

THE CARBONATES IN ALH 84001 RECORD THE EVOLUTION OF THE MARTIAN ATMOSPHERE THROUGH MULTIPLE FORMATION EVENTS. R. Shaheen¹, P. B. Niles², C. Corrigan³, M. H. Thiemens¹. ¹Department of Chemistry and Biochemistry, Univ. of California San Diego, La Jolla, California, USA. ²Astromaterial Research and Exploration Science, Johnson Space Center, Houston, Texas. ³Smithsonian Institution, Washington DC. Robina@ucsd.edu; mthiemens@ucsd.edu; paul.b.niles@nasa.gov;

Introduction: Current Martian conditions restrict the presence of liquid water due to low temperatures (~210K), a thin atmosphere (~7mb), and intense UV radiation. However, past conditions on Mars may have been different with the possibility that the ancient Martian climate was warm and wet with a dense CO₂ atmosphere [1].

The cycling of carbon on Mars through atmospheric CO₂ and carbonate minerals is critical for deciphering its climate history. In particular stable isotopes contained in carbonates can provide information of their origin and formation environment as well as possibly hinting at the composition of global reservoirs such as atmospheric CO₂.

Martian meteorite ALH 84001 contains widely studied carbonate rosettes that have been dated to ~3.9 Ga [2] and have been used to interpret climatic conditions present at that time [3]. However, there is mounting evidence for multiple episodes of carbonate formation in ALH 84001 [4, 5] with potentially distinct isotopic compositions. This study seeks to tease out these different carbonate assemblages using stepped phosphoric acid dissolution and analysis of carbon and triple oxygen stable isotopes. In addition, we report SIMS analyses of the $\delta^{18}\text{O}$ several petrographically unusual carbonate phases in the meteorite.

Materials and Methods: A slice (~1g) of ALH84001-214 was ground to fine powder and divided into two subsections. Comminuted samples were reacted with concentrated H₃PO₄ in the side arm of reaction vessels that were evacuated for 4 days to ~10⁻⁶Torr. Surface impurities were removed by allowing acid to react with the sample for 1 hour at ambient temperature (25°C). Gas released was collected at -196°C after passing through two traps (ethanol slush at -60°C to remove any traces of water). After CO₂ extraction samples were allowed to react with acid for 12 h at 25 ± 1°C to extract next batch of CO₂ from the calcite fraction. The carbonate sample was heated for 3h at 150 ± °C and CO₂ collected following above procedure. CO₂ gas was reacted with BrF₅ at 780 ± 10 °C for 48h and O₂ gas purified chromatographically [6] to allow multioxygen isotopic measurements. Carbon and O triple isotopic composition was measured using isotope ratio mass spectrometer [6].

Ion microprobe oxygen isotope measurements were obtained from two separate thin sections of ALH 84001 (,302 and ,303) using the CAMECA ims 6f at

Arizona State University and the CAMECA ims 1270 at the University of California at Los Angeles.

Results: The acid dissolution results yielded O-triple isotopic data with an excess¹⁷O ($\Delta^{17}\text{O} = 0.7\text{‰}$)[§] in both carbonate fractions (Fig. 1) with the Ca rich phase $\delta^{17}\text{O}' = 14\text{‰}$, $\delta^{18}\text{O}' = 25\text{‰}$ and Fe-Mg-Mn rich phase $\delta^{17}\text{O}' = 12\text{‰}$, $\delta^{18}\text{O}' = 21\text{‰}$. The Fe-Mg-Mn rich fraction of carbonates (3h acid digestion at 150°C with $\delta^{13}\text{C} = 39\text{‰}$) is 18‰ heavier in $\delta^{13}\text{C}$ than the Ca-rich phase (12h acid digestion at 25°C, $\delta^{13}\text{C} = 20.27\text{‰}$) after removal of surface impurities (1 hr acid digestion at 25°C).

Nearly pure Ca-rich carbonates identified in thin section were analyzed using ion microprobe which obtained $\delta^{18}\text{O}$ values of 16.5‰ and 20.3‰ with 2σ uncertainties of ±2‰ (Fig. 2).

