

**TRACE ELEMENT (REE, Y, Sr, Mn) ABUNDANCES IN CARBONATES IN CM CHONDRITES** Adrian J. Brearley, Charles K. Shearer and Grant W. Fowler, Institute of Meteoritics, Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, New Mexico 87131, USA.

**Summary** Carbonates in CM chondrites may be a possible sink for REE elements which are released from chondrule mesostases during aqueous alteration. In order to examine whether the REEs are mobile and are taken up in carbonates we have measured the abundances of Mn, Sr, Y and REE in calcites in the three CM chondrites, Murchison, Mighei and ALH 84034 by SIMS. These three meteorites cover the range of degrees of alteration observed in the CM chondrites from the least altered (Murchison) to highly altered (ALH 84034). Our analyses for Mn and Sr are consistent with the data reported by [5] from carbonates in other CM chondrites. Our results for the REE elements show that these elements are present in extremely low abundances ( $3 \times \text{CI}$  to less than  $0.1 \times \text{CI}$ ) in calcite in all three meteorites and in most cases are below detection limits for our instrument ( $0.02$  to  $0.41 \times \text{CI}$  for LREE and  $0.2 \times \text{CI}$  for most of the HREE).

**Introduction** Although carbonate minerals are extremely common in CM carbonaceous chondrites [1-3], the details of the mineral chemistry of these phases has only recently been investigated in any detail [4]. The dominant carbonate phase present is calcite, which exhibits a relatively restricted range of compositions with minor solid solution with  $\text{MgCO}_3$  and  $\text{FeCO}_3$ . Dolomite has also been shown to be present in a few CM chondrites, but is relatively rare in comparison with calcite. These carbonate phases are widely believed to have precipitated at equilibrium from aqueous solutions during low temperature aqueous alteration in a parent body environment [2,4,5]. Consequently their trace element geochemistry can provide useful information about the fluid composition from which they grew. [5] have used ion microprobe techniques to measure the concentrations of Fe, Mg, Mn, Sr, Na, B and Ba in calcites and dolomites in four CM chondrites. These data show that the carbonates precipitated from saline solutions, but calcite and dolomite did not precipitate at the same time and are not in equilibrium. These data have lead to a better understanding of carbonate genesis in CM chondrites as a result of aqueous alteration.

A further area of interest in regard to the geochemistry of carbonates in CM chondrites concerns their REE abundances. It is widely recognized that one of the earliest alteration reactions which occurs in CM chondrites is the hydration of chondrule mesostasis to form serpentine group minerals (or spinach). Mesostasis is the host of the incompatible REE (excluded during olivine and low-Ca pyroxene crystallization) and often contains extremely elevated abundances of these elements (up to  $100 \times \text{CI}$ ) [6], so that alteration of the glass phase should release significant concentrations of REE and Ca into the fluid phase. For example, analyses of slightly altered chondrules from the CM chondrite Y-793321 show that they have very significant depletions in LREE [7], which is probably attributable to the aqueous alteration of glass. The HREE appear to be preferentially retained in these chondrules. The final resting place of REE released by alteration of glass is poorly understood. However, with the exception of carbonates there are few secondary phases, present in CM chondrites which can satisfactorily incorporate REE elements. Carbonates have been shown to assimilate up to several hundred ppm of the REEs in terrestrial rocks depending on the concentrations in solution. Thus calcite and dolomite in CM chondrites could, at least theoretically, take up REE and would hence provide information on the REE geochemistry of the fluid phase. Since the alteration of chondrule glasses is a progressive phenomenon, the REE geochemistry of carbonates may be a sensitive indicator of the degree of alteration of chondrule glasses in a given chondrite.

**Samples** The 3 chondrites studied are Murchison, Mighei and ALH 84034, which show a range of degrees of alteration. Murchison and Mighei both show relatively mild alteration, where chondrule mesostases are essentially completely altered, but chondrule silicates are not. In comparison, ALH 84034 is a highly altered CM chondrite, in which all the primary chondrule silicates have been replaced by hydrous phases (dominantly serpentine) [8]. Calcite is common in all three meteorites and occurs dominantly in the fine-grained matrix, although it is also present in some CAI. In ALH 84034 calcite is especially common and also found in chondrules and throughout the matrix as angular, isolated grains or as subrounded aggregates of grains, which often consist of coexisting calcite and dolomite. The typical grain size of individual carbonate crystals is  $\sim 50 \mu\text{m}$ , but grains up to  $150 \mu\text{m}$  have been found.

