# SULFATE MINERALS, HEMATITE, AND SILICA IN CRATERS OF THE MOON, IDAHO BASALTIC LAVA TUBES: A POTENTIAL ANALOG FOR MARS.

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**Introduction:** Martian basalts differ in composition from most terrestrial basalts in their high Fe abundances. The high-Fe products of hot spot basaltic volcanism, including lavas from Craters of the Moon (COM), Idaho [1], are the closest analogs (Table 1) and provide an opportunity to observe how Mars-like basalts behave in different alteration environments. This is critical, as the products of alteration depend heavily on the composition of the substrate (e.g. [2]).

| Oxide | Shergotty meteorite[3] | Adirondack (Gusev)[4] | Bounce Rock (Meridiani)[5] | Maui[6] | Blue Dragon Flow, CoM |
|---|---|---|---|---|---|
| $SiO_2$ | 50.10 | 45.40 | 50.80 | 45.40 | 49.08 |
| $TiO_2$ | 0.80 | 0.45 | 0.78 | 3.32 | 2.71 |
| $Al_2O_3$ | 6.70 | 10.90 | 10.10 | 17.06 | 13.83 |
| $Fe_2O_3T$ | **21.00** | **20.00** | **17.30** | **13.29** | **17.16** |
| MnO | 0.50 | 0.38 | 0.43 | 0.20 | 0.26 |
| MgO | 9.10 | 11.90 | 6.40 | 3.61 | 3.29 |
| CaO | 9.40 | 7.42 | 12.50 | 9.13 | 6.89 |
| $Na_2O$ | 1.40 | 2.70 | 1.30 | 3.98 | 3.59 |
| $K_2O$ | 0.20 | 0.06 | 0.10 | 1.71 | 2.04 |
| $P_2O_5$ | 0.70 | 0.54 | 0.95 | 0.92 | 1.68 |
| Total | 100.00 | - | - | 97.38 | 99.43 |

Table 1: comparison of Mars meteorite, MER-analyzed rocks, high-Fe Hawaiian basalt, and COM Blue Dragon Flow compositions. Data from [3, 4, 5, 6] and the current study.

**Basalt alteration and secondary minerals on Mars:** High-Fe basalts and their alteration products dominate parts of the Martian surface. In the light-toned outcrops of Meridiani Planum, the MER Opportunity landing site, hematite and Mg- and Fe-sulfates (including jarosite) are directly associated with altered basaltic materials in an assemblage likely formed through evaporation of a saline-acidic brine and later interactions with groundwater [7]. Sulfate minerals, silica, and altered basalt have also been observed by the MER Spirit at Gusev Crater [8] and from orbit in other regions [9]. Thus, an analog displaying high-Fe basalts and a secondary mineral assemblge including these phases would be useful.

**Caves as Mars analogs:** Basaltic caves are likely common features on the surface of Mars, and cave entrances have recently been detected there [10, 11]. Such caves would make excellent astrobiological targets, as they could provide protection for organisms (or their signatures) from the UV radiation and cosmic particles that bombard the surface of Mars [12]. In arid places on Earth, basaltic caves also provide an environment where soluble Mars-analogous secondary minerals (including Na and Fe sulfates) can be formed and preserved in association with a basaltic substrate.

**Craters of the Moon:** The Fe-rich Blue Dragon Flow of the COM lava field represents the youngest volcanism in the Eastern Snake River Plain (~2.1 ka, [1]). It is also the site of numerous lava caves that preserve secondary mineral deposits of potential interest to Mars researchers, including hematite, silica, carbonates, and sulfate minerals (including jarosite, [13]).

**Methods:** Samples of fresh and altered basalt, white, brown, and dendritic cave ceiling coatings, and white powdery mounds on cave floors were collected from Blue Dragon Flow caves in October 2007-08 and June 2008. Samples were powdered and analyzed by X-ray Diffraction (XRD) using a Bruker D8 Focus to identify minerals, and Rietveld refinement was used to determine relative phase concentrations. Some powdered samples were also used to prepare Lithium Metaborate/Tetraborate glass beads for X-ray Fluorescene Spectroscopy (XRF) and analyzed using a Bruker S4 Pioneer (methods of [14]). Some samples were also mounted in epoxy, polished and analysed by Scanning Electron Microscopy (SEM), providing backscattered electron (BSE) images and Energy Dispersive Spectroscopic (EDS) compositional information.

