

SYNTHESIS OF TI OXIDES AT REDUCING CONDITIONS: IMPLICATIONS FOR BEAMLINE STANDARDS AND COSMOCHEMISTRY. K. Righter¹, K.A. Pando², A.L. Butterworth³, Z. Gainsforth³, C. E. Jilly-Rehak³, A.J. Westphal³; ¹NASA-JSC, Mailcode XI2, 2101 NASA Pkwy, Houston, TX 77058; ²Jacobs-JETS, NASA-JSC, Houston, TX 77058; ³Space Sciences Laboratory, University of California Berkeley, Berkeley, CA 94720.

Introduction: Oxygen fugacity exerts a major control on mineral major element chemistry and elemental valence of minerals in any planetary compositional system [1]. For Earth, Fe is multivalent ranging from nearly Fe⁰ at low fO₂ in the deep mantle to Fe²⁺ to Fe³⁺ at high low fO₂. For solar nebular and meteoritic materials fO₂ ranges from near IW to ~10 log fO₂ units below the IW buffer [1]. Phases in CAIs, for example, contain no Fe²⁺, but may contain Ti⁴⁺, Ti³⁺, or Ti²⁺, and Cr³⁺ or Cr²⁺, and V³⁺ or V²⁺ [1,2,3]. Detailed study of inclusions may reveal important differences in fO₂ thus reflecting different environments in the solar nebula [4]. XANES, FEG-SEM, and TEM can reveal such variations in micro and nano samples such as Stardust and cosmic dust particles [5], but successful application to reduced conditions depends upon the availability of well characterized standards. Acquiring appropriate standards for reduced phases that contain Ti³⁺ or Ti²⁺, Cr³⁺ or Cr²⁺, and V³⁺ or V²⁺ can be a challenge. Here we report our preliminary results at synthesizing reduced Ti bearing standards, and focus on the preliminary characterization.

Procedure: Experiments were conducted at constant pressure (1 GPa) and temperature (1400 °C) using a non-end-loaded piston cylinder apparatus at NASA-JSC [6]. Samples for these experiments comprised ultrapure oxide powders of TiO₂, MgO, Al₂O₃, or metallic Ti mechanically mixed and ground. Samples were encapsulated in polycrystalline MgO, and pressurized in an assembly with a BaCO₃ pressure medium and Type C W-Re thermocouple. After pressurization, samples were heated to 1400 °C for 6 hours [7], and then power quenched. Three different experiments were performed; two in which the Ti-TiO₂ ratio was varied in order to stabilize Ti metal and Ti oxide for a buffer. A third experiment utilized a 1:1 mixture of Ti and TiO₂ to intentionally produce TiO in larger quantities. All experiments were equilibrated with the MgO capsule material thus also allowing characterization of Ti in pericase.

Analysis: The metals and oxides were analyzed for major element composition using a JEOL 8530 FEG electron microprobe at NASA-JSC. A 1 μm beam was used at 20kV and 10nA. Also, a variety of natural and synthetic standards were used, including rutile for Ti and O.

FIB and TEM work was carried out at the National Center for Electron Microscopy and XANES spectra were acquired at Advanced Light Source Beamlines 10.3.2 (K-edges) and 11.0.2 (L-edges), all at Lawrence Berkeley National Laboratory. FIB liftouts were cut using an FEI Dual-Beam FIB with Ga⁺ at 30 and 6 keV. TEM imaging and EDS were acquired using an FEI Titan TEM. Atom Location by CHanneling Enhanced Microanalysis (ALCHEMI) was done on the Titan to determine the sites of cations. An FEI Tecnai with Gatan energy filter was used for EELS. EELS spectra were shifted to the same onset energy, and normalized. Ti L-edge EELS was measured on all phases possible, Ti L-edge XANES on select phases Ti >1 wt%, and Ti-K edge XANES was performed on the coarser phases. Oxidation state was determined based on the stoichiometry and EELS modeling. It is known that at low fO₂, oxygen vacancies occur in oxides, not yet accounted for in these preliminary results. Our future work will use DFT and multiplet simulation of the XANES spectra to produce an ab-initio determination of more precise oxidation state measurements.

Results and Discussion: Figure 1 shows results from the first experiment, which contained mainly MgAl₂O₄ (with ~1 wt% Ti), a Ti oxide, silicide and metal. The silicide, silicate and oxide suggest an fO₂ between IW-3.5 and IW-8, based on equilibria such as TiSi + 3/2 O₂ = TiO + SiO₂, or Ti₅Si₃ + 11/2 O₂ = 5TiO + 3SiO₂, and available thermodynamic data [8,9]. The Ti oxide is most likely TiO_x, where x represents a degree of non-stoichiometry from the end member TiO [10]. The TiO_x can be seen in Fig 1A as the green phase, and in 1B as the green spectrum. The EELS spectrum can be fit via multiplet theory

[11] as octahedral Ti^{4+} with a crystal field splitting of 2.4 eV. The magnesiospinel (red in 1A and 1B) had about 1 wt % of Ti which was octahedrally coordinated and has an EELS spectrum different than the TiO_x (Fig. 1B). This result shows an experimentally calibrated Ti-L edge spectrum for Ti in magnesiospinel at fO_2 near the solar nebula. The two distinct EELS spectra for $MgAl_2O_4$ and TiO_x (equilibrated at the same T- fO_2 conditions) highlight the importance of considering crystallography of the host phase.

