EFFECTS OF METAMORPHISM ON THE VALENCE AND COORDINATION OF TITANIUM IN ORDINARY CHONDRITES.

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Introduction: Despite years of study, the conditions under which ordinary chondrites were metamorphosed from grade 3 to grade 6 are not well defined. Wide ranges of peak temperature are inferred for each grade [e.g. 1]. The long-popular "onion shell" model, in which higher metamorphic grade is attributed to greater depths of origin, implies a corresponding decrease in cooling rate with increasing grade, and there is disagreement as to whether or not this is observed [2]. Redox conditions during chondrite metamorphism are also not well understood. Some workers have reported evidence for reduction, presumably by carbon, with increase in grade from 3-4, followed by oxidation during metamorphism to higher grades [3, 4], but other work [5] indicates little variation in fO_2 as a function of metamorphic grade.

During our investigation of the valence of Ti in planetary materials, we found high proportions of Ti^{3+} in olivine and pyroxene in chondrules in Semarkona (LL3.0) [6] and low proportions in New Concord (L6) olivine [7], suggesting that Ti was oxidized during ordinary chondrite metamorphism. We have undertaken a study of L and LL chondrites of grades 3-6 to see how Ti valence and coordination vary with grade and to see if the variations can be used to constrain conditions of chondrite metamorphism.

Methods: Suites of chondrules comprising the main petrographic types were selected for study based on examination of thin sections with the scanning electron microscope. Chondrules were classified by petrographic type based on backscattered electron imaging and quantitative energy dispersive analysis, except for the highest-grade sample (L6), in which discrete chondrules were not identified. The L chondrite suite, from lowest to highest grade, consists of LEW86158 (3.0); LEW86505 (3.4); ALHA81025 (3.6); ALHA84086 (3.8); EET87557 (4); and New Concord (6). The LL suite, all falls, consists of Semarkona (3.0); Bishunpur (3.15); Chainpur (3.4); Parnallee (3.6); Hamlet (4) and Olivenza (5). Valence of Ti in olivine, pyroxene and mesostasis, reported as values between 3 and 4, was determined directly by X-ray absorption near edge structure (XANES) spectroscopy using methods previously described [8]. Spots in olivine analyzed by XANES were found by electron microprobe to contain ≤0.1 wt% TiO_2. Typically 2-4 chondrules per sample were analyzed.

Results: Most of the chondrules analyzed are porphyritic, as barred and radial chondrules tend to be too fine-grained for XANES analysis. Valence measurements as a function of metamorphic grade, both individual analyses and their averages, are illustrated in Fig. 1 (L chondrites) and Fig. 2 (LLs). Mesostasis values (not shown) in a Semarkona chondrule range from 3.4±0.1 to 4.2±0.1, and all other mesostasis analyses are within that range.

L chondrites. Ranges in valence are seen in all grades. The average valence of Ti in olivine decreases from 4.0±0.1 to 3.7±0.1 with increase in grade from 3.0 through 3.6, and it is 3.9±0.1 in the L3.8, and 3.9±0.2 in the L4 and L6 samples.

Pyroxene valences average 3.59±0.04, 3.6±0.1 and 3.4±0.2 in the grades 3.0, 3.4 and 3.6 samples, respectively, and 3.9±0.2, 3.8±0.2 and 3.7±0.2 in the L3.8, L4 and L6 samples.

LL Chondrites. Olivine and pyroxene with high proportions of Ti^{3+} are found in Semarkona (LL3.0). Pyroxene with reduced Ti is also found in Bishunpur (LL3.15) but not in higher-grade samples (Fig. 2). Unlike the L chondrites, in which the average valence in both olivine and pyroxene decreases, increases, and levels off with increasing grade, in the LL chondrites average olivine and pyroxene valences exhibit different trends from each other. Valence increases, decreases, and levels off in olivine, while the average valence in pyroxene increases with grade.

