

**CARBONATE “ROSETTES” IN XENOLITHS FROM SPITZBERGEN: SIMS ANALYSIS OF O AND C ISOTOPE RATIOS IN A POTENTIAL TERRESTRIAL ANALOGUE TO MARTIAN METEORITE ALH84001.** S.J. Mojzsis<sup>1</sup>, C.D. Coath<sup>1</sup>, T. Bunch<sup>2</sup>, D. Blake<sup>2</sup>, A.H. Treiman<sup>3</sup>, and H.E.F. Amundsen<sup>4</sup>, <sup>1</sup>Earth and Space Sciences, UCLA, Los Angeles, CA 90095-1567 sjm@argon.ess.ucla.edu, <sup>2</sup>Exobiology Branch, NASA Ames Research Center, Moffett Field, CA 94305, <sup>3</sup>Lunar and Planetary Institute, 3600 Bay Area Blvd., Houston, TX 77058, <sup>4</sup>Saga Petroleum AS, N1301 Sandvika, Norway.

**Introduction:** We have studied the microdomain oxygen and carbon isotopic compositions by high-resolution SIMS (ion microprobe) of complex carbonate rosettes from spinel lherzolite xenoliths. These xenoliths are hosted by nepheline basanite and are from the island of Spitzbergen (Norway) [1]. Pleistocene volcanics containing the xenoliths erupted into a high Arctic environment (78°N) and through relatively thick (continental) crust which itself contains carbonate rocks. We have attempted to constrain the source of the carbonate by combined <sup>18</sup>O/<sup>16</sup>O and <sup>13</sup>C/<sup>12</sup>C ratio measurements in 25µm diameter spots and compare them to previous work based primarily on trace-element distributions which have been used to propose a primary mantle origin for the carbonates [2]. Based on our results, however, the origin of these carbonates can be interpreted in terms of either contamination by carbonate country rock during ascent of the xenoliths, or more probably by hydrothermal processes after emplacement. Isotopic compositions of these carbonates, from a combined  $\delta^{18}\text{O}_{\text{SMOW}}$  and  $\delta^{13}\text{C}_{\text{PDB}}$  standpoint, preclude a primary mantle origin of these carbonates. Here a description is given of the analysis procedure: standardization of the carbonates; major element compositions of the carbonates measured by e- microprobe; and correlated C and O isotope compositions as measured by ion microprobe. Since these carbonate rosettes may represent a terrestrial analogue to the carbonate “globules” found in the martian meteorite ALH84001 (see companion paper by Treiman *et al.* [3]) interpretations for the origin of the secondary minerals found in the Spitzbergen rocks may be of useful in understanding the origin of similar carbonate minerals on Mars..

**Methods:** Major element compositions of the carbonates were determined using the Scripps Institution of Oceanography Cameca SX50 electron microprobe equipped with four wavelength dispersive x-ray spectrometers and an energy-dispersive spectrometer (EDS). Analyses were performed under standard conditions at 15kV and 10nA with a beam spot size of 10µm and count time of 60s. Data obtained by electron microprobe for the carbonates were used to choose targets for microdomain isotope studies. Oxygen and carbon isotopic compositions were measured using the UCLA CAMECA ims 1270 ion microprobe.

Negative secondary-ions were sputtered by a Cs<sup>+</sup> primary beam focussed to a 25µm×20µm spot. A normal-incidence electron gun was used to flood the analysis area with low-energy electrons for charge compensation [4]. Secondary-ions with initial kinetic energies of ~350-375eV were collected and measured at a mass resolving power (M/ΔM, full width at 10% peak height) of ~3000, sufficient to completely resolve H<sub>2</sub><sup>16</sup>O<sup>-</sup> from <sup>18</sup>O. Each measurement comprised 50 cycles of counting <sup>16</sup>O<sup>-</sup> for 2s (~10<sup>6</sup> counts per second) and <sup>18</sup>O<sup>-</sup> for 10s. Secondary-ions were counted using an electron multiplier (EM) and analyses were corrected for deadtime in the counting system, typically 25ns. For each analysis session, the data were corrected for instrumental mass fractionation using the known  $\delta^{18}\text{O}_{\text{SMOW}}$  of +16.0‰ for UCLA carbonate standards Optical calcite and +21.5‰ for DM dolomite [5]. Details of the SIMS instrumental mass fractionation correction procedures for carbonate minerals have been given elsewhere [6,7]. Similarly, carbon isotopic compositions were measured using the ion microprobe operating at a mass resolving power of ~5000, sufficient to resolve <sup>12</sup>CH from <sup>13</sup>C. Secondary-ions with initial kinetic energies of 0-25eV were collected and measured. Each measurement comprised 20 cycles (25 in some cases) of counting <sup>12</sup>C<sup>-</sup> for 1s (~5×10<sup>5</sup> counts per second) and <sup>13</sup>C<sup>-</sup> for 10s. Optical (calcite) with  $\delta^{13}\text{C}_{\text{PDB}}$  of -11.1 ‰ and +0.9‰ of DM dolomite were again used to correct for instrumental mass fractionation.

