



Secondary sulfate mineralization and basaltic chemistry of craters of the Moon National Monument, Idaho: Potential martian analog

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ABSTRACT

Craters of the Moon National Monument (COM) basalts offer a reasonable analog to martian basalts, as they have elevated iron concentrations compared to traditional terrestrial analogs. Although secondary sulfate minerals on the evaporitic regions of Mars consist primarily of Mg-, Ca-, and Fe-bearing sulfate minerals, recent orbiter spectroscopic data have suggested Na-sulfate minerals may be present. Secondary minerals in the basaltic caves of COM in southern Idaho are white, efflorescent deposits in small cavities along the cave walls and ceilings and localized mounds on the cave floors. These deposits were examined using X-ray powder diffraction (XRD), X-ray fluorescence spectrometry (XRF), Fourier transform infrared spectrometry (FTIR), and laser desorption Fourier transform ion cyclotron mass spectrometry (LD-FTICRMS). The secondary mineral assemblages were dominated by Na-sulfate minerals (thenardite, mirabilite) with a small fraction of the deposits containing minor concentrations of Na-carbonate minerals. Based on thermodynamic modeling results, formation of the deposits was attributed to leaching of basalt minerals by meteoritic water followed by evaporation of solutions. Such deposits could form under similar conditions in basaltic caves on Mars, making caves an excellent target for astrobiological investigations.

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1. Introduction

Basaltic caves and lava tubes are widespread on Earth, offering stable physicochemical conditions for the formation and preservation of secondary minerals. Detailed investigations regarding the formation mechanisms of secondary cave deposits in basaltic environments have been limited (Forti, 2005; Hill et al., 1997; Léveillé and Datta, 2010; Léveillé et al., 2000a, b; White, 2010), even though these minerals provide valuable insight into past aqueous activity and any associated biological activity during mineral formation. Basaltic caves and lava tubes have been proposed or observed on Mars (Boston et al., 2004, 1992; Cushing et al., 2007; Léveillé and Datta, 2010; Wynne et al., 2008; Wyrick et al., 2004). Morphological characteristics of martian volcanic plains closely resemble the plains-style volcanism found in the Eastern Snake River Plain (ESRP) in size, volume, and shape of the basaltic shields (Sakimoto et al., 2003). If the basalt emplacement of COM is indeed analogous to Mars, then lava tubes

and caves should have features in common with their martian counterparts. These subsurface features could intercept groundwater and provide adequate physicochemical conditions for the mineralization and subsequent preservation of secondary minerals on Mars. Additionally, these stable environments are ideal locations to search for evidence of past biological activity, as they offer protection from the harsh oxidizing martian surface. Thus, investigating the formation of secondary mineral assemblages in terrestrial basaltic caves is valuable in the search for evidence of previous aqueous activity and possible associated biological activity in the subsurface of Mars.

In this study, we identify and characterize the secondary minerals found in the lava tubes and caves of Craters of the Moon National Monument (COM), a young basalt field in the Eastern Snake River Plain in Idaho, USA, while comparing the basaltic chemical signatures of COM to those of Mars. Speleogenic minerals at COM offer an opportunity to investigate formation mechanisms and physicochemical processes that may occur in the subsurface of Mars.

2. Site description

The lava flows at COM (43.417°N; 113.518°W) collectively cover 1600 km² along the northern flank of the eastern Snake River Plain (ESRP) in southern Idaho (Kuntz et al., 1992).

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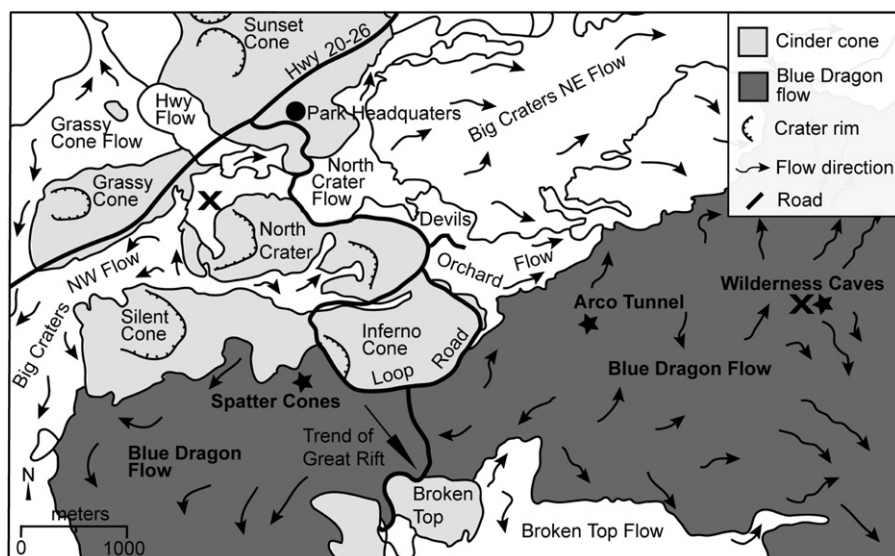


Fig. 1. Map of COM lava field showing extent of Blue Dragon flow. Location of Arco Tunnel, Wilderness Caves and spatter cones are also shown (indicated by ★s). Location of basaltic samples used for whole rock analyses are indicated by ×s. Map reproduced/modified by permission of American Geophysical Union from Kuntz (1989).

Radiocarbon dating of underlying carbonized vegetation constrains the basaltic flows between 15 and 2.1 ka, representing eight eruptive periods (Kuntz et al., 1986, 1992; Reid, 1995). These eruptive events originated along the Great Rift, a tensional feature that extends approximately 85 km, running parallel to the basin and range fault systems (Fig. 1) (Kuntz et al., 2002; Leeman et al., 1976). Unlike the majority of the basaltic flows in the ESRP, which are olivine tholeiites (Hughes et al., 1999), chemical compositions of the COM basalts are slightly more evolved (Kuntz et al., 1986; Stout et al., 1994; Stout and Nicholls, 1977) with elevated Fe and alkali-elements and depleted alkali-earth elements (Hughes et al., 1999). Since all basaltic flows in the ESRP are thought to originate from common parent magma, the variance likely reflects extensive crustal assimilation or magmatic fractionation (Kuntz et al., 1986, 1992; Leeman et al., 1976).

Of the 60 cumulative flows that comprise COM, the young Blue Dragon flow (~2.1 ka) contains the majority of the accessible caves and lava tubes. These features likely reflect the younger age of the flow because they have had less time to undergo gravitational collapse. Field observations and past reports indicate that secondary minerals are found throughout the flow in caves, lava tubes, and beneath spatter cones (Karlo et al., 1980; Peck, 1974). Their presence in the Blue Dragon flow likely results from the young age and morphological characteristics of the flow, rather than chemical and mineralogical differences between them and the older flows (Stout et al., 1994). The caves and lava tubes of the Blue Dragon flow are concentrated in a few locations (Wilderness Caves, Cave Trail caves) and vary in size from small and shallow to > 1 km in length. The extent of the Blue Dragon flow and locations of caves used in this study can be seen in Fig. 1.

