THE GROWING INVENTORY OF Ti^{3+}-BEARING OBJECTS FROM THE SOLAR NEBULA. S. B. Simon[1], S. R. Sutton[1,2] and L. Grossman[1,3], [1]Dept. Geophysical Sci., 5734 S. Ellis Ave.; [2]Center for Advanced Radiation Sources (CARS); [3]Enrico Fermi Institute, 5640 S. Ellis Ave., The University of Chicago, Chicago, IL 60637, USA (sbs8@uchicago.edu).

Introduction: The theoretical buffer curve for Ti_2O_3-TiO_2 equilibrium is ~5 log units below the iron-wüstite (IW) buffer at 1500K and ~2 log units above the curve for solar composition [1] at that temperature. Thus, a solar gas is sufficiently reducing to stabilize Ti^{3+} and allow it to coexist with Ti^{4+}, making the valence of Ti a valuable recorder of fO_2 conditions during the formation of nebular materials. For Ti-rich phases with no cation or oxygen vacancies, such as fassaite and rhönite, Ti^{3+}/Ti^{4+} ratios can be calculated by stoichiometry from electron probe analyses. For other phases, another technique is needed. The development of Ti-XANES (X-ray absorption near-edge spectroscopy) has allowed measurement of Ti valence to be performed on hibonite, spinel and olivine. These are important phases among early solar system materials, and the valence of Ti in them can tell us whether they formed in a reducing, nebular gas or under more oxidizing conditions. Over the past several years we have investigated a wide variety of materials for the occurrence of Ti^{3+}. This report is a summary of those findings. We have also recently begun an investigation of the valence of Ti as a function of metamorphic grade in L and LL chondrites, and some preliminary results are reported.

Analytical Methods: Samples were selected for analysis after characterization by scanning electron microscope and electron microprobe. Titanium K XANES spectra were collected using the GSECARS X-ray microprobe in fluorescence mode, with a 3 µm X-ray beam. Results were determined following the methods of [1, 2] and are reported as values from 3 to 4, representing the average Ti valences of the analytical volumes.

Samples: The sample suite includes chondrules, refractory forsterite (RF), Ca-, Al-rich refractory inclusions (CAIs) and amoeboid olivine aggregates (AOAs). Isolated RF grains (CaO>0.4 wt% and Al_2O_3>0.2 wt%) and RF-bearing chondrules from two CM chondrites were studied by [3]. Type IAB and type IIA porphyritic chondrules from Semarkona were studied by [4]. A coarse hibonite grain along with two spinel-hibonite and three spinel-pyroxene inclusions from Murchison were analyzed by [5]. Spinel in coarse-grained refractory inclusions from CV3s Allende, Efremovka and Vigarano was analyzed by [6] and [7]. AOAs from Allende (TS19F2) and Efremovka (Ef2) were studied in [8].

Results: *RF and chondrules.* At least 75% of the Ti is trivalent in RF, whether it is found as isolated grains or in chondrules; RF has higher Ti^{3+}/Ti^{4+} ratios than fassaite from refractory inclusions [3]. Trivalent Ti is also found in "typical" olivine in chondrules, but in lower proportions than in RF [4]. A "dusty" olivine, rich in blebs of Fe metal in a texture indicative of *in situ* reduction, in a Semarkona type IAB chondrule contains Ti^{3+} but is not anomalously Ti^{3+}-rich relative to other grains in the chondrule. Pyroxene in Semarkona type IAB chondrules also contains trivalent Ti. In the type I chondrule, Ti valences in olivine range from 3.05 to within error of 4. In type II chondrules, Ti valences in pyroxene and olivine are between 3.5 and 4. There is no correlation between Fa content and Ti valence. A grain in the type I chondrule is uniformly $Fa_{2.2}$ and zoned with increasing Ti valence from core (3.05) to rim (3.6), and a grain in the type II chondrule is strongly zoned from Fa_{12} in the core to Fa_{28} at the rim and is unzoned in Ti valence (~3.8).

Among the L chondrites, Ti valence in olivine decreases then increases with increasing metamorphic grade. It is more reduced in the L3.4 (LEW86505; avg. valence 3.7±0.2) and L3.6 (ALHA81025; 3.7±0.1) than in the L3.0 (LEW86158; 4.0±0.1), L3.8 (ALH84086; 4.0±0.1) and the L4 (EET87557; 3.9±0.2) samples we analyzed. In pyroxene, the Ti valence is low in the L3.0 (3.6±0.04), L3.4 (3.6±0.1) and L3.6 (3.4±0.2) samples, increasing to 4.0±0.2 in the L3.8 and 3.8±0.2 in the L4 chondrite.

Refractory inclusions in Murchison. It has long been known that fassaite in CV3 inclusions and pyroxene in the rims on those inclusions [1] contains trivalent Ti but little was known about Ti valence in Murchison inclusions, in which most pyroxene is Ti-poor. Results [5] show that spinel, hibonite and pyroxene in Murchison inclusions all contain Ti^{3+} and that coexisting phases (spinel-pyroxene; spinel-hibonite) tend to have similar Ti valences. Two spinel-hibonite inclusions have Ti valences ~3.8. Valences are ~3.3 in one spinel-pyroxene inclusion, ~3.5 in another, and in a third, pyroxene is ~3.5 but the coexisting spinel is ~3.6.