**Results:** The analyzed Spitzbergen carbonates are grouped into two compositional classes, (SB43690) a magnesian calcite and (SX6) a dolomite, as has been observed in these particular samples before [2,8]. The chemical, and combined oxygen and carbon isotopic compositions of sample SB43690, and the O and C isotopic composition of sample SX6 are shown in tables 1 and 2 respectively. We analyzed a restricted range of carbonate compositions clustering around magnesian calcite (SB43690) to dolomite (SX6). The measured  $\delta^{13}\text{C}_{\text{PDB}}$  values range from  $-4.1 \pm 0.9\text{‰}$  to  $+0.6 \pm 1.0\text{‰}$  relative to PDB in the Mg-calcites of SB43690 and have a more expanded range in the dolomite sample SX6 from  $-6.3 \pm 1.6\text{‰}$  to  $+7.8 \pm 1.2\text{‰}$ . The measured  $\delta^{18}\text{O}_{\text{SMOW}}$  values range from  $+20.6 \pm 1.0\text{‰}$  to  $+22.8 \pm 1.3\text{‰}$  in SB43690 and  $+24.5$

$\pm 1.3\%$  to  $+33.4 \pm 1.3\%$  in SX6. Only the cross-correlated (by spot location) O and C isotopic compositions of the two carbonate classes analyzed by SIMS from the xenoliths is represented in Figure 1. At the small spatial scale of the measurements, differences were observed between the calcites of SB43690 (range  $\delta^{13}\text{C}_{\text{PDB}} < 5\%$ ; range  $\delta^{18}\text{O}_{\text{SMOW}} < 3\%$ ) and SX6 dolomites (range  $\delta^{13}\text{C}_{\text{PDB}} \sim 14\%$ ; range  $\delta^{18}\text{O}_{\text{SMOW}} \sim 9\%$ ). All of the  $\delta^{13}\text{C}_{\text{PDB}}$  appear to suggest a kinship with sedimentary (*i.e.* crustal) carbonates. All measured carbonates in xenolith SB43690 (calcite) from Spitzbergen have  $\delta^{18}\text{O}_{\text{SMOW}}$  values greater than  $+20\%$ , typical of the marine limestone field; dolomites of sample SX6 however demonstrate a range of  $\delta^{18}\text{O}_{\text{SMOW}}$  values that is consistent with  $^{18}\text{O}$  fractionation between calcite and dolomite [9] which is normally in the range of  $\sim +4\%$  [10].

**Table 1.** Chemical and isotopic analyses SB43690 (Mg-cc)

spot	MgO <sup>#</sup>	CaO	FeO	$\delta^{18}\text{O}_{\text{SMOW}}(\text{‰})$	$\delta^{13}\text{C}_{\text{PDB}}(\text{‰})$
100.1	4.916	53.77	0.71	$+22.3 \pm 1.3^*$	$-3.1 \pm 0.9$
100.2	3.622	54.77	0.277	$+21.0 \pm 1.2$	$-2.1 \pm 0.8$
n1.1	4.592	52.82	0.655	$+21.7 \pm 1.2$	$-1.7 \pm 1.0$
n1.2	5.392	49.94	0.606	$+22.2 \pm 1.3$	$+0.6 \pm 0.9$
n1.3	5.684	50.62	0.66	$+22.8 \pm 1.3$	$-0.6 \pm 1.0$
n1.4	4.744	54.62	0.633	$+22.1 \pm 1.3$	$-4.1 \pm 1.0$
n1.5	3.567	53.41	0.529	$+20.6 \pm 1.0$	$-2.2 \pm 0.8$

**Table 2.** Isotopic analyses of carbonates in SX6 (dolomite)

spot	$\delta^{18}\text{O}_{\text{SMOW}}(\text{‰})$	$\delta^{13}\text{C}_{\text{PDB}}(\text{‰})$
2-1	$+26.1 \pm 1.1$	$+6.6 \pm 1.6$
2.2	$+27.7 \pm 1.2$	$-6.3 \pm 1.6$
2.3	$+24.5 \pm 1.3$	$-4.8 \pm 1.6$
2.4	$+25.9 \pm 1.3$	$-0.6 \pm 1.2$
3.1	n/a <sup>@</sup>	$+7.8 \pm 1.2$
3.2	n/a	$+7.2 \pm 1.4$
1.2	$+26.9 \pm 1.3$	n/a
1.7	$+28.6 \pm 1.0$	n/a
1.7.1	$+33.4 \pm 1.3$	n/a

<sup>#</sup> Chemical compositions are described in wt.% of oxide

\* all errors are reported in  $\pm 1\sigma$  (‰)

@ n/a = not analyzed

**Conclusions:** It has been shown that fractional crystallization or liquid immiscibility do not significantly affect the O and C isotopic compositions of carbonates presumed to be of mantle origin [11]. Large and measurable variations occur when magmas become contaminated by carbonate-rich country rocks or via isotope exchange between the carbonate and  $\text{H}_2\text{O}$  and  $\text{CO}_2$ -rich fluids. Most of the variations described here may be attributed to hydrothermal processes responsible for the precipitation of the carbonates in the xenoliths and the host basalt as suggested by the high oxygen isotopic values in the magnesian calcite from SB43690, and the overall scatter of val-

ues in SX6. We conclude that these carbonate features are not primary “mantle” carbonate (carbonatite) and that they are most likely derived from  $\text{CO}_2$ -rich hydrothermal fluids carrying and depositing carbonate of crustal origin. A means to confirm this interpretation would be to investigate the Sr-isotopic compositions of these minerals. Variations in the isotopic values of the Spitzbergen carbonates is smaller than that observed in the meteorite ALH84001 [6,7,12] and the carbonate compositions themselves are different [3]. However, studies of terrestrial examples of carbonate rosettes in ultramafic xenolithic terrestrial rocks such as these could be used to place constraints on the origin of the carbonates in ALH84001 by hydrothermal precipitation, or quite possibly, the assimilation of martian crustal carbonate during the formation of the ALH84001 protolith.

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**Figure 1 (below).**  $\delta^{18}\text{O}_{\text{SMOW}}$  vs.  $\delta^{13}\text{C}_{\text{PDB}}$  plot of carbonate rosettes in Spitzbergen xenoliths by SIMS.