3. Sample collection and analytical methodologies

3.1. Mineral collection

Samples of the secondary deposits were collected from cave floors, walls, and ceilings cavities in three caves from the Wilderness Caves area and Arco Tunnel (Fig. 1) in the Blue Dragon flow. These subsurface locations were selected based on their mineral occurrence, mineral abundance, cave accessibility, and lack of public access. The Wilderness Caves area is a collection of

roughly six small lava tubes and caves covering an area nearly 0.13 km². Arco Tunnel is located approximately 2 km west of the Wilderness Caves area. Arco Tunnel is a series of connected lava tubes that extend for over a kilometer. The physiographical sampling positions (i.e., floor, ceiling, or wall deposits) from within the caves and lava tubes are given in Table 1. Selected deposits were chosen from their deepest occurrence in the respective caves and tunnels to minimize any surficial environmental disturbances. All samples were taken from the interior of the deposit to minimize any external influence. Samples were collected biannually from 2006 to 2008 during the warmer, wetter month of June and the colder, drier month of October, with the exception of sample COM-781, which was obtained through subsampling from the mineral archive at COM Park Headquarters.

3.2. Water sampling

Water samples were collected as close to the secondary floor deposits as possible: samples from Wilderness Caves were collected from seeps directly associated with extensive deposits underneath the water source while one sample from Arco Tunnel was within 1 m of the deposit and the other two samples were 5–10 m away from small deposits. Samples were collected by placing HDPE bottles (I-Chem[®] Certified[®] HDPE Thermo Scientific[®] Nalgene[®]) under the dripping water until sufficient water was obtained. Two samples were collected per site: one for anion analysis and one for cation analysis. Water was filtered with a 0.45 µm GD/X disposable syringe filter (Whatman) and transferred to a fresh HDPE bottle. Cation samples (and one anion sample, accidentally) were acidified with concentrated Optima[®] HNO₃. Filters, syringes, and bottles were rinsed three times with Milli-Q water prior to use. Water samples were transported in a cooler and stored in a refrigerator prior to analysis to maintain cave conditions. Water temperature and pH (Orion SA 250 with Sensorex pH probe and ATC probe) were measured.

Anion concentrations were analyzed by ion chromatography (IC, Dionex DX-500 Ion Chromatograph) for F, Cl, PO₄, and SO₄ at the University of Montana Murdock Environmental Biogeochemistry Laboratory. Cation concentrations were analyzed by inductively coupled plasma emission spectrometry (ICP) for Ag, Al, As, Ba, Be, B, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Se, Si, Sn, Sr, Ti, Tl, U, V, W, Y, Zn at a commercial laboratory (SGS, Ontario, Canada).

Table 1

Mineral assemblages secondary deposits as determined by XRD, FTIR, and FTICR-MS.

Cave location ^a		Date	XRD			FTIR			FTICR-MS ^b		
			Na-sulfate	burkeite	Na-carbonate	Na-sulfate	burkeite	Na-carbonate	Na-sulfate	burkeite ^c	Na-carbonate
Floor deposits											
70604.1A	WC	Jun-07	XX	—	X	XX	+	X	XXX	—	+
070604.3A	WC	Jun-07	XXX	—	+	XXX	—	+	XXX	—	+
071010.1B	WC	Oct-07	XX	X	+	XX	X	X	XX	—	X
COM-781	AT		XXX	—	—	XXX	—	—	XXX	—	—
070605.5a	AT	Jun-07	XX	X	+	XX	+	X	XX	—	+
Ceiling and wall deposits											
071010.1A	WC	Oct-07	XXX	—	—	XXX	—	—	XXX	—	—
080607.3a	AT	Jun-08	XXX	—	—	XXX	—	—	XXX	—	+
070605.5a	AT	Jun-07	XX	X	+	XX	+	X	XX	—	X
Floor deposits											
070604.1A	WC	Jun-07	XX	—	X	XX	+	X	XXX	—	+
070604.3A ^d	WC	Jun-07	XXX	—	+	XXX	—	+	XXX	—	+
071010.1B	WC	Oct-07	XX	X	+	XX	X	X	XX	—	X
COM-781	AT		XXX	—	—	XXX	—	—	XXX	—	—
070605.5a	AT	Jun-07	XX	X	+	XX	+	X	XX	—	+
Ceiling and wall deposits											
071010.1A	WC	Oct-07	XXX	—	—	XXX	—	—	XXX	—	—
080607.3a	AT	Jun-08	XXX	—	—	XXX	—	—	XXX	—	+
070605.5a	AT	Jun-07	XX	X	+	XX	+	X	XX	—	X

XXX=abundant, XX=common, X=between common and rare, +=rare, –=not detected.

^a AT=Arco Tunnel, WC=Wilderness Caves.^b FTICR-MS identification was based on positive and negative spectra.^c Presence of burkeite was difficult due to gas phase reactions between sulfate and carbonate oxyanions.^d This site had no deposits in October 2007. Although deposits were present in June 2008, they were not sampled because insect or mammalian activity disturbed the deposits

3.3. X-ray powder diffraction (XRD)

Mineralogical analysis was conducted by X-ray powder diffraction (XRD). Samples were ground into a fine powder with a corundum mortar and pestle before being mounted on glass slides. Analyses were performed using a Philips APD 3720 X-ray diffractometer (currently PANalytical, Almelo, The Netherlands) with a step size of 0.01 2 θ with a scan rate of 0.24 2 θ /min. Environmental conditions were not controlled during sample preparation or XRD analysis. Diffraction patterns were compared to published mineral patterns from the Joint Committee on Powder Diffraction Standards (JCPDS).

3.4. Fourier transform infrared spectroscopy (FTIR)

Additional mineralogical characterization was acquired by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) using a Thermo Nicolet Nexus 670 FTIR spectrometer (Madison, WI). Samples were ground into a fine powder with a corundum mortar and pestle before being loaded into the sample pan of the ATR-FTIR. One hundred scans were collected and co-added resulting in spectra with a resolution of 4 cm^{–1} between 4000 cm^{–1} and 500 cm^{–1}.

3.5. Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS)

Fourier transform ion cyclotron resonance-mass spectrometry (FTICR-MS) spectra of the mineral deposits were obtained using a laboratory-built imaging laser desorption FTICR-MS (McJunkin et al., 2002; Scott et al., 2003; Scott and Tremblay, 2002) with a 7 T Oxford (Oxford, England) superconducting magnet. Parameters have been previously described (Kotler et al., 2008; Richardson et al., 2008, 2009a, b; Yan et al., 2007a, 2007b). All spectra were acquired with single laser shots in both positive and negative mode. Peaks were identified by systematic analysis following procedures previously described in Kotler et al. (Kotler et al., 2008).

3.6. X-ray fluorescence (XRF)

Bulk compositions of the COM basalts were analyzed by X-ray fluorescence (XRF) spectroscopy. One gram of finely ground sample powder was combined with 10 g of flux (50:50 Li-tetraborate:Li-metaborate with integrated LiBr non-wetting agent) and ~1 g of an oxidizer (ammonium nitrate). The mixture was fused in a platinum crucible in a Claise M4 fluxer with a predetermined 21 min fusion routine (high temperature ~1050 °C) before being analyzed with a Bruker S4 Pioneer WD-XRF (Milwaukee, WI). The instrument was calibrated for major and minor elements using 11 USGS rock standards. More detailed methods are reported in McHenry (2009). Because of difficulties with sulfur loss during fusion, a separate pressed pellet was prepared for XRF analysis for sulfur. The sample was powdered using a tungsten carbide shatterbox, and then 10 g of sample was mixed with a wax binder (in the shatterbox) for 30 s. The powder was pressed into a 40 mm pellet using a semiautomatic press, where it was held at 30 t for 1 min. The pressed pellet was then analyzed with a Bruker S4 Pioneer, using a calibration curve derived from six USGS rock standards with published sulfur concentrations prepared with the same method. CIPW-NORM analysis was used to estimate the mineral composition of the basalt samples.