**Analytical Methods.** Trace element analyses of Fe, Mn, Sr, Y, and REE were performed by SIMS using the CAMECA IMS 4f instrument operated by the University of New Mexico/Sandia National

Laboratories. Unlike previously reported analyses of REE in carbonates, real carbonate standards were identified and developed for this study. These standards include Penn State and CRC. These standards were documented for Mn, Fe, Sr, Ba, Y, and REE using both INAA and ICP-MS techniques. Homogeneity of these standards were documented using CL, EMP, and SIMS. SIMS analyses were conducted by bombardment of the samples with primary  $O^-$  ions accelerated through a nominal potential of 10 kV. A primary ion current of 20-40 nA was focused on the sample over a spot diameter of 25-30  $\mu m$ . Sputtered secondary ions were energy filtered using a sample offset voltage of -125 V and an energy window of 50 V to effectively eliminate isobaric interferences. Each analysis involved repeated cycles of peak counting on  $^{44}Ca^+$ ,  $^{55}Mn^+$ ,  $^{88}Sr^+$ ,  $^{90}Y^+$ ,  $^{139}La^+$ ,  $^{140}Ce^+$ ,  $^{146}Nd^+$ ,  $^{147}Sm^+$ ,  $^{153}Eu^+$ ,  $^{163}Dy^+$ ,  $^{167}Er^+$ , and  $^{174}Yb^+$ , as well as counting on a background position to monitor detection noise. Peak counting times were varied to achieve an analytical precision of at least 15% (typically 5-10%) on each element. Prior to each analysis, sample areas surrounding the spot were cleaned with a rastered primary beam to eliminate contamination from the gold coat and surface layer of the sample. Spots were also pre-sputtered for approximately 1 minute to allow secondary ion signals to stabilize. Following rastering and pre-sputtering, ten cycles of data were collected with total analysis times of 40-50 minutes. Interfering species were effectively eliminated using energy filtering. Absolute concentrations of each element were calculated using empirical relationships between concentrations and measured peak/ $^{44}Ca^+$  ratios, normalized to known CaO content, as derived from measurements of a documented standard. As previously reported by Mason [9,10], secondary ion yields are considerably lower for calcite and dolomite than for silicate minerals. Lower yields translate to lower count rates. As the precision of an analysis is a function of count rate, counting times were longer for carbonates than for similarly enriched silicates. With the exception of Ce, REE in silicates typically ionize in a systematic fashion which allows a single calibration curve to include each element. However, individual REE in carbonates ionize with significantly different yields under primary ion bombardment, requiring separate calibration curves for each element.

**Results** Mn, Sr and Y are found at concentrations in carbonates that can be readily detected by SIMS confirming the results for Mn and Sr found by [5]. The range of these initial carbonate analyses are shown in Table 1.

**Table 1** All values in ppm.

	Mn	Sr	Y
ALH 84034	283-3000	58-184	0.13-0.69
Mighei	71-87	300-483	0.04-0.025
Murchison	78-331	60-122	0.21-0.23

Our SIMS data for Mn and Sr in calcite in Murchison are very consistent with the measurements made by [5] and all our analyses fall within their ranges. Based on our thus far limited number of carbonate analyses, there appears to be no correlation among Mn, Fe, Sr and Y. The initial REE data collected on calcite is incomplete due to the low REE concentrations. Therefore the following observations are preliminary and need to be confirmed by additional analyses. LREE abundances in the carbonates range from 3.4 x CI to below the detection limit. Under optimum instrument conditions, detection limits for the LREE are approximately 0.02 x CI (Ce) to 0.41 x CI (Sm). HREE were generally below the detection limit (0.2 x CI for most of the HREE). This *may* imply that the carbonates are slightly LREE enriched. LREE appear to be higher in Mighei with lower concentrations in ALH 84034 and Murchison respectively. These preliminary data strongly indicate that the carbonate grains have not incorporated REEs in any significant abundance and that the REE content of the fluid from which they grew was extremely low. This suggests that the REEs are incorporated into silicate phases such as serpentines at approximately 1 x CI levels.

**References** [1] Fuchs, L.H. et al. (1973) *Smith. Contrib. Earth Sci.* 10. [2] Bunch, T.E. and Chang, S. (1980) *GCA* 44, 1543-1577. [3] Barber, D.J. (1981) *GCA* 45, 945-970. [4] Johnson, C.A. and Prinz, M. (1993) *GCA* 57, 2843. [5] Riciputi, L.R. (1994) *GCA* 58, 1343. [6] Alexander, C.M.O'D (1994) *GCA* 58, 3451. [7] Inoue, M. (1994) *Proc. NIPR Ant. Met.* 7, 150. [8] Llorca, J. and Brearley, A.J. (1992) *LPS XXIII* 793. [9] Mason, R.A. (1987) *Chem. Geol.* 64, 209-224. [10] Swart, P.K. (1990) *Anal. Chem.* 62, 722-728.

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