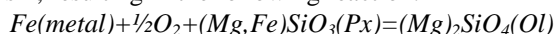


**MINERALOGICAL AND CHEMICAL EVIDENCE FOR INTRAGROUP OXIDATION STATE VARIATIONS IN EQUILIBRATED ORDINARY CHONDRITES.** T.L. Dunn<sup>1</sup>, H.Y. McSween, Jr.<sup>1</sup>, T.J. McCoy<sup>2</sup>, and G. Cressey<sup>3</sup> <sup>1</sup>Department of Earth and Planetary Sciences, University of Tennessee, Knoxville, TN, 37996 USA (tdunn@utk.edu); <sup>2</sup>Department of Mineral Sciences, Smithsonian Institution, Washington, DC, 20560, USA.; <sup>3</sup>Department of Mineralogy, Natural History Museum, London, SW7 5BD, UK.

**Introduction:** Along with bulk iron content, the oxidation state of iron varies systematically between ordinary chondrite groups, decreasing from LL to L to H. Chemical evidence, including intragroup variations in mean olivine Fa and low-Ca pyroxene Fs contents [1,2] and average Co and Ni concentrations in kamacite [2], suggest that oxidation state also changes within each chondrite group. [1] linked these intragroup redox variations to metamorphic grade and suggested that the equilibrated ordinary chondrites became progressively slightly more oxidized during metamorphism, resulting in the following reaction:



Because olivine forms at the expense of pyroxene in this reaction, changes should occur in the relative proportions of olivine and low-Ca pyroxene (with increasing petrologic type). Systematic changes in the abundances of olivine and low-Ca pyroxene have been observed in CIPW norms [3] calculated from bulk chemistries [4] and in modal abundances of a few chondrites [5,6]. However, because modal abundances of ordinary chondrites are difficult to quantify, modal data from previous studies are limited and may be unrepresentative.

Here we use X-ray diffraction-measured modal abundances of a large number of ordinary chondrites [7], along with supplemental chemical analyses, to address the question of intragroup redox state variations in the equilibrated ordinary chondrites.

**Methodology:** Modal abundances of 48 ordinary chondrite samples representing each of the ordinary chondrites groups (H, L, and LL) and corresponding petrologic categories 4-6 [8] were determined using position sensitive X-ray diffraction (PSD-XRD) [9]. Olivine and low-Ca pyroxene in 38 of these ordinary chondrites were analyzed by electron microprobe. All samples are unbrecciated falls with minimal weathering and low shock.

**Evaluation of Redox State: Modal Abundances.** Mean abundances of olivine and low-Ca pyroxene show subtle but systematic variations with petrologic type in all chondrite groups (H, L, and LL). Average olivine abundances increase with increasing metamorphic grade, while the converse trend is present in low-Ca pyroxene abundances. The subtle nature of the trends was expected, as previous studies examining normative abundances in ordinary chondrites [3] recognized only minor changes in mean abundances.

Changes in modal abundances are within the error associated with the PSD-XRD technique ( $\pm 3$  wt%), and trends are indistinct when  $1\sigma$  standard deviations are considered. However, because these intragroup trends are also present in normative data [3] and in electron microprobe-measured modal abundances of L and LL chondrites [5], we believe these subtle variations are real for all chondrite groups.

The relationship between average olivine and low-Ca pyroxene abundances can be expressed simply as a ratio of Ol/Opx. XRD-measured modal Ol/Opx ratios for the chondrites in this study are shown in Figure 1, along with ratios calculated from CIPW norms [3]. As with normative ratios, our modal Ol/Opx ratios increase with increasing petrologic type in the H, L, and LL chondrites. Like modal abundances, variations in Ol/Opx ratios are subtle and are within the error associated with the XRD technique. Trends are not linear, perhaps because temperature intervals for petrologic types differ.

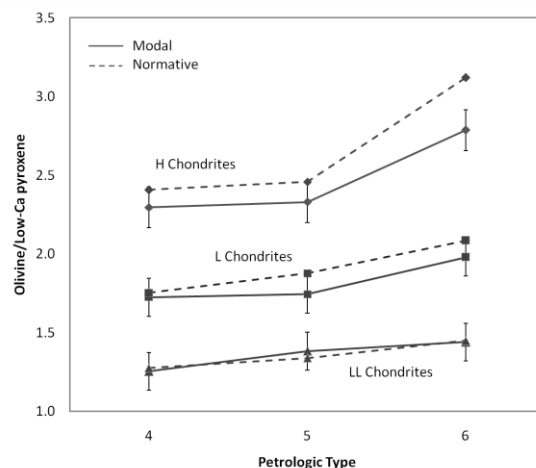


Figure 1. Ol/Opx ratios of H, L, and LL chondrites determined from modal data [9] and normative data [3]. Error bars represent  $1\sigma$  standard deviations.

**Mineral Chemistry:** Increases in the molecular ratios of olivine (mol% Fa) and low-Ca pyroxene (mol% Fs) with petrologic type have been recognized in previous studies [1,2], and have also been attributed to progressive oxidation with metamorphic type. In this study, both mean Fa content in olivine and Fs content in low-Ca pyroxene increase with petrologic type (Figure 2).

