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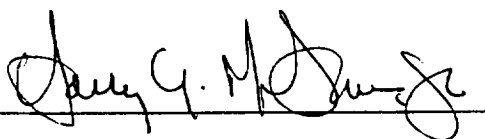
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### Light Stable Isotope Analysis of Meteorites by Ion Microprobe

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## Light Stable Isotope Analysis of Meteorites by Ion Microprobe

### Summary

The main goal was to develop the necessary secondary ion mass spectrometer (SIMS) techniques to use a Cameca ims-4f ion microprobe to measure light stable isotope ratios (H, C, O and S) *in situ* and in non-conducting mineral phases. The intended application of these techniques was the analysis of meteorite samples, although the techniques that have been developed are equally applicable to the investigation of terrestrial samples. The first year established techniques for the analysis of O isotope ratios ( $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$ ) in conducting mineral phases and the measurement of S isotope ratios ( $\delta^{34}\text{S}$ ) in a variety of sulphide phases. In addition, a technique was developed to measure  $\delta^{34}\text{S}$  values in sulphates, which are insulators. Other research undertaken in the first year resulted in SIMS techniques for the measurement of wide variety of trace elements in carbonate minerals, with the aim of understanding the nature of alteration fluids in carbonaceous chondrites. In the second year we developed techniques for analysing O isotope ratios in non-conducting mineral phases. These methods are potentially applicable to the measurement of other light stable isotopes such as H, C and S in insulators. Also, we have further explored the analytical techniques used for the analysis of S isotopes in sulphides by analysing troilite in a number of L and H ordinary chondrites. This was done to see if there was any systematic differences with petrological type.

### Publications and Abstracts Supported Solely by This Grant

- o McSween H.Y. Jr., Riciputi L.R., Johnson C.A. and Prinz M. (1993) Trace-element concentrations in calcite and dolomite from carbonaceous chondrites determined by ion microprobe, and coexisting fluid compositions. *Meteoritics* 28, 396.
- o Riciputi L. R., McSween H.Y. Jr., Johnson C.A. and Prinz M. (1994) Minor and trace element concentrations in carbonates of carbonaceous chondrites, and implications for the compositions of coexisting fluids. *Geochim. Cosmochim. Acta* 58, 1343-1351.
- o Paterson B.A., McSween H.Y. Jr., and Riciputi L.R. (1994) High spatial resolution sulphur isotopic analysis of troilite in ordinary chondrites by ion microprobe. *Lunar Planet. Sci.* XXV, 1057-1058.
- o Riciputi L.R. and Paterson B.A. (1994) In-situ analysis of oxygen isotope ratios in silicates and carbonates by ion microprobe. *Mineralogical Magazine*, in press.



## Oxygen Isotopes - Insulators and Conductors

The two techniques that have been developed for the analysis of  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  ratios in non-conducting and conducting mineral phases differ markedly from one another, although the techniques developed for non-conducting minerals could be adapted to the analysis of conducting minerals. The reproducibility and precision achieved by both methods is similar. The analysis of conducting minerals uses a 0.5 to 2nA  $^{133}\text{Cs}^+$  primary beam focussed to a spot of around 30 $\mu\text{m}$  in diameter to sputter the sample. Negative secondary ions are mass analysed at a mass resolution ( $\Delta\text{M}/\text{M}$ ) of around 6000 in order to eliminate interferences from hydrides, in particular  $^{16}\text{OH}^-$  on  $^{17}\text{O}^-$ . The transfer lens setting (150 $\mu\text{m}$ ) and the field aperture (100 $\mu\text{m}$ ) used result in only the central 8 $\mu\text{m}$  of the 30 $\mu\text{m}$  beam spot being analysed. The deadtime of the single collector counting system limits the count rate of the main isotope to around 500,000 counts per second and therefore precision is a function of the minor isotope abundance and the counting time of the analysis. Currently an analysis time of 35 minutes results in a precision of about 1‰ (1se) for  $\delta^{18}\text{O}$ , close to that predicted from counting statistics. Reproducibility from analysis to analysis is typically 1-1.5‰ (1sd).

The technique developed for analysing insulators is quite different. The main problem with analysing insulators with a positive primary beam is that of sample charging. In order to compensate for charging under the  $\text{Cs}^+$  primary beam, a normal incidence low energy electron gun is used, which delivers a supply of low energy electrons at the sample surface. However, small fluctuations in the charge compensation still occur, particularly from one analysis spot to another, resulting in poor reproducibility of isotopic analyses. This is because instrumental fractionation is strongly dependent on the energy of the secondary ions at 4500V. In order to provide immunity to these changes in charge compensation we have installed a new secondary accelerating voltage power supply that allows us to use larger energy offsets than the standard Cameca supply will allow. The Cameca power supply allows a limited range of accelerating voltage (4500 $\pm$ 125V), whereas the new supply allows the voltage to be varied from 0 to 5000V. Rather than tuning and running the mass spectrometer at 4500V, we use a 350V energy offset, ie. an accelerating voltage of 4150V. At this lower accelerating voltage small changes of a few volts in the charge compensation make no appreciable difference to the measured isotope ratios, unlike measurements made at 4500V. The use of a large voltage offset has the added benefit of eliminating molecular interferences and thus obviates the need to use high mass resolution. This means that the mass spectrometer can be run 'wide open', although a mass resolution of around 500 $\Delta\text{M}/\text{M}$  is still required to provide a flat-topped peak. The lower mass resolution results in increased transmission which compensates for the count rate loss that accompanies the use of large energy offsets. Similar count rates and counting strategies are used resulting in similar



overall precision and reproducibility to that achieved on conductors (1-1.5‰ - 1sd). The fact that high mass resolution is not required means that machine stability is less critical, as low mass resolution results in a much wider peak, meaning that a small drift of the magnet field during the analysis is less important. Also the alignment of the primary ion beam relative to the secondary ion optics is also not as critical to overall reproducibility as it is during analysis at high mass resolution. The measurement of  $\delta^{17}\text{O}$  in addition to  $\delta^{18}\text{O}$ , does not present any additional problems, although the low abundance of  $^{17}\text{O}$  results in a precision of 2‰ (1se) on  $d^{17}\text{O}$  as opposed to 1‰ on  $\delta^{18}\text{O}$ .

The combination of normal incidence low energy electron gun and a large energy offset, has allowed us to successfully analyse O isotopes *in situ* in a number of insulating silicates, carbonates and phosphates. The ion yields from these different types of mineral are remarkably similar suggesting that there may be few restrictions on the types of phases that can be successfully analysed. In exploring the potential uses of this technique we were only hampered by the dearth of homogeneous and characterised mineral standards that are currently available.

The techniques developed to overcome sample charging during the O isotope analysis of silicates and carbonates should be equally applicable to the measurement of other light stable isotope ratios in insulators, D/H, S in sulphates and possibly even C. The only problems that we would anticipate in adapting the techniques to other stable isotope systems would be the relatively poor ion yields of some elements.

### **Sulphur Isotopes in Sulphides**

For the analysis of S isotopes in sulphides a  $\text{Cs}^+$  primary beam of between 25-30 $\mu\text{m}$  in diameter is used, although as with the analysis of O in conducting minerals the arrangement of the secondary ion optics results in only the central 8 $\mu\text{m}$  being analysed. Negative secondary ions are mass analysed at a mass resolution of around 4500 $\Delta\text{M}/\text{M}$  in order to eliminate possible molecular interferences. The precision is again limited by the maximum allowable count rate of the counting system and the abundance of the minor isotope. Currently an analysis time of 10 minutes results in a precision of about 0.4‰ (1se), close to that predicted from counting statistics. However the reproducibility of standard analyses is a function of the consistency of the alignment of the primary beam relative to the secondary ion optics and is typically 0.5-0.75‰ (1sd) over the period of a day. The use of high energy offsets (as used for the analysis of O isotopes in insulators) should allow the measurement of  $\delta^{34}\text{S}$  at lower mass resolution, which would potentially remove the dependence of reproducibility on the alignment of the primary beam with the secondary ion optics. The detection of nucleosynthetic anomalies involving the





minor isotopes,  $^{33}\text{S}$  and  $^{36}\text{S}$ , is not likely due to the very low count rates and therefore poor precision.

As part of a study to test the reproducibility of the S isotope analysis technique we analysed troilite in a number of low-shock L and H ordinary chondrites. The results obtained were reproducible from day-to-day and over a period of months. In addition, the ion microprobe analyses from one sample are in agreement with a published conventional determination. However, the results are at odds with what would be expected and show no obvious correlation with petrographic type. We have found no dependence of the measured isotope ratio on small ( $\pm 25\text{V}$ ) changes in voltage offset. In an experiment to measure the effect of varying the gap between the immersion lens of the secondary ion optics and the sample surface, we did observe a correlation with measured isotope ratio. However the magnitude of the effect was insufficient to explain the measured values in the ordinary chondrites that were studied.