3.7. Electron probe microanalysis (EPMA)

Plagioclase, olivine, and titanomagnetite compositions of the COM basalts were determined using EPMA of thin sections. Thin sections were carbon coated and then analyzed using a Cameca SX-50 electron microprobe (UW Madison) operated at 15 kV and 20 nA (for oxides and olivine), or 10 nA (for plagioclase). Calibration was based on widely available mineral standards (see McHenry, in press, for details on specific standards used).

3.8. Geochemical modeling

PHREEQC equilibrium modeling software (Parkhurst and Appelo, 1999) was used to model the evolution of aqueous

solution chemistry and sequence of mineral precipitation upon evaporation under two scenarios. In the first scenario (MS 1), a model aqueous solution was allowed to equilibrate (0°C , $\sim 101\text{ kPa}$, $P(\text{CO}_2)=10^{-3.5}$, $P(\text{O}_2)=0.208$) with the mineral constituents identified in the Blue Dragon flow along with a small quantity of pyrite (0.01 mol/kg or 0.12%), as a source of sulfur. Minerals used in the modeling were based on XRF data and subsequent CIPW-NORM normative calculations; only the major minerals were used in the modeling. Plagioclase with composition An_{40} was used in the PHREEQC model. The method outlined in (Arnórsson and Stefansson, 1999) was used to estimate the equilibrium constant for the dissolution reaction for plagioclase, and dissolution of the plagioclase phase was added as a reaction to the model input file. The sequence of secondary minerals modeled to become oversaturated in the resulting solution was monitored during evaporation. Solutions were modeled under both open and closed atmospheric conditions.

In the second scenario (MS 2), the chemistry of the actual solutions collected from the Wilderness Caves and Arco Tunnel was used as the starting solution for a similar model of evaporative mineral sequences. The solutions (Table 4) were modeled under open atmospheric conditions with respect to CO_2 ; redox reactive elements were below detection in the chemical analyses and therefore, dissolved oxygen was not included in the model. Because insufficient sample was collected, alkalinity was modeled as the charge imbalance after speciation using the PHREEQC code and *llnl* database (Parkhurst et al., 1980). The resulting alkalinity was used as the bicarbonate input parameter for the PHREEQC modeling. Results from evaporation sequence models using two databases were compared; the databases were *llnl.dat* and the *pitzer.dat* included in the PHREEQC software package. The reasoning behind the comparison was that the evaporation sequence would lead to high ionic strengths as water was removed, necessitating the use of the Pitzer equations to calculate activity coefficients (Plummer et al., 1990). The modeled solutions achieved calculated ionic strengths of 0.12 and were adequately modeled using the *llnl.dat* database. A comparison of saturation indices for mirabilite showed a difference of 0.4 between the two models databases. Hence, for consistency with MS 1, *llnl.dat* was used for evaporative modeling in PHREEQC.

4. Results

4.1. Mineral deposits

The caves and lava tubes of the Blue Dragon flow host the majority of the secondary sulfate deposits found at COM. Secondary sulfate minerals occur in caves of all sizes. The more extensive caves (e.g., Arco Tunnel) were cold and humid ($< 10^{\circ}\text{C}$, $\sim 75\%$ relative humidity) with essentially the same environmental conditions in October and June, while shallow, shorter caves had variable conditions that tracked ambient surface conditions (October: $\sim 10^{\circ}\text{C}$, $\sim 26\%$ relative humidity and June: $\sim 27^{\circ}\text{C}$, $\sim 25\%$ relative humidity).

Secondary deposits were found in small cavities on cave ceilings and walls, and as localized mounds on the cave floors (Fig. 2a, and Fig. 3a). Floor deposits were found intermittently dispersed as localized, efflorescent, white, powdery mounds, with depths ranging from $\sim 1\text{ cm}$ to $\sim 10\text{ cm}$. These deposits were not a direct weathering product of the basalts because the interface between the authigenic minerals and the cave floors is quite sharp, showing no mineralogical or material gradient into the underlying basalt. Likewise, the floor deposits did not seem to form directly as precipitates from standing water because the precipitates were not necessarily found in the topographic lows. In addition to the

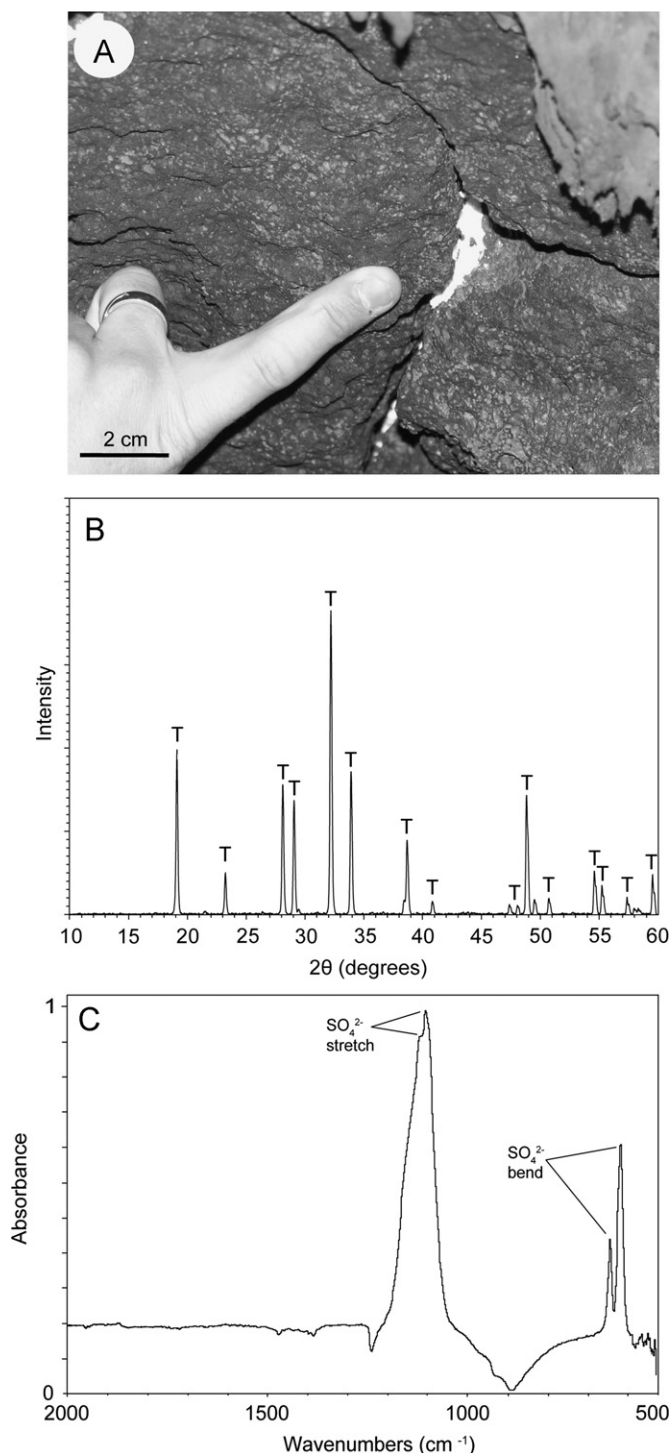


Fig. 2. (A) Photograph of secondary deposit within a ceiling cavity taken in a cave from the Blue Dragon flow. (B) Background corrected XRD pattern of corresponding deposit demonstrating the sample consists entirely of thenardite. (C) FTIR spectrum from same deposit confirms the sample is dominated by thenardite with no evidence of Na-carbonates. Sample is representative of a majority of the secondary sulfate deposits found in the caves and lava tubes of COM.

floor deposits, secondary deposits were found within small ($< 2\text{ cm}$ diameter) cavities and cracks on cave ceilings and walls (Fig. 2a). Ceiling and wall deposits, though less frequent, were coincident, but not spatially correlated with floor deposits.

