

The oxygen isotopic properties of olivines in the Semarkona ordinary chondrite

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Abstract—In order to explore the origin of chondrules and the chondrites, the O isotopic compositions of nine olivine grains in seven chondrules from the primitive Semarkona LL3.0 chondrite have been determined by ion microprobe. The data plot in the same general region of the three-isotope plot as whole-chondrule samples from ordinary chondrites previously measured by other techniques. There are no significant differences between the O isotopic properties of olivine in the various chondrule groups in the present study, but there is a slight indication that the data plot at the ¹⁶O-rich end of the ordinary chondrite field. This might suggest that the mesostasis contains isotopically heavy O. The olivines in the present study have O isotopic compositions unlike the ¹⁶O-rich olivine grains from the Julesburg ordinary chondrite. Even though olivines in group A chondrules have several properties in common with them, the ¹⁶O-rich Julesburg olivines previously reported are not simply olivines from group A chondrules.

INTRODUCTION

The O isotopic abundances of chondritic meteorites are one of their most perplexing properties but potentially among the most useful in understanding their origin and history. The various chondrite classes produce tight clusters or trend lines on the three-isotope plot ($\delta^{17}\text{O}$ vs. $\delta^{18}\text{O}$), with ordinary chondrites lying above the slope one-half terrestrial fractionation line, the carbonaceous chondrites (CI chondrites excepted) lying below the line, and enstatite chondrites plotting on the line. The chondrules of ordinary chondrites, like the ordinary chondrite classes and components from the CV chondrites, plot on lines whose slopes are close to 1.0.

A satisfactory interpretation of the O isotopic properties of meteorites has proved difficult because of the large number of processes that were possibly involved: heterogeneity of the precursors that might include interstellar grains (Nittler *et al.*, 1994); mixing of isotopically different solids (Gooding *et al.*, 1980); exchange between isotopically different solids, liquids and gases (Clayton *et al.*, 1991); isotopic fractionation between solids, liquids and gases (Clayton *et al.*, 1983, 1991); and mass-independent fractionation of the sort discussed by Thiemens (1996). Added to these possible processes, there were probably several different gaseous reservoirs and the possibility of reservoirs changing composition with time.

The bulk properties of chondrites, including those such as their O isotopes that are thought to be of particular genetic significance and are used for classification, are a reflection of the properties of the individual components. Thus, understanding the properties of the various components is crucial to understanding the origin of the meteorites. Processes like *in situ* metamorphism or chondrule formation result in reactions between individual minerals or between certain minerals and a gas or liquid phase, so it becomes essential to obtain isotopic data for individual minerals. The development of ion microprobe techniques has made it possible to examine individual minerals in thin section.

Especially significant in attempting to understand O isotopic systematics of chondrites are samples from a single meteorite that show a spread of O isotope ratios comparable to that displayed by the various chondrite groups. In this context, we can use the terrestrial fractionation line as a convenient point of reference, because

remarkably few meteorites (and none of the classes) straddle the line by more than a permil or so. The few examples that are known might represent simple contamination by foreign materials, but they might also be offering new insights into the processes affecting O isotopes and the relationships between the chondrite groups. Mayeda *et al.* (1980) reported that components from the Allan Hills A76004 LL3.4 ordinary chondrite plotted on a slope one line, but only a single poorly described inclusion plotted below the terrestrial line. More recently, Saxton *et al.* (1996b, 1998) reported that five olivine grains, containing very forsteritic cores, in the Julesburg L3.7 ordinary chondrite plotted below the terrestrial line, some with $\delta^{18}\text{O}$ values as low as -12% . These samples had been chosen on the basis of their low-Fa content and all but one showed blue cathodoluminescence (CL). Group A1,2 chondrules also contain low-Fa olivine and show bright CL but are unlike the Julesburg grains in that the group A chondrules show red CL. Cathodoluminescence is sensitive to mineralogy and composition and, thus, CL properties of chondrules afford a simple and objective means of identifying genetically significant classes without making assumptions about the host meteorite and metamorphic effects. Details are given in Sears *et al.* (1995, 1996). Thus, the differences in the CL properties of the Julesburg and Semarkona olivines could signal important genetic differences between the olivines, but O isotopic data are required to determine this.