Forsterite-bearing refractory inclusions. These objects were investigated as a possible source of RF because they have abundant, coarse, Ca–rich forsterite. It occurs, along with spinel, poikilitically enclosed in fassaite. It was found, however, that these inclusions do not contain trivalent Ti.

Spinel in CV3 inclusions. It was expected that this work would yield an estimate of the Ti^{3+}/Ti^{4+} ratio in spinel that corresponds to the nebular fO_2. It was found [6, 7] that spinel in CV3 inclusions has valences ranging from 3.5-4, generally higher than fassaite and therefore higher than expected for equilibration in a system of solar composition.

Amoeboid olivine aggregates (AOAs). These objects were investigated [8] because the presence of Ti^{3+} in them would support the long-held interpretation of them as nebular condensates [9, 10]. Results show that olivine in AOAs contains significant proportions of Ti^{3+}. Wide ranges of Ti valences were found in both TS19F2 (3.2-3.6, 3.5±0.1 avg.) and Ef2 (3.5-3.9, 3.7±0.1 avg.). As in chondrule olivine there is no correlation between Fa content and Ti valence. Olivine in Ef2 is more forsteritic (Fa_{0-5}) than that in TS19F2 (Fa_{5-32}), but it has lower proportions of Ti^{3+}.

Discussion. At least three of these results were unexpected: the occurrence of Ti^{3+} is not restricted to refractory materials or even to Fe-free phases; Fo-bearing refractory inclusions do not contain Ti^{3+}; and spinel in coarse-grained CAIs has low Ti^{3+}/Ti^{4+} ratios.

That RF might contain Ti^{3+} was suggested by [11], who calculated refractory lithophile element contents of a melt that would be in equilibrium with RF. They predicted enrichments of ~10-40xCI for most elements, but Ti enrichments of 50-65xCI would have to be inferred if it were only present as Ti^{4+}. Our measurements of Ti^{3+}/Ti^{4+} in RF combined with an olivine/liquid D of 0.355 interpolated from Ds for V^{3+} and Sc [12] indicate a liquid with 28xCI, well within the range predicted by [11] for other refractory lithophiles, supporting their model for the formation of RF.

The occurrence of Ti^{3+} in type I and type II chondrules suggests that both types had reduced precursors and that the valence of Ti in chondrules does not reflect the near-IW conditions under which FeO-bearing olivine forms. Either Fe attains redox equilibrium more rapidly than Ti, or the Fe/Mg ratio of olivine and pyroxene can increase by inward diffusion of Fe without disturbance of the Ti^{3+}/Ti^{4+} ratio. The relative rates of Fe and Ti redox equilibration are being investigated experimentally. Initial results [13] show that olivine that crystallized from a chondrule-composition partial melt held at IW-3 at 1400°C and then cooled at 500°C/h to 1078°C at IW-0.5 contains Ti^{3+} and FeO. A representative grain has core-rim zoning in Ti valence from 3.6±0.1 to 3.9±1 and in FeO from Fa_9 to Fa_{37}. This shows that Ti^{3+} can persist while Fe is oxidized. The occurrence of Ti^{3+} in chondrules and in AOAs is consistent with the suggestion that some chondrules could be related to AOAs.

Determination of redox conditions for chondrule formation will require an experimental calibration of the Ti^{3+}/Ti^{4+} ratio in olivine against fO_2 for the assemblages of interest. Temperatures of equilibration of Ti^{3+}/Ti^{4+} and compositions of coexisting phases must be known, as in the calibration of Ti^{3+}/Ti^{4+} in fassaite [14]. The necessary experiments have begun. Preliminary results [13] show that olivine and pyroxene that crystallized at IW-3 from a chondrule-composition melt held at 1400°C for 165 h have Ti valences from 3.3 to 3.7 and 3.3 to 3.6, respectively, so near-solar fO_2s are not necessary to stabilize CAI-like Ti^{3+}/Ti^{4+} ratios in these phases in chondrules. The observed ranges suggest that redox equilibrium was not attained; longer hold times will be used in future experiments.

The lack of Ti^{3+} in Fo-bearing refractory inclusions (FOBs) is not understood. One of the inclusions is an isotopically fractionated (FUN) inclusion, a type thought to have undergone evaporation, so it was probably exposed to oxidizing conditions, but the other FOB is not a FUN inclusion.

The low Ti^{3+}/Ti^{4+} ratios in CV3 spinels are also difficult to account for and will be treated in detail elsewhere [15]. Possible explanations include incorporation of Ti^{4+} from local dissolution of perovskite and growth in an oxidizing environment caused by volatilization of MgO and SiO_2, which dissociate into Mg + O and SiO + O, respectively, when evaporated.

It was concluded by [16] that ordinary chondrites underwent reduction with metamorphism from grade 3 through 4, then oxidization with continued metamorphism, but our results indicate that the most reduced chondrites are of grades <3.6, not ~4. More work on the relative rates of Ti valence equilibration in olivine and pyroxene is needed to understand the variations in the results for these phases in the L chondrite data.

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