

STABLE ISOTOPE COMPOSITION OF CARBONATES FORMED IN LOW-TEMPERATURE TERRESTRIAL ENVIRONMENTS AS MARTIAN ANALOGS. ¹Richard A. Socki, ²Everett K. Gibson, Jr., ³Eugene C. Perry, Jr., ⁴Charles Galindo, ⁴D. C. Golden, ⁵Douglas W. Ming, and ²Gordon A. McKay; ARES, NASA/JSC, ¹Lockheed Martin, Code C-23; ²Code SR, ⁵SX, ³Northern IL Univ. Dept. of Geology, Dekalb, IL 60115. ⁵Hernandez Eng., Houston., TX 77058; rsocki@ems.jsc.nasa.gov

Introduction- We examine the carbon and oxygen isotope composition of carbonate minerals that formed in two low-temperature terrestrial environments. Field locations were chosen to represent environments where microcrystalline carbonates (caliches) form. Samples include caliche crusts collected from the tsekel zone of N. Yucatan, Mexico, as well as carbonate mud from the edge of a near-by salt pan, representing both ancient and modern-precipitated carbonates. Additional field samples of surface-coating caliche were collected from two volcanic fields in Arizona. Preliminary results indicate that there is an overall depletion of ^{18}O and ^{13}C as a function of the extent of meteoric diagenesis. These data are used as terrestrial analogs to gauge whether carbonates that have been found within Martian meteorites could possibly have formed under these or similar conditions on Mars

Background- Carbonate minerals are among the most chemically reactive common minerals under Earth surface conditions. An important feature of carbonate mineral behavior in sediments and during diagenesis is the result of their unique kinetics of dissolution and precipitation. The degree of disequilibrium is one of the primary factors controlling the reaction rate of carbonate minerals in aqueous solutions and, in general, the rate of reaction tends to increase with increasing disequilibrium. Additionally, different chemical and physical processes are involved in given chemical reactions. For a given set of conditions any one of these processes could be slower than all the others, thus this process is the rate controlling, kinetic step [1].

If indeed Mars was once warm and wet [2], and if the Martian hydrologic cycle included the presence of alkali-rich oceans, which were subject to evaporation and/or freezing, the result would undoubtedly be an increase in salinity and alkalinity. Under these conditions, enrichment in the carbon isotope composition of the dissolved inorganic carbon (DIC) in the HCO_3^- fluid would be expected. Subsequent carbonates precipitating from that fluid would also be isotopically enriched. Whether this process, or subsequent alteration by ^{13}C and ^{18}O depleted HCO_3^- fluids, could explain the formation of carbonates found

in ALH84001 [3] is uncertain, since $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of the Martian CO_2 reservoir is known only with great uncertainty [4].

Low temperature carbonate precipitation:

Field studies- In Northern Yucatan, Mexico a thin, nearly impermeable calcium carbonate layer (caliche) confines much of the 250 km northern coastal part of the Yucatan aquifer. Here calcium bicarbonate-rich groundwater discharges into a coastal saline zone, locally known as tsekel. Groundwater mixes in the saline zone here and is subjected to intense evaporation. CO_2 is in turn removed from the system, the pH increases, and the result is active precipitation of a dense calcite layer. This terrestrial setting fits well within the context of an evaporating brine model, with carbonate precipitation clearly controlled by kinetic processes. Samples collected from the Northern Yucatan, Mexico include both unlithified carbonate "mud", and carbonate rocks from a quarry and "borrow" pit, located within the tsekel zone. Discharging HCO_3^- groundwater forms the calcite here that essentially cements older surficial limestone deposits, reducing porosity within this host limestone to $< 1\%$ [5].

^{18}O and ^{13}C isotope data are plotted in Figure 1. $\delta^{18}\text{O}_{(\text{SMOW})}$ values range from +23.78 to +31.07‰. $\delta^{13}\text{C}_{(\text{PDB})}$ values range from -13.64 to +1.68‰. The most ^{18}O and ^{13}C enriched carbonates are the carbonate muds that formed near the edge of an evaporating salt pan. These tend to cluster in a small zone that we have labeled "unlithified Holocene sediments" (solid diamonds in Fig. 1). These carbonates formed as a result of evaporation of HCO_3^- -rich fluids. Both ^{18}O and ^{13}C isotope composition of tsekel zone caliche are more depleted. These samples are labeled "caliche from Tsekel Zone" (Fig. 1), and consist of single hand specimens (striped squares) as well as layered samples (solid squares). The layered samples contain caliche "crusts" which most likely formed as the outermost layer within vugs and fractures in the host rock. The lines connecting the samples are paired hand/layered samples. In all cases the caliche crust samples are isotopically lighter than the hosts. We interpret this isotopic trend as the result of meteoric diage-

nesis, similar to trends seen by Allan and Mathews [6]; the so-called "Barbados Model". The depletion in ^{13}C implies alteration within the vadose zone. In the Yucatan, light soil-gas CO_2 , derived from oxidation of organic matter, dissolves in vadose water and mixes with heavier marine limestone-derived carbon. The result is HCO_3^- fluid with intermediate $\delta^{13}\text{C}$ composition. Eventually the HCO_3^- precipitates as layers of caliche crust or calcite in vugs and veins on or within the host limestone that is $\delta^{13}\text{C}$ -depleted.

