**THE VALENCE OF Ti IN ENSTATITE CHONDRITES: NOT WHAT YOU MIGHT THINK.** S. B. Simon[1], S. R. Sutton[1,2] and L. Grossman[1,3], [1]Dept. Geophysical Sci., 5734 S. Ellis Ave., The University of Chicago, Chicago, IL 60637; [2]Center for Advanced Radiation Sources (CARS), The University of Chicago, Chicago, IL 60637; [3]Enrico Fermi Institute, 5640 S. Ellis Ave.; The University of Chicago, Chicago, IL 60637 (sbs8@uchicago.edu).

**Introduction:** Because they are dominated by enstatite, a nearly FeO-free pyroxene, and Si-bearing FeNi metal, along with minor amounts of unusual monosulfides such as niningerite (MgS), oldhamite (CaS) and alabandite (MnS), the enstatite chondrites have long been thought to have formed under extremely reducing conditions [1,2]. Like the ordinary chondrites, enstatite chondrites exhibit a range of petrologic types from type 3, with sharply defined chondrules, through type 6, with no discernable chondrules. Detailed study of unequilibrated enstatite chondrites (UECs) shows that they contain minor amounts of olivine and pyroxene with significant (>3 wt%) FeO contents which has been described as a ubiquitous component of the UECs [3,4]. On the basis of cathodoluminescence (CL) characteristics three generations of enstatite have been identified within UECs [4]. Some of the FeO-rich grains have different oxygen isotopic compositions from typical UEC enstatite grains while others do not [5]. This body of work shows that enstatite chondrites are not homogeneous, highly reduced rocks, but instead are complex objects, containing materials from multiple sources that record different redox histories. We have undertaken a study of the valence of Ti in E chondrites of grades 3-6 to better understand redox conditions of the source regions of their components and to see how Ti valence and coordination vary with metamorphic grade in these samples.

**Methods:** The samples being investigated in the initial phase of the study are the falls Qingzhen (EH3), Indarch (EH4), St. Mark's (EH5) and the find Y980211 (EH6). Chondrules and areas to be analyzed were selected based on examination with the scanning electron microscope (backscattered electron imaging and energy-dispersive analysis) and were analyzed by electron probe. The valence of Ti in olivine (Ol) and pyroxene was determined directly by X-ray absorption near edge structure (XANES) spectroscopy using methods previously described [7]. Spots analyzed by XANES were also analyzed by electron microprobe and found to contain up to 0.2 wt% $TiO_2$.

**Results:** Six chondrules in Qingzhen (QZ) and two in Indarch (IN) have been analyzed by XANES thus far. In QZ, CH6 is a type IAB with subhedral, 10-50 μm Ol grains enclosed in enstatite (En) and in devitrified mesostasis. CH8 is a radial pyroxene chondrule. CH10 also is a type IAB, with coarser Ol and En and less mesostasis than CH6. CH11 is a compound chon-

drule. The main body is dominated by coarse, subhedral En, with minor Ol and mesostasis. The small, attached object has anhedral En grains with sulfide/metal rims. CH12 is very unusual, with coarse, dusty laths of FeO-rich pyroxene with interstitial En, albite and FeS. CH13 is a compound fragment with coarse En laths and a small radial pyroxene chondrule attached. The IN chondrules have coarse En and little mesostasis.

*Phase compositions*. Enstatite corresponding to the red and blue CL groups of [4] and [6] was identified in Qingzhen and Indarch, plus "black" (no CL) enstatite [4] in Qingzhen on the basis of electron albedo and minor element contents. Electron probe analysis of six Indarch chondrules shows that most of the "light" (high-albedo) En has higher $Al_2O_3$, CaO, $Cr_2O_3$, MnO and FeO contents than most "dark" En. In Fig. 1, CaO and MnO contents of light and dark En (this study) are compared to those of red and blue En from [8]. The plot shows good overlap between dark and blue En on one hand and between light and red En on the other. A difference between the present results and those of [6,8] is that here, lower FeO contents (0.4 wt% avg) are observed in dark/blue En than in red/light En (0.7 wt% avg), and both are lower than the average of 0.9 wt% reported for both types by [6]. QZ CH12 has FeO-rich pyroxene with 9-20 wt% FeO. This material would fall into the "black" CL category of [4]. Excluding CH12, FeO contents of analyzed pyroxene range from below detection to 1.5 wt%.