### **Trace Element in Carbonates**

Abundances of Fe, Mg, Mn, Sr, B and Ba in meteoritic calcites and dolomites have been determined using the ion microprobe. The compositions of these carbonates are consistent with their precipitation from, or recrystallization in equilibrium with, aqueous solutions at low temperatures. Co-existing calcites and dolomites in CM chondrites are not in equilibrium and presumably formed in distinct events. Calculated molar element/Ca ratios in equilibrium with these carbonates suggest that dolomites in CM and CI chondrites formed from compositionally similar brines. Calcite solutions were also saline but lower in Mg, Fe, and Mn; calculations suggest that these solutions became more like dolomite solutions with increasing alteration of the host CM meteorite, reflecting progressive evolution of solution compositions. Asteroid brines may have formed by membrane filtration after the formation of compacted phyllosilicates lowered permeability, by addition of components to fluids during phyllosilicate-forming reactions, or through low-pressure boiling. Occurrences of vein-filling calcite, followed by dolomite and later by sulphates, in carbonaceous chondrites represent the final stages of a protracted aqueous alteration sequence.

Further details of this work are given in Riciputi et al. (1994).





## Minor and trace element concentrations in carbonates of carbonaceous chondrites, and implications for the compositions of coexisting fluids

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**Abstract**—Abundances of Fe, Mg, Mn, Sr, Na, B, and Ba in meteoritic calcites and dolomites have been determined using the ion microprobe. The compositions of these carbonates are consistent with their precipitation from, or recrystallization in equilibrium with, aqueous solutions at low temperatures. Coexisting calcites and dolomites in CM chondrites are not in equilibrium and presumably formed in distinct events. Calculated molar element/Ca ratios for fluids in equilibrium with these carbonates suggest that dolomites in CM and CI chondrites formed from compositionally similar brines. Calcite solutions were also saline but lower in Mg, Fe, and Mn; calculations suggest that these solutions became more like dolomite solutions with increasing alteration of the host CM meteorite, reflecting progressive evolution of solution compositions. Asteroid brines may have formed by membrane filtration after the formation of compacted phyllosilicates lowered permeability, by addition of components to fluids during phyllosilicate-forming reactions, or through low-pressure boiling. Occurrences of vein-filling calcite, followed by dolomite and later by sulfates, in carbonaceous chondrites represent the final stages of a protracted aqueous alteration sequence.

### INTRODUCTION

MANY CARBONACEOUS chondrites have experienced aqueous alteration to form a complex assortment of secondary minerals, including hydrous phyllosilicates, hydroxides, oxides, carbonates, and sulfates. Whether the formation of phyllosilicates, hydroxides, and oxides occurred in the solar nebula before accretion or within parent bodies after accretion is a subject of current debate (see METZLER et al., 1992; IKEDA and PRINZ, 1993; vs. KERRIDGE and BUNCH, 1979; ZOLENSKY and MCSWEEN, 1988; for contrasting views), but there seems little doubt that vein-filling carbonates and sulfates in CI and CM chondrites precipitated from solutions migrating through asteroidal regoliths (RICHARDSON, 1978; FREDRIKSSON and KERRIDGE, 1988; LEE, 1993). In CI chondrites, carbonate veins formed earlier than sulfate veins and most of the carbonate veins have been disrupted by regolith gardening. Sulfate vein formation was also the last event in CM chondrites, but carbonates in these meteorites occur mostly as isolated grains. It seems reasonable to assume, however, that these isolated carbonate grains represent precipitates from the same or similar mineralizing solutions that formed the partly intact carbonate veins (FREDRIKSSON and KERRIDGE, 1988). This conclusion is supported by the difficulty in attaining the requisite CO<sub>2</sub> partial pressures in the nebula for carbonate stability (ARMSTRONG et al., 1982).

Previous attempts to constrain the proportions and properties (temperature, pH, Eh, and composition) of these mineralizing solutions have been based on mineralogical phase relations (DUFRESNE and ANDERS, 1962), oxygen

isotope fractionations between carbonates and phyllosilicates (CLAYTON and MAYEDA, 1984), and computer simulations of the aqueous alteration process (ZOLENSKY et al., 1989). The abundances of minor and trace elements in carbonates can also potentially provide information on the compositions of alteration fluids. However, meteoritic carbonate grains are usually small (generally <100 μm), and it is difficult to obtain reliable results from element concentrations below 500 ppm using the electron microprobe. Several recent comprehensive studies of meteoritic carbonates have determined major- and minor-element abundances using the electron probe (FREDRIKSSON and KERRIDGE, 1988; JOHNSON and PRINZ, 1993), though no attempts have been made to derive the compositions of fluids in equilibrium with these minerals.

In this paper we report ion microprobe analyses of calcites and dolomites in CM chondrites and dolomites in CI chondrites for the following elements: Fe, Mg, Mn, Sr, Na, Ba, and B. Using these data, we estimate the compositions of fluids in equilibrium with these phases and discuss implications for the alteration processes that affected carbonaceous chondrite parent bodies.

### EXPERIMENTAL

Sections of four CM chondrites (Boriskino, Murchison, Nogoya, and ALH83100) and one CI chondrite (Orgueil) from the American Museum of Natural History, previously analyzed by JOHNSON and PRINZ (1993), were coated with C for ion probe analysis. Using a Cameca ims-4f ion microprobe at Oak Ridge National Laboratory, the samples were bombarded with a 12.5 kV primary beam of <sup>16</sup>O<sup>-</sup> ions; beam currents were 0.3–5 nA, and the primary beam spot was focused to a diameter of 5–20 μm. Sample reference voltage was 4500 V, and positive secondary ions were extracted for analysis. The secondary mass spectrometer was optimized to maximize transmission, giving a mass resolution of approximately 600. <sup>44</sup>Ca, <sup>54</sup>Fe, <sup>24</sup>Mg, <sup>55</sup>Mn, <sup>88</sup>Sr, <sup>23</sup>Na, <sup>138</sup>Ba, <sup>11</sup>B, <sup>27</sup>Al, and <sup>28</sup>Si secondary ions were counted using an electron multiplier with a system deadtime of approximately

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30 ns. Analyses of Al and Si were used to screen out contaminated samples.

Peak jumping was automatically controlled by the system computer. Peak positions were calibrated each day and monitored during the presputter period of each analysis. Each spot was presputtered for 10 min to allow the secondary ion signals to stabilize and to allow the magnet to cycle so as to minimize hysteresis effects. Ten cycles of data were collected, and the total analysis time was approximately 30 min. Counting times for individual elements varied between 2 and 30 s each cycle. During each analysis, the shape of the Ca secondary ion energy distribution was monitored, and the energy offset was automatically adjusted to compensate for sample charging.

Quantitative analysis of trace elements using SIMS is hindered by the complex secondary ion spectrum, although the relatively simple chemistry of most carbonates minimizes some of the problems. Energy filtering (SHIMIZU et al., 1978; SWART, 1990) was used to compensate for or avoid secondary ion interferences. By applying an energy offset to alter the sample voltage so that high-energy ions were analyzed rather than low-energy ions, the ratio of elemental ions to molecular ions was increased. Molecular interferences were virtually eliminated from the elemental isotopic species of interest using an offset of 100 V relative to the upper edge of the energy distribution. The only major interference remaining was  $^{40}\text{Ca}^{16}\text{O}$  on the  $^{56}\text{Fe}$  peak; to avoid this problem the  $^{54}\text{Fe}$  peak was used.

Table 1. Elemental concentrations of CI & CM calcite and dolomite.