The range of valences observed does not significantly decrease with increasing grade except for the absence of valences <3.3 in LL chondrites in grades ≥3.4. Wide ranges of Ti valence are seen, even in the grade 4-6 samples. Within most chondrules, pyroxene tends to have higher Ti^{3+}/Ti^{4+} than coexisting olivine. Very Ti^{3+}-rich olivine and pyroxene are only found in Type I (Mg-rich) chondrules, but otherwise there is no correlation between Ti valence and fayalite or ferrosilite content.

The only systematic change with grade seen in both olivine and pyroxene, despite wide ranges in the individual measurements, are much higher average tetrahedral Ti^{4+} proportions (mostly 40-70%) in grades ≥3.6 than in the lower-grade samples (10-30%). In olivine in both the Ls (Fig. 3) and LLs (Fig. 4), these increases come at the expense of octahedral Ti^{4+}, but in pyroxene, tetrahedral Ti^{4+} is instead anticorrelated with Ti^{3+}.

Discussion: The ranges of Ti valence seen in equilibrated (grades 4-6) chondrites, EOCs (Figs. 1 and 2), clearly show that Ti did not attain redox equilibrium even in the highest-grade samples, which have uniform Fe/Mg ratios. The EOCs must have equilibrated with respect to Fe/Mg partitioning under conditions where FeO was stable. On the other hand, they have metal and modest proportions (up to 50%) of Ti^{3+}. In a study of H4-6 chondrites, [5] found fO_2s from 2.2 to 2.6 log units below IW for equilibration temperatures between 740 and 990°C. Such fO_2s seem reasonable for the L and LL chondrites as well, although the valence of Ti has not been calibrated against fO_2 for olivine and pyroxene in chondrule-like compositions. In a melt of L chondrite composition at IW-3, about half of the Ti is trivalent [7]; analyses of L and LL chondrite Ti average ~20% trivalent and most analyses show <50% (Fig. 1, 2), probably consistent with an fO_2 slightly higher than IW-3.

Proportions of tetrahedral Ti^{4+} are higher than those of octahedral Ti^{4+} in grades 3.8-6 L chondrites (3.6-5 in analyzed LLs), and are lower than oct Ti^{4+} in grades 3-3.6 Ls and in 3-3.4 LLs. Substitution of Ti into an octahedral site can occur along with substitution of hydrogen, which bonds with oxygen in the lattice to form hydroxyl groups [9]. The charge excess created by Ti^{4+} in an octahedral site is balanced by an adjacent Si-site vacancy coordinated with two O

