In Situ Analysis of Three Oxygen Isotopes and OH in ALH 84001: Further Evidence of Two Generations of Carbonates

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Introduction: Secondary carbonate minerals in the Martian meteorite, ALH84001 have been intensely studied and variously interpreted. Several textural forms have been described including concentrically zoned "globules" (or concretions) with distinctive white magnesite rims and "clots" of relatively homogeneous ankerite intergrown with glass and orthopyroxene (see [1]). The apparent continuum of Ca-Mg-Fe composition varying from near calcite to magnesite, has lead some workers to conclude that all textures formed by a single process, however [1] shows that compositions are not continuous if Mn is considered and that $\delta^{18}O$, measured *in situ* from 30 micron spots by CAMECA 4-f ion microprobe, also correlates to texture. Thus, there are at least two populations of carbonate. Globules were interpreted to form by aqueous precipitation at 20-190°C while clots may have formed by shock melting of globules [1].

Three oxygen isotopes have been measured by several studies of bulk silicate samples in Martian meteorites and consistently yield $\Delta^{17}O$ ~ 0.3 [2]. Bulk analyses of carbonates have also yielded $\Delta^{17}O$ values above the Terrestrial Fractionation line ($\Delta^{17}O$=0), but values average 0.8±0.05‰, indicating that carbonates precipitated from fluids that exchanged with the Martian atmosphere and that the atmosphere is not in exchange equilibrium with the silicate crust, attesting to the absence of plate tectonics on Mars [3]. There have been no previous *in situ* analyses of $\Delta^{17}O$ in Martian meteorites, in part because accuracy and precision were not sufficient to distinguish values from Earth from those on Mars, or Martian silicates from Martian carbonates.

Three-Oxygen Isotopes by Ion Microprobe: We report improved accuracy and precision for *in situ* analysis of $\delta^{18}O$ and $\delta^{17}O$ by CAMECA ims-1280. Analytical conditions are similar to [4], employ a 15μm diameter Cs^+ primary beam, MRP~ 4500 for ^{17}O and ~2200 for ^{16}O and ^{18}O, automatic focusing of secondary beam in the field aperture, NMR magnet control, and simultaneous detection with three Faraday cup detectors. After each analysis, ^{16}OH was measured to correct for tailing under ^{17}O (12-20ppm). A series of carbonate standards were run to calibrate instrumental mass fractionation (IMF), which for $\delta^{18}O$ was -4.3‰ for calcite, -16.2 for magnesite, and -11.1 for Mg-siderite (XFe=0.8). Each analysis pit was analyzed for Ca, Mg, Fe, and Mn by EMPA after ion probe analysis. SIMS analyses of carbonate were bracketed by analyses of orthopyroxene from ALH84001 ($\delta^{18}O$=4.99, $\Delta^{17}O$=0.32 [5]); IMF in opx averages 0.03±0.13 permil (n=40). Analyses were also made of terrestrial zircons, which were bracketed by analysis of the KIM-5 zircon standard ($\delta^{18}O$=5.09, $\Delta^{17}O$=0).

Results: Zircon analyses demonstrate the accuracy and precision of these *in situ* three oxygen isotope data. Values of $\Delta^{17}O$ are 0 (by definition)±0.11 (1sd, N=28, 1se=0.02‰) for KIM-5 and -0.05±0.12 for 44 zircons with ages from 4.0 to 4.35 Ga (Fig. 1a,b).

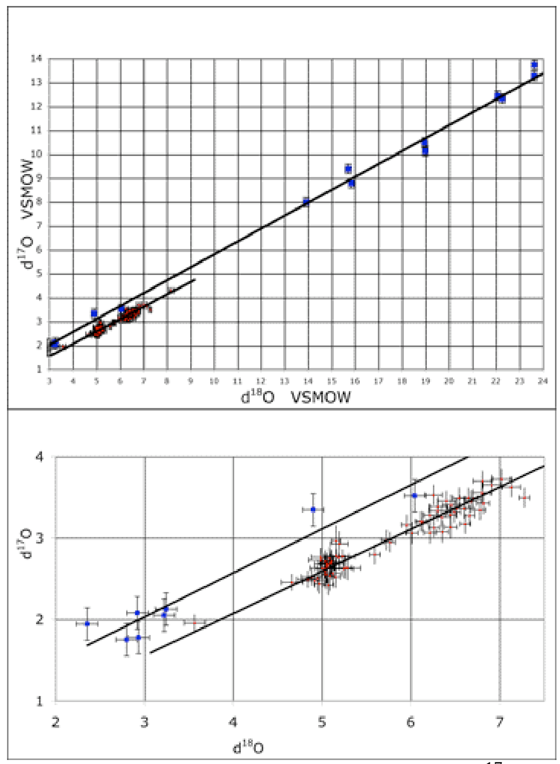

Fig. 1. In situ ion microprobe analyses of $\delta^{17}O$ vs. $\delta^{18}O$ VSMOW in carbonates from globules ($\delta^{18}O$>13) and clots ($\delta^{18}O$<6) in ALH84001 (large blue squares) and from terrestrial zircons (small red triangles). Zircons with $\delta^{18}O$ near 5 are the standard, KIM-5. All values above 6 permil are >4.0 Ga detrital zircons from the Jack Hills. **5a.** shows all data. **5b.** enlargement showing data for carbonate clots in ALH84001 and zircons.