	ppm B	ppm Na	ppm Mg	ppm Fe	ppm Mn	ppm Sr	ppm Ba
<b>CM Calcite</b>							
Boriskino A	5 ± 1	270 ± 10	630 ± 80	4050 ± 560	79 ± 5	70 ± 1	3 ± 0.3
Boriskino K	5 ± 1	440 ± 20	81 ± 9	120 ± 10	28 ± 2	42 ± 2	3 ± 0.3
Boriskino B	5 ± 2	400 ± 20	430 ± 60	1280 ± 90	110 ± 6	130 ± 3	6 ± 1
Boriskino C	10 ± 3	580 ± 10	310 ± 50	350 ± 70	99 ± 6	83 ± 3	11 ± 1
Boriskino G	8 ± 1	490 ± 20	190 ± 20	240 ± 10	360 ± 10	41 ± 3	4 ± 0.6
Boriskino G	6 ± 2	380 ± 20	420 ± 20	580 ± 60	1540 ± 20	39 ± 1	5 ± 0.9
Boriskino H	7 ± 2	530 ± 30	150 ± 30	160 ± 20	28 ± 4	36 ± 1	4 ± 0.5
ALH83100 K	7 ± 1	750 ± 10	300 ± 30	650 ± 40	520 ± 10	210 ± 4	6 ± 0.6
ALH83100 K	8 ± 2	760 ± 30	590 ± 20	3750 ± 110	870 ± 10	220 ± 4	5 ± 0.5
ALH83100 L	12 ± 2	470 ± 20	870 ± 110	1270 ± 240	160 ± 20	21 ± 1	2 ± 0.5
ALH83100 N	9 ± 2	440 ± 20	490 ± 40	1000 ± 130	180 ± 6	30 ± 2	2 ± 0.4
ALH83100 P	7 ± 2	430 ± 10	1130 ± 320	6710 ± 280	120 ± 6	65 ± 2	3 ± 0.4
ALH83100 F	6 ± 1	460 ± 10	260 ± 10	290 ± 20	550 ± 10	28 ± 1	6 ± 0.2
ALH83100 D	19 ± 3	760 ± 50	1510 ± 70	6290 ± 600	1580 ± 20	140 ± 3	5 ± 0.5
ALH83100 B	16 ± 1	450 ± 40	660 ± 100	700 ± 90	740 ± 30	240 ± 6	8 ± 1
ALH83100 A	14 ± 2	570 ± 40	550 ± 70	940 ± 60	550 ± 10	130 ± 7	6 ± 1
Nogoya L	16 ± 4	920 ± 30	1110 ± 70	4210 ± 270	410 ± 20	130 ± 8	14 ± 2
Nogoya G	8 ± 2	470 ± 10	680 ± 30	1880 ± 120	1110 ± 10	37 ± 1	3 ± 0.5
Nogoya D	28 ± 5	870 ± 30	2980 ± 120	3930 ± 170	370 ± 10	230 ± 1	17 ± 2
Nogoya M	26 ± 3	540 ± 20	3890 ± 450	6800 ± 510	380 ± 10	37 ± 2	13 ± 1
Murchison E	12 ± 3	970 ± 200	940 ± 60	2490 ± 150	66 ± 6	30 ± 6	12 ± 4
Murchison A	36 ± 10	2700 ± 41	1090 ± 250	4120 ± 700	350 ± 70	370 ± 2	29 ± 5
Murchison G	18 ± 2	1100 ± 23	890 ± 120	410 ± 80	50 ± 12	47 ± 10	
mean	13	680	880	2270	450	105	8
std.dev.	8	490	900	2230	450	93	6
<b>CM Dolomite</b>							
Boriskino D	10 ± 1	330 ± 30	106100 ± 250	27830 ± 220	22430 ± 270	130 ± 3	10 ± 0.4
Boriskino D	6 ± 1	270 ± 10	104000 ± 180	28160 ± 340	21160 ± 250	120 ± 2	4 ± 0.3
Nogoya H	15 ± 2	470 ± 30	80300 ± 3000	24010 ± 440	20460 ± 680	170 ± 5	11 ± 2
Nogoya H	11 ± 5	360 ± 10	97300 ± 1100	23540 ± 780	18530 ± 630	120 ± 8	12 ± 4
Nogoya H	10 ± 3	620 ± 90	113200 ± 200	23950 ± 160	16420 ± 990	140 ± 1	14 ± 3
mean	10	410	100200	25500	19800	140	10
std.dev.	3	140	12500	2290	2360	20	4
<b>CI Dolomite</b>							
Orgueil B	5 ± 1	370 ± 20	105500 ± 140	17370 ± 600	35460 ± 330	100 ± 2	10 ± 0.5
Orgueil A		210 ± 10	113100 ± 700	14080 ± 140	30600 ± 110	180 ± 3	4 ± 0.4
Orgueil A		230 ± 10	105800 ± 600	12740 ± 150	24100 ± 130	160 ± 2	4 ± 0.2
Orgueil A		280 ± 10	104600 ± 600	15900 ± 320	36490 ± 200	120 ± 3	5 ± 0.5
Orgueil N	7 ± 1	430 ± 10	116800 ± 110	25880 ± 500	14340 ± 110	150 ± 4	6 ± 0.6
Orgueil N		310 ± 10	115900 ± 300	19020 ± 390	12580 ± 590	140 ± 4	5 ± 0.5
Orgueil D		230 ± 10	102500 ± 500	18240 ± 350	21420 ± 90	130 ± 3	6 ± 0.5
Orgueil K		320 ± 70	105100 ± 300	14920 ± 230	20510 ± 60	100 ± 2	6 ± 0.7
Orgueil J		250 ± 10	98700 ± 900	13950 ± 200	66410 ± 430	94 ± 2	5 ± 1
Orgueil I	5 ± 1	240 ± 10	105200 ± 600	12500 ± 580	6690 ± 40	250 ± 4	14 ± 2
mean	6	290	107300	16460	26860	140	7
std.dev.	1	70	5900	3990	16960	47	3

Errors reflect both the precision of the ion probe analysis (one standard deviation) and uncertainties in the Ca concentration determined by electron microprobe (JOHNSON and PRINZ, 1993).

Quantification of secondary ion intensities requires use of standards that have major-element compositions similar to those of the unknowns. In addition, ion intensities of elements of interest must be calibrated with ion intensities of an element of known concentration in the sample. In these analyses Ca served as the reference element, since the carbonate grains had already been analyzed for Ca using an electron microprobe (JOHNSON and PRINZ, 1993). Three calcite and two dolomite standards have been developed at ORNL. Na, Ca, Fe, Mn, Mg, Sr, and Ba concentrations were measured at both Oregon State University and ORNL using neutron activation analysis. In addition, Sr, Mg, Fe, Ca, Mn, and Na concentrations were measured at ORNL using atomic absorption spectrophotometry. The ionization efficiency for B was estimated using that determined for Na. Concentration ranges for the various elements in the standards were Na (4–155 ppm), Fe (46–55,000 ppm), Mn (30–57,000 ppm), Sr (80–350 ppm), Mg (17–100,000 ppm), and Ba (1–60 ppm). Homogeneity of the standards was checked by multiple analyses of ten to twenty grains using electron and ion microprobes, and is typically 3–10% for most elements. Although the precision of the ion microprobe analyses (see Table 1) is generally good, the external accuracy (estimated to be 10–25%) is limited by the homogeneity of the standards and accuracy of the standard bulk analyses. Detection limits for most elements are typically 1 ppm or less, although this depends in part on the intensity of the primary beam. Electron microprobe analyses for Fe, Mg, and Mn (when detectable) are in reasonable agreement with the ion microprobe results, as shown in Fig. 1. Average precisions for electron microprobe analyses of calcites are  $\pm 200\%$  for MgO,  $\pm 20\%$  for FeO, and  $\pm 100\%$  for MnO.

## RESULTS OF ION PROBE ANALYSES

The petrography of the analyzed carbonate samples was previously described by JOHNSON and PRINZ (1993). The CM chondrite carbonates analyzed in this study are isolated grains dispersed in the meteorite matrix. They are a few tens of micrometers in diameter and commonly show rhombic form and polysynthetic twinning. All of the Ca-carbonate grains are optically negative, indicating that they are calcite rather than aragonite or vaterite. The dolomites in CI and CM chondrites occur as isolated grains or aggregates of grains within the matrix. Only the larger grains, measuring several micrometers in diameter, could be analyzed due to instrumental constraints on the ion beam spot size. The analyzed samples were untwinned.

### Calcites in CM Chondrites

Elemental concentrations of twenty-five analyzed calcites from CM chondrites are given in Table 1, along with mean values and standard deviations. Although multiple analyses of a few grains were made, all were too small to determine zoning patterns. The calcites contain only small quantities