The present study reports measurements with the Isolab 54 ion microprobe at the University of Manchester of O isotopic compositions of olivines in chondrules from the Semarkona LL3.0 ordinary chondrite. Primarily we wished to see if the group A1,2 olivines were isotopically similar to the Julesburg olivines, but we also hoped that such data might help clarify chondrule O isotopic systematics and their origin. We also accidentally obtained some measurements on pyroxene grains, and these data are reported, although their accuracy is less certain due to uncertainties in the matrix calibration between olivine and pyroxene.

EXPERIMENTAL

The Isolab 54 ion microprobe and techniques have been described by Saxton *et al.* (1995, 1996a) and Lyon *et al.* (1994,

1995) but may be outlined briefly here. Positive Cs primary ions (Cs^+) are produced from a Cs gun maintained at 10 kV and focused onto the sample by a series of lenses and deflector plates. The sample is held at -8 kV, so that negative secondary ions from the surface are accelerated into a second system of optics that focus the secondary ions onto the entrance slit of the mass spectrometer. The primary ion beam sputters the sample surface; the resulting crater size in these analyses was typically between 15 and 20 μm . Because the conducting coating is sputtered away, a focused electron beam (which impacts the surface with a net energy of 8 keV) is used to charge-neutralize the analyzed spot, which otherwise would rapidly charge up through gaining Cs^+ ions and losing secondary electrons and negative ions. Multicollection is used to measure the O isotopes simultaneously in different detectors; $^{16}\text{O}^-$ ions are measured in a Faraday cup and $^{17}\text{O}^-$ and $^{18}\text{O}^-$ ions by CDS detectors (Saxton *et al.*, 1996b).

Account also has to be taken of isotopic fractionation that varies with sample chemistry. This effect, known as the matrix effect, results in different measured isotopic ratios from samples of the same isotopic composition but different chemical compositions. A calibration of matrix fractionation for olivines measured using the Isolab 54 has showed no change in matrix fractionation between Fa0.7 and Fa20 (Saxton *et al.*, 1998), and so all analyses reported here were normalized to a mantle olivine standard, San Carlos (Hervig *et al.*, 1992). For some Semarkona chondrules, we obtained measurements from both olivine and pyroxene; on average, no systematic difference was found between olivine and pyroxene measurements from the same chondrule, so we have assumed zero matrix effect between olivine and pyroxene.

A polished section of Semarkona was prepared, and reflected light and CL maps were produced. These enabled chondrules to be classified using their CL (Sears *et al.*, 1995) and chondrules and grains to be located in the ion microprobe. Before and after analysis, mineral identifications and analysis locations were checked with a scanning electron microscope equipped with energy dispersive x-ray spectrometer facilities.

The present data were gathered over two time intervals, 1997 July/August and 1997 September. The standard deviations of San Carlos $\delta^{17}\text{O}$, $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ determinations were 2, 2.1, and 1.7‰ (n = 31), respectively, for the first period; and 1.5, 1.8, and 1.8‰ (n = 9), respectively, for the second. The standard deviations quoted above were derived from measurements of the standard made over the whole of the experimental period and are *as measured*, corrected only for detector deadtime and not normalized from day to day. Therefore, the scatter in the above measurements contains contributions from all potential sources of uncertainty: changes in detector efficiency, standard inhomogeneity, and changes in instrumental fractionation. Therefore, we believe that this scatter is the best representation of the accuracy of any single measurement on an unknown sample. These quoted uncertainties are obviously much larger than obtainable by bulk techniques, but the technique provides spatial resolution on the 20 μm scale of *in situ* samples.

RESULTS

Our results are shown in Table 1 and plotted on a three-isotope diagram in Fig. 1. We analyzed nine olivines from seven chondrules: two group A1, two group A2, one group A5, and two group B1.

