

EXPERIMENTAL INVESTIGATION OF Ti and Fe VALENCE IN CHONDRULE-LIKE MELTS DURING COOLING UNDER CHANGING REDOX CONDITIONS AT LOW PARTIAL PRESSURES. S. B. Simon¹, J. R. Beckett², 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; ⁴The Enrico Fermi Institute, 5640 S. Ellis Ave., Univ. of Chicago, Chicago, IL 60637.

Introduction: Detection of Ti^{3+} in type I (Fe/(Fe+Mg) of olivine and pyroxene <0.1) and type II chondrules (Fe/(Fe+Mg) of olivine and pyroxene >0.1) [1] in Semarkona suggests that both chondrule types had reduced precursors [2]. Trivalent Ti is not expected to occur in FeO-bearing silicates, as the Ti_2O_3 - TiO_2 (pure oxide) buffer lies at oxygen fugacities (fO_2 s) ~ 5 log units below the iron-wüstite (IW) buffer, in a regime where most of the Fe in a system would occur as metal. Our currently preferred explanation for the presence of Ti^{3+} in the olivine and pyroxene of type II chondrules is that their 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 the valence of Fe equilibrating more rapidly than that of Ti. This idea is being tested experimentally. Initial results were reported by [3]; here we report results for a second set of experiments.

Methods: In [3], the reactant gas species (H_2 , CO_2) were at 1 atm total pressure, much higher than nebular conditions, so the observed results and inferred reaction rates were not directly applicable to natural chondrules. Thus, in the present work, the reactive H_2 - CO_2 mix has been diluted to ~ 0.02 atm with an inert gas (Ar) to simulate more closely nebular partial pressures of reactive species. Also, here the starting materials were synthesized from pure oxides of the major and minor elements rather than natural meteoritic material. The bulk composition used is that of the liquid phase of a pyroxene + olivine + liquid system of New Concord (L6 chondrite) composition at 1400°C. Powders were melted on Fe loops. Three runs are reported here: an isothermal run (I6) at 1400°C for 66 h at 2.75 log units below the IW buffer (IW-2.75); a run (C2) held for 72 h at 1386°C and IW-3.7 and then cooled at 100°C/h to 980°C in the same gas composition; and one (C3) held for 72 h at 1386°C and IW-2.5 and then cooled at 100°C/h to 1000°C at IW-0.48. The fO_2 s of the initial and final gases were checked before and after each run using an SIRO2 oxygen sensor. Run products were mounted in epoxy, polished, observed with the 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 using methods previously described [4,5].

Sample descriptions: The isothermal sample (I6) consists of green glass. No crystals are visible in the section, and EMP analyses show no evidence of ol or pyx fractionation. The charge gained FeO, containing 5.7 wt% FeO rather than the nominal 3.1 wt%. The run cooled under very reducing conditions (C2) has vesicles, abundant, prismatic opx ($Fs_{1.4}$) grains ~ 50 μm across, olivine ($Fa_{1.6}$) hopper crystals and laths, and metal blebs 10-20 μm across in a glass matrix. The run cooled under oxidizing conditions (C3) also has skeletal opx ($Fs_{2.8}$) and olivine laths ($Fa_{2.4}$) in a glass matrix. Thus, the silicate minerals and the glass in C3 are slightly more FeO-rich than their counterparts in C2. The glass in C2 is, however, more CaO-rich than that in C3, and the C2 section contains more crystals than C3, indicating that the former has undergone more extensive crystal/liquid fractionation than the latter. Unfortunately the crystals in both C2 and C3 are too small for definitive measurement of zoning profiles.

Results: Measurements of Ti valence in the run products are presented in Table 1. The isothermal run is the most oxidized of the materials, with an average Ti valence of 3.7 ± 0.1 . Not surprisingly, C2, the run held and cooled at IW-3.7, is the most reduced. In it both olivine and pyroxene have an average Ti valence of 3.2 ± 0.1 . The Ti in the glass in C2 averages 3.4 ± 0.1 , slightly higher than the crystalline phases. Run C3, held at IW-2.5 and cooled under oxidizing conditions, is more oxidized than C2 but it does not appear to have extensively reacted with the ambient gas during cooling. One C3 pyroxene grain has a Ti valence of 3.9 ± 0.1 , but the others range from 3.53 to 3.66, averaging 3.6 ± 0.1 , olivine averages 3.5 ± 0.1 and the glass has a similar Ti valence, 3.6 ± 0.1 . The XANES results are consistent with the SEM observations, which show that the pyroxene and olivine crystals do not exhibit strong core-to-rim increases in FeO. This is quite unlike our previous results [3], in which olivine in a run cooled at 100°C/h at IW-0.5 after being held at IW-3 did show strong zoning, e.g., from Fa_{22} (core) to Fa_{37} (rim).