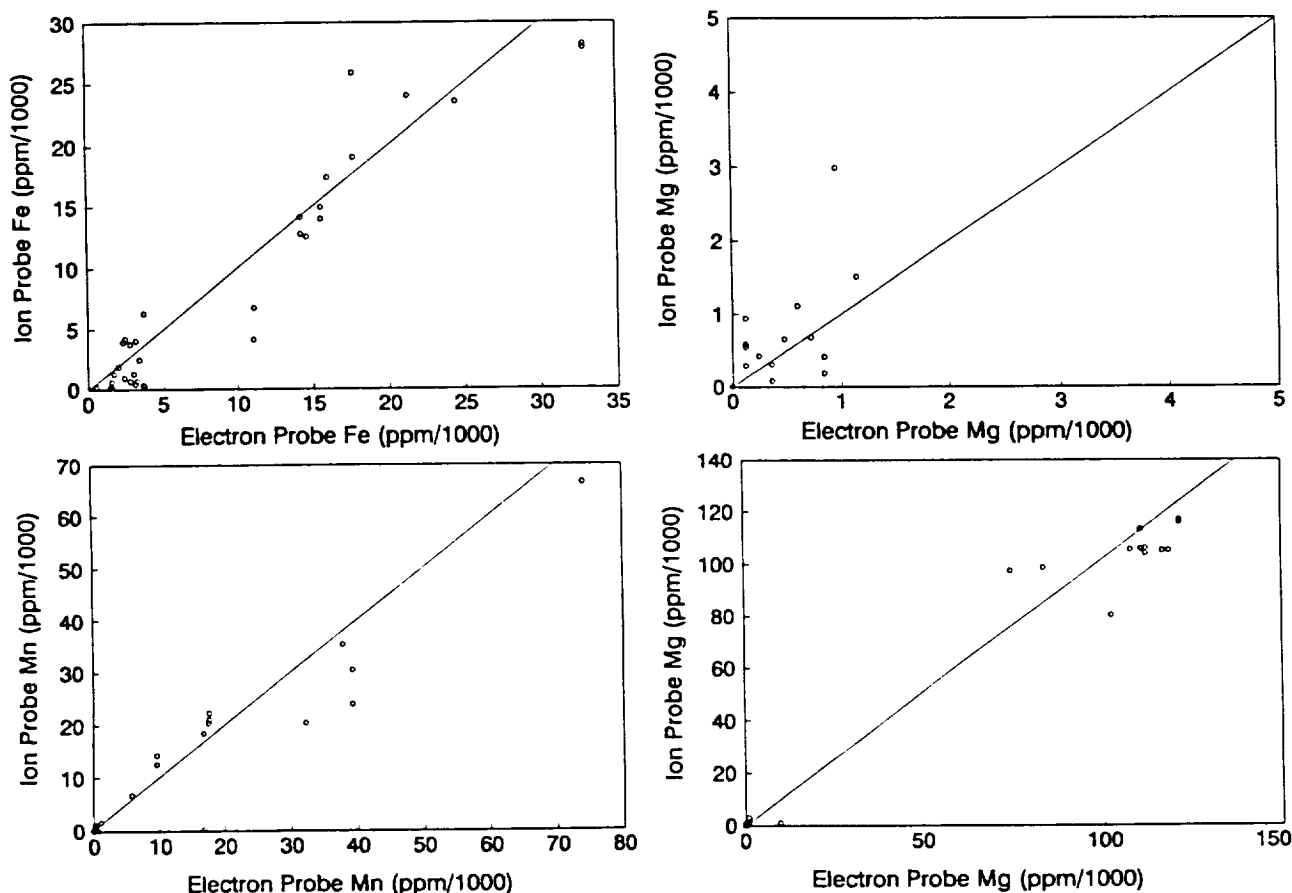


FIG. 1. Comparisons between electron microprobe analyses of carbonates (JOHNSON and PRINZ, 1993) and ion microprobe analyses of the same grains show reasonably good agreement. The Mg comparison diagram in the upper right shows an expanded field of data for calcites which are clustered near the origin in the diagram at lower right.

of Fe, Mg, and Mn, consistent with the idea that calcite precipitated as a stable phase at low temperature (<20°C, CLAYTON and MAYEDA, 1984). The higher concentration of Fe relative to Mg and Mn is consistent with the relative solubilities of these components in calcite (ANOVITZ and ESSENE, 1987), though these phase relations have only been determined at higher temperatures (250°C and above). Most calcites contain considerable quantities of Na, although whether the Na is structurally bound or present along grain boundaries or in minute fluid inclusions is unknown. (We did presputter grain surfaces to clean them before starting the analysis, and the Na signals during analysis were steady, so we doubt that this is terrestrial contamination.) Calcite grain compositions are highly variable, even within the same chondrite. ALH83100 is visibly brecciated, but the range of calcite compositions in this sample is no greater than in the other meteorites, and calcites within one clast show appreciable compositional scatter.

It is instructive to compare the concentrations of elements that have different calcite/fluid partitioning behavior, as trends in these elements can provide information on whether such systems approached equilibrium (VEIZER, 1983). Although there is a great deal of scatter in the data, some systematic relationships emerge. For example, Mn and Sr, which have very different calcite/fluid  $K_D$  values (see below), appear to have been differentially partitioned within the calcites. As an illustration, Nogoya G, with the highest Mn of any calcite grain in this meteorite, has the lowest Sr (as well as the lowest Ba and B, which also have  $K_D$  values similar to Sr), whereas Nogoya D has the lowest Mn and highest Sr, Ba, and B (Table 1). These covariation patterns do not form linear trends on graphs—they are only evident from inspection of the highest or lowest concentrations. However, modelling of Sr and Mn variations in limestones resulting from water-rock interaction during diagenesis indicates that the covariation should not be linear; Sr is almost quantitatively removed before Mn is added (see Fig. 6 of BANNER and HANSON, 1990), so there is no reason to expect statistical fits. Strontium, Ba, and B appear to have been partitioned together in calcites from Boriskino and Murchison as well, and Mn values are low in grains where the other three elements are high. However, this relationship is not evident in calcites from ALH83100, perhaps reflecting modification of carbonates under Antarctic weathering conditions. These covariations among trace elements with very similar or very different calcite/fluid partitioning behavior suggest that individual calcite grains approached equilibration with the associated fluids.

#### Dolomites in CM and CI Chondrites

Results of analyses of five dolomites in CM chondrites and ten dolomites in Orgueil are given in Table 1. The dolomites are more restricted in composition compared to calcites, and CI dolomites are consistently less Fe-rich and usually more Mn-rich than those in CM chondrites. Average molar  $\text{CaCO}_3$  values in dolomite, calculated by difference from the sum of  $\text{FeCO}_3 + \text{MgCO}_3 + \text{MnCO}_3$ , are as follows: for CI chondrites, 49.0 mol%; and for CM chondrites, 52.4 mol%. This confirms the observation of JOHNSON and PRINZ (1993) from electron probe analyses that CI dolomites are slightly subcalcic and

CM dolomites contain excess Ca. It also agrees with previous observations that ferroan dolomites have Ca excesses (ANOVITZ and ESSENE, 1987) and manganous dolomites have Ca depletions (GOLDSMITH and GRAF, 1960), although, again, these phase relations have been determined only at high temperatures (500°C and above). JOHNSON and PRINZ (1993) suggested that the excess Ca in CM dolomites results from metastable growth. Covariations between Mn, Sr, Ba, and B in dolomites do not follow their expected partitioning behavior (compare the values in Table 1 with  $K_D$  values given below) and may support this idea.

#### COMPOSITIONS OF COEXISTING FLUIDS

The grain-to-grain variability in composition shown by calcites and dolomites indicates that all the carbonate grains in any one meteorite were never in equilibrium with a pervasive, chemically homogeneous fluid. However, trace-element covariations discussed above suggest that each carbonate grain may have equilibrated with its own associated fluid. There were certainly changes in temperature and/or solution composition over time that allowed precipitation of carbonates followed by sulfates in carbonaceous chondrite parent bodies (RICHARDSON, 1978; LEE, 1993). There may have been other, less drastic temporal and spatial changes in fluids that account for the variations in the compositions of individual carbonate grains. The isolated calcites and dolomites now lie within regolith breccias (FREDRIKSSON and KERDRIDGE, 1988), so they probably formed at various depths and at various times over a wide area and then were mixed during impacts.

For the purpose of the calculations given below, we assume that calcites precipitated stably from solutions with which they were in equilibrium at low temperature. In terrestrial studies, dolomite is generally thought to form either as a diagenetic mineral through reaction of calcite with a Mg-bearing fluid or by precipitation from a brine. We do not know the formation mechanism of meteoritic dolomite, but we assume that it formed in contact with an aqueous solution.

Trace element concentrations of calcite and dolomite allow the molar ratios of analyzed elements, relative to Ca, in co-existing solutions to be calculated, if distribution coefficients (carbonate/fluid, relative to Ca) for the various elements are known. As discussed by MORSE and BENDER (1990), determination of distribution coefficients for carbonate-fluid systems, particularly at low temperatures, has proven to be extremely difficult. At low temperatures, it is unlikely that true thermodynamic equilibrium is achieved and that measured distribution coefficients reflect a variety of additional factors including solid and fluid compositions and reaction rates. VEIZER (1983) compiled distribution coefficients for calcite/fluid that had been determined at low (<100°C) temperatures. The difficulties of experimental work at low temperatures, and the probable lack of true equilibrium in these systems, are reflected in the range of distribution coefficients that he reported. The  $K_D$  values that we have used, with the highest and lowest values reported by Veizer in parentheses, are as follows: Na =  $2.85 \times 10^{-5}$  ( $2 \times 10^{-5}$ – $3 \times 10^{-5}$ ), Mg = 0.044 (0.013–0.060), Fe = 10 (1–20); Mn = 20 (5.4–50), Sr = 0.13 (0.027–0.4), and Ba = 0.25 (0.1–0.4). We have

generally used values in the midrange of those reported, unless a specific value was recommended for an element (VEIZER, 1983). The calcite  $K_D$  value for B = 0.1 (0.01–1) was determined in an empirical study of marine carbonates (HEMMING and HANSON, 1992). The wide range in reported  $K_D$  values (up to an order of magnitude) adds a large uncertainty to fluid compositions calculated from calcite compositions. The problem is even worse for dolomite calculations, as almost no experimental work on dolomite distribution coefficients

exists due to difficulties with getting dolomite to form at low temperatures. For this reason, dolomite distribution coefficients were calculated based on the calcite  $K_D$  values chosen above and crystal chemistry considerations, as discussed by KRETZ (1982): Na =  $2.3 \times 10^{-5}$ , Mg = 0.29, Fe = 22.2, Mn = 33.3, Sr = 0.12, Ba = 0.25, and B = 0.1 (assumed to be the same as for calcite). The calculated value for Sr (0.012) agrees with an empirical value of 0.0118 determined by VAHRENKAMP and SWART (1991). Although large uncer-

Table 2. Molar element/Ca fluid ratios calculated in equilibrium with CM & CI calcite and dolomite.

