

**ION MICROPROBE ANALYSIS OF OXYGEN AND CARBON ISOTOPE RATIOS IN THE ALH84001 METEORITE.** J. W. Valley<sup>1</sup>, J. M. Eiler<sup>2</sup>, C. M. Graham<sup>3</sup>, E. K. Gibson Jr.<sup>4</sup>, C. S. Romanek<sup>5</sup>, <sup>1</sup>Dept. of Geology, Univ. of Wisconsin, Madison, WI 53706, USA, <sup>2</sup>Div. of Geological and Planetary Sci., Calif. Inst. Tech., Pasadena, CA 91125, USA, <sup>3</sup>Dept. of Geology and Geophysics, Univ. of Edinburgh, Edinburgh, EH9 3JW, Scotland, <sup>4</sup>NASA-JSC, Houston, TX 77058, USA, <sup>5</sup>Savannah River Lab., Univ. of Georgia, Aiken, SC 29802, USA.

Carbonate and silicate minerals in the martian meteorite, ALH84001, have been analyzed in situ for  $^{18}\text{O}/^{16}\text{O}$  and  $^{13}\text{C}/^{12}\text{C}$  using a Cameca ims 4f ion microprobe. Previous analyses of this sample, made by acid dissolution or thermal decrepitation of whole rock powders or mineral separates, have varied from  $-9$  to  $26\%$  SMOW in  $\delta^{18}\text{O}$  and  $-21$  to  $53\%$  PDB in  $\delta^{13}\text{C}$  [1–4]. No spatial information was obtained and these values may represent mixtures of heterogeneous material. The size for our ion probe pit is  $20\text{--}40\ \mu\text{m}$  diameter by  $6\text{--}8\ \mu\text{m}$  deep (volume =  $1600\text{--}2500\ \mu\text{m}^3$ , mass =  $5\text{--}8\ \text{ng}$ ). The high spatial resolution of ion microprobe analysis permits textural and chemical correlation, and optimizes efforts to avoid terrestrial contamination. Instrumental mass fractionations (IMF) are standardized as a function of Fe content and calibrated through detailed analysis of carbonate standards [5]. Analytical procedures are reviewed elsewhere [6].

Our sample of ALH84001 is dominantly composed of orthopyroxene ( $\text{En}_{70}\text{Fs}_{27}\text{Wo}_3$ ) with minor chromite, maskelynite, pyrite,  $\text{SiO}_2$  and multiple generations of carbonate, including disk-shaped carbonate concretions reported to contain submicroscopic grains of magnetite and greigite [7,8]. The sample is heterogeneously fractured. Concretions are precipitated along fractures and show pronounced concentric mineralogical, textural, and chemical zonation [7,8]. Two concretions were analyzed: Carb. #1, a composite concretion of two intergrown disks measuring ca.  $250 \times 150 \times 10\text{--}50\ \mu\text{m}$ ; and Carb. #2, a single disk measuring ca.  $150\ \mu\text{m}$  dia. by  $10\text{--}20\ \mu\text{m}$  thick. Electron microprobe analysis and imaging were performed before and after ion probe analysis. With the exception of one pit that overlapped the outer white magnesite rim, the carbonates analyzed by ion probe were orange-colored ferroan-magnesite (breunnerite),  $(\text{Mg}_{51\text{--}63}\text{Ca}_{6\text{--}13}\text{Mn}_{0.3\text{--}3}\text{Fe}_{30\text{--}35})\text{CO}_3$ .  $\text{Si}_2$ , presumably quartz (glass?), is found as irregularly shaped grains up to  $50\ \mu\text{m}$  dia. in orthopyroxene (not necessarily associated with maskelynite) and in an irregular veinlet cross-cutting Carb#1.

Approximately 400 spot analyses were made of  $^{18}\text{O}/^{16}\text{O}$  on carbonate standards in preparation for 7 analyses of Carb.#1 and 2 of Carb. #2. Analytical precision is controlled by counting statistics and is better than  $1\%$  (1sd) ( $1.5 \times 10^6$  atoms detected of  $^{18}\text{O}$  in a typical analysis of 80 cycles,  $^{18}\text{O}$  vs.  $^{16}\text{O}$ ). IMF varies by less than  $2.5\%$  among the analyzed orange carbonates as a function of chemical composition [5]. Corrected values of  $\delta^{18}\text{O}$  range from  $9.5$  to  $20.6\%$  SMOW. Five of 6 analyses of orange carbonate in Carb.#1 average  $16.7 \pm 1.3\%$ , one spot is  $12.2$ . Two analyses of Carb.#2 average  $11.5 \pm 2\%$ . Thus the isotopic composition of the interior of each disk appears to be largely homogeneous, but the disks are  $5\%$  different. The values we observe are in general agreement with bulk conventional analyses and suggest that variability in previous data may in part reflect real differences among individual carbonate concretions. No correlation of  $\delta^{18}\text{O}$  is seen with chemical composition for the orange carbonates.