**Results:** The XRD data reveal a range of minerals in the coatings and mounds, including calcite (dendritic and some white coatings), silica (some white coatings), hematite and silica (brown coatings, Figure 1), and Na-sulfates and carbonates (mounds, Figure 2). Jarosite or other Fe-sulfates were not observed.

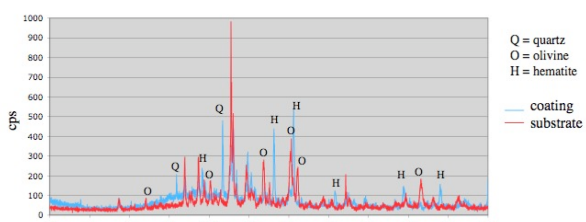


**Figure 1**: XRD patterns for a brown cave ceiling coating (blue) and the underlying basaltic substrate (red).

The XRF bulk compositional data indicates a Mars-like high-Fe basaltic composition for the substrate with similar Si, Mn, and Ca concentrations but higher Ti, Al, Na, K, and P and lower Mg (Table 1) compared to Mars. White coatings were either dominated by Ca (for the calcite) or Si (for the silica), while the brown (hematite and silica dominated) coatings were enriched in Si, Na, and K relative to the substrate but showed a decrease in all other elements analyzed (Table 2).

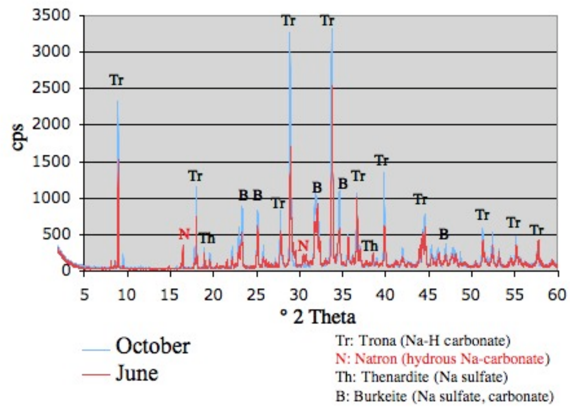


Figure 2: XRD pattern for one Na-carbonate/sulfate mound sampled in October and June. Natron (a hydrous Na-carbonate) is present during the cooler spring but absent in the warmer fall. Trona and burkeite dominate year round.

| Oxide | $SiO_2$ | $TiO_2$ | $Al_2O_3$ | $Fe_2O_3T$ | MnO | MgO | CaO | $Na_2O$ | $K_2O$ | Total |
|---|---|---|---|---|---|---|---|---|---|---|
| brown coating | 53.61 | 2.35 | 11.12 | 14.34 | 0.18 | 2.73 | 5.82 | 3.83 | 2.21 | 98.04 |
| fresh basalt | 47.79 | 2.95 | 12.51 | 17.12 | 0.21 | 3.32 | 7.04 | 3.14 | 1.89 | 98.28 |

Table 2: comparison between brown ceiling coating and fresh Blue Dragon basalt composition (XRF data).

The SEM BSE images and EDS analysis confirmed the presence of calcite and silica coatings and showed fine layering (Figure 3). For the brown coatings, hematite was concentrated in a thin layer coating the surface of the basalt, with a thin layer of silica coating on the outside. XRD analysis of the substrate and coating (Figure 1) reveals plagioclase and pyroxene in both, olivine in the basalt (but not the coat), and hematite and quartz in the coat (but not the basalt).

