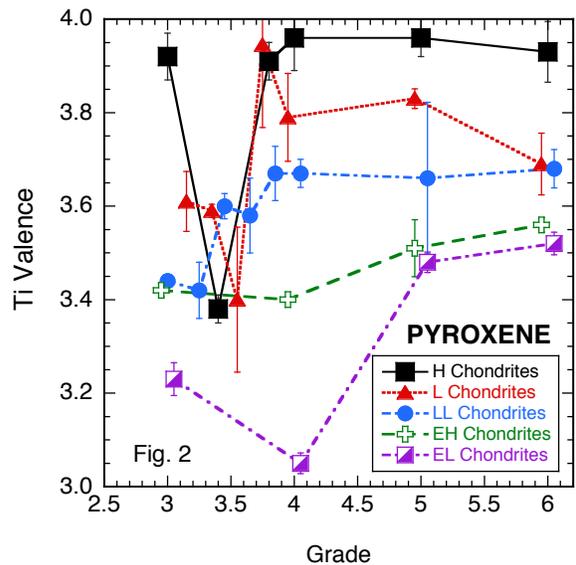
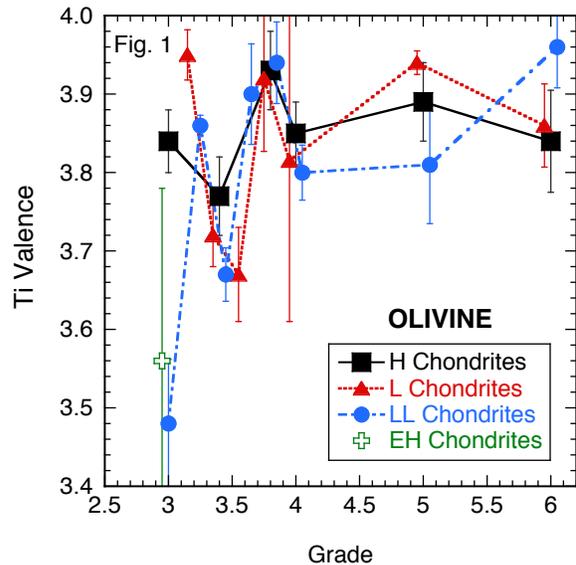


THE VALENCE AND COORDINATION OF Ti IN OLIVINE AND PYROXENE IN ORDINARY AND ENSTATITE CHONDRITES AS A FUNCTION OF METAMORPHIC GRADE. S. B. Simon¹, S. R. Sutton^{1,2} and L. Grossman^{1,3}, ¹Dept. Geophysical Sci., 5734 S. Ellis Ave.; ²Cntr. Adv. Radiation Sources (CARS); ³Enrico Fermi Institute, 5640 S. Ellis Ave., The University of Chicago, Chicago, IL 60637, USA (sbs8@uchicago.edu).

Introduction: Knowledge of the conditions to which chondrites were subjected and their responses to them is necessary for an understanding of the evolution of their parent bodies and early planetary processes in general. One way to better understand processes related to chondrite metamorphism is to evaluate changes in chondrite features, such as oxidation state, as a function of metamorphic grade. It has been suggested that ordinary chondrites underwent reduction during metamorphism from grade 3 to 4 [1] and oxidation during metamorphism from grade 4 through 6 [2, 3, 4], although [5] found no systematic variation of recorded oxygen fugacities (f_{O_2} 's) with metamorphic grade. In [1], Mössbauer spectroscopy was used, and the other studies used petrographic and mineral chemical data. We have undertaken a study of chondrites of grades 3-6 to see how Ti valence and coordination in olivine and pyroxene vary as a function of metamorphic grade and to see if the variations can be used to constrain conditions and effects of chondrite metamorphism. Results for L, LL and E chondrites have been reported [6, 7]; herein new data for H chondrites are presented and compared with all previous results.

Methods: Suites of chondrules 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. The suite of H chondrites studied, from lowest to highest grade, consists of Asuka-881026 (3.0); Sharps (3.4); Dhajala (3.8); Weston (4); Lost City (5); and Guareña (6), all falls except for Asuka. Valence of Ti in olivine, pyroxene and mesostasis, reported as values between 3 and 4, was determined *in situ* by X-ray absorption near edge structure (XANES) spectroscopy using methods previously described [8], except now the beam diameter is just $\sim 1 \mu\text{m}$, for improved spatial resolution. Spots analyzed by XANES were found by electron probe to contain $\leq 0.2 \text{ wt\% TiO}_2$ (olivine) or $\leq 0.5 \text{ wt\%}$ (pyroxene). Orientation effects can cause spurious Ti valence determinations, especially in samples with significant tetrahedral Ti components. Analysis of multiple grains of a phase within a sample and use of merged spectra can mitigate this effect if the grains are randomly oriented, which is assumed to be the case for the porphyritic chondrules. A total of 37 chondrules (4 - 8 per H chondrite) were analyzed, with an average of 5.3 XANES analyses/chondrule.