Six of the nine olivines plot within 1σ of the equilibrated chondrite line, whereas eight are within 2σ . The outlier is a grain from chondrule O (referred to as O27 in Table 1 and Fig. 1), which lies $\sim 5\%$ to the high ^{17}O or low ^{18}O side of the equilibrated chondrite line. An additional measurement from chondrule O (overlapping both pyroxene and olivine) also shows high $\Delta^{17}\text{O}$.

We also analyzed pyroxene grains in four chondrules, one each of group A1, A2, A5 and B1. In three cases (A, AA and AH), we

TABLE 1. Oxygen isotopic data for olivine and pyroxene grains in Semarkona chondrules.

Point	Chondrule group	$\delta^{17}\text{O} \pm 1\sigma$ (‰)	$\delta^{18}\text{O} \pm 1\sigma$ (‰)	$\Delta^{17}\text{O}$ (‰)	Dataset*
Olivines					
A26	A5	3.2 ± 1.4	1.9 ± 1.7	+2.2	(2)
G18	A1	3.0 ± 2.0	5.6 ± 2.1	+0.1	(1)
O27	A2	6.4 ± 1.4	1.6 ± 1.7	+5.6	(2)
X14	B1	-0.3 ± 2.0	2.4 ± 2.1	-1.5	(1)
AA28	A2	4.1 ± 1.4	5.2 ± 1.7	+1.4	(2)
AE9	B1	-1.4 ± 2.0	0.5 ± 2.1	-1.6	(1)
AE15	B1	2.1 ± 2.0	4.2 ± 2.1	-0.1	(1)
AE16	B1	1.5 ± 2.0	4.0 ± 2.1	-0.6	(1)
AH25	A1	1.9 ± 1.4	3.6 ± 1.7	+0.0	(2)
Pyroxenes					
A19	A5	1.7 ± 2.0	2.1 ± 2.1	+0.7	(1)
AA10	A2	-1.5 ± 2.0	2.1 ± 2.1	-2.5	(1)
AH6	A1	1.8 ± 2.0	4.3 ± 2.1	-0.4	(1)
AI8	B1	-0.6 ± 2.0	3.4 ± 2.1	-2.4	(1)
O29†	A2	5.3 ± 1.4	2.5 ± 1.7	+4.0	(2)

*Data set (1) 1997 July 24–August 20 and (2) 1997 September 19–24 (see text).

†Overlaps with olivine.

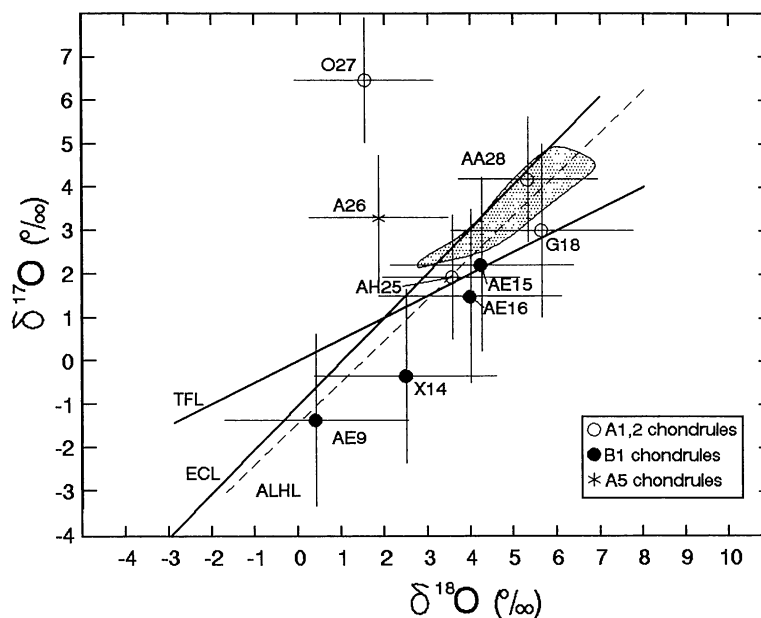


FIG. 1. Plot of O isotopic compositions in olivines from Semarkona chondrules. The chondrule group, the field for chondrules from equilibrated ordinary chondrites (Clayton *et al.*, 1991), and three lines are indicated; ECL, equilibrated chondrite line; TFL, terrestrial fractionation line; ALHL, a line defined by inclusions and other separates from the Allan Hills A76004 meteorite. The error bars refer to 1σ uncertainties.

also have measurements of the O isotopic ratios of olivine in the same chondrule. The uncorrected pyroxene values are very similar to the olivine measurements; from this, we infer that there is no significant matrix effect between olivine and pyroxene. We have no olivine measurement for type B1 chondrule AI; but assuming zero matrix effect for pyroxene, we find its pyroxene to be isotopically very similar to that of the olivine in the other three B chondrules we analysed.

