

CHONDRULE-COMPOSITION MELTS: RESPONSE OF Fe AND Ti VALENCE TO CHANGING REDOX CONDITIONS. S. B. Simon¹, J. R. Beckett², W. M. Vaughan¹, S. R. Sutton^{1,3} and L. Grossman^{1,4}, ¹Dept. of the Geophysical Sci., 5734 S. Ellis Ave., Univ. of Chicago, Chicago, IL 60637 (sbs8@uchicago.edu), ²Div. Geol. Planet. Sci., Caltech, Pasadena, CA 91125, ³CARS, Univ. of Chicago, Chicago, IL 60637, ⁴The Enrico Fermi Institute, 5640 S. Ellis Ave., Univ. of Chicago, Chicago, IL 60637.

Introduction: Chondrules in highly unequilibrated chondrites can be classified as either type I [Fe/(Fe+Mg) of olivine and pyroxene <0.1] or type II [Fe/(Fe+Mg) of olivine and pyroxene >0.1] [1]. A major question in the study of chondrule origin is: Did type I and type II chondrules have different precursor assemblages (reduced and oxidized, respectively), or did they have similar source compositions but crystallize in different environments? Detection of Ti³⁺ in type I and type II chondrules in Semarkona [2] suggests that the latter is the case. Trivalent Ti is not expected in FeO-bearing silicates, as stabilization of significant concentrations of Ti³⁺ in these phases likely requires fO_2 s well below the iron-wüstite (IW) buffer where most of the FeO in the silicates would be reduced to metal. Our currently preferred explanation for the presence of Ti³⁺ in the silicates of type II chondrules is that the precursors formed in a reducing environment, such as a solar gas, but that cooling following the chondrule melting event occurred in a relatively oxidizing environment, with Fe undergoing redox equilibration more rapidly than Ti. This is the first report on a series of experiments we are conducting to test this idea.

Methods. Powdered aliquots of New Concord (L6) were used as an analog to a type IIA (olivine-rich) chondrule composition. Powders were melted on Fe loops in a gas-mixing furnace and held at 1400°C and three log units below IW (IW-3). A set of 24-165 h isothermal runs was obtained for characterization of the assemblage at 1400°C. Dynamic crystallization experiments were initially held at 1400°C and IW-3 for a 15-24 h “soak” at those T- fO_2 conditions to allow devolatilization (Na, S, K) and at least partial crystal/liquid equilibration, followed by cooling at 10-1000°C/h in a constant composition H₂-CO₂ gas whose fO_2 was set equal to that of IW-0.5 at 1400°C, except for one cooled at IW-3. Quench temperatures ranged from 709 to 1296°C. The fO_2 of both the IW-0.5 and IW-3 gases were checked before and after each run using an SIRO2 oxygen sensor. Run products were mounted in epoxy, polished, documented with a scanning electron microscope and analyzed by electron probe (EMP). Valence of Ti in olivine, pyroxene and glass was determined directly by X-ray absorption near edge structure (XANES) spectroscopy as previously described [3].

Sample descriptions. In polished section, New Concord is dominated by olivine (Fa₂₄₋₂₈ with 0.02 wt% CaO) and low-Ca pyroxene (pyx, Fs₂₁), with minor high-Ca-pyx (En₄₇Wo₄₅Fs₈), feldspar (Ab₈₃An₁₁Or₆), metal and sulfide. Isothermal experiments run at 1400°C and IW-3 consist of rounded to subhedral olivine (Fa₂, 0.15 wt% CaO) and low-Ca pyx (Fs₂), and metal blebs in a glass matrix. Olivine in the IW-0.5 dynamic cooling runs is normally zoned, with Mg-rich cores and Fe-rich rims, even in the 1000°C/h run. Rims of Fa₃₅₋₄₀ with ~0.25 wt% CaO are typical. The run cooled at 10°C/h and IW-0.5 has weakly zoned olivine (Fa~40-45, CaO 0.2-0.4 wt%). Olivine in the one cooled at IW-3 has a very narrow range of Fa contents (2.8-4) with CaO ranges

similar to those of grains in the IW-0.5 runs. Pyroxene (enstatite and minor Al-diopside) occurs in runs cooled to below 1100°C before quenching. Glass compositions become increasingly CaO-, Al₂O₃-rich and FeO-poor with decreasing quench temperature.

