

OXYGEN ISOTOPIC COMPOSITIONS OF OLIVINE AND PYROXENE FROM CI CHONDRITES; Laurie A. Leshin<sup>1</sup>, Alan E. Rubin<sup>2</sup>, and Kevin D. McKeegan<sup>1</sup>, <sup>1</sup>Department of Earth and Space Sciences, <sup>2</sup>Institute of Geophysics and Planetary Physics, University of California, Los Angeles, CA 90095-1567, USA.

**Introduction:** The oxygen isotopic compositions of carbonaceous chondrites are complicated since individual components of these meteorites have distinct isotopic compositions that have been affected, to varying degrees, by both nebular and parent body processes [1]. In principle, these preserved O-isotopic heterogeneities can be used to place quantitative constraints on the physical processes that occurred during formation of these meteorites. An example of this approach is provided by the detailed study of oxygen isotopic distributions in CM chondrites [2]. This study showed that the variation of oxygen isotopic compositions of different mineralogical components in CM samples can be understood as resulting from multiple interactions of two initial end-members: a solid component enriched in  $^{16}\text{O}$  (with  $\delta^{18}\text{O} \approx -40$  and  $\delta^{17}\text{O} \approx -41$ ) and a gaseous component depleted in  $^{16}\text{O}$  relative to terrestrial materials (with  $\delta^{18}\text{O} \approx +30$  and  $\delta^{17}\text{O} \approx +24$ ). According to the model, these two components partially equilibrated isotopically in a two-stage process [2]. First, high-temperature, incomplete exchange between the  $^{16}\text{O}$ -enriched solids (or liquids) and  $^{16}\text{O}$ -depleted gas produced "anhydrous" minerals which lie along a mixing line with slope  $\sim 1$  on an oxygen 3-isotope plot (e.g., chondrules fall nearly along the carbonaceous chondrite anhydrous minerals line, or CCAM). This high-temperature exchange was followed by interaction of the anhydrous minerals with liquid water at low temperatures, presumably on the CM parent body, that produced secondary minerals which lie along a slope-1/2 mass-dependent fractionation line. The isotopic composition of the water, fluid:rock ratio, and the approximate temperatures of equilibration were estimated from the O-isotopic data [2].

CI chondrites are primarily composed of the products of aqueous alteration. In addition to the whole-rock, separated magnetite and matrix silicates in CIs fall slightly above the terrestrial line and form slope-1/2 arrays with  $\Delta^{17}\text{O}$  values distinct from one another [2,3]. The O-isotopic composition of the secondary minerals in CI chondrites have also been interpreted within the framework of the CM model. This model of CI O-isotopic evolution assumes the O-isotopic compositions of the high-temperature, anhydrous minerals to be the same as those measured in CM chondrites because olivine and pyroxene grains (the likely precursors to the altered minerals) in these samples are extremely rare, precluding previous measurements of their O-isotopic compositions by gas-phase mass spectrometry. Presented here are the first oxygen isotopic data for separated olivine and pyroxene grains from CI chondrites.

**Experimental procedure:** Olivine and pyroxene grains were separated from  $\sim 0.75$  grams of Orgueil (Muséum National D'Histoire Naturelle, Paris; sample #235). An additional two separated and mounted pyroxenes from Ivuna were provided by J.N. Goswami. Aliquots of Orgueil were ground and ultrasonically suspended in a solution of 3% Na-metaphosphate and water. Grains larger than  $60\ \mu\text{m}$  were separated by filtration and material with density  $>2.96$  was concentrated using heavy liquids. Olivine and pyroxene candidates (i.e., clear grains) were hand picked from this separate, mounted in epoxy along with oxygen isotope standards for olivine and pyroxene, and polished. Major-element chemistry of the olivine and pyroxene grains was analyzed with the UCLA CAMECA electron probe.

Oxygen isotope ratios were measured for seven Orgueil olivines, two Orgueil pyroxenes, and two Ivuna pyroxenes with the UCLA CAMECA ims1270 ion microprobe. Negative secondary ions were sputtered by an  $\sim 1$  nA  $\text{Cs}^+$  primary beam defocused to a  $\sim 30\ \mu\text{m}$  diameter spot. A normal-incidence electron gun was used for charge compensation [4]. Secondary ions with initial kinetic energies of  $\sim 95$ - $120$  eV were measured at a mass resolving power of  $\sim 6100$ , sufficient to completely eliminate hydride interferences. Each measurement comprised 50 cycles of counting  $^{16}\text{O}$  for 1 second,  $^{17}\text{O}$  for 15 s, and  $^{18}\text{O}$  for 10 s. For each analysis session the olivine data were corrected for instrumental mass fractionation using the known  $\delta^{18}\text{O}$  value for San Carlos olivine ( $+5.25$ ; [5]) and pyroxene data were corrected in a similar fashion using our diopside standard ( $\delta^{18}\text{O} = +8.25$ ; [6]) and assuming a linear mass fractionation law ( $^{17}\text{O}/^{16}\text{O}_{\text{SMOW}}$  from [7]). A preliminary correction to account for changes in instrumental mass discrimination due to deviations of Fe-content of some of the CI olivine grains from that of the standard was included in the correction procedure (this additional correction, calibrated by measurement of San Carlos and nearly pure fayalite of known O-isotopic composition, resulted in shifts of  $<1\%$  from the values produced by correcting only to San Carlos). No such correction was made for the CI pyroxene grains.

