THE EFFECT OF CARBONATE ON THE DETERMINATION OF $\delta^{13}C$ BIOSIGNATURE IN LOW-ORGANIC LOW-CARBONATE SOILS FROM THE ATACAMA: RELEVANCE TO THE SEARCH FOR PAST LIFE ON MARS. R. Bonaccorsi[1,2], C. P. McKay[1], and A. P. Zent[1] - [1]Space Science Division, NASA Ames Research Center M.S. 245-3-1000 Moffett Field, CA 94035 USA. [2]SETI Institute - 189 Bernardo Avenue Mountain View, CA 94043 Rosalba.Bonaccorsi-1@nasa.gov.

Introduction:

A key goal of the next decade planetary missions is to determine whether life developed on any planetary body in the solar system other than Earth. The 2011 Mars Science Laboratory (MSL) and the ESA 2016/18 Pasteur ExoMars missions will seek information on the geological and biological history of Mars at landing sites with the expected highest preservation potential of organics [1].

Detailed information on the abundance and $^{13}C/^{12}C$ isotope ratios ($\delta^{13}C$) of inorganic (IC) and organic carbon (OC) mixed in geological materials is essential for modeling planetary formation and geochemical evolution and, in particular, for the search for past/present life on Mars.

On Mars carbonates have been detected at 1-5% as background component, or even in higher amounts in localized settings e.g., at Nili Fossae [5-8]; these carbonates could be mixed with the organic-poor Martian soil.

The MSL Sample Analysis at Mars (SAM) payload will characterize the $\delta^{13}C$ of the total CO_2 gas evolved from combusted/pyrolized geological samples [12] and bearing a mixed IC (less negative $\delta^{13}C$) and OC (more negative $\delta^{13}C$) signature. As a result, the instrumental capability of unraveling IC and OC from measured total carbon pools (TC=IC+OC) will be challenged by amount and type of carbonate minerals in geological samples.

In this context, of most relevance is the understanding of carbonate removal effects on the $\delta^{13}C$ signature of environmental samples characterized by a Low Organic Carbon/Low Carbonates content (herein referred as to LOCC).

Novel aspects of " LOCC Mars-like" materials:

We first present Elemental Analyzer-Ratio Mass Spectrometer (EA-IRMS) data from carbonate removal/combustion tests on a suite of LOCC soil analogs from the "Mars-like" [e.g., 1-2, 11] Atacama Desert, Chile (Figure 1). As these soils contain very low levels of refractory organics (at the 0.1% level), they have been suggested to represent key analogs of possible Martian organics [e.g., 1-2]. However, their amount of carbonate carbon have been overlooked.

In the second part of this paper, we compare LOCC soil from the Atacama with other mineralogically and biologically diversified LOCC environments worldwide. These includes: *a*) cyanobacteria-colonized/non colonized quartz sandstone (Antarctic Dry Valleys) and rhyolitic beach deposits from the peri-Antarctic Shetland Islands; *b*) clay-rich/Fe-oxyhydroxides-rich units from the hyperacidic drainage system of the Rio Tinto (Spain); and *c*) sub-lava-flow fossil soil rich in nontronite clay (Hawaian Islands) and subaerial analogues from the Mojave Desert.

Background & Study Site: The Atacama desert extends across 1000 km (30ºS to 20ºS) along the Pacific coast of South America (Figure 1) within the rain shadow of the Andes. This desert is one of the oldest and driest deserts on Earth, has been considered a renowed analog model for constraining the limits of life/ or its preserved remnants on Earth as well as on an early/ present-day Mars [1-2].

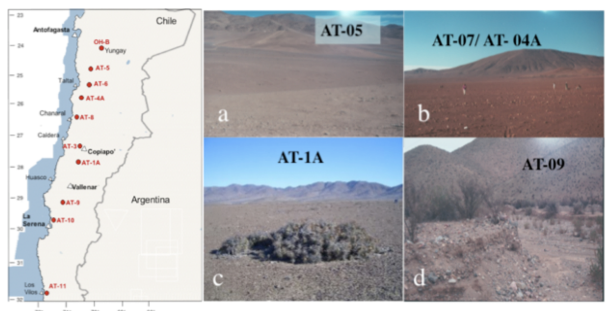

Figure 1. Left: Map showing location of tested samples. Right-hand side: (a) Representative hyperarid soil (~24ºS and ~0.5mm/y rain); and (b-d) arid sites (~32ºS and >120 mm/y rain).

Approach and Methods:

The elemental CN and naturally occurring stable isotopes of TC and OC were determined with a Carlo Erba NA-1500 Elemental Analyzer coupled with a Finnigan Mat Delta Plus XL IRMS instrument. Up to 50 to 100 ml of acid was added to the sample into silver boats in small increments until effervescence stopped and oven dried at T<60°C. Several cycles were repeated until no release of CO_2 was observed from the samples. To determine the efficiency of carbonate carbon removal sub samples were independently tested with sulfuric acid (2N H_2SO_4) and hydrochloric acid (1N HCl), which are commonly used for carbonate removal [9-10]. Solid samples were flash combusted (>1600°C) in a stream of pure O_2 (He carrier) to complete oxidation of organic matter and inorganic carbon [e.g., 9] to gases reduced and chromatographically separated (CO_2, N_2) prior injection into the MS unit.