Results: Most of the chondrules analyzed are porphyritic, as barred and radial chondrules tend to be too fine-grained for XANES analysis. Valence measurements (sample averages and standard errors based on merged spectra for each chondrule) as a function of metamorphic grade are shown in Fig. 1 (olivine) and Fig. 2 (pyroxene). Grades are offset by +0.05 (LL) and -0.05 (L) for clarity. With one exception (Sharps pyx), the average Ti valence in H chondrites is ~ 3.8 , with no redox trend or reduction of ranges of chondrule averages with increasing grade, and no correlation between Ti valence and Fa or Fs contents.

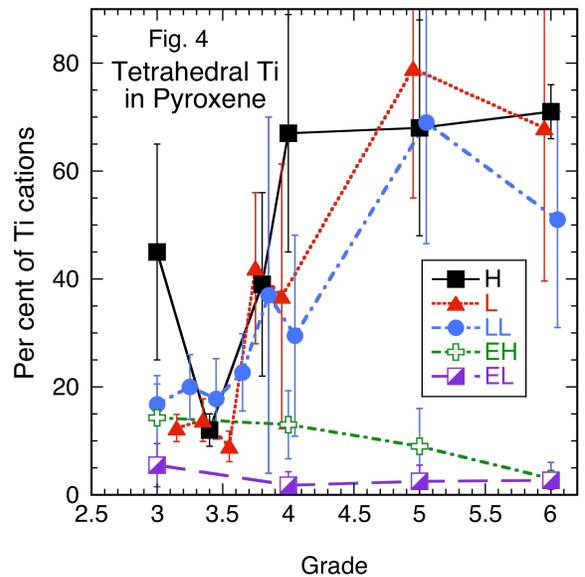
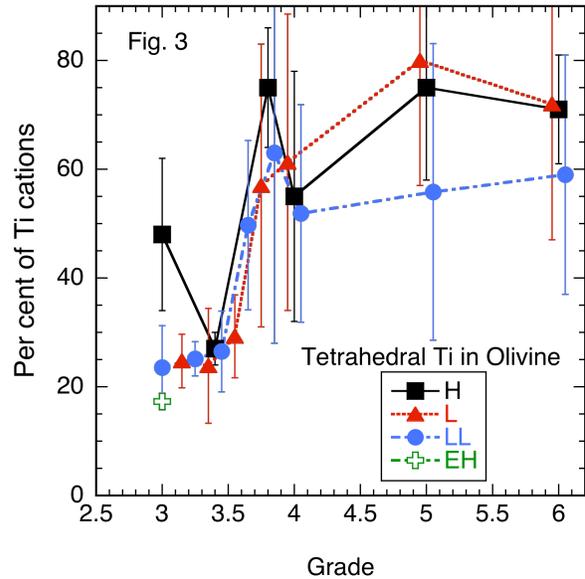


The H chondrite pyroxene results are similar to those for the L chondrites, with valence decreasing then increasing between grades 3 and 4. Three mesostasis analyses were obtained, all within error of 4. A systematic change seen in all three types of ordinary chondrites (OC) is that between unequilibrated and equilibrated members there are sharp increases in the proportions of Ti in tetrahedral (tet) coordination in both olivine (Fig. 3) and pyroxene (Fig. 4). Error bars in these plots are 1σ . This feature is not observed in either EH or EL chondrite pyroxene (high-grade E chondrites do not contain olivine). Except for the LL pyroxene, these increases are accompanied by decreases in Ti^{3+} , which are seen as valence increases in Figs. 1 and 2. The H3.0 chondrite is anomalous, with much higher tet Ti^{4+} proportions in both olivine and pyroxene than in the other unequilibrated OCs. The Ti in Sharps (H3.4) pyroxene is more reduced than that in the other H chondrites but its proportion of tet Ti^{4+} is typical for a low-grade OC.

Discussion: Interchondrule variations in Ti valence are seen in all equilibrated OC and E chondrites, and the use of merged spectra makes it very unlikely that this observation is due to orientation effects. The standard deviations of the valence measurements do not decrease with increasing grade. Once established, Ti valence did not completely reequilibrate, unlike that of Fe, even under grade 6 conditions. The average valence of Ti in E chondrites, ~ 3.0 – 3.5 , indicates that their formation and metamorphic conditions were very different from the OCs. Our results (Figs. 1, 2), unlike those of [1] for Fe, show onset of oxidation in OCs at grades lower than 4, with the lowest average Ti valences occurring at grades 3.4–3.6. The uniform valence of grade 4–6 H chondrites is consistent with fO_2 calculations based on measured chromite activities [5] that yielded a limited range of fO_2 s and no trend as a function of grade.

In the OCs, most of the sharp increases in tet Ti are accompanied by increases in valence in both olivine and pyroxene. The mechanism for the change in coordination is unclear, and different processes may be at work in olivine and pyroxene; what is clear is that the event was associated with oxidation of Ti. The occurrence of this feature in all OC groups and its absence from E chondrites is an important clue. As noted by [9], E chondrites are even drier than OCs, consistent with accretion in the relatively warm inner nebula, whereas OCs probably formed further from the Sun. The E chondrites therefore did not accrete ice, whereas the least equilibrated OCs contain small amounts of phyllosilicates in their matrices, evidence of incipient hydration [9]. The observed OC valence and coordination trends may thus be due to a sequence of hydration

followed by dehydration or dehydrogenation, processes that did not occur in the E chondrites.



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