The secondary sulfate deposits appear to be seasonal in that deposits were consistently observed at sites in the caves in June

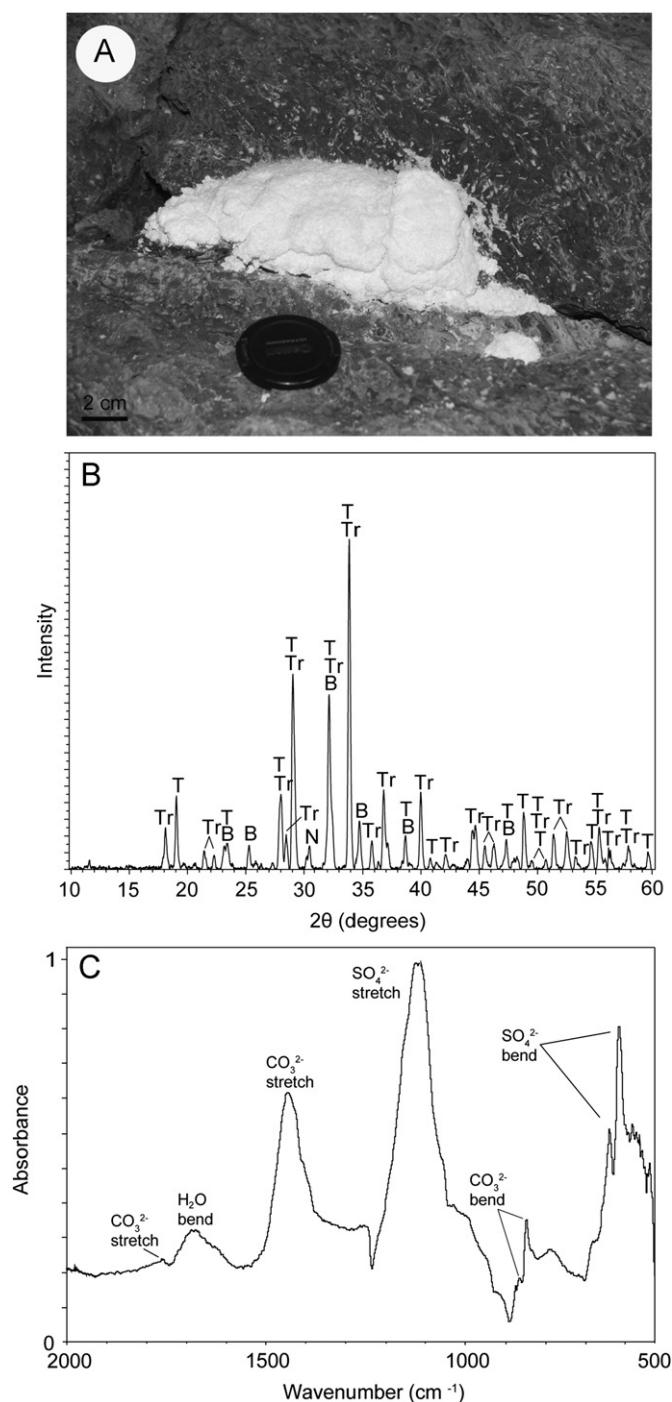


Fig. 3. (A) Photograph of a secondary floor deposit in a cave within the Blue Dragon flow. (B) Background corrected XRD pattern of corresponding deposit demonstrating the sample is dominated by Na-sulfate with minor concentrations of Na-carbonate minerals and possibly double salt burkeite (thenardite=T; burkeite=B; trona=Tr; natron=N). (C) FTIR spectrum from same deposit confirming the sample is dominated by thenardite with peaks corresponding to Na-carbonates and burkeite.

but not always observed at the same sites in October. In October, mineral deposits were generally smaller and less abundant than in June. It appears that the sulfate minerals form in winter and spring and disappear during the summer and fall. Appearance and disappearance of sulfate minerals correlate with a change in temperature and relative humidity in the caves between October and June.

Mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), a hydrous, low-temperature Na-sulfate mineral, was observed during June visits when the cave temperatures and relative humidity were more conducive for mirabilite formation and preservation. For example, temperature and relative humidity of an unnamed cave in the Wilderness Caves area were recorded to be $\sim 8^\circ\text{C}$ and 73%, respectively. Conversely, in October, the same cave was slightly warmer ($\sim 15^\circ\text{C}$) and drier (67% relative humidity) and thenardite was present instead of mirabilite. The dehydration–rehydration transition between thenardite and mirabilite is controlled by temperature and relative humidity; mirabilite dehydrates to form thenardite within minutes, depending on air temperature and relative humidity (Rodríguez-Navarro et al., 2000). The observed changes in cave temperature and relative humidity between October and June visits would be consistent with the conversion of mirabilite to thenardite and vice versa.

4.2. Secondary mineral identification

Secondary deposits at COM were dominated by Na-sulfate minerals (thenardite, mirabilite) with or without minor concentrations of Na-carbonate minerals (i.e., trona, natron) (Table 1). The XRD pattern shown in Fig. 2b represents about half of secondary deposits analyzed. Peak assignments showed the sample was composed entirely of thenardite with no other detectable minerals. FTIR spectra (Fig. 2c) of the same sample showed bands indicating SO_4^{2-} with the ν_3 stretch at 1109 cm^{-1} and the ν_4 at 639 cm^{-1} and 621 cm^{-1} . These bands were consistent with synthetic thenardite in this study and with previously reported spectra of thenardite (Farmer, 1974; Lane, 2007; Vassallo and Finnie, 1992). Of all the XO_4^{2-} ions, sulfate anions have the highest frequencies for stretching and bending (Farmer, 1974). FTIR spectra of mirabilite can be distinguished from thenardite spectra because of the additional presence of ν_1 (1000 cm^{-1}), $\nu\text{H}_2\text{O}$ (3570 cm^{-1} and 3440 cm^{-1}), and $\delta\text{H}_2\text{O}$ (1635 cm^{-1}) bands (Farmer, 1974).

Although all samples consist primarily of thenardite or mirabilite, depending on cave conditions, approximately half of the samples analyzed also have minor concentrations of Na-carbonate minerals (e.g., trona and natron). Na-carbonate minerals were identified by XRD (Fig. 3b). As with the XRD pattern in Fig. 3b, the FTIR spectrum (Fig. 3c) had absorbance bands that were attributed to carbonate and sulfate moieties. The doublet bands of sulfate near 1169 cm^{-1} , 1130 cm^{-1} , 637 cm^{-1} , and 614 cm^{-1} are reminiscent of thenardite (Farmer, 1974; Lane, 2007; Vassallo and Finnie, 1992). Additional bands suggested the presence of Na-carbonate species. The most prominent bands of the carbonate anion were seen at 1691 cm^{-1} , 1451 cm^{-1} and 847 cm^{-1} , with minor bands at 1764 cm^{-1} , 1032 cm^{-1} , 875 cm^{-1} , and 680 cm^{-1} . Definitive assignment of which cations (i.e. $\text{Na}_2\text{-}$ or NaH-carbonate) are present in the carbonate mineral could not be made using FTIR because bands of Na-carbonate and bicarbonate species have overlapping IR bands, making accurate identification difficult.

