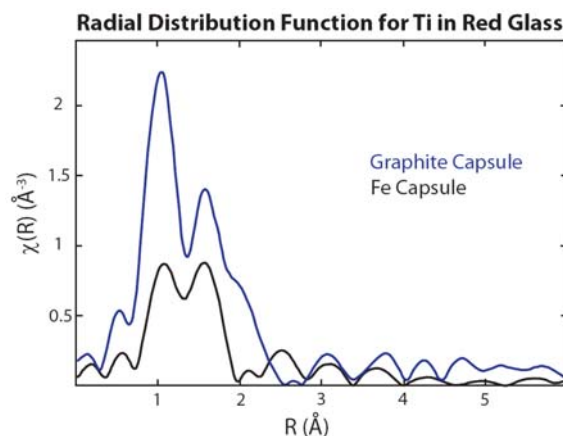


Figure 2: The radial distribution functions for 2 red glass experiments, one in graphite and one in an Fe capsule. Functions are from transmitted X-ray spectrum near the Ti K-edge region. Both experiments were performed at similar P-T conditions, thus the difference is due to Ti oxidation state.