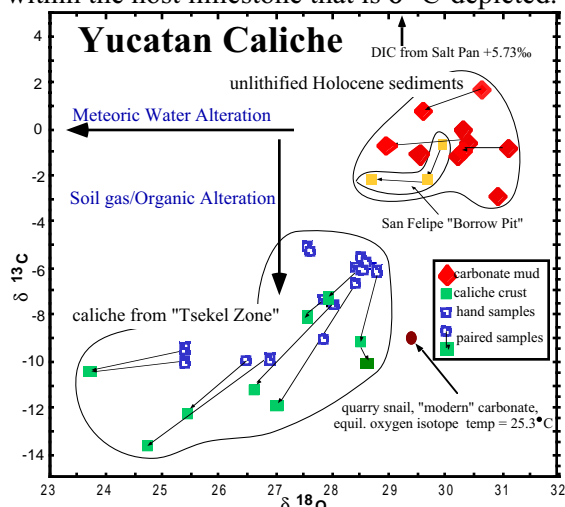


Figure 1. O and C isotope data of carbonates from Northern Yucatan, Mexico.

The $\delta^{18}\text{O}$ depletion seen in the older carbonates collected from the tsekel zone is likely the effect of alteration by meteoric water. However, these samples are, on average, 2‰ lighter than the $\delta^{18}\text{O}$ composition of a terrestrial snail collected on the ground near the tsekel zone. $\delta^{13}\text{C}$ of the snail is roughly identical to the average of the tsekel samples. This snail shell presumably would represent "modern" carbonate. The calculated equilibrium oxygen isotope temperature (25.3°C) is within reasonable agreement of the mean annual air temperature for this region, as estimated from the $\delta^{18}\text{O}$ value of local precipitation (-3.22‰) measured by Socki et al. [7].

Wide variations in ^{18}O and ^{13}C isotopes have recently been shown within the weathering products (caliche) on < 1 Ma basalts in three volcanic fields in Arizona by Knauth et al. [8]. We have re-examined a few of these field locations within the context of this study. Our samples consist of carbonate caliche collected from two of these volcanic fields. $\delta^{18}\text{O}$ values range from +22.88 to +33.56‰, while $\delta^{13}\text{C}$ values range from -5.02 to +11.21‰. The pedogenic samples, that are presumed to have been in contact with isotopically

light soil gas, are $\delta^{13}\text{C}$ -depleted, similar to what we have observed in the Yucatan carbonates. Carbonates with heavier ^{18}O and ^{13}C values showed the effects of forming from ^{18}O -rich evapo-concentrated HCO_3^- waters. Our data suggest ^{13}C enrichment due either to removal of ^{12}C by photosynthesizers in the evaporating drops [8], evaporation effects [9] or during freezing [10].

Implications for Mars- We report the isotopic composition of microcrystalline carbonates from two terrestrial environments. We examine these as analogs within the context of Martian carbonate mineral formation. ^{13}C and ^{18}O enriched carbonates form in these environments where HCO_3^- -rich fluids are subjected to intense evaporation processes. Diagenetic alteration of these carbonates can take place within the vadose zone where meteoric precipitation mixes with ^{13}C -depleted soil gas CO_2 , resulting in ^{13}C and ^{18}O depleted carbonates. If indeed Mars once had a hydrologic cycle where HCO_3^- fluids could have been subjected to evaporation and/or freezing, precipitated carbonate minerals would in turn be ^{18}O - and ^{13}C -enriched. Subsequent alteration of these Martian carbonates could produce carbonates whose $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ composition is highly fractionated (depleted) with respect to the evaporation-produced carbonates. Without a more precise measurement of the isotopic composition of the CO_2 reservoir, however, it remains speculative as to whether the carbonates found in ALH84001 are the result of an evaporating and/or freezing bicarbonate fluid, or the products of subsequent alteration. A thorough understanding of the effects of carbonate mineral precipitation and subsequent alteration on the isotopic composition of carbonates associated with these terrestrial analogs will allow us to better decipher those data collected from Martian carbonates. This in turn can reveal which processes contributed to the precipitation of those minerals on the Martian planetary surface.

References: [1] Morse and Mackenzie, *Geochemistry of Sedimentary Carbonates*. Elsevier, NY, 707pp., 1990 [2] Baker *Nature* **412**, 228-236 [3] Romanek et al. *Nature* **372**, 655-657, 1994 [4] Owen et al. *J. Geophys. Res.* **82**, 4635-4639. [5] Perry et al. *Geol.* **17**, 818-821, 1989 [6] Allen and Mathews *Sedimentol.* **29**, 797-817, 1982 [7] Socki et al. *Limnol. Oceanogr.* **47**, 6 2002 [8] Knauth et al. *GCA*, **67**, 185-195 2003 [9] Stiller et al. *Nature* **316**, 434-435, 1985 [10] Clark and Lauriol *Chem. Geol. (Isot. Geosci. Sec.)* **102**, 217-228, 1992