DISCUSSION

Comparison with Julesburg Oxygen-16-rich Olivines

Figure 2 compares the present data with the Julesburg data from Saxton *et al.* (1996b, 1998). Julesburg is a fairly metamorphosed ordinary chondrite (type 3.7) whose olivines are mostly a fairly uniform Fa₂₃ (Graham, 1993). Therefore, the olivines analyzed by Saxton *et al.* stood out in the backscattered electron images because of their very low Fa (typically, Fa1). Also because of their low Fa, all but one displayed a bright blue cathodoluminescence similar to that of the olivines described by Steele (1986). Most noteworthy, their O is isotopically light, having $\delta^{18}\text{O}$ values extending down to approximately -12‰ and $\delta^{17}\text{O}$ down to approximately -10‰ .

The present olivines, whether group A or group B, have O isotopic compositions unlike the ^{16}O -rich olivine grains from the Julesburg meteorite (contrary to Saxton *et al.*, 1996b, we now believe that all the olivines analysed in Julesburg are in chondrules or in chondrule fragments). Two olivines in chondrules analyzed by Saxton *et al.* (1996b, 1998), J4 and J5, have O isotopic data more similar to the

present data—these objects were probably originally group A chondrules (Saxton *et al.*, 1998).

Clearly the ^{16}O -rich olivine grains in Julesburg are not grains from group A chondrules. As previously suggested by their unusual cathodoluminescence, they are unrelated to any of the major chondrule classes in ordinary chondrites.

Comparison with Data for Bulk Chondrules

The present data plot in the same general region of the three-isotope plot as whole-chondrule samples from ordinary chondrites previously measured by other techniques. Just as most are within 2σ of the terrestrial line, most are within 2σ of the bulk chondrules measured by Clayton *et al.* (1991). The data are also similar to several group B chondrules from Semarkona reported by Huang *et al.* (1996) and chondrules of both groups reported by Sears *et al.* (1997).

Although the error bars on the present measurements are rather large, there is some indication that the present data are plotting to the lower end of the equilibrated chondrite chondrule field of Clayton *et al.* (1991). The mean ($\pm 1\sigma$ of population) for the $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ of olivine for these chondrules is 2.59 ± 2.10 and 3.31 ± 1.69 ($n = 9$), respectively, which does not overlap entirely with the equilibrated chondrite chondrule field. This simply might reflect the uncertainties in our data. However, it might also be an indication that the data plot at the light end of the ordinary chondrite field and that the mesostasis contains isotopically heavy O. This speculation is almost certainly an oversimplification, however, because Bridges *et al.* (1997, 1998) recently reported correlations between O isotopes and chondrule class, and reported that the mesostasis was ^{16}O -poor, for chondrules separated from the Chainpur (LL3.4) and Parnallee (LL3.6) chondrites.

Class Comparisons

The chondrule classes are indicated in Fig. 1. The four olivines from group B1 chondrules have $\delta^{17}\text{O}$ values below 2.5‰ , whereas olivines from the group A1, A2 and A5 chondrules have values generally above this. Such a ready distinction is not made in $\delta^{18}\text{O}$, although the two olivines with the highest $\delta^{18}\text{O}$ are group A and the lowest is an olivine from a group B1 chondrule. Thus, there is only the slightest indication that group B1 chondrules contain lighter O than the other groups, but it is not significant within the uncertainties of our data. The same considerations and conclusions apply to the pyroxenes.

