

INFLUENCE OF GEOCHEMISTRY ON DETECTION OF BIO/ORGANIC SIGNATURES. C. D. Richardson¹, N. W. Hinman¹, J. M. Kotler¹, T. R. McJunkin², and J. R. Scott². ¹Department of Geosciences, University of Montana, Missoula, MT 59812 (nancy.hinmna@umontana.edu). ²Idaho National Laboratory, Idaho Falls, ID 83415 (jill.scott@inl.gov).

Introduction: Our primary interest is in determining how the geochemistry on Mars may affect the ability to detect signs of life via laser desorption/ionization mass spectrometry (LD-MS) techniques. The first LD-MS instrument that is scheduled to visit the martian surface is part of the Mars Organic Molecule Analyzer (MOMA), which is part of the ExoMars payload.

In conjunction with mineralogical data, the detection and identification of bio/organic signatures can assist in linking biochemical and geochemical processes. Geomatrix-assisted laser desorption/ionization (GALDI) in conjunction with laser desorption Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) is a method of obtaining bio/organic signatures from a range of geological materials with little or no sample preparation [1]. A variety of laboratory and natural samples have been investigated to determine how well bio/organic signatures can be detected when associated with different minerals using GALDI-FTICR-MS [2]. Because the minerals essentially play the role of “matrix” to assist desorption and ionization of the bio/organic compounds, it is not surprising that some bio/organic-mineral combinations work better than others. Even for the minerals that work well, one of the key challenges is that the bio/organic constituents are not homogeneously distributed.

Approach: Laboratory or natural samples were analyzed with a 7T imaging laser desorption FTICR-MS, which has been described previously [3,4]. Each spectrum was acquired with a single laser shot using a wavelength of 355 nm with a 6 ns pulse for an irradiance of $\sim 10^8$ W/cm² for 10 μ m spot. In survey or mapping mode, the mass resolution was typically $\sim 10,000$ with a mass accuracy of 3 ppm.

Results & Discussion: Six general types of ionization reactions have been observed. (1) Organic compounds, such as polyaromatic hydrocarbons (PAHs), tend to self-ionize and not be dependent on the geomatrix present [5]. (2) Not unexpectedly, evaporitic minerals with alkali metals present tend to produce cation attached bio/organic signatures [1]. (3) While this is generally true of alkyl halides, if sulfate is the counterion, then larger inorganic cluster ions are formed (usually noticed in the negative mode) that can have gas-phase basicities that allow them to abstract a proton from a bio/organic molecule to produce a deprotonated bio/organic ion [6]. (4) The presence of sulfate can also lead to the production of complex cluster ion bio/organic signatures, similar to that observed with

glycine and jarosite [2]. (5) Fragmentation of bio/organic compounds has also been observed, predominantly with iron oxide minerals [1]. (6) It is also possible for the presence of certain bio/organic compounds (i.e., PAHs) to assist in the ionization of other bio/organic compounds [1].

Because a combination of these reactions may be possible in a natural sample, the bio/signature ultimately observed via GALDI-MS is dependent on the competitive nature of the possible ionization mechanisms. A key example of the competition between reaction mechanisms is the case of aromatic amino acids with the mineral thenardite (Na₂SO₄). Aromatic amino acids by themselves behave similar to PAHs and will self-ionize with UV laser desorption/ionization (Fig. 1A). When mixed with the mineral thenardite, the aromatic amino acid, tyrosine (Tyr, C₉H₁₁NO₃), is preferentially ionized by cation attachment (Fig. 1B).

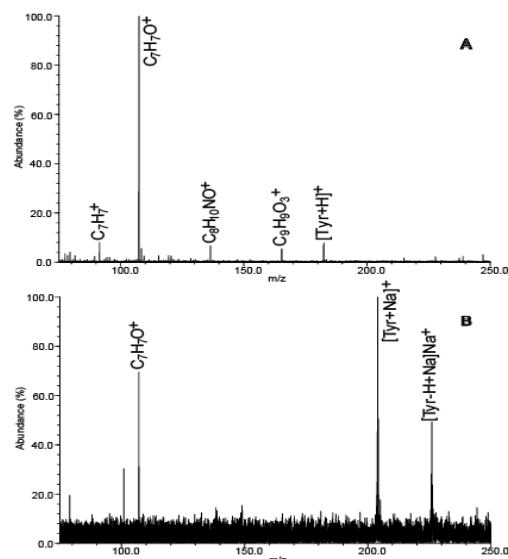


Figure 1. FTICR-MS spectra of (A) tyrosine alone and (B) tyrosine with thenardite [7].

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