**Results and discussion:** Separated Orgueil olivine grains range from  $\text{Fa}_{0.8-24.6}$ ; most exhibit normal igneous zoning in FeO. Grains analyzed for oxygen isotopes have the following mean Fa contents: 7.6, 8.5, 8.6, 9.4, 12.4, 13.2, 24.6. Pyroxene grains include low-Ca and high-Ca varieties from Orgueil ( $\text{Fs}_{5.9}\text{Wo}_{0.2}$ ;  $\text{Fs}_{4.9}\text{Wo}_{41.1}$ ) and Ivuna ( $\text{Fs}_{7.7}\text{Wo}_{4.6}$ ;  $\text{Fs}_{16.0}\text{Wo}_{46.5}$ ). Of the four pyroxene grains analyzed for oxygen isotopes, only one Ivuna grain is of the low-Ca variety.

Orgueil olivine major-element compositional data, combined with previous work [8,9] show correlated variation in CaO and Fa content closely resembling that observed in olivine phenocrysts from CM, CO, and LL3 chondrules [10,11]. Our observations of highly altered regions of CM chondrites show that they contain "ghost chondrules" in which the mesostases of some porphyritic olivine chondrules have been transformed almost completely to phyllosilicate. It is possible that higher degrees of alteration on the CI parent body could have freed mafic phenocrysts from CI chondrules producing the grains we have studied.

The oxygen isotopic compositions of CI olivine and pyroxene grains are reported and compared to other CI components in Fig. 1. The error bars represent one sigma uncertainties and reflect both the internal precision of each measurement and an uncertainty in the instrumental mass fractionation correction due to scatter in the standard measurements. All olivine points except one are the weighted mean of two measurements in the same spot. The remaining olivine measurement and all of the pyroxene data represent single analyses.

The  $\delta^{18}\text{O}$  values of six of the olivines range from  $\sim+3$  to  $+7$  and the  $\delta^{17}\text{O}$  values range from  $\sim+1$  to  $+4$ , while the most Fe-rich olivine (Fa<sub>24.6</sub>) is significantly more enriched in heavy isotopes ( $\delta^{18}\text{O}=+13$ ;  $\delta^{17}\text{O}=+7$ ). The  $\delta^{18}\text{O}$  values of the pyroxenes range from  $\sim+4$  to  $+10$  and the  $\delta^{17}\text{O}$  values range from  $\sim+2$  to  $+5$ . Observations that must be explained in the interpretation of the data are: (1) CI pyroxene and olivine grains have essentially identical oxygen isotopic compositions which are distinct from those measured in other carbonaceous chondrites [1]. (2) All data points except two are indistinguishable from terrestrial values at the one sigma level, and the two exceptions fall only slightly below the terrestrial fractionation line. We consider the data taken as a whole to be consistent with terrestrial values, as well as the slightly positive  $\Delta^{17}\text{O}$  values reported previously for matrix and magnetite in CI chondrites [3] (Fig. 1). (3) Due to the small range in  $\delta$  values observed relative to the uncertainties, it is not possible to distinguish whether these data fall on a line of approximately slope 1 or slope 1/2.

Although the similarity of the  $\Delta^{17}\text{O}$  values of the olivine and pyroxene grains to the secondary phases in CI chondrites (Fig. 1) suggests the possibility that the mafic silicates could have exchanged O with  $^{16}\text{O}$ -depleted fluids during the low-temperature formation of the secondary phases, O diffusion data [12] shows that this exchange would be far too slow. Thus, the isotopic signature of the mafic silicates is not the result of low-temperature exchange.

The oxygen isotopic composition of the high-temperature, anhydrous minerals from CI chondrites are clearly distinct from similar phases in other carbonaceous chondrites, which typically lie below the terrestrial fractionation line and fall near the CCAM [1]. Note however that our data are consistent with extension of the CCAM line to higher  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  values. This means that even prior to alteration and formation of secondary minerals, the CI chondrites were the most  $^{16}\text{O}$ -depleted carbonaceous chondrites. In the context of previous models for the evolution of carbonaceous chondrite minerals [2,3], this would imply that the precursors to the high-temperature, anhydrous phases in CI chondrites underwent a higher degree of exchange with a gaseous  $^{16}\text{O}$ -depleted reservoir than did their analogs in other carbonaceous chondrites. Considering results of laboratory diffusion experiments [13], the coincidence of the olivine and pyroxene data presented here are consistent with this hypothesis, but suggest that isotopic exchange took place either between the  $^{16}\text{O}$ -depleted gas and a liquid (i.e., chondrule melt) from which the olivine and pyroxene crystallized or between the gas and chondrule precursor solids. In addition, the observation that the most fayalitic olivine grain studied is also the most  $^{16}\text{O}$ -depleted is consistent with previous observations of a similar correlation between the bulk Fe/Mg and oxygen isotopic ratios in chondrules [14-16]. This has been interpreted to represent more complete exchange of relatively Fe-rich chondrule melts (which would have lower liquidus temperatures and thus would remain molten longer) with nebular gas [15]. Future work, which will include analysis of more forsteritic CI olivines, will test the preliminary conclusion that CI olivines and pyroxenes fall along an extension of the CCAM to more  $^{16}\text{O}$ -depleted values.

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Figure 1. The oxygen isotopic compositions of olivine and pyroxene from CI chondrites Orgueil and Ivuna. Error bars represent  $1\sigma$  uncertainties. Fields for other CI components represent the compositions of magnetite (CIM) and non-magnetic matrix and whole rock (CIS) from CI chondrites [3]. The terrestrial fractionation line (TF) and the carbonaceous chondrite anhydrous minerals line (CCAM; from [3] dashed to include the data presented here) are shown for reference.

