

Isotopic Composition of Carbonates in Antarctic Ordinary Chondrites and Miller Range Nakhrites: Insights into Martian Amazonian Aqueous Alteration. M. E. Evans^{1,2}, P. B. Niles², D. R. Locke³, P. Chapman¹; (michael.e.evans@nasa.gov) ¹Texas A&M University, College Station, Tx; ²NASA Johnson Space Center, Houston, Tx; ³HX5-Jacobs JETS Contract–NASA Johnson Space Center, Houston, Tx.

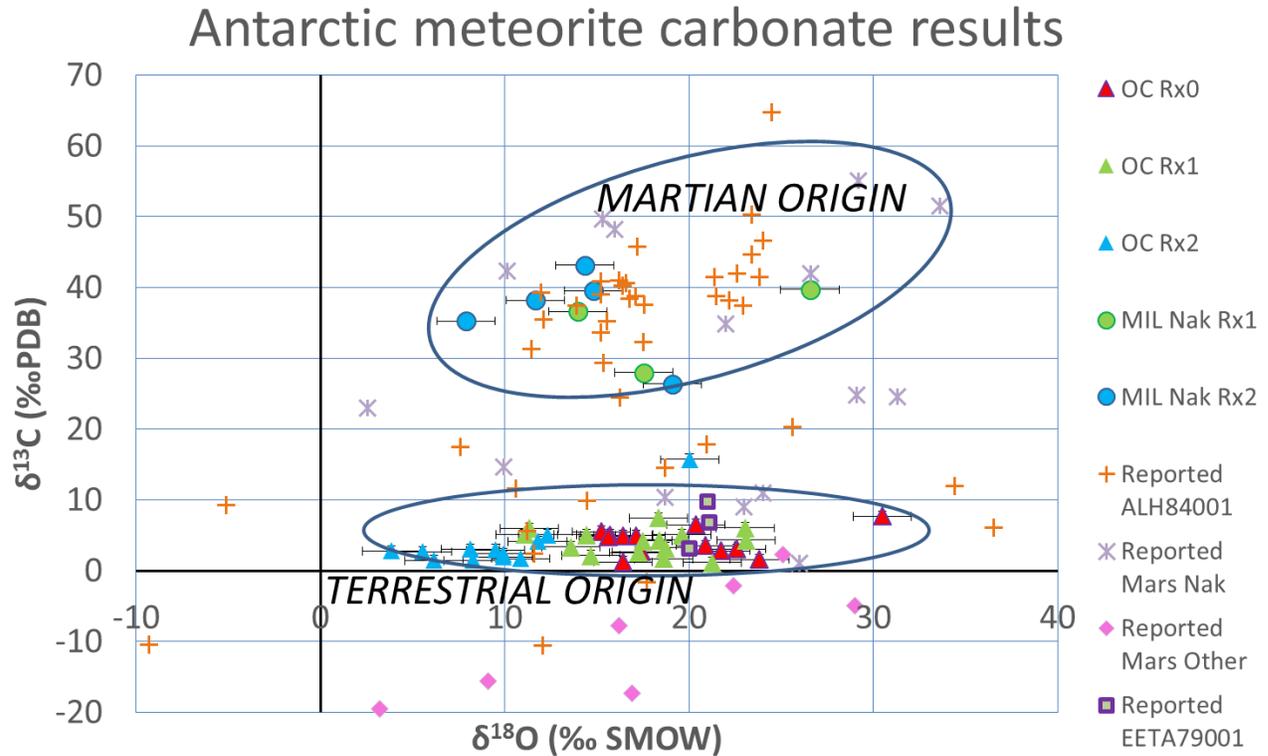


Figure 1: Comparison of new results for Ordinary Chondrite (OC) meteorites, new results for Miller Range (MIL) Nakhrites, and prior martian meteorite results, show carbonate stable isotope values from distinct carbon reservoirs

Introduction: The martian surface contains features of ancient fluvial systems. Stable isotope analysis of carbonates that form in aqueous systems can reveal their formation conditions. The Nakhlite meteorites originally formed on Mars 1.3 Ga and were later exposed to aqueous fluids that left behind carbonate minerals [1], thus analysis of these carbonates can provide data to understand Amazonian climate conditions on Mars. Carbonates found in the Nakhlite meteorites contain a range of $\delta^{13}\text{C}$ values, which may be either martian carbonates or terrestrial contamination. To better understand terrestrial weathering products and martian carbonate formation processes, we conducted a set of carbonate isotope analyses on Antarctic meteorites focusing on Miller Range (MIL) Nakhrites as well as Ordinary Chondrites (OCs) (Figure 1)[1-11] [12]. OCs of petrology type H, L, and LL 3-6 were selected since they are not expected to contain preterrestrial carbonates, yet they have visible evaporite minerals on the fusion crust

indicating terrestrial alteration. These cryogenically formed terrestrial carbonates may also provide an analog for cryogenic carbonate formation on Mars.