Values of $\delta^{18}O$ range from 2.3 to 6.0 for carbonate in clots (fig. 1b) and 13.9 to 24.6 in globules (fig. 1a).

As seen in previous studies, $\delta^{18}O$ in globules increases with XMg [1]. Values of $\Delta^{17}O$ average 0.46±0.20 (1sd) for clots, 0.61±0.36 for ankeritic domains of globules, and 0.96±0.16 for magnesite-rich domains including rims.

Discussion:

Terrestrial zircons. The detrital Hadean zircons are the only terrestrial materials that are similar in age to silicates and carbonates in ALH84001. There is no significant difference in $\Delta^{17}O$ between KIM-5 which represents oxygen from the Earth's mantle at ~0.1Ga and the $\Delta^{17}O$ of Jack Hills (Western Australia) detrital zircons, which preserve values of oxygen isotope ratio from magmas that were contaminated by supracrustal oxygen at > 4Ga in the Hadean [6]. Thus there is no evidence in these data for a secular trend in $\Delta^{17}O$ on Earth for the mantle, crust, or hydrosphere.

Martian carbonates. Figs. 1a and 1b show that the new *in situ* analyses of three oxygen isotopes from the Martian meteorite, ALH84001, are clearly distinct in $\Delta^{17}O$ from those for terrestrial samples. The average for all samples is close to that reported for bulk analyses [4], however differences are seen among the textural and chemical sub-groups. There are three possible explanations for these differences.

1. Hydride interferences. The count rate on OH was consistently higher for carbonate globules than clots (Fig. 2). The uncertainty in correction for tailing on ^{17}O is estimated at ±~0.1 permil.

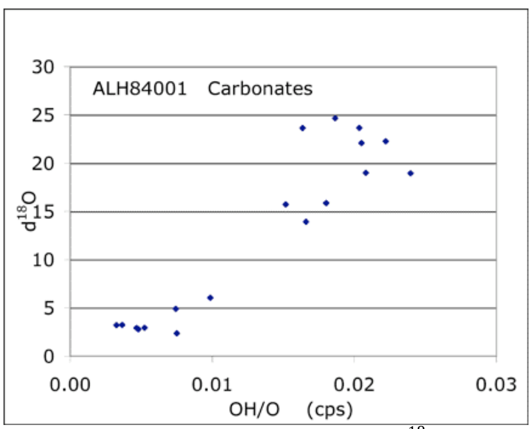

Fig. 2. Ion microprobe analysis of $\delta^{18}O$ VSMOW vs. count rate on OH normalized to oxygen for carbonates in ALH84001. Carbonate globules ($\delta^{18}O$>13) contain significantly more OH than clots ($\delta^{18}O$<6).

2. The magnesite standard data are anomalously high in $\Delta^{17}O$ by 0.3 permil.
3. The data may represent real heterogeneity of ~0.5 permil in $\Delta^{17}O$ within and among carbonates in ALH84001. This hypothesis is supported by the bulk data [4] that equal the average of our new in situ analyses.

Further analysis will evaluate analytical effects (#1 & 2), but heterogeneity cannot be ruled out at this time.

If carbonates are variable, this would confirm the conclusions that there are multiple generations of carbonate formation with globules formed by low temperature aqueous precipitation [1].

Water in Martian carbonates. Bulk analysis of Martian meteorites shows significant H_2O contents with elevated D/H. In situ analysis of δD in ALH84001 carbonates yields values from +182 to 2092 permil, but the 60μm spot size was too large to test for zonation [7]. High D/H is confirmed by microanalysis of bulk samples of carbonate, and leaching experiments suggest that the main carrier of H in globules is hydromagnesite [8]. Figure 2 shows that H is concentrated in the Mg-rich globules ($\delta^{18}O$ >13) over the relatively Mg-poor clots ($\delta^{18}O$ <6). Imaging of individual analysis pits shows that H is homogeneously distributed over the 15μm domains analyzed, ruling out late hydrous alteration along cracks. These observations show that the water in carbonate globules is largely Martian in origin and concentrated in the white rims probably as hydromagnesite. The lower water content of ankeritic clots is consistent with dehydration of impact melt.

References: [1] Eiler, JM, Valley, JW, Graham, CM, and Fournelle, J (2002) Geochem. Cosmochim. Acta, 66, 1285-1303. [2] Clayton RN and Mayeda TK (1996) Geochim. Cosmochim. Acta, 60, 1999-2017. [3] Farquhar J, Thiemens MH, and Jackson T (1998) Science. 280, 1580-1582. [4] Kita NT, Nagahara H, Tomomura S, Tachibana S and Valley JW (2006) LPS *XXXVII* Abstract #1496. [5] Spicuzza MJ, Day JMD, Taylor LA, and Valley JW (2007) LPS *XXXVIII*. [6] Cavosie AJ, Valley JW, Wilde SA, and EIMF (2005) Ear. Plan. Sci. Lett. 235, 663-681. [7] Sugiura N and Hoshino H (2000) Meteoritics & Plan. Sci. 35, 373-380. [8] Eiler JE, Kitchen N, Leshin L and Straussberg M (2002) Meteoritics & Plan. Sci. 37, 395-405.