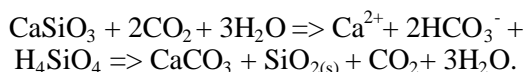


CONTRIBUTION OF ORGANIC MATERIAL TO THE STABLE ISOTOPE COMPOSITION OF SOME TERRESTRIAL CARBONATES AS ANALOGS FOR MARTIAN PROCESSES

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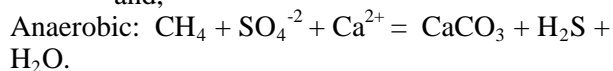
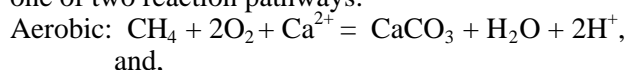
Introduction: Understanding the isotopic geochemistry of terrestrial carbonate formation is essential to understanding the evolution of the Martian atmosphere, hydrosphere, and potential biosphere. Carbonate minerals, in particular, are important secondary minerals for interpreting past aqueous environments, as illustrated by the carbonates present in ALH84001 [1]. Models for the history of Mars suggest that the planet was warmer, wetter, and possessed a greater atmospheric pressure within the first billion years as compared to present conditions [2],[3],[4], and likely had an active hydrologic cycle. Morse and Marion [5] point out that associated with this hydrologic cycle would be the active chemical weathering of silicate minerals and thus consumption of atmospheric CO₂ and deposition of carbonate and silica, for example by the reaction:



It is during this warmer and wetter period of Martian history that surface and/or near-surface conditions would be most favorable for harboring possible microbiological life. Carbonates within ALH84001 offer evidence that fluids were present at 3.9 Gy on Mars [6]. A more thorough understanding of the effects of aqueous weathering and the potential contribution of organic compounds on the isotopic composition of Martian carbonate minerals can be gained by studying some terrestrial occurrences of carbonate rocks.

Organic influence on low temperature calcite precipitation: Knauth [7] suggests that the wide isotopic variations seen in terrestrial microcrystalline calcite (caliche) is a strong indicator of biological activity, and therefore carries implications for astrobiological prospecting on Mars. Recently, Mars Express has detected the presence of methane in the Martian atmosphere that could be attributed to a possible biogenic source [8]. Additional evidence indicates that methane abundances on Mars are greater above basins that have enhanced water concentrations [8]. Indeed, calcite formed from the oxidation of organic material (i.e., methane in soil gas) is typically strongly depleted in ¹³C owing to influence of the source hydrocarbon. Schumacher [9] reports that depending on the proportion of oxidized

hydrocarbon incorporated, the isotopic composition of the resultant carbonate can range from -10 to -60‰. These near-surface pore-filling calcite and replacement calcites are formed principally by using one of two reaction pathways:



Precipitated carbonate or carbonate cement in turn (caliche) has an isotopic signature that is principally derived from the parent hydrocarbon(s).

Isotopically light carbonates have also been documented occurring in association with U.S. Gulf coast salt dome cap rocks, a result of microbial oxidation of petroleum. $\delta^{13}\text{C}$ of calcite within the cap rocks of salt domes as light as -53‰ has been reported [10],[11]. We have recently measured the isotopic composition of a cap rock calcite drill core taken from the High Island salt dome, High Island, TX. $\delta^{13}\text{C}$ of this calcite is -42.30‰, clearly indicating that this calcite was formed as a result of microbial oxidation of isotopically light hydrocarbons.

Perry, et al [12] discuss the mechanism responsible for the growth of a thin, nearly impermeable calcium carbonate layer (caliche) that confines much of the 250 km northern coastal part of the Yucatan aquifer of Mexico. Here calcium bicarbonate saturated groundwater discharges into a coastal saline zone, locally known as "teskel". Discharging groundwater mixes in the saline zone here and is subjected to intense evaporation. CO₂ is in turn "pumped" from the system and the result is active precipitation of a dense calcite layer that essentially cements older surficial limestone deposits, reducing porosity within this host limestone to less than 1%. The geochemistry of the groundwater here has been recently examined by Socki, et al [13]. They note that sulfate-reducing and sulfide-oxidizing bacteria living within narrow bands within the water column of deep water-filled sinkholes, tend to cycle between sulfate reduction and sulfide oxidation, depending on type and availability of nutrients. These bacterial-induced sulfur redox reactions could play an important role during secondary carbonate formation within the context of this environment.

