

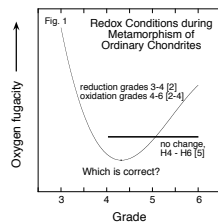
Effects of Metamorphism on the Valence and Coordination of Titanium in Ordinary Chondrites

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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. Estimates of peak temperatures range from 500-800°C for types 4 and 5, and from 800-1000°C for type 6 [1]. Redox conditions during chondrite metamorphism are also not well understood. As illustrated schematically (after [2]) in Fig. 1, it has been suggested that reduction of iron, presumably by reaction with carbon, occurred with increase in grade from 3-4 [2], followed by oxidation during metamorphism to higher grades [2-4], but a study of H chondrites by [5] showed no systematic variation in f_{O_2} as a function of metamorphic grade in the 4-6 range.



The discoveries of high proportions of Ti^{3+} in olivine and pyroxene in Semarkona (LL3.0) chondrites [6] and low proportions in New Concord (L6) olivine [7] suggest 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

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. Valence results were determined following the methods of [8] and are reported as values from 3 to 4, representing the average Ti valences of the analytical volume.

Samples

The sample suite is listed in Table 1 and representative images are shown in Fig. 2. Typically 2-4 chondrules per sample were analyzed, except for the grade 6 samples, in which discrete chondrules were not identified (e.g., Fig. 2d). Chondrules were classified by petrographic type based on backscattered electron imaging and quantitative energy dispersive analysis. Most of the chondrules analyzed are porphyritic, as barred and radial chondrules tend to be too fine-grained for XANES analysis of pure phases.

Table 1. Sample suite and their petrologic grades		
Grade	L chondrites	LL chondrites
3.0	LEW86158	Semarkona
3.15	—	Bishunpur
3.4	LEW86505	Chainpur
3.6	ALHA81025	Parnallee
3.8	ALHA84086	LAR06674
4	EET87557	Hamlet
5	Park Forest	Olivenza
6	New Concord	St. Severin

References

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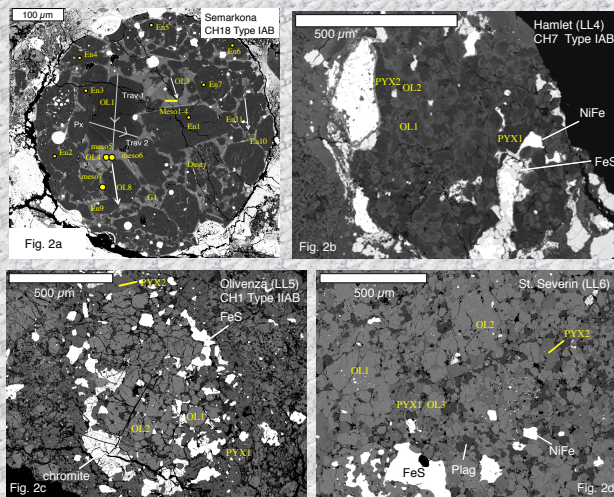


Fig. 2. Backscattered electron images of LL3-6 chondrites illustrating textural changes with grade and showing locations of XANES analysis spots (yellow). Arrows indicate analytical traverses. Brightness of a mineral is proportional to the average atomic number of the elements in it. (a) Semarkona (LL3.0) type IAB chondrule. (b) Hamlet (LL4) type IAB chondrule. (c) Olivenza (LL5) type IAB chondrule. (d) St. Severin (LL6) chondrule. Abbreviations: OL: olivine; PYX: pyroxene; En: enstatite; meso: mesostasis; Plag: plagioclase; G: glass.

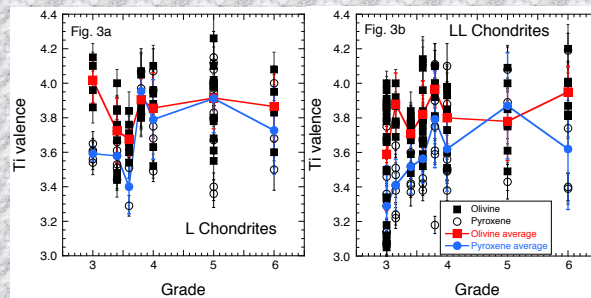


Fig. 3. Plots of Ti valence determined by XANES, as a function of petrologic grade in (a) L chondrites and (b) LL chondrites. Wide ranges are seen in all samples. Lines connect averages for olivine (red squares) and pyroxene (blue circles). Error bars are 1 σ .

Results: Ti valence

General: Wide ranges of valence are seen within most samples, even those of grades 4 – 6. Pyroxene generally has lower average valences (higher Ti^{3+}/Ti^{4+}) than olivine in most samples, especially in the low-grade ones (Fig. 3). Within most chondrules, pyroxene tends to have higher Ti^{3+}/Ti^{4+} than coexisting olivine. Very Ti^{3+} -rich olivine and pyroxene grains are only found in type I (Mg-rich) chondrites in low-grade LL samples, but otherwise there is no correlation between Ti valence and fayalite or ferrosilite content.