Several researchers have looked for evidence for a difference in O isotopic properties between group A and group B chondrules. Sears *et al.* (1997) suggested that whereas group B chondrules from Semarkona plotted within the field of equilibrated chondrules, group A chondrules tended to scatter about the field in all directions. In contrast, group B chondrules from Chainpur and Parnallee are ^{16}O -poor relative to group A chondrules (Bridges *et al.*, 1997, 1998), but these are relatively metamorphosed meteorites. It seems clear that although the data are still meager and details uncertain, if there is a difference in O isotopic properties between chondrules of group A and group B, it is fairly subtle. If, as we suggest, the olivines in group A and group B chondrules are very similar in O isotopic properties, then any difference in bulk chondrule O isotopes must be due to differences in the properties of their mesostases.

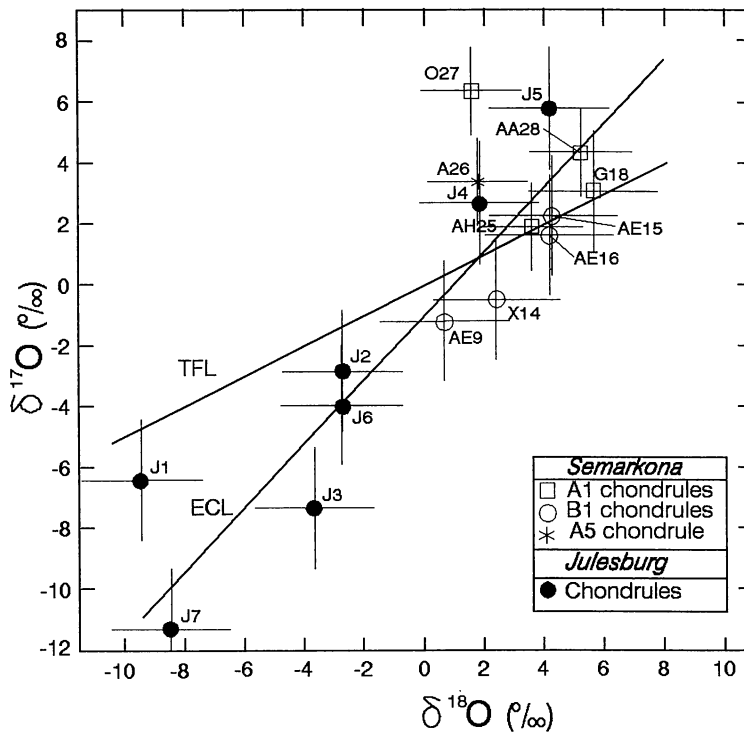


FIG. 2. Plot comparing the O isotopic composition of olivine in the present chondrules from the Semarkona LL3.0 chondrite with olivines from the Julesburg L3.7 chondrite (Saxton *et al.*, 1996a). Julesburg olivines J4 and J5 have compositions very similar to the present olivines, but the ^{16}O -rich Julesburg olivines contain significantly lighter O. The error bars refer to 1σ uncertainties.

Implications for Origin

The fact that the Julesburg ^{16}O -rich olivines are not simply and directly related to one of the major chondrule groups in primitive meteorites means that they are most probably "contaminants" from another class. In addition, there is still no observational evidence that chondrule formation is a means of moving material from one side of the terrestrial line to the other (*i.e.*, from the CV to the ordinary chondrite region of the diagram). In other words, the ordinary and carbonaceous chondrite classes are not simply related through chondrule formation. Of course, these data do not preclude a more primitive connection that predated the formation of the present chondrules.

The present data also might be indicating that group A and group B chondrules shared a common precursor and that the reduction and evaporation that accompanied chondrule formation resulted in the loss of O without significant isotopic fractionation. This seems reasonable because the amount of O involved in the reduction of Fe is small compared with the total amount of O in the olivine. The mass-dependent fractionation due to reduction is readily calculated. It is only $\sim 0.5\%$ in $\delta^{18}\text{O}$ assuming C is the reducing agent (Clayton *et al.*, 1991), and H_2 reduction will cause fractionations of a similar magnitude. It seems unlikely that such isotopic similarity would result from producing chondrules from different mixes of precursor material or from reacting the chondrule liquids with local gases.

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