Ti valence. Glass, representing quenched residual liquids, has a Ti valence within error of 4 in all the runs cooled at IW-0.5, but in the run cooled at IW-3 it is 3.49±0.07. The lowest Ti valences in both olivine (3.25±0.06) and pyx (3.31±0.07) are found in the run held for 165 h at 1400°C and IW-3. Valence ranges found for olivine and pyx in the cooling runs are given in Table 1. The highest valence in pyx (3.69±0.10) is found in the run cooled at 100°C/h to 800°C at IW-0.5, although that run also yielded pyx with a Ti valence of 3.30±0.07, unchanged from the IW-3 starting condition. Ti valence in olivine in that sample ranges from 3.44±0.07 to 4. In general, olivine tends to have higher valences than pyx in the run products and in the New Concord meteorite (ol, 4.08±0.10; pyx, 3.68±0.13). It should be noted, however, that the synthetic olivine is finer-grained than the pyroxene, and some Ti valences in run product olivine may be overestimated due to contribution from adjacent glass.

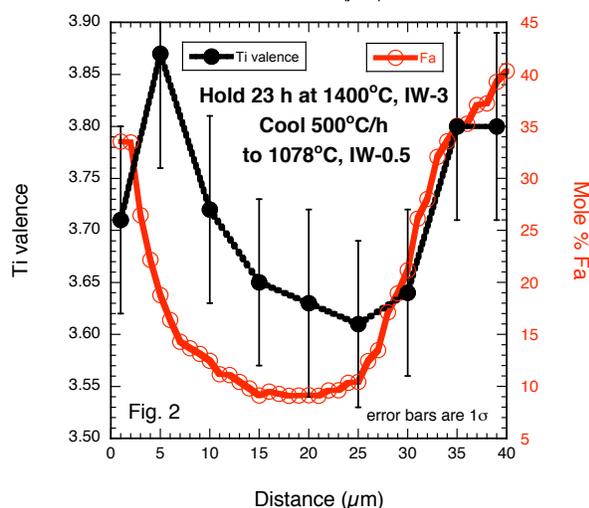
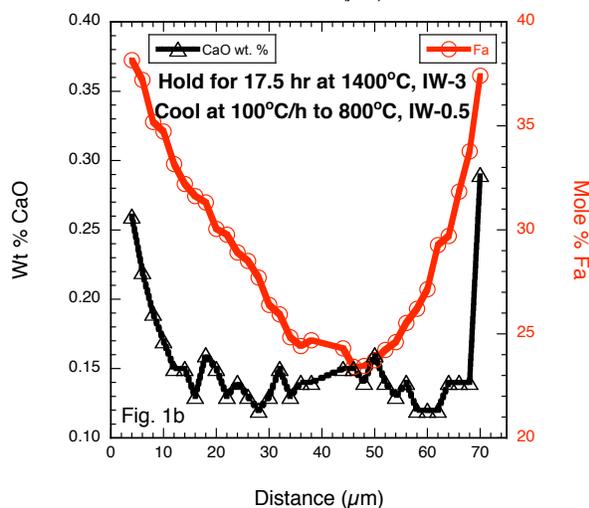
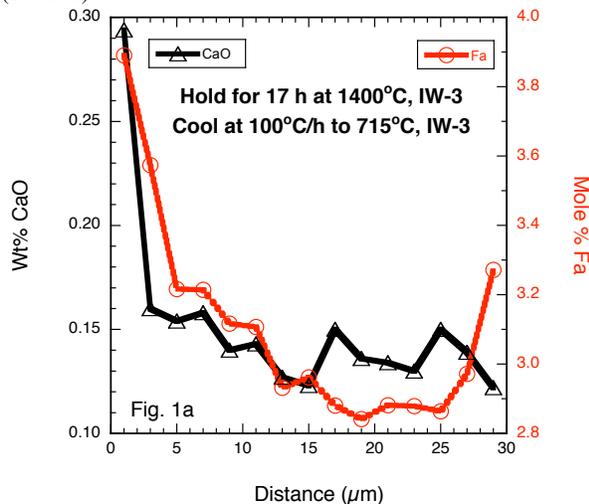
Table 1. Ti valence ranges in cooling experiments.

Cool rate, °C/h	Quench T, °C	Ti valence range, ol	Ti valence range, pyx
1000	821	3.87±0.09-4.06±0.11	3.50±0.07-3.68±0.08
500	1078	3.61±0.08-3.87±0.11	3.49±0.09 (one analysis)
100	1296	3.78±0.08-4.19±0.12	
100	800	3.44±0.07-4.14±0.12	3.35±0.07-3.69±0.10
10	709	3.84±0.10-3.93±0.11	
100 (IW-3)	715	3.56±0.07-3.62±0.07	3.40±0.07-3.63±0.07

Figure 1 shows the results of two electron probe traverses: one across a grain in a run cooled at 100°C/h to 715°C at IW-3 (Fig. 1a), and another from a run cooled at 100°C/h to 800°C at IW-0.5 (Fig. 1b) after being initially held at IW-3. The run cooled at IW-3 reflects fractional crystallization alone whereas zoning in the IW-0.5 run records fractionation and oxidation. Note the factor of ten difference in the Fa scales. The contrast between the very weak zoning of olivine grown at IW-3 (Fig. 1a) and the strong zoning in Fa but not in CaO in the IW-0.5 olivine (Fig. 1b) suggests that much of the range in fayalite content seen in the IW-0.5 runs is due to oxidation of Fe rather than fractionation.

