CONSTRAINTS ON THE OXIDATION STATE OF CHONDRULE PRECURSORS FROM TITANIUM XANES ANALYSIS OF SEMARKONA CHONDRULES.

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; [3]Enrico Fermi Institute, 5640 S. Ellis Ave.; The University of Chicago, Chicago, IL 60637, USA (sbs8@uchicago.edu).

Introduction: Chondrules are very important because they formed in the solar nebula and are a major component of chondrites, the most common type of meteorite. In unequilibrated chondrites, the ferromagnesian silicates in chondrules exhibit wide ranges of fe# (Fe/(Mg + Fe)). On this basis, chondrules can be divided into type I (fe# <0.1) and type II (fe# > 0.1) [1]. Because a metal must be oxidized to enter a silicate, mafic silicates with low fe#s are inferred to have formed in environments where little oxidized iron was available, implying reducing conditions. Therefore, type I and type II chondrules record different oxidation states. A fundamental question in the study of chondrules is whether this difference was established during chondrule formation, or if it reflects differences in their precursors [1, 2].

Last year [3], we reported the presence of trivalent Ti in refractory forsterite found in the dense fraction of the Tagish Lake CM chondrite. In addition, in the corresponding oral presentation, we reported high Ti^{3+}/Ti^{4+} in refractory forsterite containing 0.4-0.7 wt% FeO, present in a type I chondrule. Even these low FeO contents reflect a much higher f_{O2} than that at which pyroxene with equivalent Ti^{3+}/Ti^{4+} would be stable [4]. This suggests that either: the equilibrium Ti^{3+}/Ti^{4+} is higher in olivine than in pyroxene for a given f_{O2}; or the grains formed under highly reducing conditions and the valence of Ti in chondrule olivine is a robust recorder of the oxidation state of chondrule precursors, not easily reset during chondrule formation.

To improve our understanding of the origin of chondrules we have used XANES (X-ray absorption near edge structure) spectroscopy to measure the valence state of Ti in a type I and a type II chondrule in Semarkona (LL3.0). If olivine from type I chondrules contains Ti^{3+} and that from type II chondrules does not, that would tell us that either their precursors formed under different conditions, or that type IIs were more strongly oxidized during formation. If olivine in type II chondrules contains Ti^{3+}, that would probably mean that the precursors of these chondrules were originally reduced and that oxidation occurred during chondrule formation.

Analytical methods: Chondrules were documented by SEM and analyzed by electron probe. Titanium K XANES spectra were collected using the GSECARS X-ray microprobe in fluorescence mode, with a 3 μm X-ray beam. Valences were determined following the results of [5]. That study demonstrated that Ti K-edge XANES spectra of pure Ti^{4+}-bearing minerals fall into two, distinct valence-coordination clusters on a plot of pre-edge peak intensity *vs.* energy. Those with all Ti in tetrahedral coordination have high intensities and low energies, whereas those with all Ti in octahedral coordination have low intensities and high energies. Any Ti^{3+} present in olivine is expected to be in octahedral coordination, yielding a third data cluster, pre-edge peaks with relatively low intensity and low energy [3]. Titanium valences in unknowns were determined by applying the lever rule to mixing lines for XANES results for standards representing these three endmember occurrences.

Samples: Two porphyritic olivine chondrules in Semarkona thin section USNM 18 were selected for study. Chondrule 18 (CH18), a type I, is ~525 μm in diameter and consists of mostly subhedral olivine, (Fa_{0-8}, avg 1.9), from ~1-200 μm across and low-Ca pyroxene ($Fs_{2.8}$ avg), with round blebs of Fe,Ni metal and overgrowths of Ca-rich pyroxene in a glassy mesostasis. Several olivine grains are "dusty" (rich in fine Fe blebs), and one grain of refractory forsterite ($Fa_{0.2}$, 0.75 wt% CaO) is present.

The type II chondrule, CH8, is a rounded fragment, ~950 x 700 μm, with subhedral olivine (Fa_{9-38}, avg 17.2) 10-300 μm across, enclosed in a mesostasis of glass and fine, skeletal olivine. Most phenocrysts have large, uniform cores of $Fa_{~15}$ and thin, FeO-rich rims.

In both chondrules, single crystals with uniform birefringence and extinction were selected for study. XANES analytical traverses were conducted across grains, and point analyses of small grains and of mesostases were also obtained.

Reference materials with were also analyzed - endmember Ti^{3+}: synthetic $NaTi^{3+}Si_2O_6$, isostructural with acmite [6]; endmember tetrahedral Ti^{4+}: synthetic forsterite produced in air (Ito); endmember octahedral Ti^{4+}: natural titanite; and with octahedral $Ti^{3+}/(Ti^{3+} + Ti^{4+})$ = 0.6: Allende fassaite [7].

Results: Olivine in both chondrules was found to contain Ti^{3+}, but in different proportions and with different spatial distributions. In type I chondrule CH18, there is a strong inverse correlation between grain size and Ti valence in the cores of crystals (Fig. 1). The refractory forsterite (avg Ti valence = 3.12±0.08) and another relatively large olivine grain have high

Ti^{3+}/Ti^{4+} ratios, while among smaller grains the Ti^{3+}/Ti^{4+} ratio decreases with decreasing grain size. The one pyroxene grain analyzed also falls on this trend. Traverses across grains show that, within grains, Ti^{3+}/Ti^{4+} decreases from crystal cores to rims (Fig. 2).