Discussion: The high temperature acid dissolution step likely sampled an Fe-, Mg-rich carbonate composition, and the isotope values measured in this step correspond to those measured previously in $\Delta^{17}\text{O}$, $\delta^{13}\text{C}$, and $\delta^{18}\text{O}$ [7, 8]. However, the low temperature dissolution step likely sampled Ca-rich carbonate with isotopic compositions that differ from those measured previously in this meteorite. Nearly all Ca-rich carbonates previously measured by ion microprobe analysis possess $\delta^{18}\text{O}$ values less than 10‰ [5, 9-11] while our acid dissolution measurement measured a $\delta^{18}\text{O}$ of +25‰ (Figure 1). Furthermore, we measured a significant $\Delta^{17}\text{O}$ anomaly in this carbonate fraction confirming a likely martian origin [12]. The presence of a distinct population of $\delta^{18}\text{O}$ rich carbonates is further supported by the ion microprobe measurements which revealed $\delta^{18}\text{O}$ -rich Ca-rich phases with unusual petrographic relationships. These Ca-rich carbonates occur as isolated domains inside of a Mg-rich carbonate matrix (Fig. 3). This departure from the typical rosette morphology suggests a separate aqueous precipitation event [4]. The Ca-rich carbonates also possess carbon isotope compositions which are substantially lower than those measured in the more abundant carbonate rosettes. The $\delta^{13}\text{C}$ measured in the Ca-rich phase is +20.27‰ compared to the range of $\delta^{13}\text{C}$ measured by

[§] Excess ¹⁷O ($\Delta^{17}\text{O} = \delta^{17}\text{O}' - 0.524 \delta^{18}\text{O}'$) in carbonates. Here $\delta^{17}\text{O}' = 10^3 \ln(1 + \delta^{17}\text{O}/10^3)$ and $\delta^{18}\text{O}' = 10^3 \ln(1 + \delta^{18}\text{O}/10^3)$.

ion microprobe of +27 to +64‰ [13] with an average composition near +40‰ [8].

These differences in carbon isotope composition between carbonates deposited in distinct events suggest that either the different carbonate formation events sample different carbon reservoirs or that the isotopic composition of the carbon reservoir is changing with time. The only known carbon reservoir with the potential to have $\delta^{13}\text{C}$ values of +20‰ or above is the martian atmosphere which could potentially have become enriched in ^{13}C through atmospheric loss [14].

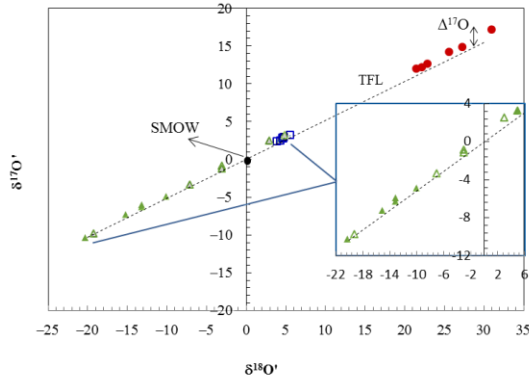


Fig. 1. Oxygen triple isotopic composition (a) O- carrying reservoirs, CO_3 (ALH84001 this study), SNC CO_3 and silicate (Farquhar et al., 2000), mineral water from SNC meteorites [16]. The insert shows slight offset of water O-isotopic composition from terrestrial fractionation line with $\Delta^{17}\text{O} \sim 0.52 \delta^{18}\text{O}$. Red circles denote CO_3 , blue square = silicate, open triangle = mineral water released during pyrolysis at 600 °C, filled triangle = mineral water released at 1000 °C.

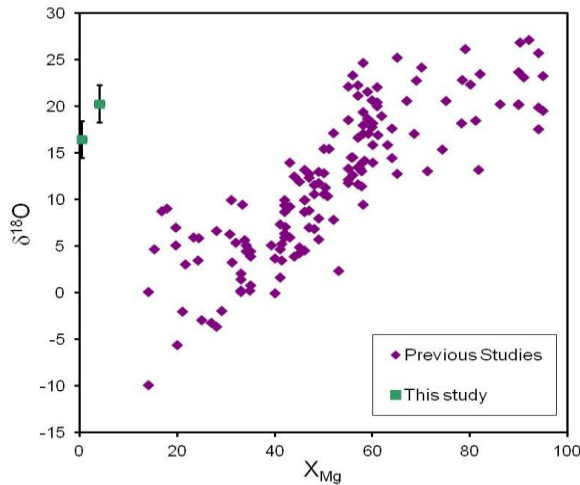


Fig. 2. Ion Microprobe measurements of ALH 84001 carbonates compared to new ion microprobe data reported in this study. The new data have more Ca-rich compositions than have been previously measured, and also show enriched $\delta^{18}\text{O}$ values.