Several peaks in the XRD diffraction pattern (Fig. 3b) were attributed to the presence of the carbonate-sulfate salt, burkeite ($\text{Na}_6\text{CO}_3(\text{SO}_4)_2$). The FTIR band at 1764 cm^{-1} (Fig. 3c) is characteristic of the ν_3 bend of CO_3^{2-} in burkeite and cannot be attributed to thenardite, mirabilite, trona, or natron (Farmer, 1974; Lane, 2007). Other CO_3^{2-} and SO_4^{2-} spectral bands characteristic of burkeite are seen (at 1128 cm^{-1} , ν_3 stretch of SO_4^{2-} ; at 637 cm^{-1} and 614 cm^{-1} , ν_4 bend of SO_4^{2-} ; at 1477 cm^{-1} , ν_3 of CO_3^{2-} ; and at 875 cm^{-1} , ν_2 of CO_3^{2-}). However, these bands could also correspond to other Na-sulfate and Na-carbonate species; thus, the presence of burkeite could not be definitively established by FTIR. However, the presence of burkeite was confirmed by XRD.

In addition to XRD and FTIR, mineral deposits were characterized using imaging laser desorption/ionization FTICR-MS (Table 1). This technique has been used successfully in previous studies of synthetic and natural sulfate minerals (Kotler et al., 2008; Richardson et al., 2008, 2009a, b; Yan et al., 2007a), demonstrating its ability to characterize inorganic minerals at a microscopic level. Imaging mass spectrometry is a useful technique for micron-scale identification of compounds and minerals, especially compared to more conventional methods that tend to have problems identifying individual mineral species in heterogeneous mixtures (Van Vaeck et al., 1998). Also, it is a sensitive technique (Richardson et al., 2008) that can detect the presence of minor elements that may be missed by other techniques (Hinman et al., 2009).

Fig. 4 shows the positive and negative mode FTICR-MS spectra of a representative secondary deposit. The sample appears to be dominated by Na-sulfate moieties, consistent with XRD and FTIR analyses. Peaks were identified following the detailed procedures of Kotler et al. (2008) and were systematically compared to a suite of synthetic reference samples. The major peaks in the positive spectrum (Fig. 4a) are clearly attributed to Na-sulfate ions, with the exception of peaks at m/z 130, 175, 225, 310, and 393, which contain carbonate adduct ions. Generally, these peaks are less abundant than peaks consisting entirely of Na-sulfate ions. No

peaks in the spectrum consist entirely of Na-carbonate constituents, possibly reflecting the lower concentration of carbonate minerals in the sample. Peaks at m/z 62, 110, 165, and 227 comprise Na-sulfate ions and have been identified in previous mass spectrometry studies of Na_2SO_4 (Poels et al., 1998; Richardson et al., 2009a, b; Van Vaeck et al., 1998).

The negative-mode spectrum of the secondary deposit (Fig. 4b) shows similar adduct ions to those observed in the positive mode spectrum. The major peaks in the spectrum are dominated by Na-sulfate adduct ions, while peaks at m/z 166 and 351 contain the carbonate moiety. Peaks consisting entirely of Na-sulfate adduct ions have been previously reported in Na_2SO_4 studies (Poels et al., 1998; Van Vaeck et al., 1998). As with the positive spectrum, the negative spectrum suggests that the sample consists of Na-sulfate with a minor amount of Na-carbonates. Quantification of the oxyanions is difficult using laser desorption mass spectrometry (LDMS) practices, as the abundance of the ions in the spectrum is not only dependent on the amount of the substance in the sample, but also by its ionization efficiency (Yan et al., 2006) and subsequent gas-phase interactions between the ions (Richardson et al., 2009a, b). No peaks consistent with other elements, besides some organic peaks, were detected. Thus, the general consistency between the FTICR-MS spectra and the bulk analyses of the XRD and FTIR results suggest that the samples are composed of sulfate and carbonate minerals.

4.3. Bulk composition and primary igneous mineralogy

XRF whole-rock analysis of the COM basalts (Table 2) reveals a high Fe concentration, coupled with higher alkali concentrations than other ESRP basalts. Abundant phenocrysts include Fe-rich olivine, intermediate plagioclase, and magnetite, and some samples contained Fe-rich augite. Example phenocryst compositions from the Blue Dragon flow and North Crater flow, a flow with a bulk composition similar to that of the Blue Dragon flow and of similar age (Kuntz et al., 1986), are also reported in Table 3. Significantly, a small quantity of sulfur is detected in the COM basalts; sulfur for sulfate mineral formation must come from either the infiltrating water solutions or from the basalt that comes in contact with such water.

Table 2
Comparison of COM, Hawaii, and Mars basaltic compositions

Oxide	BD1 ^a	COM flows		BC ^b	Hawaii	Mars basalts			
		NC ^a	BD2 ^b			Spirit ^d	Sherg ^e	Merid ^f	Bounce ^g
SiO ₂	47.8	48.7	49.0	51.3	49.7	45.4	51.3	48.2	50.8
TiO ₂	3.0	2.7	2.9	2.5	2.8	0.5	0.9	1.0	0.8
Al ₂ O ₃	12.5	12.7	13.4	14.2	17.4	10.9	6.8	8.1	10.1
Fe ₂ O ₃ T	17.1	16.9	15.3	14.6	12.0	20.0	19.4	20.8	17.3
MnO	0.2	0.3	0.2	0.3	0.2	0.4	0.5	0.4	0.4
MgO	3.3	3.1	3.3	2.9	3.9	11.9	9.3	10.4	6.4
CaO	7.0	6.7	6.9	6.4	6.6	7.4	9.6	6.5	12.5
Na ₂ O	3.1	2.9	3.6	3.6	4.3	2.7	1.4	2.2	1.3
K ₂ O	1.9	2.1	2.0	2.2	1.9	0.1	0.2	0.8	0.1
P ₂ O ₅	–	1.8	1.8	1.6	0.9	0.5	0.7	1.4	1.0
Cr ₂ O ₃	–	–	–	–	–	0.6	0.2	0.3	0.1
Cl	–	–	–	–	–	0.1	–	–	0.1
SO ₃	0.02	–	–	–	0.1	1.2	0.1	–	0.5
Total	96.0	97.9	–	99.5	99.7	–	100.3	–	–

Fe₂O₃T=all Fe reported as Fe₂O₃.

^a Blue Dragon (BD1) and North Crater (NC) Flows, COM. This study.

^b Blue Dragon (BD2) and Big Crater (BC) flows, COM. From Stout et al. (1994).

^c Average unaltered Hawaiitic tephra from Mauna Kea (MK). From Morris et al. (2000).

^d MER Spirit analysis of Adirondack (RAT). From Gellert et al. (2004).

^e Shergotty meteorite, calculated volatile free. From Lodders (1998).

^f Extrapolated outcrop precursor basalt, Meridiani, Morris et al. (2006).

^g MER Opportunity analysis of Bounce Rock. Rock from Rieder et al. (2004).

