

**POTENTIAL FOR FINDING EVIDENCE OF BIO/ORGANIC COMPOUNDS IN EXTRATERRESTRIAL MATERIALS.** N. W. Hinman<sup>1</sup>, C. D. Richardson<sup>1</sup>, D. Aspden<sup>1</sup>, K. Kouri<sup>1</sup>, J. M. Kotler, L. J. McHenry<sup>3</sup>, and J. R. Scott<sup>1,4</sup>, <sup>1</sup>Department of Geosciences, The University of Montana, Missoula, MT 59812, nancy.hinman@umontana.edu, <sup>2</sup>North American Palladium, Thunder Bay, ON P7C 4T8, mkotler@napalladium.com; <sup>3</sup>Department of Geosciences, University of Wisconsin-Milwaukee, WI 53201, lmchenry@uwm.edu, <sup>4</sup>Department of Chemical Sciences, Idaho National Laboratory, Idaho Falls, 83415, jill.scott@inl.gov.

**Introduction:** We have been seeking to better understand mineral-bio/organic compound interactions in laboratory-based, biologically induced, and natural samples and to understand bio/organic compound stability upon exposure to thermal, gamma, and UV radiation. This understanding will lead to improved ability to detect such compounds and determine their biogenicity, predict which landing sites are most likely to provide evidence for life, and detect bio/organic compounds for decontamination procedures for planetary protection.

Herein, we present results of experiments to determine mass spectral patterns for bio/organic compounds associated with different mineral salts, which are representative of secondary minerals that have been or might be found on Mars. Additionally, we report results of natural, mineral terrestrial samples and how these might be related to extraterrestrial settings. Specifically, we emphasize that the basalts and secondary minerals at Craters of the Moon (COM) National Monument are analogous to martian basalt and that the secondary minerals associated with such basalts are a potential target for finding bio/organic compounds derived from microbial activity.

**Approach:** Both laboratory and natural samples were analyzed. For laboratory samples, sulfate (jarosite, alunite, thenardite, gypsum, and anhydrite) and phosphate minerals were synthesized. Organic compounds were physically mixed or added to synthetic solutions. Natural samples were collected from various sites (e.g., COM). X-ray diffraction (XRD) patterns and geomatrix-assisted laser-desorption Fourier transform ion cyclotron mass spectrometry (GALDI-FTICR-MS) spectra were collected for pure synthetic minerals, laboratory samples with added organic compounds, and natural samples. The resulting diffraction patterns and spectra were compared to distinguish the mineral from the organic signatures. These results were then compared to those obtained from natural samples. In some cases, a mechanism for the observed ionization method or fragmentation pattern could be determined or hypothesized. Other analytical techniques employed include Fourier transform infrared spectroscopy (FTIR) and sulfur isotope ratio mass spectrometry (IRMS).

**Methods:** Minerals were synthesized according to the following procedures:

*Jarosite:* reflux FeCl<sub>3</sub> solution with sulfate salt following Kotler et al. (2009).

*Alunite:* modified from jarosites procedure by substitution of AlCl<sub>3</sub> for FeCl<sub>3</sub> in Kotler et al. (2009).

*Thenardite:* Na<sub>2</sub>SO<sub>4</sub> was purchased from Fisher Scientific (Pittsburgh, PA).

*Gypsum:* saturated mixtures of CaCl<sub>2</sub> and Na<sub>2</sub>SO<sub>4</sub> solutions were prepared and filtered.

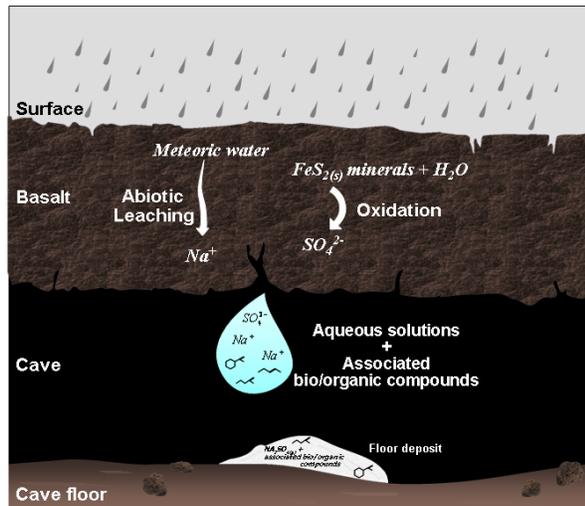
*Anhydrite:* saturated mixtures of CaCl<sub>2</sub> and Na<sub>2</sub>SO<sub>4</sub> solutions were prepared, heated to 60 C for three hours, and filtered.

*Apatite:* saturated mixtures of Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O and (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> solutions were prepared with a Ca:P ratio of 1.67 and heated to 200 C for 24 hours, followed by filtration.

