

**SECONDARY MINERALS IN BASALTIC CAVES: ANALOG FOR MARS SURFACE AND SUBSURFACE MINERALOGY.** L. J. McHenry<sup>1</sup>, J. M. Ruffini<sup>1,2</sup>, T. L. Gerard<sup>1</sup>, and G. L. Walters<sup>1</sup>. <sup>1</sup>Department of Geosciences, University of Wisconsin- Milwaukee. PO Box 413, Milwaukee, WI 53201. [lmchenry@uwm.edu](mailto:lmchenry@uwm.edu), [tlgerard@uwm.edu](mailto:tlgerard@uwm.edu). <sup>2</sup>Current employer: Kensington gold mine, Juneau, Alaska.

**Introduction:** Lava tubes provide excellent environments for the formation and preservation of Mars-relevant sulfate, oxide, and silica minerals with a basaltic substrate. These minerals form by alteration and precipitation under both high and low temperature conditions, with or without water or microbial activity, and as such could help constrain the conditions of formation of similar mineral assemblages on Mars.

**Relevance to Mars:** Extensive basaltic lava flows on Mars suggest that associated lava tubes could be commonplace, and skylights into Martian lava tubes have been observed remotely [1,2]. These have been suggested as potential targets for astrobiological investigations [3], or as habitats for humans on future Mars missions [4]. On Earth they provide a stable environment that preserves otherwise soluble minerals such as sulfates (e.g. thenardite, mirabilite, jarosite). Basalt compositions in some terrestrial lava fields (e.g. Craters of the Moon, CoM) are Fe-rich, similar to those observed on Mars (Table 1). Hematite, sulfates (e.g. gypsum, mirabilite, thenardite, jarosite), amorphous silica, and carbonates are common secondary minerals in these environments; the detection of some of these on Mars has often been interpreted as evidence of ancient Martian aqueous activity [e.g. 5,6,7].

Oxide	Shergotty (Mars)	OCBP1 (Mars)	Kula Kai (Hawaii)	G. Dome (LBNM)	BDF, CoM
SiO <sub>2</sub>	50.10	48.19	51.40	54.47	47.79
TiO <sub>2</sub>	0.80	1.01	1.95	0.71	2.95
Al <sub>2</sub> O <sub>3</sub>	6.70	8.06	13.33	16.80	12.51
Fe <sub>2</sub> O <sub>3</sub> T	<b>21.00</b>	<b>20.23</b>	<b>11.67</b>	<b>8.07</b>	<b>17.12</b>
MnO	0.50	0.43	0.17	0.14	0.21
MgO	9.10	10.40	7.18	7.08	3.32
CaO	9.40	6.46	10.27	8.59	7.04
Na <sub>2</sub> O	1.40	2.19	2.03	2.73	3.14
K <sub>2</sub> O	0.20	0.75	0.43	1.11	1.89
P <sub>2</sub> O <sub>5</sub>	0.70	1.37	0.23	0.10	1.68
SO <sub>3</sub>	0.48	*	n.a.	n.a.	0.05
Total	100.00	99.09	97.38	99.88	98.28

Table 1: Basalt compositions. Shergotty Mars meteorite [8]. OCBP1, calculated fresh Meridiani basalt end member, S-free, [9]. Hawaii, Lava Beds (LBNM), Blue Dragon Flow (BDF, at Craters of the Moon (CoM)) from present study.

**Study sites:** To date we have sampled basalts (Table 1), ceiling and wall surface coatings, and secondary mineral mounds (Figure 1) from lava caves in the Blue Dragon Flow (BDF) at CoM, Idaho, from Catacombs,

Golden Dome, and Valentine caves at Lava Beds National Monument (LBNM), California, and Kula Kai Caverns, lower SW slopes of Mauna Loa, Hawaii. All are in semi-arid regions. CoM's Blue Dragon Flow and Kula Kai have similar ages (less than 2000 years), while most LBNM caves are in older (30-40,000 yr) flows. Some CoM caves were sampled twice, in different seasons (June and October).



Figure 1: Sample types. A. CoM dendritic ceiling coating; B. Hawaii orange sulfate coating; C. CoM sulfate powder mound; D. CoM metallic hematite and white coating; E. CoM jarosite and hematite; F. Hawaii calcite "puffballs."

**Methods.** All samples were powdered for X-ray Diffraction (XRD) for phase identification, and some were mounted in epoxy and polished for electron probe microanalysis (EPMA) and scanning electron microscopy (SEM) for imaging and grain-discrete chemical analysis or fused for X-ray fluorescence (XRF) for substrate bulk compositions. Methods following [10].

**Results.** Minerals observed in the cave coatings are reported in Table 2. Coatings represent a variety of compositions, even within the same caves. While hematite, calcite, gypsum, and some Si-rich phase were present in all three localities, other minerals (Na-sulfates, jarosite, Na-carbonates) varied. Sulfate mounds in CoM caves changed in size (and Na-sulfate mineral assemblage) between visits, indicating seasonal changes [11]. At CoM, bulk analysis showed little

difference between hematite-rich (and olivine-poor) wall coatings and the underlying basaltic substrate, suggesting in-situ alteration with only minor leaching. SEM imaging shows that the coatings form discrete layers, with hematite in direct contact with the substrate while calcite and silica formed later (Figure 2).