Results and Conclusions:

1. Total carbon, organic and inorganic carbon. Figure 3a plots the compositional field of total and organic carbon pools with respect to the total amount of carbonate minerals (as %$CaCO_3$). Samples fall into three different compositional fields of the OC-carbonate diagram. 1. Extremely low OC (<0.06 wt.%) – low $CaCO_3$ (< 0.1-1 wt.%); 2. very low OC (< 0.1%) – low $CaCO_3$ (<1 wt.%); 3. relatively low OC (~0.1-1 wt.%) – $CaCO_3$ (~1-3 wt.%); and 4. higher OC (~1-2 wt.%) – $CaCO_3$ (~10-20 wt.%). The carbonate amount is directly correlated with the total carbon in samples i.e., open red circles symbols (R^2 = 0.97).

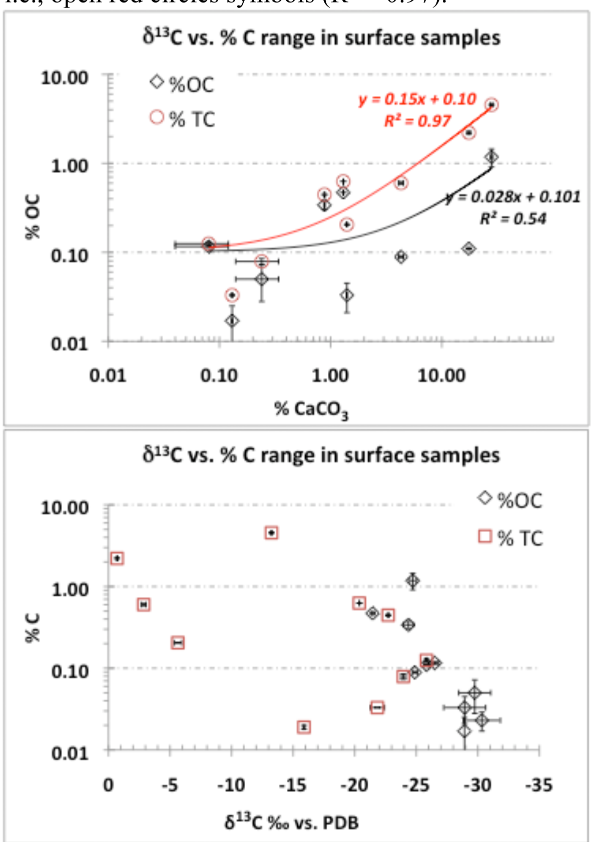

Figure 2ab. Organic geochemistry results in acid processed (%OC) and not processed bulk samples (%TC) from the Atacama Desert.

2. Stable isotopic composition of total and organic carbon. In Figure b we distinguish two different groups of soil based on their OC% vs. δ^{13}C-OC composition. 1) Soil with an extremely low amount of OC (<0.06 wt.%) and more negative values of δ^{13}C-OC (–30‰ to –28‰); these are from the plant-barren and low in active bacterial biomass e.g., 10^5 - 10^6 cell/gram [11]; 2) arid soils with a higher amount of OC (<0.6 wt.% to 2.2wt.%) and less negative OC- δ^{13}C (-21.5‰ to -26.5‰); these surface soils are mostly vegetated and contain higher living microbial biomass e.g., 10^7 - 10^8 cell/gram [11]. The less negative values of TC (δ^{13}C-TC ~15‰ to ~ -1 ‰) reflect a consistent fraction of carbonates relatively to the total carbon fraction (28% to 95%).

3. Effect of carbonate removal on bulk organic and inorganic δ^{13}C signature. Results from carbonate removal experiments show that the carbon isotopic composition can significantly shift (from 2‰ up to 5-7‰) even for small amounts of carbonate (<0.01-0.1%) left in the soil matrix. Understanding and mitigating this effect is necessary for the correct interpretation of bulk organic geochemistry data in organic-poor/carbonate-poor ground from Martian and planetary surfaces.

References: [1] http://marsoweb.nas.nasa.gov/landingsites; Navarro-González, R., F. et. al. (2003) *Science*, 302:1018-1021); [2] McKay, C. P. (2002) *Ad Astra*; [3] McKay, C. P., et al. (2003), *Astrobiology,* 3, 393-406; [4] Warren-Rhodes et al.(2006) *Microbial Ecology* 52:389-398; [5] Bandfield et al., (2003) *Science*, 301, 1084–1087; [6] Boynton et al., (2009). *Science*, 325, 61-64; [7] Ehlmann, et al., (2008). *Science*, 322, 1828-1832; [8] Morris et al. (2010). *Science*, 329, 421-424; [9] Nelson and Sommers (1996) Part 2, A.L. Page et al., Ed. *Agronomy*, 9:961-1010. Am. Soc. of Agron. Madison; [10] U.S. EPA. (1974); [11] Bonaccorsi and McKay (2008) *LPSC* XXXIX, #1489; [12] Mahaffy (2009) *Geochemical News*, 141.