**Results & Discussion:** In general, six types of ionization reactions have been observed for bio/organic compounds associated with minerals when analyzed via GALDI-FTICR-MS. (1) Self-ionization: typical of aromatic organic compounds, such as polycyclic aromatic hydrocarbons (PAHs) and amino acids such as Tyr and Trp [1,2]. (2) Cationization: common for evaporitic minerals with alkali metals present [3]. (3) Deprotonation: inorganic cluster ions formed from the mineral matrix can have gas-phase basicities that allow them to abstract a proton from a bio/organic molecule to produce a deprotonated bio/organic ion [4]. (4) Complex cluster ion formation: the presence of sulfate can lead to the production of bio/organic signature ions that have adducts from the mineral attached [5]. (5) Fragmentation: predominantly observed with iron oxide minerals [3]. (6) Co-bio/organic assisted ionization: the presence of certain bio/organic compounds (i.e., PAHs) can assist the ionization of other bio/organic compounds [1]. While a particular ionization scheme is usually associated with a particular mineral, multiple ionization methods can be observed with some minerals, such as thenardite. Thenardite has been observed to produce ions via cation attachment, deprotonation, and complex cluster ion formation [2, 4].

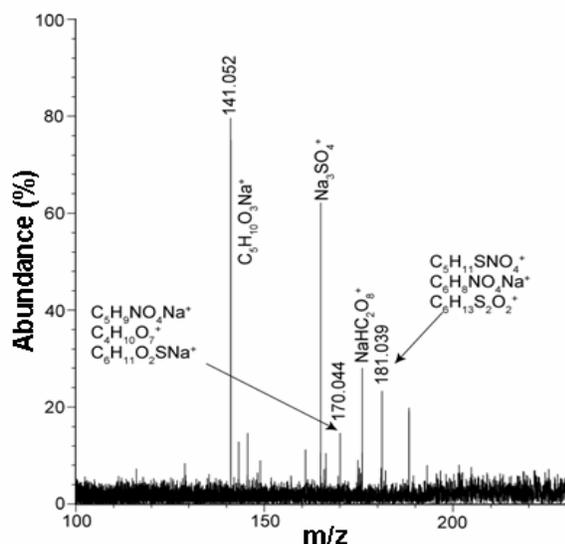
Besides the laboratory results for observing bio/organics in thenardite, natural samples of thenardite have also produced bio/organic signatures

[4]. Currently, thenardite samples collected from basalt lava tubes at COM have been examined for bio/organics based on the hypothesis that the thenardite deposits are formed by a combination of abiotic and biotic physiochemical weathering of the overlying basalt as illustrated in Figure 1.



**Figure 1.** Schematic illustration of potential formation mechanism for thenardite in basalt lava tubes at COM.

XRD patterns revealed that the COM thenardite deposits contain some carbonate minerals. Evidence for the carbonate minerals was also observed in the GALDI-FTICR-MS spectra. Analysis of thenardite deposits collected from several caves within COM revealed that the deposits also contain mass spectral peaks that have bio/organic compositions as shown in Figure 2.



**Figure 2.** GALDI-FTICR-MS spectrum from a thenardite deposit collected from COM.

Peak identification was obtained by comparing the observed mass defects with theoretical mass defects. Using this method, the peak at  $m/z$  141.052 was found to have only one likely composition with a theoretical weight of 141.053 u, corresponding to a formula of  $C_5H_{10}O_3Na^+$ . The peaks at  $m/z$  170.044 and 181.039 have several likely formulas could account for these mass defects.

Additional evidence of associated bio/organic compounds in the secondary deposits was investigated using FTIR. Even though FTIR does not have the sensitivity and resolution of FTICR-MS, several bands were observed to support the presence of organic compounds. Furthermore, sulfur fractionation between the COM host basalts and the secondary minerals was determined. The greatest fractionation difference between the host basalt and the secondary deposits is 4.5%, with several additional values exceeding 3.5%. These small but significant differences may imply biological oxidation as inorganic fractionation of sulfidic minerals generally do not exceed 3%.

**Conclusions:** Understanding the type of bio/organic signature that can be observed from different minerals is important both for future laser desorption mass spectrometer (LDMS) instruments, such as the Mars Organic Molecular Analyzer (MOMA) selected for the upcoming ExoMars rover, and analysis of samples returned to Earth. This knowledge will assist in the selection of which minerals offer the highest probability of detecting bio/organic compounds. For example, because the chemical composition of the COM basalts is similar to that of their martian counterparts, the occurrence of biological activity in the formation of sulfate minerals at COM has direct implications for the search for life on Mars. In addition, the presence of caves on Mars suggests the importance of these environments as a possible location for the growth and preservation of microbial activity because of shielding from UV and solar radiation.

#### References:

- [1] Yan et al. (2007) *Talanta*, 72, 634–641.
- [2] Richardson, C. D. (2009) *Int. J. Astrobiol.*, 8, 291–300.
- [3] Yan, B. et al. (2007) *Geomicrobiol. J.*, 24, 379–385.
- [4] Richardson, C. D. et al. (2008) *Geomicrobiol. J.*, 25, 432–440.
- [5] Kotler, J. M. et al. (2008) *Astrobiology*, 8, 253–266.