Site-specific carbon isotope measurement of organics by gas source mass spectrometry

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Most isotopic measurements constrain the bulk compositions of molecules or minerals, averaging over non-equivalent sites. Site-specific isotope measurements potentially could add new constraints regarding the sources and reaction histories of molecules. For example, previous studies demonstrate that biosynthetic reactions, such as decarboxylation of pyruvate, lead to even/odd ordering and more complex pattens of ^{13}C enrichment within fatty and amino acids, with differneces of up to 30‰ between adjacent C positions. Such variations are potentially preserved in the products of thermal degredation of biomolecules (e..g, propane). And isotopic structures of these products may also reflect the mechanisms and conditions of the 'cracking' reactions by which they are produced from larger biomolecules at elevated temperatures, and/or measure their later consumtion by thermal or bio-degredation.

We have developed a new mass spectrometric tecnique for measuring the difference in ^{13}C enrichment between the terminal central C position in propane. Our measurement based on comparison of the δ^{13}C values of one- and two-carbon fragment ions, each of which is analyzed using a new high resolution mass spectrometer, the MAT 253 Ultra. We appiled this technique to a sample suite of wet (i.e., ethane and propane-rich) natural gases. Conventional interpretations of δ^{13}C values of these components of these gases suggest they are a single suite that varies only in its level of thermal maturity. However, we find these samples can be divided into two populations that differ by 5 ‰ in the δ^{13}C of their central carbon position. Within each of these populations, the δ^{13}C of the terminal carbon position can vary by up to 7 ‰. Several interpretations of these data are possible; a simple hypothesis we suggest is that the central carbon position samples the δ^{13}C of the source rocks (which are known to be a mix of lacustrine and marine rocks in this suite), whereas variations in δ^{13}C of the terminal carbon within any set of samples from a given source increases with increasing thermal maturity. We are now exploring this and other hypotheses through experiments, modeling, and measurements of other suites. More generally, this work suggests a path toward site-specific measurements of a variety of organic molecules.

Evaluating the fossilization potential of Fe(II)-oxidizing bacteria

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The hunt for microfossils in the rock record has been pursued for several decades to reconstruct the individual steps in life evolution as well as the appearance of microbial metabolisms [1]. Given the small cell size and the limited morphological diversity in the microbial world, the biogenicity of microbial-like structures has always been questioned. Fossilization experiments have shown that microorganisms can be well preserved in silica [2]. However the presence of Fe^{3+} appears essential during the fossilization process in silica [3, 4]. In this study, we investigate the fossilization potential of Fe(II)-oxidizing bacteria after exposition to pressure (P) and temperature (T) conditions simulating diagenetic processes during sediment burial and rock formation. Within this project we seek to propose a "biosignature" for microbial Fe metabolism to be compared to the rock record. *Gallionella*-like microorganisms produce twisted stalks – structures made of a polysaccharide bone and coated with Fe(III) oxyhydroxides – as a result of growth and Fe(II) oxidation [5]. A Fe(II)-oxidizing microbial mat containing twisted stalks was collected at the Segen Gottes mine (SW Germany) and incubated at various P/T conditions in a hydrothermal autoclave. Twisted stalks were preserved at the highest P/T conditions tested (1 week at 250°C/140 MPa) and after the longest incubation (4 months at 170°C/120 MPa). Fe(III) minerals evolved from ferrihydrite to hematite with increasing P/T conditions. Polysaccharidic and peptidic components were altered at the highest P/T conditions tested. However organic carbon was relatively well preserved. It seems that Fe(III) oxyhydroxides covering the organic carbon are acting as a protectant to maintain the morphology and organic components of the twisted stalks and might be able to preserve these structures over geological times.

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