L chondrites: 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, L5 and L6 samples. Average Ti valences in pyroxene are also lowest in grades 3.0 – 3.6: 3.59 ± 0.04 (L3.0); 3.6 ± 0.1 (L3.4); 3.4 ± 0.2 (L3.6), and close to 4 in the higher grades: 3.9 ± 0.2 (L3.8); 3.8 ± 0.2 (L4); 3.9 ± 0.2 (L5) and 3.7 ± 0.2 (L6).

LL chondrites: The range of valences does not significantly decrease with increasing grade except for the near-absence of valences <3.3 in grades ≥ 3.4 . Semarkona (LL3.0) olivine has the lowest average valence, 3.6, with a large standard deviation because individual measurements span a wide range, from 3.05 ± 0.06 to 4.00 ± 0.07 . Other average valences in olivine range from 3.7 ± 0.1 (LL3.4) to 4.0 ± 0.1 (LL3.8). The average valence in pyroxene increases with grade more smoothly than in the Ls. It is lowest in Semarkona, 3.3 ± 0.2 , and highest in Olivenza, 3.9 ± 0.4 .

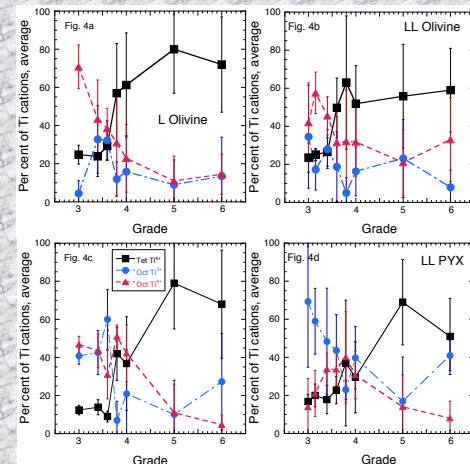


Fig. 4. Average percentages of octahedrally coordinated and tetrahedrally coordinated Ti in olivine and pyroxene in L and LL chondrites as a function of metamorphic grade. Note increase in tetrahedral Ti^{4+} and decrease in octahedral Ti^{4+} with increasing grade in both phases in L and LL chondrites. a) Olivine in L chondrites. b) Olivine in LL chondrites. c) Pyroxene in L chondrites. d) Pyroxene in LL chondrites.

Results: Ti coordination

Similar trends in average percentages of octahedrally coordinated and tetrahedrally coordinated Ti in olivine and pyroxene are seen with increasing grade in both L and LL chondrites despite wide ranges in individual measurements that cause large standard deviations in the averages (Fig. 4). The average tetrahedral Ti^{4+} proportions are much higher (mostly 40 – 70% in grades ≥ 3.8 than in the lower-grade samples (10 – 30%). In olivine in both the Ls (Fig. 4a) and LLs (Fig. 4b), these increases come mainly at the expense of octahedral Ti^{4+} , but in pyroxene (Figs. 4c, d), tetrahedral Ti^{4+} proportions are instead more strongly anticorrelated with Ti^{3+} proportions.

Discussion

Measurements on these suites of L and LL chondrites show that internal variation in Ti valence in olivine and pyroxene persists to metamorphic grades at which Mg/Fe ratios are equilibrated. These results and analyses of chondrules [6] show that the Ti valence of olivine and pyroxene is not easily reset.

In forsterite, high proportions of tetrahedral Ti^{4+} have been associated with formation under anhydrous conditions, where direct substitution of Ti^{4+} for Si^{4+} is energetically favored over other substitutions [9]. In contrast, substitution of Ti^{4+} into octahedral sites in olivine tends to occur along with substitution of hydrogen, which bonds with oxygen in the lattice to form hydroxyl groups.

The charge excess resulting from substitution of Ti^{4+} for a divalent cation is balanced by an adjacent Si-site vacancy coordinated with two O^{2-} anions and two OH groups [10] instead of four O^{2-} anions. The H_2 -rich environment in which chondrules formed could have favored this substitution mechanism. The decrease in octahedral Ti^{4+} proportions with increasing grade would then be explained by H loss from olivine during metamorphism accompanied by filling of Si-site vacancies by Ti^{4+} .

The results for pyroxene are not yet understood. The relatively high proportions of tetrahedral Ti^{4+} are surprising, because fassalite in refractory inclusions has only octahedrally coordinated Ti [11,12]. The decreasing proportions of Ti^{3+} with increasing grade from 3 to 4 suggest oxidation occurred, and they imply a mechanism different from that which occurred in olivine.

Conclusions

- Ordinary chondrites retain Ti^{3+} through grade 6. The valence of Ti is not as easily reset as that of Fe.
- The observation of increasing tetrahedral Ti^{4+} /octahedral Ti^{4+} ratios in olivine with increasing grade is consistent with diffusive loss of hydrogen during heating and entry of Ti^{4+} into adjacent tetrahedral vacancies.
- 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.

Acknowledgments

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