Methodology: Meteorite samples of ~1.2g were gently crushed and sieved to a size of <700 μm , acidified, reacted, and extracted to collect CO_2 cryogenically using standard techniques [7]. The carbonates were reacted with 1.2-1.5 ml of 100% H_3PO_4 at 30°C and 150°C. The CO_2 was extracted at three different steps: 1) Rx0 after 1 hour at 30°C; 2) Rx1 after 18 hours at 30°C, and 3) Rx2 after 3 hours at 150°C. The CO_2 was separated from other condensable gases using a TRACE GC with a Restek HayeSep Q 80/100 6' 2mm stainless column. Stable isotope measurements were then made on a Thermo MAT 253 IRMS in Dual Inlet mode. The carbonate concentration was determined based on calcite standard correlations to the GC CO_2 peak count. Study accuracy is $\delta^{13}\text{C} \pm 0.76\%$, $\delta^{18}\text{O} \pm 1.58\%$ (with 2σ standard deviation).

Results and Discussion: Ten OC meteorite samples from three Antarctic regions (RBT, ALH, and MIL) were analyzed. These contain terrestrial Ca-rich carbonates with $\delta^{13}\text{C}$ values clustering around +6‰, which is consistent with equilibrium formation from Earth atmospheric CO_2 at 15°C. Siderite or magnesite fractionation may create slightly heavier carbonate $\delta^{13}\text{C}$, as seen in the OC Rx2 results, but fractionation values for these minerals are not well understood at low temperatures.

The range of measured $\delta^{18}\text{O}$ from OC terrestrial carbonates is +3‰ to +30‰. This is heavier than the expected $\delta^{18}\text{O} < 0\text{‰}$ if Antarctic meteoric melt water $\delta^{18}\text{O} < -50\text{‰}$ and equilibrium fractionation at 0°C-15°C [13]. A possible explanation is that the heavier OC carbonates form in a thin-film environment with such small amounts of water that there is a substantial contribution of $\delta^{18}\text{O}$ from atmospheric CO_2 with $\delta^{18}\text{O} \approx +41\text{‰}$ [14].

A $\delta^{18}\text{O}$ mixing model can be created with Earth atmospheric CO_2 and meteoric water as end members (Figure 2). Mixing various ratios of each known end member produces boundary lines that can be mapped onto measured OC results. This model predicts the OC Ca-rich carbonates form with 60%-90% contribution from atmospheric CO_2 at 0°C, and the Fe/Mg-rich carbonates form with 40-60% contribution from atmospheric CO_2 . The predicted Ca-rich carbonate $\delta^{13}\text{C}$ in equilibrium with the atmospheric CO_2 at 0°C and 15°C is also shown on Figure 2.

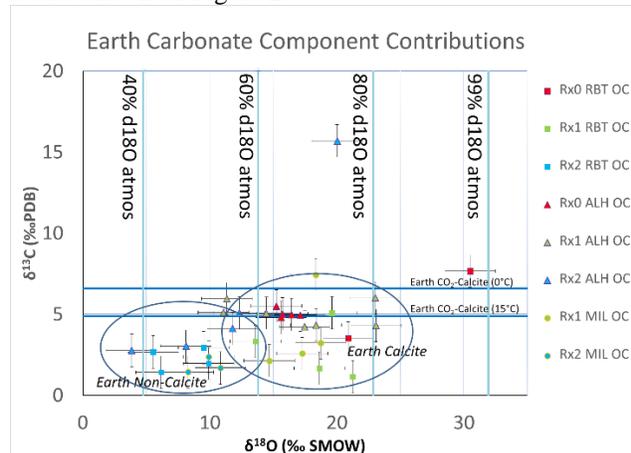


Figure 2: OC carbonate $\delta^{18}\text{O}$ mixing model for terrestrial carbonates showing predicted calcite $\delta^{13}\text{C}$

Four paired Nakhilites from the Antarctic Miller Range (MIL 03346, 090030, 090032, 090036) contain low carbonate concentrations (avg. 0.007% by wt). These carbonates, ranging from $\delta^{13}\text{C} = +26.4\text{‰}$ to +43.2‰, are distinctively heavier than terrestrial (Fig 3) [15]. Using the recently reported Mars atmospheric value ($\delta^{13}\text{C} \text{ CO}_2 = 48\text{‰}$) [16], these carbonate $\delta^{13}\text{C}$ values are lighter than expected if formed in atmospheric equilibrium (expect $\delta^{13}\text{C} \approx +59\text{‰}$).