Both the Ca-rich and Fe-Mg-Mn rich phases possess 0.7‰ O-isotopic anomaly, and $\delta^{18}\text{O}$ varies by 4‰ between the two phases, suggesting that processes responsible for generating the O-isotopic anomaly of the hydrosphere and atmosphere. The interaction of

anomalous CO_2 with surface adsorbed water on mineral grains to generate μm sized carbonates is known to occur on aerosol surfaces in terrestrial environment [6] and may be relevant on Mars, especially if water is limited.

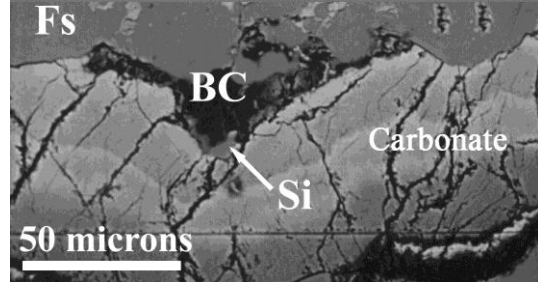


Figure 3. Backscattered Electron image of Ca-rich carbonates showing their unusual petrographic relationships. The most Ca-rich carbonates are the brightest material on the upper (inner) edge of the carbonate material in the image. Fs = feldspathic glass, Si = silica glass, and BC = black carbonate from [5]. Image adapted from [5].

This suggests, therefore, that atmospheric evolution is the source of the carbon isotope differences between the Ca-rich phase measured in this study and the more widely studied rosettes. Without knowing the age of the Ca-rich carbonates measured in this study it is difficult to make firm conclusions, however, a potential record of the $\delta^{13}\text{C}$ evolution of the martian atmosphere may be constructed between the carbonates in ALH 84001 and the recent measurements of the modern atmosphere [15]. This suggests that the early atmosphere of Mars was enriched in ^{13}C through atmospheric loss processes to about +30‰ or greater. This is the atmospheric reservoir sampled by the carbonate rosettes. Later, the $\delta^{13}\text{C}$ of the atmosphere was lowered to near 10‰ which is the reservoir sampled by the Ca-rich carbonates measured in this study. Finally the modern atmosphere has obtained a $\delta^{13}\text{C}$ value of about -2‰ which may reflect the effects of volcanic degassing and carbonate formation [15].

References: [1] Pollack J.B., 1987, *Icarus*, 71, 203-224. [2] Borg L.E. et al., 1999, *LPSC 31*, #1430. [3] Niles P.B. et al., 2009, *EPSL* 286, 122-130. [4] Corrigan C.M. and Harvey R.P., 2004, *MAPS* 39, 17-30. [5] Holland G. et al. 2005 *GCA* 69, 1359-1370. [6] Shaheen R. et al., 2010, *PNAS* 107, 20,213-18. [7] Farquhar J. et al., 1998, *Science* 280, 1580-1582. [8] Romanek C.S. et al., 1994, *Nature* 372, 655-657. [9] Eiler J.M. et al., 2002, *GCA* 66, 1285-1303. [10] Leshin L.A. et al., 1998, *GCA* 62, 3-13. [11] Saxton J.M. 1998, *EPSL* 160, 811-822. [12] Farquhar J. and Thiemens M., 2000, *JGR-Planets* 105, 11,991-11,997. [13] Niles P.B. et al., 2005, *GCA* 69, 2931-2944. [14] Jakosky B. et al., 1994, *Icarus* 111, 271-288. [15] Niles P.B. et al., 2010, *Science* 329, 1334-1337. [16] Karlson et al., 1992, *Science* 255, 1409-1411.