In contrast, in type II chondrule CH8, all grains analyzed have very low Ti^{3+} contents (avg Ti valence 3.7-3.9) regardless of their size (Fig. 1). Traverses across grains in CH8 show that they are unzoned with respect to Ti valence.

In both chondrules, the Ti^{3+} content of the mesostasis is negligible; all titanium occurs as Ti^{4+}.

Discussion. The systematics observed in the data for the type I chondrule (CH18) are precisely what would be expected for oxidation during crystallization. Assuming that smaller grains began crystallizing later than larger ones, they record progressive oxidation of the residual liquid, as do the core-rim trends within grains. Chondrule formation began with highly reduced (possibly relict) crystal nuclei having almost no Ti^{4+} and ended with quenching of a liquid having almost no Ti^{3+}. Other studies have also concluded that type I chondrules formed under open-system conditions [e.g., 8], possibly exchanging with an ^{16}O-poor nebular gas [9] during crystallization.

Most grains in the type II chondrule (CH8) have small Ti^{3+} components, but there is no correlation of Ti valence with grain size or with position within a grain, arguing against oxidation during crystallization. The precursors of CH8 either: were originally more oxidized than those of CH18, yet contained Ti^{3+}; or were originally reduced and became relatively oxidized prior to crystallization, perhaps during melting. The latter case would imply exposure to a strongly oxidizing environment.

Detection of Ti^{3+} in olivine with such high FeO contents, Fa_{15}, suggests that the precursors of CH8 were reduced and that the valence of Ti is more resistant to resetting by oxidation than that of Fe. Experiments are planned in which we will 1) investigate the relative rates of change of Ti^{3+}/Ti^{4+} and Fe^0/Fe^{2+} ratios in chondrule-composition melts at relatively high f_{O2}; and 2) calibrate the Ti^{3+}/Ti^{4+} ratio in olivine as a function of oxygen fugacity.

Also of interest is the dusty olivine in CH18. Does it represent a generation of relatively oxidized precursor grains that underwent reduction and predated the reduced phenocryst cores? In future work we will measure the Ti valence in this dusty olivine.

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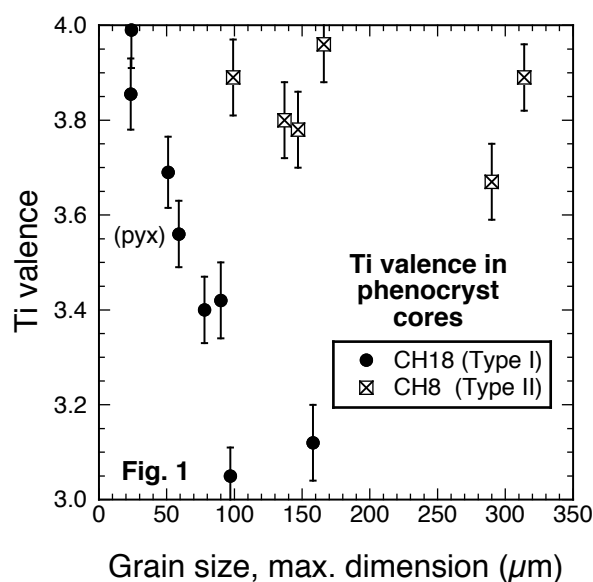

Fig. 1. Plot of Ti valence measured by XANES in crystal cores as a function of grain size. There is a strong inverse relationship in the type I chondrule but not in the type II chondrule. All data are for olivine except for one pyroxene (pyx) grain. Error bars are 1σ.
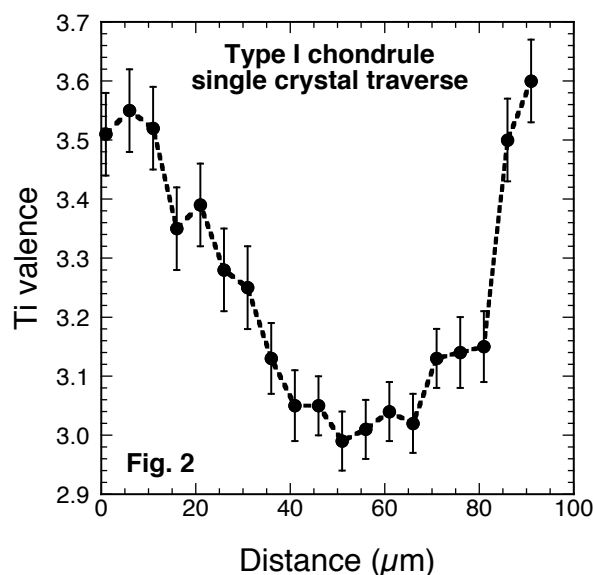

Fig. 2. Results of a XANES traverse from rim to rim across an olivine grain in type I chondrule CH18. Error bars are 1σ.

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