Analyses of "teskel" zone caliche indicates that pore- and vein-filled caliche is depleted in

^{13}C with respect to the host limestone. $\delta^{18}\text{O}_{(\text{SMOW})}$ values range from +23.78 to +31.07‰. $\delta^{13}\text{C}_{(\text{PDB})}$ values range from -13.64 to +1.68‰. The 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. Similar isotopic trends have been seen by others in Barbados carbonate rocks [14].

Hydrothermal Environments (Nevada Hot Springs):

Preliminary field work was conducted in the Spring of 2004 to collect carbonate material from several hydrothermal (hot spring) environments in N. Nevada. In these hydrothermal terrestrial environments carbonate minerals precipitate as a result of heating of bicarbonate-rich water. During this heating process the solubility of CO_2 is lowered resulting in CO_2 de-gassing at the spring and an increase in the pH of the water. As the pH is raised solid carbonates in turn precipitate, typically near the edges of the springs. Another factor which may influence the carbon chemistry here is the presence of methane, produced under either biogenic or thermogenic conditions within the hot springs.

Collected samples include: 1.) solid carbonate from travertine deposits along the edges of hot springs (both modern and fossil deposits), 2.) bicarbonate-rich fluids from the springs for $\delta^{13}\text{C}$ of dissolved inorganic carbon (DIC) measurements, 3.) CO_2 and methane (where present) collected from bubbles emanating from the springs using a custom-designed gas harvesting devise for $\delta^{13}\text{C}$ measurements, and 4.) pH of the hot spring water where samples were taken.

DIC measurements indicate that in all cases the $\delta^{13}\text{C}$ DIC composition becomes heavier away from the source; i.e., the source has the lightest ^{13}C . We interpret this as a decrease in the CO_2 solubility the further from the source and subsequent degassing that favors light C removal, thus leaving the pool heavier in ^{13}C . pH measurements confirm this in at least one location. The most pronounced C isotope enrichment is seen in the Soldier Meadow Hot Creek, Nevada. Here the source DIC $\delta^{13}\text{C}$ is -5.35‰, while the DIC ~1 km away is at +4.88‰. These data are consistent with

a kinetic fractionation model controlling the carbonate precipitation.

CO_2 /methane gas mixtures were harvested from selected hot springs using a custom-designed gas collecting devise consisting of a ~2000 ml volume flask attached to a telescoping aluminum pole. The flask was submerged in the spring and positioned over a gas bubble train. The gas bubbles eventually displace the air in the flask and then transferred to pre-evacuated glass vials using a syringe needle. $\delta^{13}\text{C}$ of the methane ranges from -23.66‰ to -71.90‰, while the $\delta^{13}\text{C}$ of the CO_2 ranges from -4.92‰ to -23.62‰. We interpret variations in $\delta^{13}\text{C}$ composition of the methane/ CO_2 as an indication of a biogenic vs. thermogenic source for the sampled methane. Alternatively, $\delta^{13}\text{C}$ variations of the CO_2 may be indicative of kinetic processes operating at the surface of the spring. Analyses of layered solid samples (carbonate minerals) collected at these sites will further help to decipher the chemistry associated with these hot spring carbonate precipitation processes.

Implications for Mars: These data provide valuable information not only for better understanding of the processes that control organically-influenced carbonate mineral precipitation, but also how these processes affect the mineral's stable isotope composition and mineralogy. Having a thorough understanding of the effects of organically-controlled carbonate precipitation on the carbonate minerals will allow us to better decipher data collected from Martian carbonates, revealing which processes contributed to the precipitation of those minerals on or near the Martian planetary surface.

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