Fig. 1
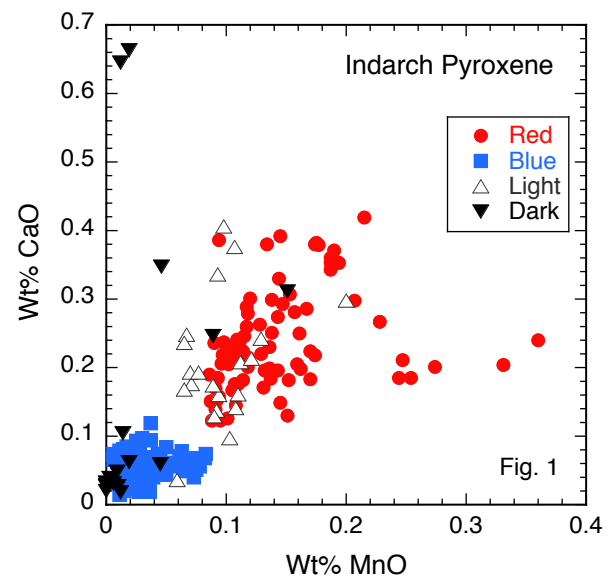
*Ti valence.* XANES results are summarized in Fig. 2, sorted by inferred CL color and plotted against FeO content. Valences range from 3.12±0.05 to 3.72±0.07 except for the one analysis of CH8, at 4.04±0.08. The FeO-rich pyx of CH12 (not plotted due to its off-scale FeO contents) averages 3.7±0.1, indistinguishable from blue (pure) En in the same chondrule. This is unlike other chondrules, where the red En, with an average Ti valence of 3.4±0.2, tends to be more reduced than the blue, which averages 3.7±0.1. CH11 has Ol with a Ti valence of 3.8±0.1 and red En that averages 3.2±0.1, the largest intrachondrule range. Within the color groups there is no correlation between FeO content and Ti valence. No differences are seen between the Qingzhen and Indarch data sets, although the latter is small. Several measurements of Ti valence in olivine were obtained and they range from 3.40±0.07 to 3.78±0.07.



Fig. 2
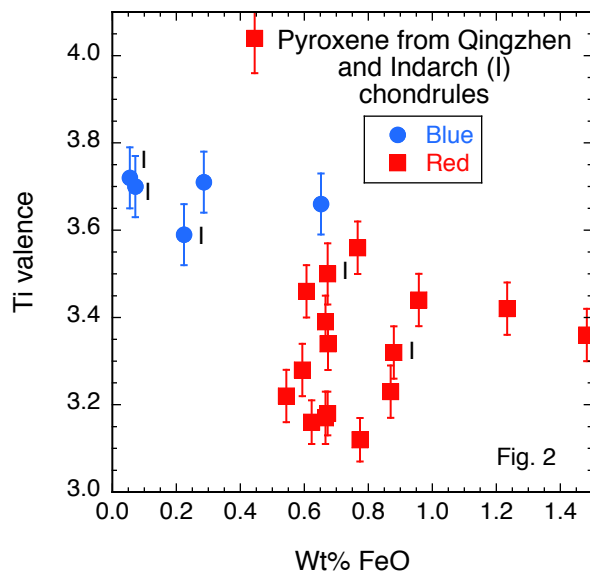
**Discussion:** The $fO_2$s inferred from typical E-chondrite (EC) mineral assemblages (pure En, Si-bearing metal, Mg-sulfides) are several orders of magnitude below those of a system of solar composition [2]. This leads to the reasonable expectation that all Ti in E-chondrites is trivalent. In contrast, the presence of $Ti^{4+}$ in all pyroxene and olivine analyzed supports previous suggestions, based on observations of FeO-bearing pyroxene and olivine, that materials in ECs formed from originally oxidized precursors that underwent reduction [3,4]. The present results show that some oxidized Ti survived this event. The reverse sequence has been inferred for chondrules in ordinary chondrites (OC): that their precursors formed in reducing environments, and that they contain reduced Ti that survived chondrule formation in an environment where $Fe^{2+}$ was stable [9]. Both the EC and OC chondrule studies are consistent with the interpretation that redox equilibra-

tion of Ti is sluggish relative to that of Fe, does not go to completion on the time scale of chondrule formation, and therefore can be a useful tool for unraveling multi-stage redox histories. The range of valences observed (Fig. 2) indicates that Ti redox equilibration was not attained in ECs. If the valences at least approached equilibrium, the subequal proportions of $Ti^{3+}$ and $Ti^{4+}$ more likely represent near-solar conditions rather than a system lower in $fO_2$ by several orders of magnitude. Solar $fO_2$s, 6-8 log units below the IW buffer, are also indicated by the model of [10] for the silicate sulfidation of E-chondrites.

The difference in valence between red and blue En supports previous suggestions that they represent different generations of materials and that redox conditions varied within the E-chondrite formation region [4]. In the context of the model of [4], in which red En formed by solid-state reduction of black, followed by condensation of blue En, our data imply that the reduction step occurred at a lower $fO_2$ than the condensation step and was of sufficient duration to allow significant reduction of both Fe and Ti, but not equilibration of the latter. The blue En may have formed under slightly more oxidizing conditions than those to which the red En was exposed, and with lower proportions of minor elements available than when the earlier pyroxene formed, leading to its purer compositions.

The $Ti^{3+}$-free analysis of CH8, if representative of the rest of the chondrule, provides additional evidence for sampling of an oxidizing environment. As an RP chondrule, it was probably once completely molten or very nearly so [11] and could have equilibrated with its solidification environment. On the other hand, its texture indicates that it cooled very rapidly, so it may not have equilibrated and may instead record the Ti oxidation state of its precursors.

In future work, we will analyze higher-grade EH chondrites to assess the effect of metamorphism on Ti valence in enstatite chondrites, and conduct a similar study of EL chondrites.

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