	B/Ca	Na/Ca	Mg/Ca	Fe/Ca	Mn/Ca	Sr/Ca	Ba/Ca
<b>CM Calcites</b>							
Boriskino A	4.82e-04	4.07e+01	5.78e-02	7.16e-04	7.10e-06	6.03e-04	8.59e-06
Boriskino K	4.34e-04	6.67e+01	7.47e-03	2.08e-05	2.50e-06	3.65e-04	8.76e-06
Boriskino B	4.83e-04	6.22e+01	4.08e-02	2.33e-04	1.00e-05	1.19e-03	1.77e-05
Boriskino C	9.45e-04	8.63e+01	2.85e-02	6.17e-05	8.80e-06	7.13e-04	3.05e-05
Boriskino G	7.39e-04	7.52e+01	1.72e-02	4.28e-05	3.23e-05	3.57e-04	1.26e-05
Boriskino G	5.70e-04	5.81e+01	3.90e-02	1.03e-04	1.40e-04	3.43e-04	1.45e-05
Boriskino H	6.14e-04	7.99e+01	1.41e-02	2.88e-05	2.50e-06	3.13e-04	1.16e-05
ALH83100 K	6.07e-04	1.11e+02	2.69e-02	1.14e-04	4.67e-05	1.79e-03	1.74e-05
ALH83100 K	7.04e-04	1.14e+02	5.41e-02	6.57e-04	7.78e-05	1.90e-03	1.55e-05
ALH83100 L	1.05e-03	7.02e+01	7.92e-02	2.23e-04	1.40e-05	1.79e-04	5.39e-06
ALH83100 N	8.52e-04	6.62e+01	4.54e-02	1.76e-04	1.63e-05	2.61e-04	6.98e-06
ALH83100 P	6.41e-04	6.69e+01	1.09e-01	1.24e-03	1.16e-05	5.93e-04	8.29e-06
ALH83100 F	6.06e-04	7.06e+01	2.50e-02	5.25e-05	5.11e-05	2.49e-04	1.87e-05
ALH83100 D	1.72e-03	1.13e+02	1.38e-01	1.10e-03	1.41e-04	1.23e-03	1.29e-05
ALH83100 B	1.53e-03	6.96e+01	6.22e-02	1.26e-04	6.75e-05	2.12e-03	2.38e-05
ALH83100 A	1.29e-03	8.41e+01	4.97e-02	1.61e-04	4.86e-05	1.07e-03	1.69e-05
Nogoya L	1.46e-03	1.39e+02	1.03e-01	7.47e-04	3.67e-05	1.11e-03	4.03e-05
Nogoya G	7.36e-04	7.16e+01	6.32e-02	3.34e-04	1.01e-04	3.23e-04	8.69e-06
Nogoya D	2.58e-03	1.30e+02	2.73e-01	6.88e-04	3.29e-05	1.94e-03	4.93e-05
Nogoya M	2.38e-03	8.21e+01	3.60e-01	1.21e-03	3.43e-05	3.22e-04	3.75e-05
Murchison E	1.17e-03	1.54e+02	9.19e-02	4.67e-04	6.24e-06	2.72e-04	3.50e-05
Murchison A	3.48e-03	4.30e+02	1.06e-01	7.72e-04	3.31e-05	3.38e-03	8.84e-05
Murchison G	1.70e-03	1.68e+02	8.38e-02	7.33e-05	4.89e-06	4.16e-04	1.29e-03
<b>CM Dolomites</b>							
Boriskino D	1.84e-03	1.20e+02	2.86e+00	4.28e-03	2.34e-03	2.33e-03	5.66e-05
Boriskino D	1.13e-03	9.72e+01	2.81e+00	4.33e-03	2.20e-03	2.17e-03	2.12e-05
Nogoya H	2.47e-03	1.61e+02	2.06e+00	3.50e-03	2.02e-03	2.91e-03	5.92e-05
Nogoya H	1.76e-03	1.22e+02	2.49e+00	3.43e-03	1.83e-03	2.05e-03	6.36e-05
Nogoya H	1.75e-03	2.13e+02	2.90e+00	3.49e-03	1.62e-03	2.31e-03	7.56e-05
<b>CI Dolomites</b>							
Orgueil B	9.57e-04	1.43e+02	3.09e+00	2.90e-03	4.01e-03	1.99e-03	6.03e-05
Orgueil A		8.35e+01	3.35e+00	2.37e-03	3.50e-03	3.52e-03	2.44e-05
Orgueil A		9.15e+01	3.13e+00	2.15e-03	2.75e-03	3.10e-03	2.44e-05
Orgueil A		1.10e+02	3.10e+00	2.68e-03	4.17e-03	2.27e-03	3.05e-05
Orgueil N	1.24e-03	1.56e+02	3.17e+00	4.00e-03	1.50e-03	2.76e-03	3.36e-05
Orgueil N		1.12e+02	3.15e+00	2.94e-03	1.32e-03	2.52e-03	2.80e-05
Orgueil D		8.96e+01	3.01e+00	3.05e-03	2.43e-03	2.45e-03	3.63e-05
Orgueil K		1.20e+02	2.94e+00	2.37e-03	2.21e-03	1.94e-03	3.45e-05
Orgueil J		9.43e+01	2.82e+00	2.27e-03	7.31e-03	1.79e-03	2.94e-05
Orgueil I	8.76e-04	8.57e+01	2.82e+00	1.91e-03	6.92e-04	4.48e-03	7.73e-05

Calculated compositions are probably order-of-magnitude estimates due to uncertainties in distribution coefficients (see text for discussion).

tainties in the distribution coefficients exist and our knowledge of the conditions under which the carbonates formed is very limited, the general characteristics (order of magnitude) of the solutions can be evaluated using the carbonate compositions.

Calculated element molar ratios (relative to Ca) for fluids in equilibrium with meteoritic calcites and dolomites are given in Table 2 and illustrated in Figs. 2 and 3. For comparison, the element ratios in average terrestrial seawater, surface waters, subsurface waters, and brines (VEIZER, 1983) are also shown in these figures.

IMPLICATIONS FOR CARBONATE FORMATION

A number of interesting features are apparent from inspection of Figs. 2 and 3. For CM chondrites, dolomites indicate fluids having consistently higher molar Fe/Ca, Mg/Ca, and Mn/Ca ratios than do coexisting calcites. Moreover, the mean Sr content of CM dolomite (135 ppm) is higher than that of calcite (104 ppm). The large Sr ion is confined to the Ca crystallographic sites of both calcite and dolomite (JACOBSON and USDOWSKI, 1976), leading to twice as much Sr in calcite as in associated dolomite (KRETZ, 1982). Thus, the calcites and dolomites in CM chondrites were clearly not in equilibrium. These observations imply that the calcites

and dolomites did not form from the same fluids, and so presumably represent distinct mineralizing events on the CM parent body (as they normally do in terrestrial occurrences). Unfortunately, because of the brecciation we have no preserved textural relationships between calcite and dolomite that would allow conclusions about the relative timing of these events. In nearly all terrestrial situations, however, calcite precipitation events precede dolomite formation.

Several alteration scales for CM chondrites have been proposed (MCSWEEN, 1979a, 1987; TOMEOKA and BUSECK, 1985; BROWNING et al., 1993). Of the chondrites studied here, Nogoya is significantly more altered than the other CM meteorites. Fluids in equilibrium with calcites in highly altered meteorites like Nogoya appear to have higher Mg/Ca, Mn/Ca, and possibly Fe/Ca than those calculated for less-altered meteorites like Murchison (Fig. 2). This observation, plus the earlier conclusion that the fluids that produced calcites and dolomites in CM chondrites were distinct, reinforces previous suggestions that fluid compositions in the parent asteroids were locally and temporally variable (RICHARDSON, 1978; FREDRIKSSON and KERRIDGE, 1988; JOHNSON and PRINZ, 1993). Calcite solutions appear to have become more like dolomite solutions with increasing alteration of the host CM meteorite, and CI chondrites, which appear to be more heavily altered than most CM chondrites (MCSWEEN,