In C2 the olivine and pyroxene contain very little Ti^{4+} , and consequently low proportions of tetrahedrally coordinated (tet) Ti, but most of the Ti^{4+} is in tet sites (Table 1). High proportions of the Ti^{4+} in C3 are in tet sites as well. This contrasts with meteoritic fassaite from refractory inclusions, in which both Ti^{3+} and Ti^{4+} are in octahedral sites, with no tet Ti [6]. This differ-

ence in Ti^{4+} behavior is probably due to the much greater availability of Al (for coupled substitution with Ti^{4+}) during CAI formation. CAIs typically contain about three times as much Al_2O_3 as the run products, ~30-35 wt% [7] vs. ~10 wt%. Tet Ti values are calculated assuming there can only be tet and oct coordination, but 5-fold coordination may also be possible in glass, so the glass tet Ti values should be considered upper limits.

Discussion: These initial results indicate, as we suspected, that the previous experiments had much higher reaction rates than would be relevant to the low ambient pressures of the solar nebula. Run C3, which cooled in a constant gas composition that started at IW-0.5, underwent little oxidation because the partial pressures of the oxidizing gas species were decreased by a factor of ~50 by dilution with Ar. This is ~20x the nominal nebular total pressure, yet neither the Fe nor the Ti in the charge equilibrated with the surrounding gas. Additional experiments will investigate different combinations of cooling rates and partial pressures of reactant species in a search for conditions under which iron would oxidize while preserving Ti^{3+} during chondrule crystallization.

Over the last few years, exhaustive attempts have been made to find possible conditions, thermal histories, etc. that, in a nebular setting, can account for the FeO contents of olivine in chondrules [e.g., 8-10]. These have been largely unsuccessful, and along with absences of isotopic fractionation and Na loss that would result from evaporation during melting of chondrule precursors in a nebular setting have lead to serious consideration of impact plumes as a chondrule-forming environment [11]. The present observations further illustrate the difficulties in forming FeO-bearing chondrules in a low-pressure, nebular environment. Given the high cooling rates that chondrules underwent, they may not have been molten long enough for the Fe present to oxidize and enter olivine even if sufficiently oxidizing conditions were attained. Ambient pressures higher than those expected for the nebula may be needed for both Fe oxidation and suppression of evaporation of Mg, Si and Na.

The present results also show that, at least in these chondrule-composition melts, solar fO_2 s of ~IW-7 [12] are not necessary for generation of high Ti^{3+}/Ti^{tot} ratios in olivine and pyroxene. In run C2, at IW-3.7, 80-90% of the Ti in these phases is trivalent (Table 1). These are higher proportions than are found in the fassaite of refractory inclusions, which have been found to be quantitatively consistent with crystallization at solar fO_2 s [12]. It is not yet understood why, unlike C3, the olivine and pyroxene in C2 have higher Ti^{3+}/Ti^{4+} ratios than the coexisting glass.

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. (2011) *LPS XLII*, Abstract #1271. [4] Simon S. B. et al. (2007) *GCA* 71, 3098-3118. [5] Berry A. J. et al. (2003) *J. Synch. Rad.*, 10, 332-336. [6] Dowty E. and Clark J. (1973). *Am. Min.* 58, 230-242. [7] Grossman L. et al. (2000) *GCA* 64, 2879-2894. [8] Fedkin A. and Grossman L. (2004) *LPS XXXV*, Abstract #1823. [9] Fedkin A. and Grossman L. (2006) *MESS II*, 279-294. [10] Grossman L. et al. (2012) *MAPS* 47, 2160-2169. [11] Fedkin A. and Grossman L. (2013) *GCA* 112, 225-250. [12] Grossman L. et al. (2008) *RiMG* 68, 93-140.

Table 1. XANES analyses of run products.

	Ti Valence	1 σ	Tet %
C2			
A3 GL1	3.50	0.08	29
A4 GL2	3.46	0.08	26
A1 GL1	3.39	0.07	23
A2 GL1	3.38	0.07	24
GL mean	3.43	0.06	26
A3 PX1	3.34	0.07	19
A1 PX1	3.11	0.06	12
A2 PX1	3.12	0.06	12
A2 PX2	3.25	0.06	15
A3 PX4	3.22	0.05	4
A1 PX2	3.14	0.06	12
A1 PX3	3.12	0.06	12
PX mean	3.19	0.09	12
A4 OL1	3.07	0.05	7
A4 OL2	3.10	0.05	5
A1 OL1	3.31	0.06	23
OL mean	3.16	0.13	12
C3			
A3 GL1	3.55	0.07	25
A3 OL3	3.56	0.08	27
A1 GL3	3.67	0.08	24
GL mean	3.59	0.07	25
NPYX8	3.64	0.08	31
NPYX8	3.66	0.08	29
NPYX7A	3.65	0.09	34
NPYX7B	3.53	0.08	33
NPYX6	3.91	0.12	46
A1PYX4	3.55	0.08	33
NPYX8B	3.61	0.08	29
PX mean	3.64	0.05	34
A1 OL1	3.47	0.08	29
OL10	3.52	0.08	27
OL11	3.43	0.08	27
A1 OL2	3.48	0.09	39
OL mean	3.48	0.05	31
I6			
Chip A	3.71	0.07	21
Chip B	3.77	0.08	25