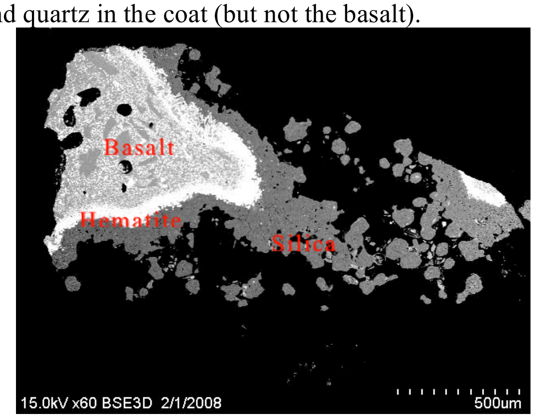


Figure 3: SEM BSE image of a basaltic speleothem, showing the underlying basalt, thin hematite layer, and silica coat.

**Discussion:** *Sulfate Mounds.* The sulfate mounds were composed almost exclusively of Na-sulfate and Na-carbonate minerals, including thenardite, mirabilite, trona, and burkeite (e.g. Figure 2). Samples of the same mounds collected in June and October revealed subtly different mineral assemblages. The hydrous Na-carbonate mineral natron was present in June but not October, perhaps indicating dehydration during the warmer summer months. The origin of these mounds is likely biological, as they are not found at the lowest points on the floor (where evaporation would be expected), do not underly obvious ceiling mineral occurrences, and show clear breaks with the substrate (and thus are not formed directly through local basalt alteration). It is interesting to note within these caves, calcite is the dominant carbonate in the ceiling mineral deposits, with Na-carbonate precipitates on the floors.

*Hematite-rich coatings.* These thin hematite coats directly overlying the basalt substrate likely formed at the expense of olivine in the high-temperature environment of the lava tubes shortly after formation, while the overlying silica coating likely formed afterwards in a groundwater environment. This hydrothermal and groundwater scenario could be relevant to formation of hematite and silica at Meridiani Planum [e.g. 15]

**Contrast to Mars:** The Na-sulfate minerals sampled in COM lava tubes are not representative of Fe-, Mg-, and Ca-sulfate minerals that dominate the surface and potentially the subsurface of Mars. This difference is likely attributable to different starting compositions (COM basalts are richer in Na and K) and different weathering conditions (Na-sulfates are favored under higher pH condiditon typical of terrestrial basaltic weathering as opposed to more acidic conditions on Mars). Additionally, microbes were likely involved in the formation of the COM mounds. Water availability alone cannot explain the difference, as thenardite has a solubility between Mg-sulfates epsomite and kieserite [16], both identified on Mars [17]. However, the brown ceiling coatings, with their hematite, silica, and basaltic minerals, could be a potential analogue for the light-toned outcrop materials at Meridiani Planum.

**References:** [1] Kuntz M.E. et al. (1986) *GSA Bulletin 97*, 579-594. [2] Tosca N.J. et al. (2005) *EPSL 240*, 122-148. [3] Lodders K. (1998) *Meteoritics & Planet. Sci., 33*, A138-A190. [4] Gellert R. et al. (2004) *Science 305*, 829-832. [5] Rieder R. et al. (2004) *Science 306*, 1746-1749. [6] Bishop J.L. et al. (2007) *Clay Clay. Miner. 55*, 1-17. [7] McLennan S.M. et al. (2005) *EPSL 240,* 95-121. [8] Ming D.W. et al. (2006) *JGR 111,* E02S12. [9] Ehlmann B.L. et al. (2009) *JGR 114,* E00D08. [10] Wyrick D. et al. (2004) *JGR 109,* E06005. [11] Cushing G.E. et al. (2007) *GRL 34,* L17201. [12] Boston P. et al. (2001). *Astrobiology 1*, 25-55. [13] Peck S.B. (1974), *NSS Bulletin 36*, 19-24. [14] McHenry L.J. (2009) *Chem. Geol. 265,* 540-552. [15] Golden D.C. et al. (2008) *Am. Mineral. 93*, 1201-1214. [16] Spencer R.J. (2000) *In:* Alpers C.N. et al. *Sulfate Minerals*. MSA, Washington, 173-192. [17] Peterson R.C. et al. (2007) *Am. Mineral. 92*, 1756-1759.