We have thus far performed both XANES and electron probe traverses across one olivine grain (Fig. 2). This run was cooled at 500°C/h from 1400 to 1078°C at IW-0.5 after a 23 h soak at IW-3. The grain is zoned in composition from Fa₉ (core) to Fa₃₇ (rim), in CaO from 0.14 to 0.23 and in Ti

valence from 3.61 ± 0.08 to 3.87 ± 0.11 . Count rates for Ca, obtained during XANES analysis, show that signal contribution from adjacent glass is minor and that the core-rim variation in valence is real. Individual point analyses of olivine in other run products show that Ti valence in olivine reaches 4 in most of the IW-0.5 runs but not in the run cooled at IW-3 (Table 1).



Discussion. Experimental results. It is notable that the Ti^{3+} -bearing olivine and pyroxene in the isothermal runs are not FeO-free, but contain ~ 2 mol% of the Fe endmember component. Thus, such grains found in chondrules may not have had multistage histories. On the other hand, the experiments further suggest that fayalitic olivine that contains Ti^{3+} (e.g. Fig. 2) likely did have a two-stage history, with exposure to both reducing and oxidizing conditions. It is clear from this work that Fe readily begins oxidizing to FeO upon exposure to an IW-0.5 atmosphere. Cores of synthetic olivine grains cooled at different $f\text{O}_2$ s exhibit a wider range of Fa contents than is consistent with their uniformly low CaO contents. Occurrence of relatively fayalitic olivine with low CaO contents (e.g. Fig. 1b) suggests that oxidation occurred very early, prior to extensive fractionation. Ti valence in olivine in the two shortest-duration runs (~ 35 min-cooling at $1000^\circ\text{C}/\text{h}$ to 821°C ; and ~ 1 hour-cooling at $100^\circ\text{C}/\text{h}$ to 1296°C) reach values within error of 4.0. These rates are not directly applicable to chondrule formation, however, because experiments were conducted at 1 atm total pressure; at solar nebular pressures, $\leq 10^{-3}$ atm, reactions would likely be much slower.

Analysis of the run products and the New Concord meteorite shows that the valence of Ti in low-Ca pyx in a chondritic system at IW-3 is similar to that of fassaite found in refractory inclusions, and even at 1 atm the valence of Ti in pyx did not change significantly during cooling at IW-0.5.

Another difference between the IW-3 and the IW-0.5 runs is Ti valence in the glass. In the former it is reduced while in the latter it is within error of 4, or very nearly so, in all cases, despite coexistence with cogenetic Ti^{3+} -bearing phases. Either Ti was progressively oxidized during cooling, reaching a valence of 4 regardless of run time, or electron exchange reactions occurred in the liquid upon quenching, analogous to those observed by [4]. There is a known tendency in Fe-bearing liquids for Fe to donate or receive electrons such that the valence of each of the minor element multivalent cations converges to a single value. This did not occur at IW-3 because there was insufficient Fe^{3+} available for exchange.

Conditions of chondrite metamorphism. The valence of Ti in New Concord olivine indicates that it equilibrated at an $f\text{O}_2 > \text{IW-3}$, assuming curves of $\log f\text{O}_2$ relative to IW vs. T are concentric for different Ti valences in olivine. With additional experiments, and measurements on natural chondrites of different metamorphic grades, quantitative constraints can be placed on temperatures and $f\text{O}_2$ s of chondrite metamorphism.

Conclusions. 1) Much of the Ti in a chondritic melt is trivalent at IW-3. 2) Ti^{3+} -bearing, fayalitic olivine can form in a two-stage process in which a reduced precursor assemblage is melted and then cooled in a relatively oxidizing environment. 3) The valence of Ti in precursor pyroxene experiencing such a history would likely change little, providing evidence of its formation in a reducing environment. 4) A Ti valence of 4 in a chondrule glass is not a reliable indicator of the $f\text{O}_2$ of its formation.

References: [1] Hewins R. H. (1997) *Ann. Rev. Earth Planet Sci.*, 25, 61–83. [2] Simon S. B. et al. (2008) *LPS XXXIX*, Abstract #1352. [3] Simon S. B. et al. (2007) *Geochim. Cosmochim. Acta*, 71, 3098–3118. [4] Berry A. J. et al. (2003) *J. Synch. Rad.*, 10, 332–336.