

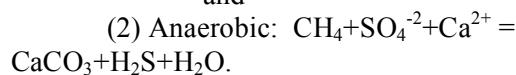
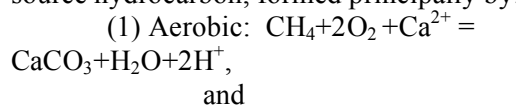
## ISOTOPE VARIATIONS IN TERRESTRIAL CARBONATES AND THERMAL SPRINGS AS BIOMARKERS: ANALOGS FOR MARTIAN PROCESSES

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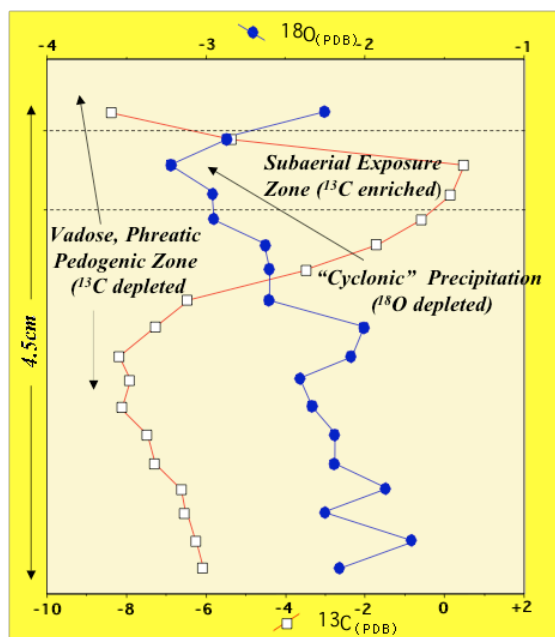
**Introduction:** Stable isotope measurements of carbonate minerals contained within ALH84001 [1] suggest that fluids were present at 3.9 Gy on Mars [2, 3, 4, 5]. Both oxygen and carbon isotopes provide independent means of deciphering paleoenvironmental conditions at the time of carbonate mineral precipitation. In terrestrial carbonate rocks oxygen isotopes not only indicate the paleotemperature of the precipitating fluid, but also provide clues to environmental conditions that affected the fluid chemistry. Carbon isotopes, on the other hand, can indicate the presence or absence of organic compounds during precipitation (i.e. biogenically vs. thermogenically-generated methane), thus serving as a potential biomarker.

We have undertaken a study of micro scale stable isotope variations measured in some terrestrial carbonates and the influence of organic compounds associated with the formation of these carbonates. Preliminary results indicate that isotope variations occur within narrow and discrete intervals, providing clues to paleoenvironmental conditions that include both biological and non-biological activity. These results carry implications for deciphering Martian isotope data and therefore potential biological prospecting on the planet Mars. Recently, Fourier Transform Spectrometer observations have detected methane occurring in the Martian atmosphere [6] that could be attributed to a possible biogenic source. Indeed, Mars Express has detected the presence of methane in the Martian atmosphere [7], with evidence indicating that methane abundances are greatest above those basins with high water concentrations.

**Micro-scale isotope variations in carbonates:** Calcite formed from the oxidation of organic material (i.e., methane in soil gas) is typically strongly depleted in <sup>13</sup>C owing to the influence of the source hydrocarbon, formed principally by:



In the Yucatan, light soil-gas CO<sub>2</sub>, derived from oxidation of organic matter, dissolves in vadose water and mixes with heavier marine limestone-derived carbon. The result is HCO<sub>3</sub><sup>-</sup> fluid that eventually precipitates as layers of caliche crust or calcite in vugs and veins on or within the host limestone that is δ<sup>13</sup>C-depleted. δ<sup>18</sup>O<sub>(PDB)</sub> and δ<sup>13</sup>C<sub>(PDB)</sub> analyses of micro milled growth layers in a 4.5 cm long thick section of caliche collected from Dzilam de Bravo, NW Yucatan, range from -3.23 to -1.71‰, and -8.29 to +0.33‰, respectively (Fig. 1). Variations in <sup>13</sup>C imply alteration within the vadose zone, with <sup>13</sup>C-depletions attributed to light soil gas CO<sub>2</sub> derived