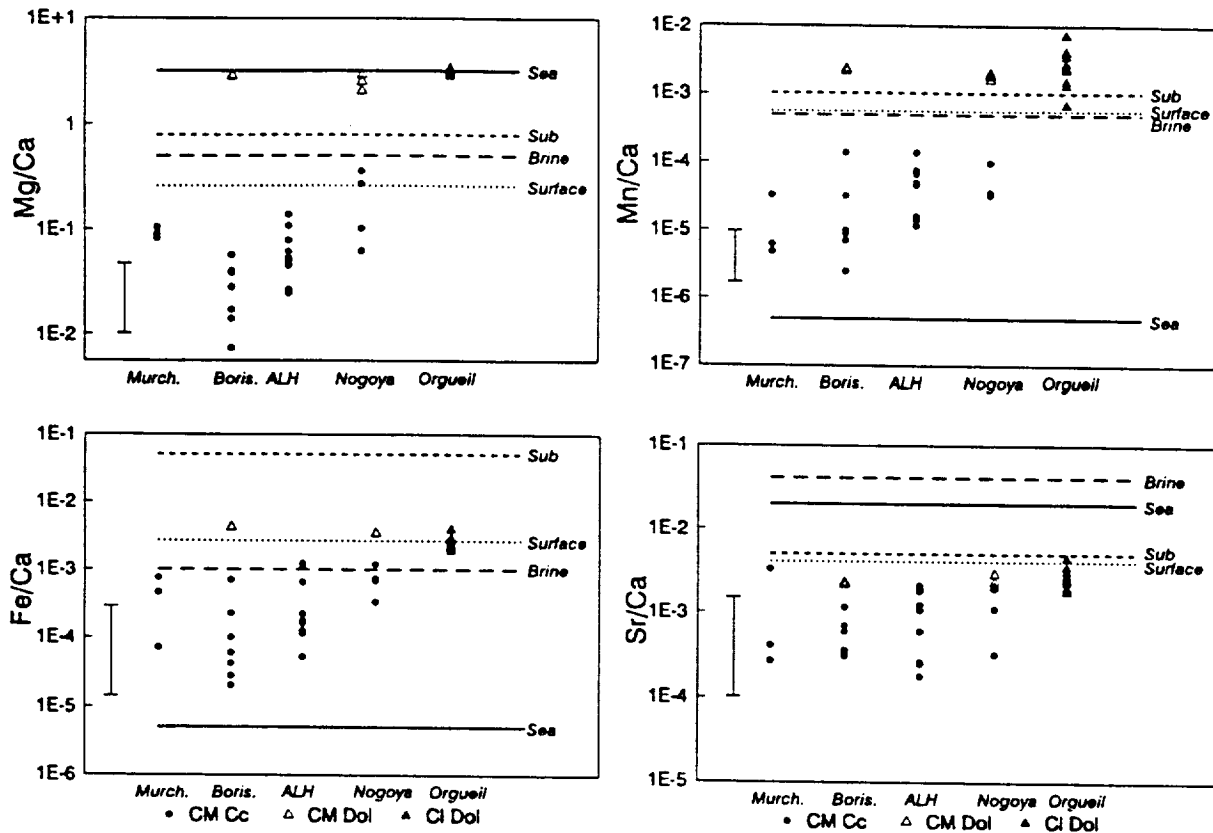


FIG. 2. Calculated molar ratios (relative to Ca) of Mg, Fe, Mn, and Sr for fluids in equilibrium with meteoritic calcites and dolomites. Potential range in calculated compositions based on uncertainties in published distribution coefficients and analytical error are illustrated by the error bars on the left of each plot. Shown for comparison are horizontal lines representing average molar ratios in terrestrial seawater, subsurface waters, brines, and surface waters (VEIZER, 1983).



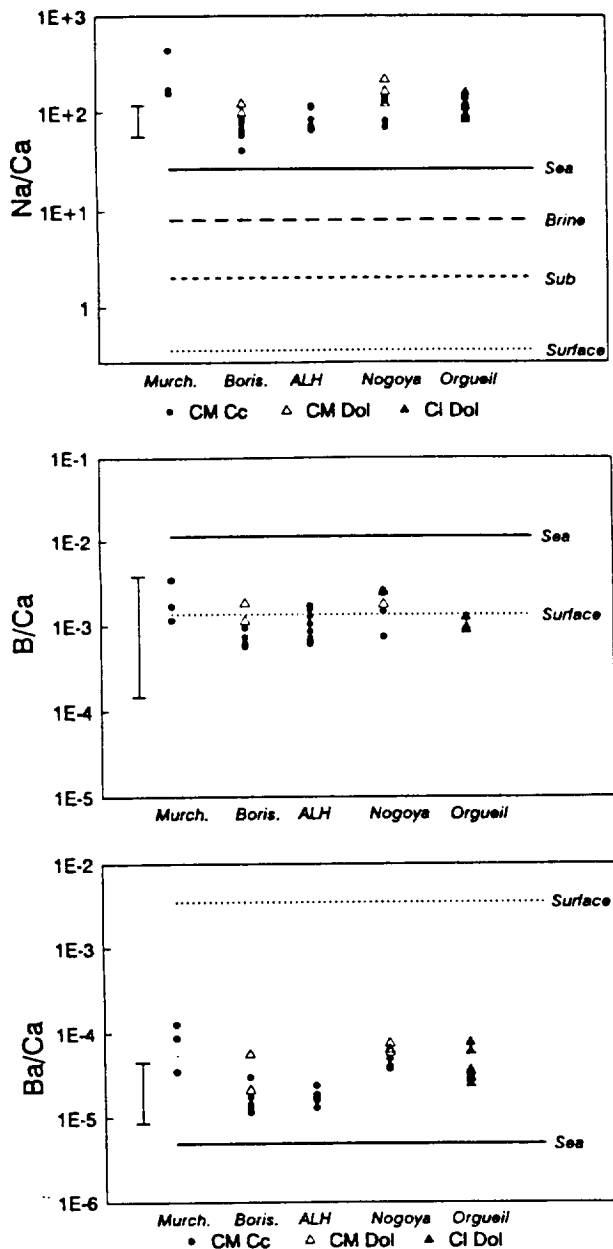


FIG. 3. Calculated molar ratios (relative to Ca) of Na, B, and Ba for fluids in equilibrium with meteoritic calcites and dolomites. Potential errors and average molar ratios in terrestrial solutions are also shown (VEIZER, 1983).

1979b), contain mostly dolomite. We might therefore conclude that calcite formed before dolomite in CM chondrites.

Calculations for dolomites in CI chondrites suggest fluids very similar to those in equilibrium with CM dolomites. LEE (1993) also noted the similarity between later-formed sulfate veins in the Cold Bokkeveld CM chondrite with those in CI chondrites. These similarities could be used to speculate that both kinds of chondrite formed within a shared parent body, or at least had been assembled into the same body by the time of late-stage vein formation. However, LEE (1993) suggested that fracturing and mineralization were common

events on asteroids, and preferred different parent bodies for CM and CI chondrites. Based on differences in dolomite Ca contents and systematic differences in oxygen isotopic composition, we also prefer different asteroids with parallel alteration histories.

#### FORMATION OF BRINES

The dolomitic fluids have very high Na/Ca ratios (Fig. 3), and appear similar in many respects to terrestrial brines. ("Brines" are strictly defined as waters containing >100 g/L of total dissolved substances, HANOR, 1983; here, we will use the term brine to describe highly saline solutions without implying formal limits in the concentration of dissolved salts.) Although we can specify only the ratio of Na to Ca, it seems probable that the absolute concentration of Na was also high, because the Mg/Ca ratio was probably similar to that of seawater in which the absolute concentration of Mg is sufficient to promote dolomitization. The concentration of Na in terrestrial dolomites is especially sensitive to salinity variations in associated fluids (SASS and BEIN, 1988), and the nearly stoichiometric or slightly Ca-depleted compositions of meteoritic dolomites are also consistent with the hypothesis that they formed through reaction with brine-like fluids (LUMSDEN and CHIMAHUSKY, 1980). Fluids in equilibrium with CM calcites also had high Na/Ca ratios (Fig. 3) but had lower Mg/Ca, Fe/Ca, and Mn/Ca ratios. The correspondence between the meteoritic solutions and terrestrial brines is certainly not exact, but terrestrial brines vary considerably in composition, and there is no reason to assume that meteoritic fluids would be similar in composition to any specific terrestrial solution in terms of every element ratio.

Three generalized processes have commonly been invoked to explain the origin of terrestrial brines (HANOR, 1983): subsurface dissolution of evaporites, subaerial evaporation of seawater, and shale membrane filtration. Of these possibilities, only the last seems possible in an asteroidal setting. In shale membrane filtration, water molecules are preferentially forced through semipermeable, compacted clay layers, and dissolved ions are concentrated in a residual saline pore fluid. Once phyllosilicates had formed through the alteration of CM and CI chondrite precursor materials, membrane filtration might have produced local pockets of brine as solutions percolated upward during hydrothermal circulation or venting (GRIMM and MCSWEEN, 1989). However, it is not known whether serpentines that dominate the matrix of CM chondrites would be as effective a membrane as clay minerals.

Alternatively, the alteration reactions that formed the phyllosilicates may have released components directly into the associated fluids, thus forming brines. Hydration reactions have also been implicated in the formation of brines in sea-floor hydrothermal systems (e.g., HOLLAND, 1978, pp. 190–200). Such hydrothermal brines are typically high in Ca (HARDIE, 1990), and the lower Mg/Ca, Fe/Ca, Mn/Ca, and Sr/Ca values in meteoritic carbonates relative to terrestrial sedimentary brines might reflect high Ca concentrations. In principle, the phyllosilicate-producing reactions in carbonaceous chondrites could be modelled to test whether they can produce the brine compositions needed; however, the precise reactions are not yet known, although some progress

in this area has been made (e.g., ZOLENSKY et al., 1989). In this case, as in shale membrane filtration, formation of phyllosilicates within the parent bodies is indicated.

