

# The Valence of Ti in Enstatite Chondrites: Not What You Might Think

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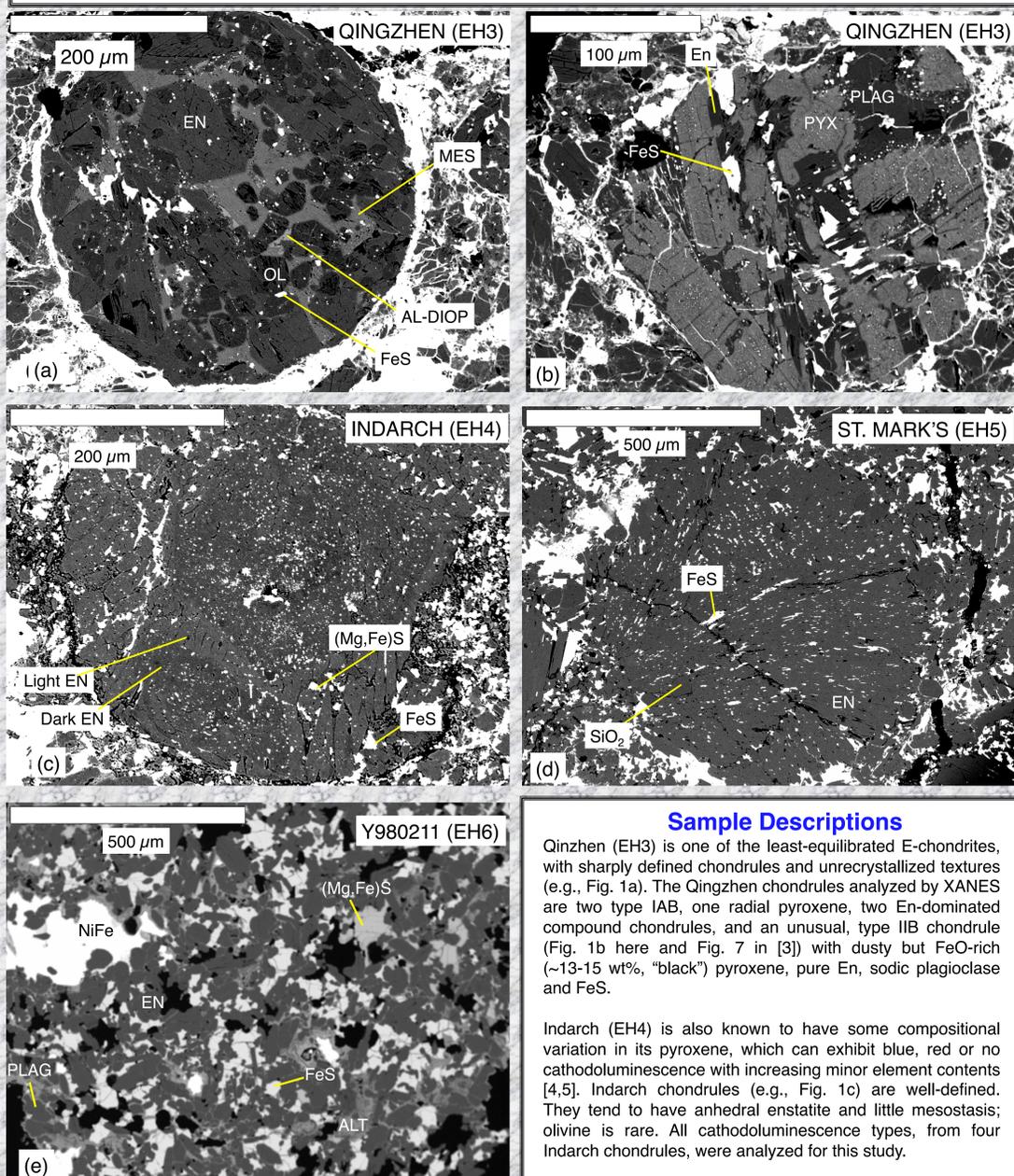
## Introduction

Enstatite chondrites are dominated by nearly FeO-free pyroxene and olivine, FeS and Si-bearing metal. Minor phases include monosulfides of elements that are typically lithophile, such as Ca, Mg and Mn [e.g. 1]. Thus the mineral assemblages found in E chondrites have long been thought to have formed under extremely reducing conditions, at oxygen fugacities possibly as low as 9 log units below the IW buffer [2]. There are numerous reports, however, of FeO-bearing silicates in unequilibrated enstatite chondrites (UECs), and they have been called a ubiquitous component of UECs [3]. On the basis of cathodoluminescence (CL) and minor element characteristics, first two (red and blue) [4] and later three (red, blue and none/black) [5] generations of pyroxene have been identified in some UECs, and some O-isotopic variations among them have been reported [6]. E chondrites are not simple, highly reduced rocks; they are complex objects consisting of materials from multiple sources with different redox states. It has also been suggested that sulfidization was important in their histories [7].