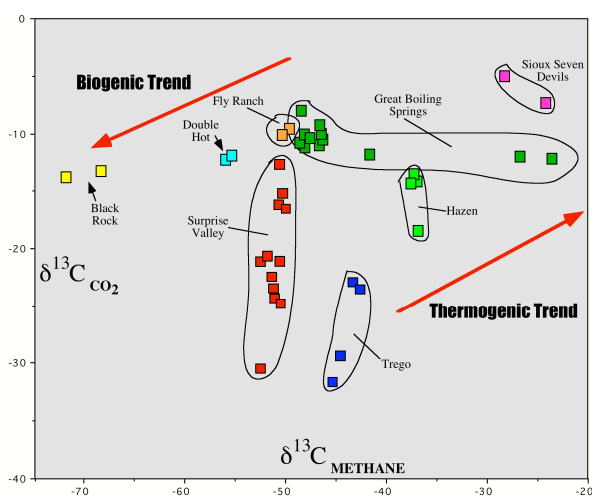


**Figure 1.** Micromilled O and C isotope composition of a 4.5 cm long caliche thick section from Dzilam de Bravo, Yucatan.

from oxidation of organic matter by either reaction (1) or (2), and <sup>13</sup>C enrichments attributed to subaerial exposure during precipitation. O isotope variations are indicative of meteoric diagenesis with <sup>18</sup>O enrichments due to evaporation effects, and <sup>18</sup>O depletions due either to sulfate reduction [8] (reaction 2), or the influence of <sup>18</sup>O-depleted meteoric precipitation (tropical cyclones) [9].

***C isotope variations in CO<sub>2</sub>-methane fluids from hot springs:***

In order to more fully understand the influence of methane on the C isotope composition of carbonate precipitation we have collected additional material for this study from thermal springs in N. Nevada, USA. CO<sub>2</sub>/methane gas mixtures were harvested from selected hot springs using a custom-designed gas collecting device 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 are then transferred to pre-evacuated glass vials using a syringe needle.  $\delta^{13}\text{C}$  of the methane from these springs ranges from -23.2‰ to -71.9‰, while the  $\delta^{13}\text{C}$  of the CO<sub>2</sub> ranges from -4.9‰ to -31.7‰ (Fig 2). Variations in  $\delta^{13}\text{C}$  composition of



**Figure 2.** C isotope composition of methane/CO<sub>2</sub> mixtures from N. Nevada, USA hot springs.

the methane could indicate a biogenic vs. thermogenic source for the sampled methane. Indeed, one of the most  $\delta^{13}\text{C}$ -enriched methane samples was taken where hot spring surface temperatures were among the highest recorded (Great Boiling Springs, T =96.0 °C).

The isotopic composition of the “harvested” gases from the hot springs suggests that both sources (biogenic vs. thermogenic) are plausible. The bacterial process contributed significantly to the very light C methane samples (~-70‰) that plot to the left on figure 2, whereas the thermal process contributed significantly to

the heavy C methane samples (~-23‰) that plot to the right on figure 2. Whether the heavy methane was co-generated as deep thermal methane and migrated with the ascending hydrothermal fluids of the hot springs, or originated as light (shallow) methane that fractionated as a consequence of in-situ distillation under the contact thermal effects of the hot fluids at the site of the hot springs, remains to be determined.

**Implications for Mars:** Our study of micro-scale isotope variations in caliche provide valuable information not only for better understanding the processes that control organically-influenced carbonate mineral precipitation, but also how these processes affect the mineral's stable isotope composition. Oxygen isotopes provide clues to help decipher paleoenvironmental conditions present during mineral precipitation. Carbon isotope measurements provide a means of determining the presence of organic compounds such as methane, either biogenically or thermogenically-generated, and thus serve as potential biomarkers. These data will in turn provide a basis for interpreting present and future isotope measurements from Martian carbonates, and for possible bio-prospecting on the planet Mars.

**References:** [1] Romanek, C.S. et al, *Nature* **372**, 655-657, 1994. [2] Carr, M. *Water on Mars*, Oxford University Press, New York, 1996. [3] Head, J. et al. *Meteoritics & Planetary Sci.*, **33**, A66, 1998. [4] Head, J. et al, *LPSC XXX*, Abstr. No.1352. [5] Borg, L.E. et al, *Science*, **286**, 90-94, 1999. [6] Krasnopolsky, V.A. et al, *Icarus*, **172**, 537-547, 2004. [7] Formisano, V. et al, *Science*, **306**, 1758-1761, 2004. [8] Socki, R.A. et al, *Limnol. Oceanogr.* **47**, 6 2002. [9] Perry, E.C., Jr. et al, *W#8, Workshop on Isotope Tracers and Remote Sensing Tech., VIIth Scientific Ass. of IAHS in Foz do Iguacu, Brazil, 2005.*