It is also possible that brines were concentrated during low-pressure boiling of less saline fluids as they rose toward the asteroid surface. Alteration temperatures for CI chondrites are estimated at 50–150°C (HAYATSU and ANDERS, 1981; CLAYTON and MAYEDA, 1984; ZOLENSKY et al., 1989), although CM chondrites apparently were altered at much lower temperatures. Escape of these brines into the overlying regolith then resulted in precipitation of carbonate (and later sulfate) veins. This mechanism decouples the formation of phyllosilicates and carbonates, allowing phyllosilicates to have formed in the nebula.

The inferred sequence—calcite, dolomite, sulfates—suggests that solutions became progressively more saline as alteration proceeded. Either shale membrane filtration or boiling should also enrich the residual brine in  $^{18}\text{O}$ , so we might expect these minerals to show isotopic fractionation if the brine formed by one of these mechanisms. The formation of brines capable of precipitating carbonates and sulfates in carbonaceous chondrite asteroids may have been critically dependent on the earlier formation of phyllosilicates, and these veins might thus represent the ultimate step in a protracted alteration sequence.

Contaminants are more highly soluble in liquid water than in water ice. If the original source of the aqueous fluid in carbonaceous asteroids was ice accreted along with silicate material (GRIMM and MCSWEEN, 1989), the contaminants were probably added to the fluid after melting of the ice. The brine-like compositions of these fluids may then imply that dissolution of soluble components was pervasive, and that the preservation of “cosmic” bulk compositions for carbonaceous chondrites is more apparent than real.

#### SUMMARY

The concentrations of minor and trace elements in meteoritic calcites and dolomites are variable, but appear to be consistent with their stable formation in equilibrium with aqueous solutions at low temperatures. The fluids coexisting with these carbonates contained appreciable amounts of Na, Mg, Fe, and Mn (relative to Ca), and were similar in many respects to buried terrestrial brines. The compositions of these mineralizing fluids were probably temporally and spatially variable. The concentrations of dissolved species may have increased through shale membrane filtration as the fluids tried to pass upward through compacted phyllosilicate material, during phyllosilicate-forming reactions as Ca and Mg were released into the fluids, or through low-pressure boiling. The formation of vein carbonates and of later sulfates represents the final stage in the alteration of carbonaceous chondrite asteroids.

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# HIGH SPATIAL RESOLUTION SULPHUR ISOTOPIC ANALYSIS OF TROILITE IN ORDINARY CHONDRITES BY ION MICROPROBE

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**Rationale.** Sulphur is the fifth most abundant element found in meteorites and it occurs in a wide variety of chemical forms, including sulphides, sulphates and organic material. Partly due to the very restricted isotopic composition of S in bulk meteorites of all types [1] (the standard deviation on the range is  $<0.1\text{‰}$ ), there have been comparatively few studies of the composition of constituent phases, although the studies that have been published have observed small but significant differences between phases [2]. In addition to the restricted isotopic composition, the extraction of S for isotopic analysis usually relies on chemical extraction [3] or stepped combustion [4] techniques. There are a number of drawbacks to these methods: 1) it is not always certain which phases are being sampled; 2) spatial information is lost; and 3) the demands of minimum sample size mean that it is virtually impossible to analyse single grains, let alone parts of single grains, and thus it is not possible to detect inter-grain variability within one phase. S isotopic analysis using the ion microprobe can overcome some of these problems, although the precision is poor in comparison with conventional and laser combustion techniques [5]. Here we report initial *in situ* analyses of troilite from ordinary chondrites using an ion microprobe. This has enabled us to study inter and intra-grain variations in S isotopic composition.

**Methods.** The S isotopic values were obtained with a Cameca ims-4f ion microprobe [6]. A Cs<sup>+</sup> primary beam focussed to a spot of between 25-30 $\mu\text{m}$  in diameter, although the secondary ion optics result in only the central 8 $\mu\text{m}$  being analysed. The S isotope standard Cañon Diablo Troilite (CDT) was analysed at the beginning and end of each analytical session in order to measure the degree of instrument-induced isotopic fractionation (usually -20 to -25 $\text{‰}$ , although this varies from session to session), overall reproducibility (usually in the range  $\pm 1-1.5\text{‰}$  ( $2\sigma$ ), occasionally better) and to check for drift over the period of an analytical session (~12 hours). None of the standard analyses presented here displayed any such drift. The reproducibility is the measure of the consistency of the instrument conditions over an analytical session, in particular the alignment of the primary beam relative to the secondary ion optics. In any one analytical session the ratio of the number of standard analyses to the number of unknowns is always better than 1:2. In addition to being used to correct the unknown analyses for instrument-induced fractionation, the reproducibility of the measured value of CDT is incorporated in the error for each unknown in order to obtain a measure of the accuracy. All errors are quoted at the  $2\sigma$  level. The relatively poor precision obtainable using the ion microprobe means that the detection of nucleosynthetic anomalies involving the minor isotopes, <sup>33</sup>S and <sup>36</sup>S, is not likely.

**Results.**  $\delta^{34}\text{S}_{\text{CDT}}$  data have been obtained from troilite grains in six ordinary chondrites, three relatively low-shock Antarctic L chondrites (ALH85045 (L3), LEW86024 (L4) and QUE90210 (L5)) and three H chondrites (Tieschitz (H3), Forest Vale (H4) and Limerick (H5)). The results obtained thus far are summarised in Figure 1.

**Discussion.** For the purposes of discussion the samples can be divided into three categories: 1) Those samples (Tieschitz, Forest Vale and ALH85045) whose absolute  $\delta^{34}\text{S}_{\text{CDT}}$  values are not significantly different from CDT and that show a range of variation not significantly greater than that expected from the reproducibility of the standard. The Forest Vale analyses were obtained on troilite both within chondrules and within the matrix. The Tieschitz analyses came from troilite on chondrule rims and within the matrix.

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2) Those samples (Limerick and LEW86024) that show significant differences in absolute values of  $\delta^{34}\text{S}_{\text{CDT}}$ , although again the variation within a sample is not significantly greater than would be expected given the standard reproducibility. Limerick gave values consistently heavier than CDT by an average of approximately +2.5‰, and the results from two separate analytical sessions are in agreement. In contrast, troilite in LEW86024 is isotopically light, giving an average of approximately -2.7‰. In both samples troilite was a matrix phase.

3) The only sample which has a significant variation in troilite  $\delta^{34}\text{S}_{\text{CDT}}$  values greater than that observed in the standard analysed concurrently is QUE90210. The 12 standard analyses gave a standard deviation of 1.3‰, and the standard deviation of the 21 unknown analyses, which were all from matrix troilite, was 2.2‰. The last 8 analyses (see Figure 1), which are displaced to lighter isotopic values, were all from a single grain or grain aggregate. At the present scale of study there is no indication of within-grain heterogeneities.

Differences in the S isotopic composition of troilite from that of bulk meteorites could have two extreme interpretations: either the variations observed are due to nebular heterogeneity, or that they are due to secondary alteration of the primary S-containing phases. The differences in troilite S isotopic composition presented here and in particular the apparent heterogeneities within a single section of QUE90210 support a secondary alteration mechanism. If such small-scale, within-phase heterogeneities commonly exist in chondrites and they are due to variable secondary processes, then it would suggest that similar heterogeneities may exist in coexisting S containing phases and that the internal variations between phases, identified using chemical extraction and stepped combustion techniques, may locally be larger than has previously been reported.

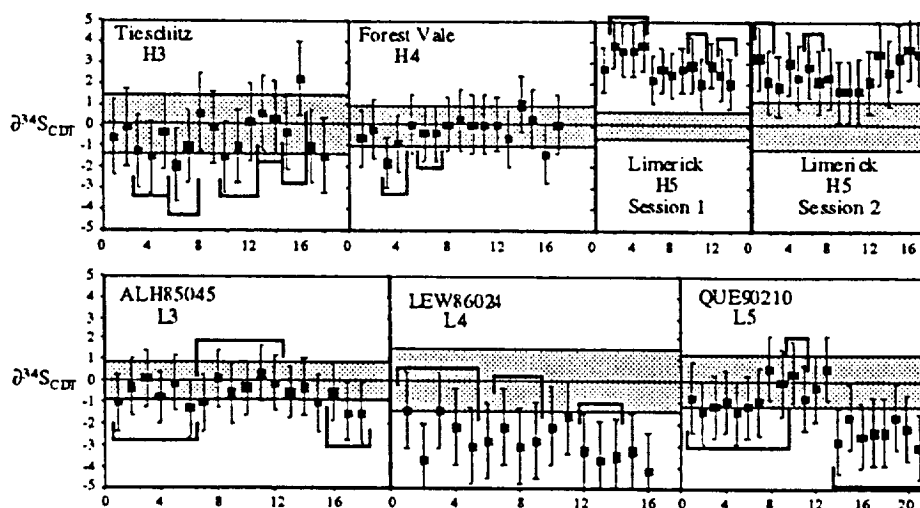


Figure 1. Summary of S-isotope data obtained on troilites from ordinary chondrites. Shaded bands represent the  $2\sigma$  reproducibility of analyses on the CDT standard. Error bars on the analyses include both the error on the sample and the reproducibility on the standard. Grouped analyses were obtained from different areas on the same grains or grain aggregates.