Redox state in the H, L, and LL chondrites can also be examined using molar Fe/Mn and molar Fe/Mg

ratios in silicate minerals [10]. Fe addition (as a result of oxidation) is indicated by the presence of a linear trend, which passes through the origin ( $y$  intercept = 0) and is defined by constant Mn/Mg ratios. In the H and LL chondrites, data fall on lines that pass naturally through the origin. However,  $R^2$  values are less than 0.90 in both groups, suggesting that there is a poor correlation between variables. Molar ratios of Fe/Mn and Fe/Mg in the H chondrites are presented in Figure 3. The L chondrite data is best fit with a line that does not pass through the origin. In all three chondrite groups, petrologic types 4, 5, and 6 data generally plot in an Fe-enrichment sequence, although there is considerable overlap between molar Fe/Mn and Fe/Mg ratios. Individual data are too variable and  $R^2$  values are too low to constitute convincing evidence for or against oxidation, especially in the L chondrites.

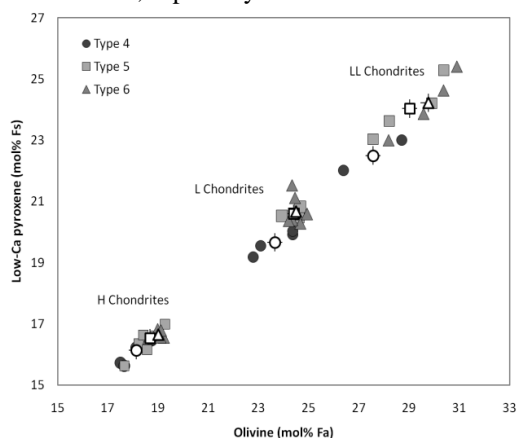


Figure 2. Mol% Fa versus mol% Fs. Symbols are average analyses from each chondrite analyzed in this study. Averages for each petrologic type are shown as open symbols with crosshairs.

Enrichment trends of Co and Ni in kamacite with increasing petrologic type [2] and increasing mean ratios of Ni/Fe and Co/Fe in bulk metal [1] have also been cited as evidence for progressive oxidation. Weight ratios of Ni/Fe and Co/Fe in thirty-nine of our sample were determined from bulk chemical analyses collected by [4]. Although mean ratios of Ni/Fe and Co/Fe increase with petrologic type in the H chondrites, this is not the case in the L and LL chondrites. An increasing trend can be discerned in the L chondrites when standard deviations are considered, but because only one LL4 and one LL5 sample were analyzed chemically by [4], there is insufficient data to determine if Ni/Fe and Co/Fe increase with increasing metamorphic type in the LL chondrites. Based on our data, it is unclear whether compositional ratios in metal support the oxidation hypothesis in all chondrite groups.

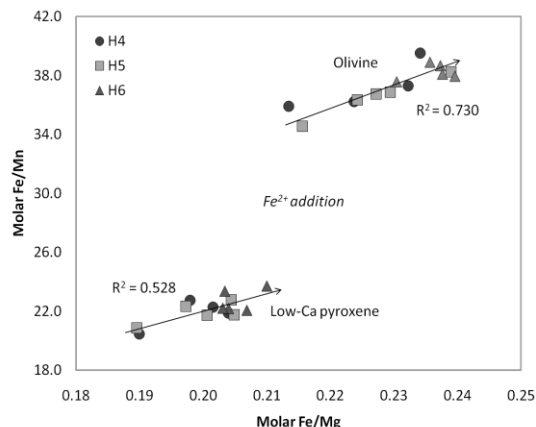


Figure 3. Molar Fe/Mn versus Fe/Mg in the H chondrites. Each line is a linear regression of data, where the  $y$ -intercept equals zero.

**Conclusions:** Based on modal mineralogies and chemical analyses, we suggest that progressive oxidation likely occurred during metamorphism in the equilibrated ordinary chondrites. Ratios of olivine to low-Ca pyroxene abundances increase subtly but systematically from type 4 to type 6 in all chondrite groups, suggesting that olivine was produced at the expense of pyroxene during progressive oxidation. In all three chondrite groups, mean Fa in olivine and mean Fs in low-Ca pyroxene increase with increasing petrologic type, indicating that silicate phases became progressively enriched in Fe as a result of oxidation. Linear trends indicative of Fe addition appear to be present in the H and LL chondrites, but individual data are too variable to constitute convincing evidence for or against oxidation in the L chondrites. Mean ratios of Ni/Fe and Co/Fe in bulk metal increase with petrologic type in the H chondrites; however, it is unclear whether compositional ratios in metal support the oxidation hypothesis in the L and LL groups. Water is the most plausible agent responsible for oxidation in the ordinary chondrite parent bodies. Based on mass balance calculations, 0.3-0.4 wt% water is required to convert low-Ca pyroxene to olivine during oxidation.

**References:** [1] McSween H.Y. and Labotka T.C. (1993) *GCA*, 57, 1105-1114. [2] Rubin A. (1990) *GCA*, 54, 1217-1232. [3] McSween H.Y. et al. (1991) *Icarus*, 90, 107-116. [4] Jarosewich E. (1990) *Meteoritics*, 25, 323-337. [5] Gastineau-Lyons H. et al. (2002) *MAPS*, 37, 75-89. [6] Menzies O.N. et al. (2005) *MAPS*, 40, 1023-1042. [7] Dunn T.L. et al. (2007) *MAPS*, 42, A37. [8] Van Schmus W.R and Wood J.A. (1967) *GCA*, 31, 747-765. [9] Dunn T. L. et al. (2007) *XXXVIII LPSC, Abstract # 1137*. [10] Goodrich C.A. and Delaney J.S. (2000) *GCA*, 64, 149-160.