The MIL Nakhilite carbonates vary in $\delta^{18}\text{O}$ from +7.9‰ to +26.6‰. This is not typical for formation from hydrothermal environments, but may be explained using the OC carbonate mixing model with 1) same Mars mixing ratios as terrestrial carbonates, and 2) Mars meteoric water $\delta^{18}\text{O} \approx -65\text{‰}$ (see Figure 3) [1, 3, 8, 9].

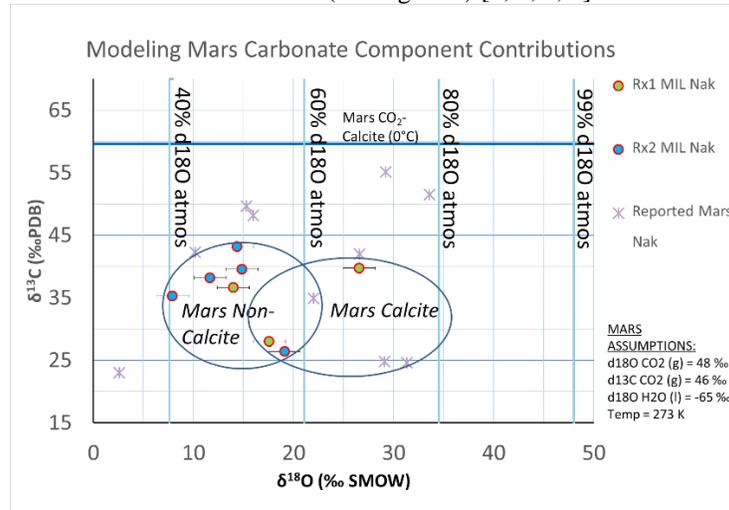


Figure 3: Mars Nakhilite carbonate $\delta^{18}\text{O}$ mixing mode showing predicted calcite $\delta^{13}\text{C}$ based on measured atmos. CO_2

Conclusions: OCs contain terrestrial Ca-rich and Fe/Mg-rich carbonates possessing variable $\delta^{18}\text{O}$, and $\delta^{13}\text{C}$ consistent with formation at 15°C in equilibrium with Earth atmospheric CO_2 . MIL Nakhilites contain Ca-rich and Fe/Mg-rich carbonates possessing variable $\delta^{18}\text{O}$ that can be explained with a mixing model of endmembers for Mars meteoric water and Mars atmospheric CO_2 . The variability in MIL Nakhilite $\delta^{18}\text{O}$ values could be the result of low temperature, low water conditions during the Amazonian period on Mars.

References: [1] Grady, M.M., et al. (2007) *LPS XXXVIII*, Abstract #1826. [2] Romanek, C.S., et al. (1994) *Nature*, 372(6507), 655-657. [3] Jull, A.J.T., et al. (1995) *Meteoritics*, 30(3), 311-318. [4] Jull, A.J.T., et al. (1997), *Journal of Geophysical Research-Planets*, 102(E1) 1663-1669. [5] Wright, I.P., et al. (1998) *Meteoritics & Planetary Science*, 33(4) A169-A169. [6] Niles, P.B., et al. (2005) *Geochimica et Cosmochimica Acta*, 69(11) 2931-2944. [7] Shaheen, R., et al., (2015) *Proceedings of the National Academy of Sciences*, 112(2) 336-341. [8] Wright, I.P., et al. (1992) *Geochimica Et Cosmochimica Acta*, 56(2) 817-826. [9] Jull, A.J.T., J.W. (2000) *Geochimica et Cosmochimica Acta*, 64(21) 3763-3772. [10] Clayton, R.N. and T.K. Mayeda (1988) *Geochimica et Cosmochimica Acta*, 52(4) 925-927. [11] Wright, I.P., et al. (1988) *Geochimica Et Cosmochimica Acta*, 52(4) 917-924. [12] Jull, A.J.T., et al. (1992) *LPS XXIII*, 641. [13] Friedman, I. and J. O'Neil (1977) *Data of Geochemistry*, 6. [14] Brenninkmeijer, C., P. Kraft, and W. Mook (1983), *Chemical Geology*, 41, 181-190. [15] Hallis, L.J. and G.J. Taylor, (2011) *Meteoritics & Planetary Science*, 46(12), 1787-1803. [16] Mahaffy, P.R., et al. (2013), *Science*, 341(6143), 263-266.