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Author(s): Tomasz Durakiewicz, Zach Sharp, John Papike

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THE EFFECT OF THERMAL DECARBONATION ON THE STABLE ISOTOPE COMPOSITION OF CARBONATES

Z.D. Sharp¹, T. Durakiewicz^{2, 3}, J.J. Papike¹, 1 - Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM 87131, 2 – Maria Curie Sklodowska University, 20-031 Lublin, Poland, 3 - Los Alamos National Laboratory, Los Alamos NM 87544.

The unusual texture and stable isotope variability of carbonates in AH84001 have been used as evidence for early life on Mars (Romanek *et al.*, 1994; McKay *et al.*, 1996). Oxygen and carbon isotope variability is most commonly attributed to low-temperature processes, including Rayleigh-like fractionation associated with biological activity. Another possible explanation for the isotopic variability in meteoritic samples is thermal decarbonation. In this report, different carbonates were heated in a He-stream until decomposition temperatures were reached. The oxygen and carbon isotope ratios ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values) of the resulting gas were measured on a continuous flow isotope ratio mass spectrometer. The aim of this work is to evaluate the possibility that large isotopic variations can be generated on a small scale abiogenically, by the process of thermal decarbonation.

Oxygen isotope fractionations of $>4\text{‰}$ have been measured during decarbonation of calcite at high temperatures (McCrea, 1950), and in excess of 6‰ for dolomite decarbonated between 500 and 600°C (Sharma and Clayton, 1965). Isotopic fractionations of this magnitude, coupled with Rayleigh-like distillation behavior could result in very large isotopic variations on a small scale. To test the idea, calcite, dolomite and siderite were heated in a quartz tube in a He-stream in excess of 1 atmosphere. Simultaneous determinations of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values were obtained on 250 μl aliquots of the CO_2 -bearing He gas using an automated 6-way switching valve system (Finnigan MAT GasBench II) and a Finnigan MAT Delta Plus mass spectrometer.

It was found that decarbonation of calcite in a He atmosphere begins at 720°C, but the rate significantly increases at temperatures of 820°C. After an initial light $\delta^{18}\text{O}$ value of -14.1‰ at 720°C associated with very early decarbonation, $\delta^{18}\text{O}$ values increase to a constant -11.8‰ , close to the accepted value of -12.09‰ (PDB). After 10 minutes at 820°C, the $\delta^{18}\text{O}$ values and signal strength both begin to decrease linearly to a $\delta^{18}\text{O}$ value of -14.75 and very low amounts of CO_2 (Fig. 1). In contrast, the $\delta^{13}\text{C}$ values are extremely constant ($0.12 \pm 0.25\text{‰}$) for all measurements, in very good agreement with accepted values of 0.33‰ (PDB).

There is much less isotopic variability during dolomite decarbonation. CO_2 is first detected at 600°C. The signal strength increases by an order of magnitude between 670 and 700°C and again at 760°C. Both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are nearly constant over the entire temperature range and sample size. For oxygen, the measured $\delta^{18}\text{O}$ values averaged $-20.9 \pm 0.7\text{‰}$ ($n = 30$). Including only samples over 700°C, the average is $-21.2 \pm 0.2 \text{‰}$ compared to the accepted value of -21.0‰ . Carbon is similarly constant. The average $\delta^{13}\text{C}$ value is -2.50‰ compared to the accepted value of -2.62‰ .

Far more variability is seen during the decomposition of siderite. Two samples were analyzed. In both samples, the initial $\delta^{18}\text{O}$ values were far lower than expected.

For one sample, the $\delta^{18}\text{O}$ values quickly stabilized at the accepted value, while for a second sample, the $\delta^{18}\text{O}$ values were 6‰ higher than those measured conventionally. The $\delta^{13}\text{C}$ values were observed to increase logarithmically with time (Fig. 2), covering a range of ~7‰, with final values greater than 6‰ above those measured conventionally.

The carbon isotope data for siderite can be explained in terms of auto-oxidation of Fe^{2+} to Fe^{3+} by the reaction $3 \text{FeCO}_3 \rightarrow \text{Fe}_3\text{O}_4 + 2 \text{CO}_2 + \text{CO}$ (Fig. 3). The equilibrium $\Delta^{13}\text{C}$ ($\text{CO}_2 - \text{CO}$) value is ~20‰ (450°C), so that the $\delta^{13}\text{C}$ value of CO_2 should be given by $\delta^{13}\text{C}_{\text{tot}} = 2/3(\delta^{13}\text{C}_{\text{CO}_2}) + 1/3(\delta^{13}\text{C}_{\text{CO}_2} - \Delta^{13}\text{C}(\text{CO}_2-\text{CO}))$, or $\delta^{13}\text{C}_{\text{CO}_2} = (\delta^{13}\text{C}_{\text{total}} - 20/3)\text{‰}$. In other words, the $\delta^{13}\text{C}$ value of the evolved CO_2 should be 6‰ greater than the carbonate. CO is detected in the mass spectrometer, with very scattered $\delta^{13}\text{C}$ values.

Thermal decarbonation of iron-free carbonates will not cause a significant shift in either $\delta^{13}\text{C}$ or $\delta^{18}\text{O}$ values of remaining carbonates. Decarbonation of siderite (and ankerite) can cause a shift in both carbon and oxygen isotope ratios *and* can explain magnetite inclusions in carbonate. However, it is unlikely that thermal decarbonation can explain the high variability observed in AH84001. Instead, low temperature effects remain the most favorable explanation for the high degree of isotopic variability.

Ref. cited: McCrea, J. Chem. Phys. 18, 849; McKay *et al.*, Science 273, 924; Romanek *et al.*, Nature 372, 655; Sharma & Clayton, Geochim. Cosmochim. Acta 29, 1347.

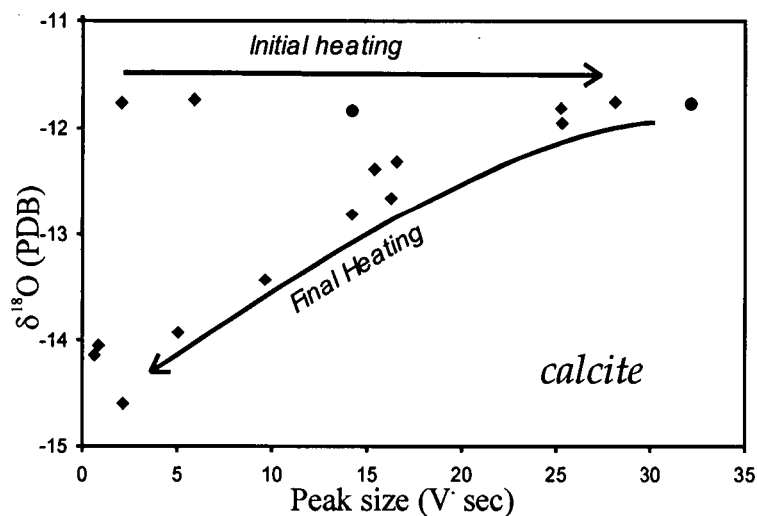


Fig 1 (left). $\delta^{18}\text{O}$ values during heating. Final heating may produce CO, lowering the $\delta^{18}\text{O}$ value.

Fig 2 (bottom left). C & O isotope values of siderite during decomposition. $\delta^{13}\text{C}$ values increase due to CO production.

Fig 3 (bottom). BSE image of thermally decomposed siderite in iron oxide (magnetite?) matrix.