A second experiment produced $MgAl_2O_4$ without Ti, $MgTi_2O_4$, TiFe metal, and periclase (with Ti). This suggests a mix of Ti oxidation states; we plan additional studies to evaluate the utility of $MgTi_2O_4$ as a standard or as part of a buffer.

Conclusions: These initial experiments demonstrate the great potential for synthesizing customized compounds for use as standards, or in

buffering experiments at reducing conditions. We are also investigating Cr and V oxides, as well as compounds containing these elements such as FeV_2O_4 and $FeCr_2O_4$ [12].

References: [1] Righter, K. et al. (2016) *Amer. Mineral.* 101, 1928-1942 [2] Papike, J.J. et al. (2005) *Amer. Mineral.* 90, 277-290 [3] Paque, J. et al. (2013) *MaPS* 48, 2015-2043. [4] Dyl, K. (2011) *GCA* 75, 937-949. [5] Gainsforth, Z. et al. (2015) *MaPS* 50, 976-1004. [6] Righter, K. et al. (2006) *Amer. Mineral.* 91, 1643-1656; [7] Righter, K. et al. (2011) *Amer. Mineral.* 96, 1278-1290; [8] Liang, H. and Chang, Y. A. (1999) *Intermetallics* 7, 561-570; [9] Chen, C. C. (2014) *Atlas Jour. Mat. Sci.* 1, 1-11; [10] Doyle, N.J. et al. (1968) *Phys. Letters* 26A, 604-605; [11] E. Stavitski and F.M.F. de Groot, (2010) *Micron* **41**, 687; [12] Jacob, K.T. and Alcock, C.B. (1975) *Met Trans. B6*, 215-221.

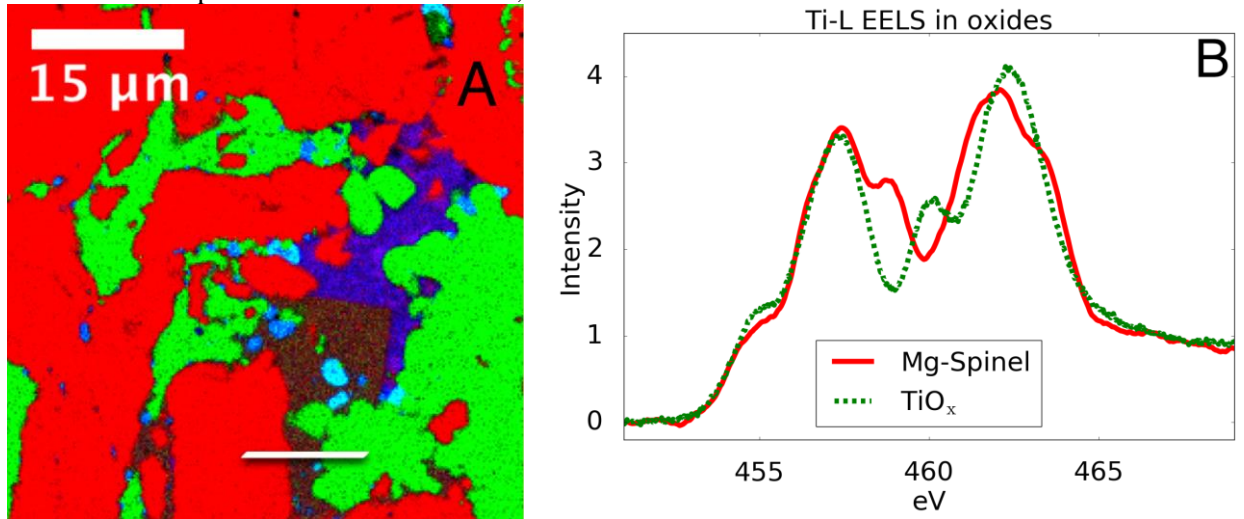


Fig. 1A) EDS map with Al (red), Ti (green), Si (blue) showing $MgAl_2O_4$ (red-Al), TiO_x (green-Ti), unknown phase (dark red equant crystal), FeTi silicide (cyan), and melt (blue-Si). The white line shows the location of FIB section. B) EELS spectra comparing Ti L-edge EELS from $MgAl_2O_4$ spinel and TiO_x .

Table 1: All characterized phases in both synthesis experiments (1400 °C) which contain Ti

† Coordination and oxidation state are likely variable. Only one location has been characterized as yet.

Experiment # / phase	Ti-L (EELS)	Ti-L (STXM)	Ti-K (XANES)	Coord.	Oxid. state
1 / $MgAl_2O_4$ (Minor Ti)	Y	Y	N	Oct	Unk.
1 / TiO_x	Y	Y	Y	Oct [†]	4+ [†]
1 / Silicide	Y	N	N	Unk.	Metallic
2 / $MgAl_2O_4$ (No Ti)	N	N	N	N/A	N/A
2 / $MgTi_2O_4$	Y	Y	Y	Oct	3+
2 / Periclase (minor Ti)	Y	Y	Y	Unk.	Unk.