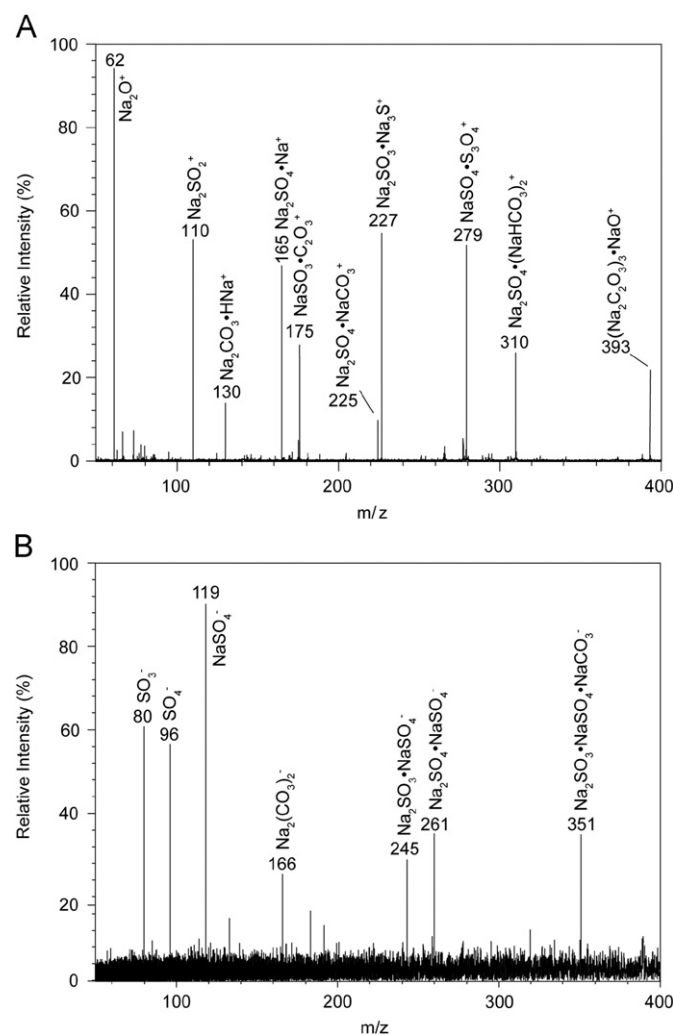


Fig. 4. Laser desorption FTICR-MS spectra of secondary sulfate deposits from floor deposit within a cave in the Wilderness Caves area. (A) Positive mode spectrum and corresponding. (B) Negative mode spectrum.

Table 3
Blue Dragon (BD) and North Crater (NC) bulk XRF and phenocryst EPMA compositions.

	<i>n</i>	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃ T	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	BaO	Cr ₂ O ₃	V ₂ O ₃	SUM
NC bulk	1	48.70	2.70	12.70	16.90	0.30	3.10	6.70	2.90	2.10	1.80	0.17	n.d.	n.d.	98.07
BD1 bulk	1	47.80	3.00	12.50	17.10	0.20	3.30	7.00	3.10	1.90	1.96	0.15	n.d.	n.d.	98.01
	<i>n</i>	SiO ₂	TiO ₂	Al ₂ O ₃	FeOT	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	BaO	Cr ₂ O ₃	V ₂ O ₃	SUM
NC plagioclase	8	56.97	n.d.	27.04	0.78	n.d.	n.d.	9.26	5.52	0.72	n.d.	0.18	n.d.	n.d.	100.46
StDev		0.83		0.51	0.17			0.59	0.22	0.13		0.11			0.58
NC olivine	5	33.58	n.d.	n.d.	41.64	0.73	21.92	0.36	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	98.23
StDev		0.45			1.53	0.10	1.47	0.04							0.89
NC magnetite	3	0.12	22.90	2.68	67.56	0.56	1.81	0.04	n.d.	n.d.	n.d.	n.d.	0.04	0.34	96.05
StDev		0.02	0.28	0.16	0.29	0.03	0.46	0.05					0.02	0.09	0.57

Bulk data from XRF; plagioclase, olivine, and magnetite data from EPMA.

n=number of analyses.

n.d.=not determined.

Fe₂O₃T=all Fe reported as Fe₂O₃.

FeOT=all Fe reported as FeO.

Table 4
Chemistry of solutions collected from caves.

Sample ID	Cave	Date	Cave Rel. Humidity (%)	Water Temp	pH	HCO ₃ ^c mg/L	Cl mg/L
1 C	Blank						< 0.2
2 B	Wilderness	7-Jun	25	18	7.4	522	2.3
3 B	Wilderness	7-Oct	26	19	7.3	14	3.6
4 B	Arco	7-Jun	75	16	7.4	354	0.89
12 B	Arco	8-Jun	75	17	7.6	1,650	1.6
Model				0	8.9	354.1	n.c.
Sample ID	Ba mg/L	B mg/L	Ca mg/L	Cu mg/L	K mg/L	Mg mg/L	Na mg/L
1C	0.0019	< 0.002	< 0.03	< 0.001	0.02	< 0.003	0.09
2 B	0.185	0.039	4.35	0.002	1.05	< 0.003	8.83
3 B	0.118	0.028	1.05	0.004	3.87	< 0.003	2.4
4 B	0.0562	0.02	0.88	0.006	0.68	< 0.003	1.54
12 B	0.236	0.024	4.29	0.004	0.81	< 0.003	5.73
Model	n.c.	n.c.	89.9	n.c.	n.c.	54.6	0.26
Sample ID	P mg/L	S mg/L	Si mg/L	Sr mg/L			
1C	< 0.01	< 0.01	0.01	< 0.0001			
2 B	0.05	1.58	6.02	0.0254			
3 B	0.03	0.3	0.12	0.0059			
4 B	0.04	0.19	1.49	0.0046			
12 B	0.12	1.33	4.85	0.0248			
Model	n.c.	34.7	19.4	n.c.			

n.c.=not included in calculation.

^c =calculated by PHREEQC.

4.4. Aqueous geochemistry and geochemical modeling

Dissolved constituents were detected in low concentrations in aqueous solutions collected from Wilderness Caves and Arco Tunnel (Table 4). Elements for which all analyses were less than three times the detection limit are not included in the table; see Table 5 for limits of detection. Waters collected from cave ceilings were dilute sodium-sulfate solutions with lesser amounts of calcium and chloride (Table 4).⁴ The pH values were slightly above neutral. Sodium concentrations range from 1.54 to 8.83 mg/L. Sulfate concentrations range from 0.79 to 4.60 mg/L. The compositions of these waters were

modeled with PHREEQC (Parkhurst and Appello, 1999) to determine the saturation indices of sulfate, carbonate, and chloride minerals.

MS 1 addressed the question of whether basalt minerals, upon equilibration with water in an atmosphere open with respect to CO₂ and O₂, would provide sufficient dissolved components to produce sulfate and carbonate minerals upon evaporation. As mentioned above, a small quantity of sulfur was detected in the Blue Dragon basalt. The phase bearing the sulfur was below the detection limit of XRD so a small quantity of pyrite (0.01 mol/kg or 0.12%) was added to provide an appropriate amount of sulfur for the calculation. Calculated solution composition is shown in Table 4 (Model). The calculated composition was calcium-bicarbonate with significant amounts of sulfur, as sulfate, and magnesium. In the simulation, minerals were allowed to precipitate as saturation was reached. Initially, the solution exceeded saturation with respect to calcite (saturation index

⁴ Elements for which all analyses were less than three times the detection limit are not included in the table; see Table 5 for limits of detection.

Table 5
Limits of detection for analytes.