We have undertaken a study of the valence of Ti in E chondrites of grades 3–6 to better understand redox conditions of their source regions and to see how Ti valence and coordination vary with metamorphic grade. We begin with a suite of EH chondrites comprising the falls Qingzhen (E3), Indarch (E4), St. Mark's (E5) and the find Y980211 (E6).

## Methods

Samples were selected based on descriptions in the literature and 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 1  $\mu$ m X-ray beam. 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 volumes. TiO<sub>2</sub> contents of analyzed phases range from below detection by electron probe to ~0.2 wt%. The average Ti content of St. Mark's enstatite is 50 ppm [9], but recent beamline upgrades enabled measurement of valences in such Ti-poor pyroxene.



**Fig. 1.** Backscattered electron images of chondrules in Qingzhen, Indarch and St. Mark's and an area in Y980211 that were analyzed by XANES. (a) Porphyritic olivine (OL)-pyroxene (EN) chondrule in Qingzhen. (b) Chondrule with FeO-rich, "black" pyroxene (PYX) in Qingzhen. (c) Indarch. (d) St. Mark's. (e) Y980211. AL-DIOP: aluminous diopside; ALT: alteration, mainly terrestrial Fe-oxide(s); MES: mesostasis; PLAG: plagioclase.

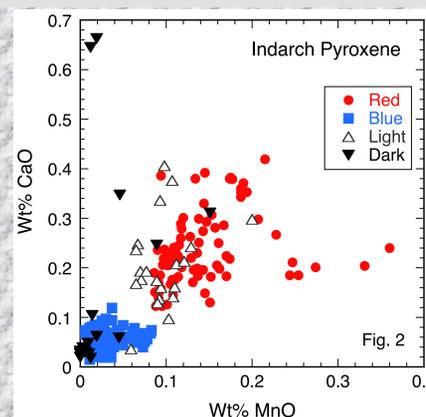
## Sample Descriptions

Qingzhen (EH3) is one of the least-equilibrated E-chondrites, with sharply defined chondrules and unrecrystallized textures (e.g., Fig. 1a). The Qingzhen chondrules analyzed by XANES are two type IAB, one radial pyroxene, two En-dominated compound chondrules, and an unusual, type IIB chondrule (Fig. 1b here and Fig. 7 in [3]) with dusty but FeO-rich (~13-15 wt%, "black") pyroxene, pure En, sodic plagioclase and FeS.

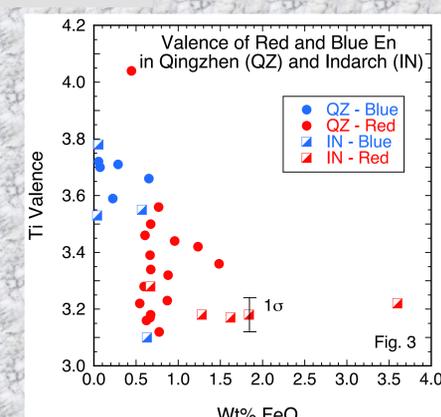
Indarch (EH4) is also known to have some compositional variation in its pyroxene, which can exhibit blue, red or no cathodoluminescence with increasing minor element contents [4,5]. Indarch chondrules (e.g., Fig. 1c) are well-defined. They tend to have anhedral enstatite and little mesostasis; olivine is rare. All cathodoluminescence types, from four Indarch chondrules, were analyzed for this study.

St. Mark's (EH5) has recrystallized and radial pyroxene chondrules (e.g., Fig. 1d), typically consisting of pure En with very low minor element contents, and interstitial FeS.

Y980211 (EH6) contains no discernable chondrules, so representative areas (e.g., Fig. 1e) were analyzed. The sample consists of anhedral to subhedral En and plagioclase intergrown with NiFe metal, FeS, and iron oxides from terrestrial weathering.



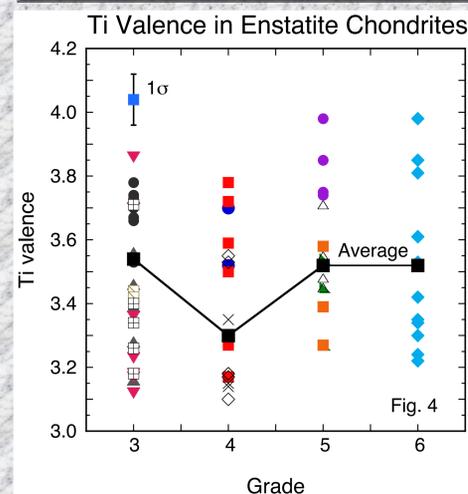
**Fig. 2.** Plot of electron probe analyses of Indarch chondrule enstatite identified as light and dark based on BSE albedo (this work) compared to analyses of pyroxenes with red or blue CL [4].