	n	Basaltic	Fe-oxides	Na-sulfates	Ca-sulfates	Jarosite	Calcite	Na-carbonate	Amorphous	Cristobalite
<b>CoM</b>										
Metallic	5	XX	XX	-	-	-	-	-	-	-
Yellow	1	XX	XX	-	-	+	-	-	-	-
White coat	2	-	-	-	XX	-	-	-	-	-
White coat	2	-	-	-	-	-	XX	-	-	-
Powder	4	-	-	XX	-	-	-	-	-	-
Powder	1	-	-	-	-	-	XX	-	-	-
Powder	1	-	-	XX	-	-	-	-	-	-
Powder	1	-	-	+	-	-	-	XX	-	-
<b>Kula Kai</b>										
Dark coat	2	XX	XX	-	-	-	-	-	-	X
yellow/white coat	3	-	-	-	XX	-	-	-	-	-
Orange coat	1	-	-	XX	-	-	-	-	-	-
Dendritic	1	XX	+	-	-	-	-	-	XX	-
Soft puffballs	2	-	-	-	+	-	XX	-	-	-
Soft puffballs	1	-	-	-	-	-	XX	-	-	-
<b>Lava Beds</b>										
Orange coat	1	+	-	-	+	-	X	-	XX	-
Orange coat	1	XX	XX	-	-	-	-	-	-	-
White coat/powder	1	-	-	-	-	-	-	-	XX	-

Table 2: XRD results. n = number of samples analyzed with similar mineral assemblages.

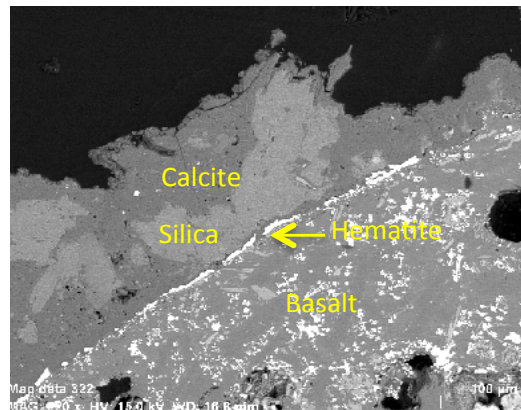


Figure 2: Backscatter electron (BSE) image of a CoM cave coat, with a thin layer of hematite at the boundary between the basalt and the amorphous silica and calcite coating.

**Discussion.** Despite similarities in age, substrate composition, and semi-arid environment, lava caves at CoM, LBNM, and Kula Kai exhibit different secondary mineral assemblages. Powdery Na-sulfate deposits are common in CoM caves, while thick ceiling coat Na-sulfates occur in one short section of Kula Kai. Na-sulfates are absent in the LBNM caves analyzed to date

in this study. Silica at CoM and LBNM appears to be amorphous, while Kula Kai coatings include cristobalite. Jarosite has so far only been observed at CoM. Iron oxide is ubiquitous in the metallic surface coatings, as hematite at Kula Kai and CoM and maghemite at LBNM.

The life cycle of a basaltic cave includes an initial high-T stage, when high-T (both dry and hydrothermal) processes drive the oxidation of basaltic  $\text{Fe}^{2+}$ -bearing minerals into hematite and when less stable secondary minerals precipitate [12,13]. Gypsum and other sulfates form at high and intermediate temperatures. As the temperature drops, less stable high-T minerals are destroyed and replaced by lower-T, more stable minerals [12]. Once the cave is cool, calcite, gypsum, Na-sulfate and carbonates, opal, and (in cooler regions) water ice can precipitate from seeping water or sublimating ice [11,14].

The secondary minerals present in these caves on a basaltic substrate make this a relevant Mars analog. Soluble sulfate minerals are often preserved, including jarosite, an abundant mineral at the Opportunity landing site at Meridiani Planum [5]. The most interesting comparison is likely the presence of hematite formed by the alteration of a basaltic substrate, presumably at high temperatures. Meridiani Planum hematite is most often interpreted as a low-T phase [e.g. 15], though a hydrothermal origin has also been suggested [e.g. 16].

We will continue analysis of newly collected samples (additional caves at LBNM and Hawaii) and will collect additional samples, hopefully at higher (and drier) elevations in Hawaii where preservation might be much improved.

**References:** [1] Wyrick D. et al. (2004) *JGR* 109, E06005. [2] Cushing G.E. et al. (2007) *GRL* 34, L17201. [3] Boston P. et al. (2001). *Astrobiology* 1, 25-55. [4]. Léveillé J. & Datta S. (2010) *PSS* 58, 592-598. [5] McLennan S. et al. (2005) *EPSL* 240, 95-121. [6] Ming D. et al. (2006) *JGR* 111, E02S12. [7] Ehlmann B. et al. (2009) *JGR* 114, E00D08. [8] Lodders K. (1998) *Meteoritics & Planet. Sci.* 33, A138-A190. [9] Morris R. et al. (2006) *JGR* 111, E12S15. [10] McHenry L. (2009) *Chem. Geol.* 265, 540-552. [11] Richardson C. et al. (2011) *Planet. Space Sci.* 65, 93-103. [12] Forti P. (2005) *J. Karst Cave Stud.* 67 3-13. [13] Minitti M. et al. (2005) *Meteoritics & Planet. Sci.* 40, 55-69. [14] Hill C. & Forti P. (1997) *Cave Minerals of the World, 2<sup>nd</sup> ed.* National Speleological Society. [15] Glotch T. et al. (2006) *Icarus* 181, 2006. [16] Golden D. et al. (2008) *Am. Mineral.* 93, 1201-1214.