anions and two OH⁻ groups. This mechanism has been shown to occur under hydrous conditions, where water is the hydrogen provider. Although chondrules likely formed in gases having higher H_2O/H_2 ratios than a gas of solar composition [10], H_2 was still abundant. It is possible, though not experimentally demonstrated, that either molecule may have been the source of hydrogen for coupled substitution of Ti^{4+} into the octahedral site of olivine. Under anhydrous conditions, substitution of Ti^{4+} into the tetrahedral site of olivine is energetically favored over other coupled substitutions [11]. The observation of increasing tet Ti^{4+}/oct Ti^{4+} ratios with increasing grade is consistent with diffusive loss of hydrogen during metamorphism and entry of Ti^{4+} into adjacent tetrahedral vacancies, presumably accompanied by entry of Mg or Fe cations into the vacated octahedral sites. Theoretical and experimental investigation of this process as a function of time and temperature could provide important constraints on L and LL chondrite thermal histories.
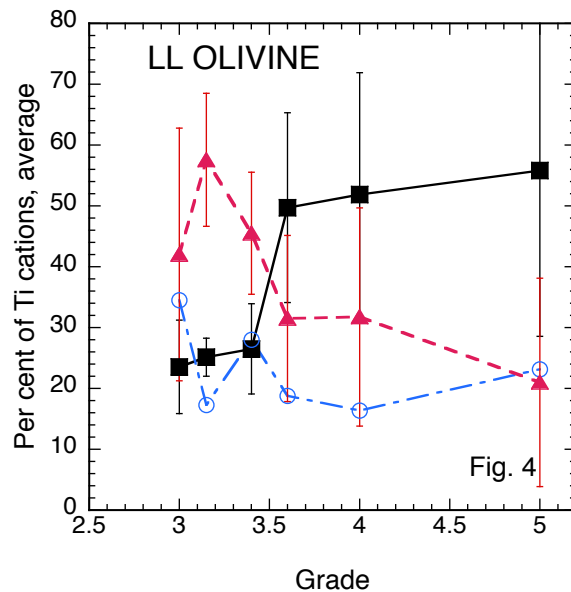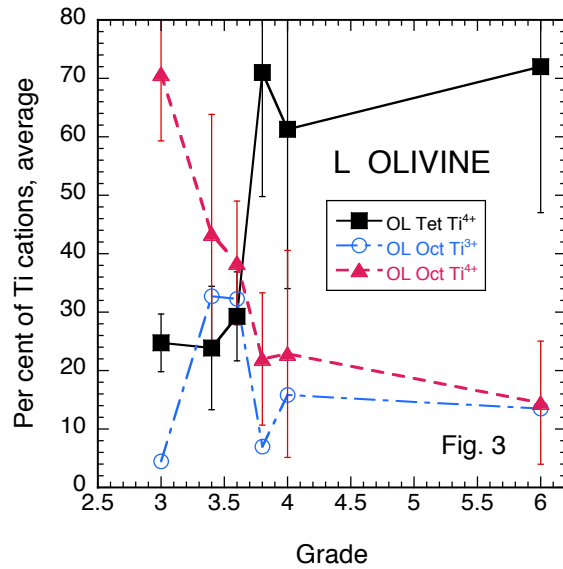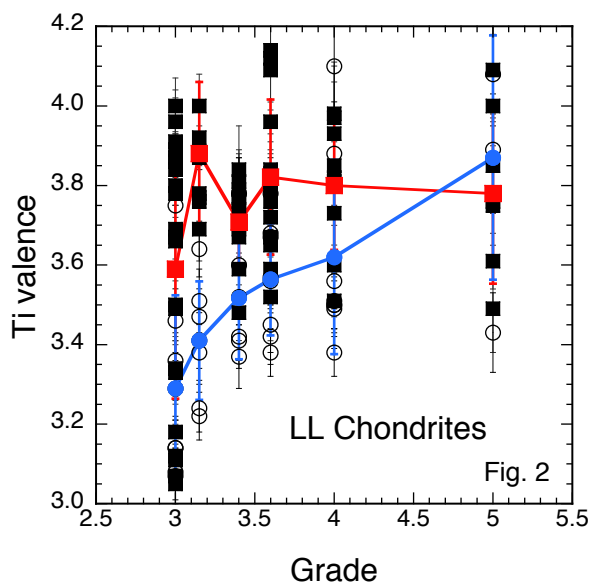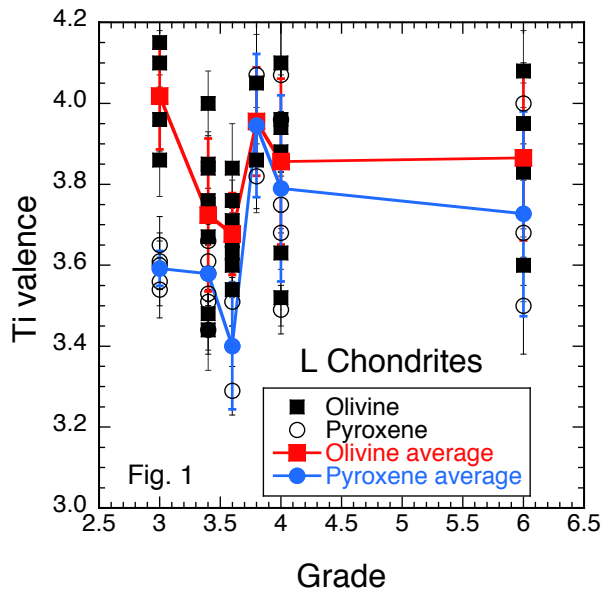
Fig. 1

Fig. 2

Fig. 3

Fig. 4

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