**Fig. 3.** Plot of valence of Ti in En, grouped by inferred CL color based on BSE albedo, in Qingzhen (QZ) and Indarch (IN) chondrules. Ti in red pyroxene tends to be more reduced than that in blue pyroxene. A representative error bar ( $\pm 0.06$ ) is shown.

## Results

**Phase compositions.** In Fig. 2, CaO and MnO contents of light and dark En (this study) are compared to those of red and blue En from [4]. The plot shows good overlap between dark and blue En on one hand and between light and red En on the other. This shows that our analyses and BSE observations can be used as a proxy for CL classification. In addition to CaO and MnO, "light" En tends to have higher contents of Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub> and FeO than "dark" En. The FeO contents of dark En range from below detection to 0.7 wt%, and the range in light En is 0.2–3.7. The FeO-rich pyroxene found in Qingzhen (Fig. 1b), with Fs>6 mole%, is classified as "black" pyroxene [5].



**Fig. 4.** Plot of valence of Ti in enstatite as a function of metamorphic grade. For grades 3–5, analyses with the same symbol are from the same chondrule. No chondrules were observed in the grade 6 sample. A representative error bar ( $\pm 0.06$ ) is shown.

**Ti valence.** XANES results for En in low-grade samples are illustrated in Fig. 3 (above), sorted by inferred CL color. Ti in red En tends to be more reduced than that in the blue. The QZ FeO-rich pyx (not plotted) has Ti valences between 3.5 and 3.7 (three analyses); the average valence of Ti in En in that chondrule is 3.7. Within each CL group there is no correlation between FeO content and Ti valence.

Results for all samples are illustrated as a function of metamorphic grade in Fig. 4 (left). The ranges of Ti valence do not decrease with increasing grade, and the average valences neither increase nor decrease as a function of metamorphic grade. Valence differences between and within chondrules are observed through grade 5, and the grade 6 sample, with no recognizable chondrules, has a range and average similar to those of the grades 3 and 5 samples.

**Ti coordination.** Unlike our results for L and LL chondrites [10], there is no increase in the proportions of tetrahedral Ti<sup>4+</sup> with increasing grade. In the present study, all tetrahedral Ti<sup>4+</sup> proportions are <20% and in most cases are <10%.

## Discussion

The finding that all pyroxene contains some Ti<sup>4+</sup> is consistent with previous observations [e.g. 4, 5] that E chondrites contain oxidized components. The conditions under which E chondrites were metamorphosed from grade 3 through 6 did not affect the valence of Ti; there is no indication of oxidation or reduction with increasing grade. This contrasts with our results for L and LL chondrites [10], where the Ti in pyroxene was found to be more oxidized in equilibrated samples than in unequilibrated ones.

The difference in valence between red and blue En is consistent with previous work [5] in the sense that variations in redox conditions existed during E chondrite formation. The red En has more reduced Ti but higher FeO contents than the blue; therefore, Ti and Fe valences were not established under the same conditions.

If the high proportions of tetrahedral Ti<sup>4+</sup> found in olivine and pyroxene in equilibrated L and LL chondrites [10] resulted from filling of OH-coordinated tetrahedral site vacancies during dehydration, then the low tetrahedral Ti<sup>4+</sup> proportions found here for all pyroxene can be explained by a lack of such vacancies in E chondrites due to their extreme dryness.

The valence of Ti in En shows no evidence that E chondrites either formed at or later equilibrated with anomalously low  $f_{O_2}$ s. Rather than a system lower in  $f_{O_2}$  by several orders of magnitude, the sub-equal proportions of Ti<sup>3+</sup> and Ti<sup>4+</sup> of most of the analyses most likely represent formation under near-solar redox conditions.

## Conclusions

1. There is no decrease in range of Ti<sup>3+</sup>/Ti<sup>4+</sup> nor convergence to a preferred value with increase in metamorphic grade. The valence and coordination of Ti in pyroxene are primary features that were not modified by the conditions of E chondrite metamorphism. The Ti valence therefore indicates the presence of oxidized components among the E chondrite precursors.
2. Enstatite with red CL tends to have higher Ti<sup>3+</sup> proportions than that with blue CL. These En types had different sources with different Ti<sup>3+</sup>/Ti<sup>4+</sup> ratios.
3. Enstatite chondrites of all grades exhibit a range of Ti<sup>3+</sup>/Ti<sup>4+</sup> ratios; Ti did not record uniform, anomalously low oxygen fugacities. The valence of Ti provides no evidence that E chondrites either formed at or equilibrated with extremely sub-solar oxygen fugacities.

## References

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