Ten analyses of orthopyroxene show homogeneity at  $\delta^{18}\text{O} = 4.6 \pm 1.3\%$ , standardized against conventional analyses [8]. One analysis of quartz shows  $\delta^{18}\text{O} = 20.4\%$ , standardized against ion probe analysis of Amelia albite ( $\Delta\text{IMF} = 3.2\%$  [9]).

Preliminary carbon isotope analyses were made of four spots of orange carbonate in Carb.#1. Approximately 100 analyses of standards were used to calibrate IMF [5]. In each measurement, initial count rates and isotope ratios were steady, but after 17 to 56 cycles (at  $1\text{--}4\ \mu\text{m}$  depth), count rates were observed to increase by a factor of  $2\text{--}5\times$  and then decrease, and measured isotope ratios decreased by  $48 \pm 2\%$ . Since these sample analyses are bracketed by good analyses of carbonate standards, the cause of this phenomenon must be real changes at depth within the sample. The initial cycles of the four analyses yield  $\delta^{13}\text{C} = 47.3 \pm 8\%$ , at the upper end of the previous range of estimates from mineral separates. Changes in measured  $^{13}\text{C}/^{12}\text{C}$  with depth in the sample may result from (1) contamination by C-bearing epoxy or polishing materials (necessary and acceptable for oxygen analysis), (2) differences in chemical composition that affect count rate and IMF, or (3) the presence of reduced carbon phases

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inherent to the specimen with drastically lower  $\delta^{13}\text{C}$  (~50‰) than the carbonate. Resolution of this question awaits preparation of a sample with carbon-free mounting medium.

The  $\delta^{13}\text{C}$  of orange carbonate is significantly higher than values measured on Earth and proves that these concretions have an extraterrestrial origin as previously suggested based on the presence of fractures that are presumably of impact origin and which cross-cut the carbonates displacing chemical zonation [7,8,11] and based on high  $\delta\text{D} = 4000\text{‰}$  [4]. The genesis of other carbonates in this sample is less certain and thus textural relations are important to resolve different events that have affected this meteorite.

The high values of  $\delta^{18}\text{O}$  in Carb.#1 cannot represent isotopic equilibrium with the host orthopyroxene at temperatures above 100–200°C, and the chemical and isotopic heterogeneity among carbonates was not equilibrated at any temperature. On Earth, such high and variable  $\delta^{18}\text{O}$  is proof of low-temperature exchange because isotopic fractionations are small at high temperature. However, the nature of low-temperature processes on Mars is poorly understood; the  $\delta^{18}\text{O}$  of the atmosphere/hydrosphere may be higher and show more temporal change than on Earth. Chemical compositions of carbonate in ALH84001 are reported in the fields of low-temperature immiscibility of the Ca-Mg-Fe carbonate system [11,12]. Since the crest of the Cc-Dol solvus is over 1000°C, these compositions can only represent equilibrium at extremely high temperatures. In contrast, sulfide stability in ALH84001 requires lower temperatures: pyrite  $T < 750$ ; greigite  $T < 280$  [13]. Carbonates within the Dol-Mg solvus are not stable at any temperature. The only explanation that is consistent with all of these otherwise conflicting observations is that carbonates precipitated in a disequilibrium system, most likely below 100°C. On Earth, low-temperature, biologically mediated processes are well known that commonly produce isotopic disequilibrium as well as metastable carbonate compositions that fall within the calcite-dolomite solvus [14].

**REFERENCES.** [1] Grady, M.M., et al. (1994) *Meteoritics* 29, 469; [2] Romanek et al. (1994) *Nature* 372, 655; [3] Jull, A.T. (1995) *Meteoritics* 30, 311; [4] Leshin, L.A., et al. (1996) *GCA* 60, 2635; [5] Eiler, J.M. et al. (1997) *LPSC Abst*; [6] Valley, J.W. et al. (1997) in M.A. McKibben et al. (eds.) *Soc. Econ. Geol. Reviews in Econ. Geol.* 7, in press; [7] Mittlefehldt, D.W. (1994) *Meteoritics* 29, 214; [8] McKay D.S. et al. (1996) *Science* 273, 924; [9] Clayton, R.N. and Mayeda, T.K. (1996) *GCA* 60,199; [10] Eiler, J.E., et al. (1997), *Chem. Geol.*, in press; [11] Treiman, A.H. (1995) *Meteoritics* 30, 294; [12] Harvey, R. and McSween, H.P. (1996) *Nature* 382, 49; [13] Craig J.S. and Scott S.D. (1974) in P.H. Ribbe (ed.) *M.S.A. Rev. in Mineralogy* 1, CS1; [14] Mackenzie, F.T., et al. (1983) in R.J. Reeder (ed) *M.S.A. Rev. in Mineralogy* 11, 97.