F	IC	mg/L	0.07
Cl	IC	mg/L	0.2
PO ₄ -P	IC	mg/L	0.1
SO ₄	IC	mg/L	0.6
Ag	ICP	mg/L	0.005
Al	ICP	mg/L	0.01
As	CIP	mg/L	0.008
Ba	ICP	mg/L	0.01
Be	ICP	mg/L	0.0001
B	ICP	mg/L	0.002
Bi	ICP	mg/L	0.03
Ca	ICP	mg/L	0.03
Cd	ICP	mg/L	0.002
Co	ICP	mg/L	0.003
Cr	ICP	mg/L	0.001
Cu	ICP	mg/L	0.001
Fe	ICP	mg/L	0.01
K	ICP	mg/L	0.10
Li	ICP	mg/L	0.002
Mg	ICP	mg/L	0.003
Mn	ICP	mg/L	0.001
Mo	ICP	mg/L	0.005
Na	ICP	mg/L	0.05
Ni	ICP	mg/L	0.01
P	ICP	mg/L	0.01
Pb	ICP	mg/L	0.005
S	ICP	mg/L	0.01
Sb	ICP	mg/L	0.01
Se	ICP	mg/L	0.02
Si	ICP	mg/L	0.10
Sn	ICP	mg/L	0.03
Sr	ICP	mg/L	0.0001
Ti	ICP	mg/L	0.001
Tl	ICP	mg/L	0.01
U	ICP	mg/L	0.1
V	ICP	mg/L	0.001
W	ICP	mg/L	0.01
Y	ICP	mg/L	0.0004
Zn	ICP	mg/L	0.01

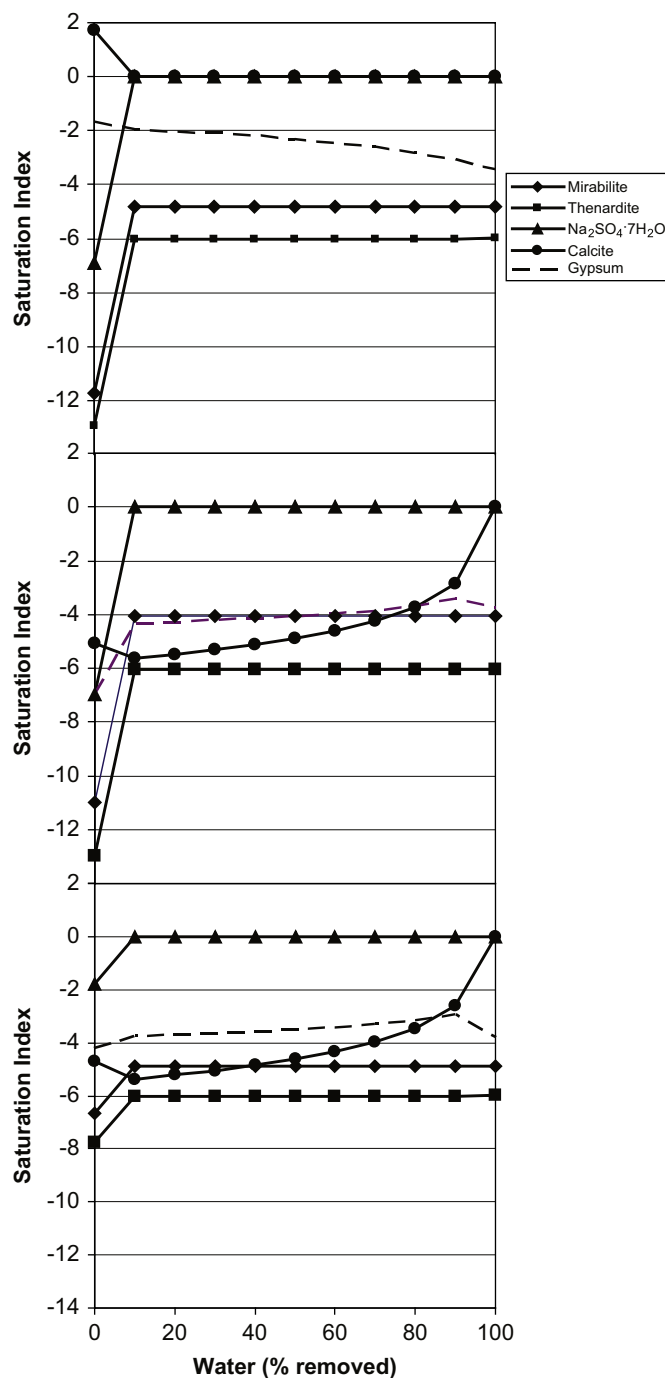


Fig. 5. Saturation indices for calcite, gypsum, sodium heptahydrate, and mirabilite as a function of the systematic evaporation of water using PHREEQC modeling software for evaporation of modeled and natural solutions. (a) Saturation indices upon evaporation of water previously equilibrated with basalt according to the equations: Diopside, $\text{CaMgSi}_2\text{O}_6 = \text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{H}_2\text{O} + 2\text{SiO}_2$; Fayalite, $\text{Fe}_2\text{SiO}_4 + 4\text{H}^+ = \text{SiO}_2 + 2\text{Fe}^{2+} + 2\text{H}_2\text{O}$; Ilmenite, $\text{FeTiO}_3 + 2\text{H}^+ + \text{H}_2\text{O} = \text{Fe}^{2+} + \text{Ti}(\text{OH})_4$; Quartz, $\text{SiO}_2 = \text{SiO}_2$; Pyrite, $\text{FeS}_2 + \text{H}_2\text{O} = 0.25\text{H}^+ + 0.25\text{SO}_4^{2-} + \text{Fe}^{2+} + 1.75\text{HS}^-$; Plagioclase, $\text{Na}_{0.6}\text{Ca}_{0.4}\text{Al}_{1.4}\text{Si}_{2.6}\text{O}_8 + 5.6\text{H}^+ = 0.6\text{Na}^+ + 0.4\text{Ca}^{2+} + 1.4\text{Al}^{3+} + 2.8\text{H}_2\text{O} + 2.6\text{SiO}_2$. (b) Saturation indices upon evaporation of Arco Tunnel, June 2007 water sample. (c) Saturation indices upon evaporation of Wilderness Caves, June 2007 water sample.

5. Discussion

Craters of the Moon basalts are high in Fe by Earth standards (Kuntz, 1989) and thus are more comparable to martian basalts than other traditional terrestrial analogs (e.g., Hawaii,

(SI)=1.72) after equilibration with basalt minerals and prior to evaporation (Fig. 5a); during the first step of evaporation, calcite precipitated to achieve a saturation index of 0. During evaporation, saturation indices for gypsum, thenardite, and mirabilite increased to -3.4 , -4.8 , and -5.8 , respectively, but did not reach saturation even after complete evaporation. In fact, gypsum saturation index decreased during evaporation as sulfate was removed by another phase, invoking the common ion effect. Sodium heptahydrate ($\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$), a metastable sodium sulfate salt from which mirabilite and thenardite form (Hall and Hamilton, 2008), was undersaturated after solution equilibration with basalt minerals (SI = -6.92) but rapidly reached saturation after the first evaporation step (SI=0).

MS 2 demonstrated that calcite and sodium heptahydrate reached saturation during the modeled evaporation of water, but that mirabilite, thenardite, and gypsum did not reach saturation over the course of the modeling exercise (Fig. 5b, c). The June 2007 water sample from Arco Tunnel reached saturation with respect to calcite but not gypsum (Fig. 5b). Thenardite and mirabilite reached saturation indices of -6.0 and -4.1 , respectively. Sodium heptahydrate reached saturation at the first evaporation step. The June 2007 water sample from Wilderness Caves (Fig. 5c) reached saturation with respect to calcite but not gypsum. Thenardite and mirabilite reached saturation indices of -6.2 and -4.2 , respectively, while sodium heptahydrate became oversaturated at the first evaporation step. The other samples, Arco Tunnel June 2008 and Wilderness Caves October 2007, behaved the same way with respect to saturation of minerals.

Antarctica; (Chevrier et al., 2006; Morris et al., 2000)). Table 5 compares the bulk compositions of COM and martian basalts. Although COM and the martian basalts have similar Fe concentrations, they differ substantially in other potentially important elements as do other terrestrial analogs. COM basalts are higher in Al, Ti, Na, and K and lower in Mg, Ca, and S than their martian counterparts, which is consistent with previous studies of COM basalts (Hughes et al., 1999; Kuntz et al., 1986; Stout et al., 1994). Despite these differences, the COM basalts are closer to martian basaltic chemical compositions than previously and frequently used terrestrial basalts that suffer from the same limitations, but also have lower Fe concentrations.