**References.** [1] Pillinger (1984) *GCA*, **48**, 2739. [2] Monster et al. (1965) *GCA*, **29**, 773. [3] Gao & Theimens (1993) *GCA*, **57**, 3171. [4] Burgess et al. (1991), *Meteoritics*, **26**, 55. [5] Kelley et al. (1992) *Scanning Microscopy*, **6**, 129. [6] Graham & Valley (1991) *Chem Geol.* **101**, 169-172. **Acknowledgements.** NASA grant NAGW 2800, and Geoscience Research Program and Division of Chemical Sciences, Office of Basic Energy Sciences, US Department of Energy under Contract DE-ACO5-85OR21400 with Martin Marietta Energy Systems, Inc.

## In-situ Analysis of Oxygen Isotope Ratios in Silicates and Carbonates by Ion Microprobe

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A long held aim of ion microprobe analysis techniques has been the *in situ* analysis of  $\delta^{18}\text{O}$  in a variety of minerals. The principal advantage of the ion microprobe is the high spatial resolution of the primary ion beam (10-30  $\mu\text{m}$  wide). The ability to routinely determine  $\delta^{18}\text{O}$  on small volumes of material permits study of inhomogeneous mineral grains and allow analysis of single mineral grains in fine-grained rocks. Analysis of  $\delta^{18}\text{O}$  by ion microprobe has been carried out on conducting mineral phases, for example magnetite (Valley and Graham, 1992). However, severe sample charging and the resulting instability has presented major problems in attempts to analyze non-conducting mineral phases such as silicates and carbonates. Both high (Hervig et al., 1992) and low (Migeon et al., 1990) energy electron guns have been used in an attempt to overcome the sample charging problem. However use of these devices has met with limited success, since even small instabilities in charge compensation can result in large changes in measured  $\delta^{18}\text{O}$  under normal operating conditions. Hervig et al. (1992) analyzed  $\delta^{18}\text{O}$  in silicates using a high energy electron gun in combination with applying a large voltage offset, as this provides an immunity to small variations in the charge compensation. However, the high energy and currents of the electron gun may prevent analysis of beam sensitive phases (Migeon et al., 1990). Here we report on the use of a normal incidence, low energy electron gun and large voltage offsets, which has allowed for the relatively routine analysis of  $\delta^{18}\text{O}$  in non-conducting minerals with precision similar to counting statistics ( $\pm 1\%$ ).

Analyses were done using a Cameca ims-4f ion microprobe (#176), equipped with a Cs gun, normal incident electron gun, and dual sample airlock interchange. We have modified the instrument so that sample accelerating voltages can be varied between 0 and 5 keV, in contrast to standard instruments which have an accelerating voltage range of  $4.5 \pm 0.125$  keV. The sample was sputtered with a primary beam of  $^{133}\text{Cs}$  accelerated at 10 keV. Primary beam currents were typically around 5 nA, with a spot size of 20 to 30  $\mu\text{m}$ . The secondary mass spectrometer was tuned for  $4.5 \pm 0.2$  keV ions, and an offset voltage of 350 eV was applied. Mass resolution was set at  $\sim 500$  m/ $\Delta m$  as the presence of molecular interferences at large offset energies is negligible. Secondary ions were detected using a 14 month old Balzers SEV217 electron multiplier and a deadtime of 33 ns. Count rate on the  $^{18}\text{O}$  peak was 500,000 cps. Magnetic peak jumping was used to change masses (0.7 s settle time). Each analysis consisted of 200 ratios, counting 1 second on  $^{18}\text{O}$  and 5 seconds on  $^{16}\text{O}$ , resulting in a total of  $\sim 1 \times 10^6$   $^{18}\text{O}$  counts for a theoretical precision of 1%. Samples were pre-sputtered for five minutes before starting an analysis, and total sputter time was 35 minutes. Sample charging was neutralized using the normal incident electron gun, producing a cloud of low energy electrons (a few volts) over an area  $\sim 125$   $\mu\text{m}$  in diameter, and total sample current was at most a few tens of nA. During the first analytical period, room temperature fluctuated by as much as  $5^\circ\text{C}$  during a day.

We have analyzed  $\delta^{18}\text{O}$  in several minerals during two separate one week periods (Table 1). The reproducibility ( $1\sigma_{n-1}$ ) for three to seventeen analyses for a particular phase ranges from 0.6 to 1.7%, with most falling in the range of 0.9 to 1.2%. Internal precision is similar to that predicted by counting statistics (0.9 to 1.2%). Our precision is comparable to published results for magnetite (0.76 to 1.9%; Valley and Graham, 1992), and is more consistent than that obtained using a high energy electron gun on insulators (Hervig et al., 1992). In contrast

to the results obtained on magnetite, we observed no systematic drift in measured isotope ratios with time. Although our data is relatively limited, our results suggest that instrumental fractionation both for a single phase and between different phases is similar from day-to-day when the energy slits are properly tuned. No sample damage due to the electron gun was observed, even on calcite.

Closer examination of daily runs suggests that some of the variation in measured isotope ratios may not be entirely random (Fig. 1). The instrument appears sensitive to temperature variation, as the results obtained during the morning when the instrument and the room were warming up are more variable than the results obtained in the afternoon and evening when conditions were more stable. We apparently obtain rare "flyers", which lie more than  $2\sigma$  from the mean. The cause of these is currently uncertain, but they may be due to sample imperfections. Rejection of such outliers considerably improves the calculated standard deviation (see Table 1), but until a method to detect suspect analyses is found, inclusion of these outliers is a more honest assessment of our precision.

This technique has several advantages over using either a high energy electron gun or using a low energy electron gun and low energy ions. Unlike a high energy electron gun, low energy electrons do not damage beam sensitive materials such as carbonates and phosphates. Also, different minerals reach charge equilibrium at different sample voltages under bombardment by high energy electrons, making analysis of heterogeneous materials potentially difficult (Migeon et al., 1990). Compared to analyzing low energy secondary ions (w/a low energy electron gun), analysis using high energy secondary ions is much simpler for two reasons. First, the instrumental fractionation is not nearly as sensitive to changes in charge compensation. Secondly, since the instrument is operated at low mass resolution, alignment of the primary beam spot relative to the secondary optics is much simpler.

Our results indicate that we can routinely analyze  $\delta^{18}\text{O}$  in silicates and carbonates with a precision that is similar to that predicted by counting statistics for an individual analysis ( $\pm 1\%$ ), with spatial resolutions of 20 to 30  $\mu\text{m}$ . This precision and spatial resolution has many potential applications, particularly in studies of low temperature processes such as diagenesis, and in studies of meteorites where large isotopic variations are expected.

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Table 1: Summary of Isotope ratios

Date	Sample	n	$^{18}\text{O}/^{16}\text{O} \times 10^{-3}$	$\delta_{\text{SMOW}}$	$1\sigma_{n-1}$	$10^3 \ln \alpha_{\text{inst}}$
4-15-94	Braz Qtz	6	1.8981	-53.39	0.71	
4-18-94	Braz Qtz	6	1.8984	-53.26	0.68	
4-19-94	Braz Qtz	7	1.9075	-48.74	1.74 (-1.11 <sup>‡</sup> )	-63.34
4-20-94	Braz Qtz	3	1.8947	-55.11	0.65	
4-21-94	Braz Qtz	17	1.9068	-49.08	1.29 (-0.98 <sup>‡</sup> )	-63.68
4-22-94	Braz Qtz	5	1.8979	-53.51	0.85	
5-2-94	Braz Qtz	6	1.9021	-51.44	1.08	
5-3-94 <sup>†</sup>	Braz Qtz	7	1.9190	-43.01	1.49	
5-4-94	Braz Qtz	4	1.8959	-54.51	1.27	
5-5-94	Braz Qtz	5	1.9008	-52.08	1.05	
5-6-94	Braz Qtz	6	1.9020	-51.48	1.01	
4-20-94	S.P. Albite	8	1.8796	-62.62	1.41	
5-5-94	S.P. Albite	4	1.8823	-61.30	0.99	
5-6-94	S.P. Albite	4	1.8825	-61.18	0.57	
5-2-94	U.T. Calcite	6	1.8829	-60.98	0.95	
5-3-94 <sup>†</sup>	U.T. Calcite	6	1.9093	-47.83	1.37	
5-4-94	Cpx 437	3	1.8693	-67.76	1.20	
5-5-94	Cpx CN183	4	1.8797	-62.61	0.90	
5-6-94	Cpx CN183	6	1.8800	-62.46	0.90	
5-5-94	G.M. Gnt	4	1.8965	-54.20	1.63	

Table lists mean value for the daily  $^{18}\text{O}/^{16}\text{O}$  ratio measured on a variety of samples, where n is the number of analyses. The measured ratios are also expressed relative to SMOW. The instrumental fractionation for each day is shown in the last column.

† Energy slits not centered during instrument tuning.  
‡ One outlier ( $>2\sigma$ ) removed from the set of analyses.

Figure 1:  $\delta^{18}\text{O}$  values of Brazilian Quartz, April 21, 1994.