Because of their similar chemical composition, caves at COM are expected to precipitate secondary minerals representing the secondary minerals found in martian caves. These minerals, found in cracks and on the surfaces of walls, ceilings, and floors, provide an opportunity to reconstruct groundwater compositions through inverse geochemical modeling.

Léveillé and Datta (2010) reviewed mineral assemblages in basaltic caves while considering caves as astrobiological targets. The assemblage observed in caves at Craters of the Moon bears some similarity to assemblages observed in other basalt caves. White (2010) observed similar assemblages: calcite, gypsum, mirabilite, and thenardite, along with a hydrated copper–vanadium silica mineral. Léveillé et al. (2000a, b, 2002) reported kerolite, a talc-like clay mineral, along with numerous carbonate minerals (aragonite, calcite, hydromagnesite, monohydrocalcite, magnesite, and dolomite) in caves in Hawaii. Of these reported minerals, only calcite was identified in the caves at Craters of the Moon (McHenry et al., 2010); silica and calcite are observed on cave walls at Craters of the Moon (McHenry et al., 2010). Similar to White's (White, 2010) study, thenardite and mirabilite were observed in caves at Craters of the Moon. Additionally, natron, trona, and burkeite were observed. These minerals are more commonly found in evaporitic sequences in terrestrial environments. The secondary Na-sulfate mineral thenardite (Na_2SO_4), which is found at COM, is typically found in non-marine environments such as evaporitic salt flats (sabkhas, playas), fumarolic exhalations (Hill et al., 1997), and subsurface Antarctic ice (Ohno et al., 2006).

Such sulfate minerals have relevance to martian environments as well. Recently, Na-sulfate minerals were suggested to form on Mars in evaporitic environments (Mangold et al., 2008; Zhu et al., 2006) and possibly as a constituent of the martian regolith, based on chemical/mineralogical modeling (Tosca and McLennan, 2006). Such salts would indicate the past occurrence of water on Mars.

The evaporitic assemblages observed on the surface of Mars consist primarily of secondary Mg-, Ca-, and Fe-bearing sulfate minerals and silica; however, minor concentrations of Na-sulfate species cannot be ruled out in evaporitic environments on Mars based on spectroscopic signatures (Mangold et al., 2008; Zhu et al., 2006). Seasonal variations of vapor pressure, temperature, and humidity of the martian atmosphere cover the stability fields of thenardite, mirabilite, and the heptahydrated species ($\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$) reported here. These minerals may all be present but not detected on the martian surface (Hall and Hamilton, 2008; Kuzmin et al., 2004) because spectroscopic signatures of Mg-, Ca-, and Na-bearing sulfate minerals are sufficiently similar to prevent precise mineral identification (Mangold et al., 2008). Furthermore, chemical/mineralogical modeling indicates that Na-sulfates could form through primary basaltic weathering on Mars (Tosca and McLennan, 2006). These modeling results suggest that thenardite, along with bloedite, glauberite, and polyhalite, may subsequently precipitate from a low-pH, sulfate-rich brine solution, after the initial precipitation of siderite, gypsum, melanterite and magnesite (Tosca and McLennan, 2006). The general lack of Na-sulfate and Na-carbonates signatures on Mars

could also reflect differences in environmental conditions because terrestrial thenardite is typically an evaporitic mineral formed in neutral to alkaline non-marine environments (Spencer, 2000), while Mg- and Fe-sulfates, which are common on Mars, more typically form in acidic environments on Earth (Chevrier et al., 2006; Clark et al., 2005; Hill et al., 1997). Nevertheless, whether alkaline or acidic, any detection of thenardite, like jarosite, an Fe-sulfate mineral detected on Mars by the Opportunity rover at Meridiani Planum (Klingelhofer et al., 2004; Morris et al., 2006), on Mars would suggest the prior presence of water.

6. Mineral formation

Previous hypotheses have suggested that the secondary sulfate deposits form as a result of fumarolic activity during basaltic emplacement (Stearns, 1963), by influx of brine-type groundwater (Peck, 1974), or by a combination of the two (Karlo et al., 1980). These hypotheses seem unlikely at COM as no volcanic activity has occurred in over 2000 years. The secondary sulfate deposits appear to be seasonal in that deposits were consistently observed at sites in the caves in June but not always observed at the same sites in October. Likewise, evidence of brine-type groundwater infiltration and subsequent mineral precipitation was not observed in any of the caves. The secondary sulfate deposits more likely formed from the primary weathering of the overlying basaltic host.

Solution composition calculated by PHREEQC from reaction of the observed mineral assemblage at COM with water was different from the composition analyzed in ceiling drips; PHREEQC calculated a calcium-bicarbonate solution, while the sampled waters were sodium-sulfate. This suggests that calcium and bicarbonate were removed from solution by precipitation prior to sampling. Indeed, calcite is observed on cave ceilings and walls (McHenry et al., 2010) where it is removed through precipitation, as calculated in MS1 using the PHREEQC code. Calcite reaches saturation under both scenarios: (1) equilibration with basalt minerals and subsequent evaporation, and (2) evaporation of observed cave-water solutions. Another common cave mineral, gypsum, was not modeled to achieve saturation in either MS1 or MS2, suggesting that weathering of COM basalt does not provide sufficient calcium and sulfate for gypsum formation under ordinary conditions. Neither mirabilite nor thenardite was calculated to achieve saturation in either scenario. Instead, another sodium sulfate phase, sodium heptahydrate ($\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$), was calculated to precipitate from solutions upon limited evaporation (< 10–20%) in both MS1 and MS2, providing a means to remove sodium and sulfate into a solid phase. Sodium heptahydrate reportedly alters to mirabilite under suitable conditions during dehydration (Hall and Hamilton, 2008). This phase may have an important role in ice formation in caves or polar regions on Mars as it has a eutectic point with water-ice of -3.11°C (Hall and Hamilton, 2008). White (2010) observed sodium sulfate phases in Hawaiian basaltic caves and invoked their formation from seepage of rainfall into caves during cooling; he suggested that the more soluble phases would only be found over time in higher and drier caves. This work provides an alternative mechanism for formation of sodium sulfate salts in caves through an as yet undetected sodium sulfate phase, sodium heptahydrate. In evaporitic environments, the formation of sodium sulfate minerals is invoked through chemical divides, which may help explain the lack of gypsum in the secondary deposits. A chemical divide occurs when a binary salt precipitates from solution removing the ionic constituents in a set ratio. As the more abundant ion is removed, its concentration increases sharply while the less abundant ion is removed to undetectable concentrations (Eugster, 1980). The starting ratios of the cave drippings at Craters

of the Moon lead to a solution in which Ca and Mg concentrations are sufficiently low as to preclude the precipitation of gypsum or Mg-sulfate phases.

The abrupt contact between the sulfate mounds and the basaltic floor, in addition to the absence of intermixing between the sulfate mounds and the authigenic basaltic minerals, further supports that secondary mineralization occurs via precipitation rather than direct mineralogical replacement. The presence of minerals on the cave floor may suggest biogenically mediated formation through alteration of bat guano. However, the lack of associated ammonium, nitrate, or phosphate minerals precludes the latter possibility as these are the most common minerals formed through alteration and leaching of bat guano (Forti, 2005; Hill et al., 1997). Additionally, the occurrence of thenardite in wall and ceiling cavities (Fig. 2) make any interaction and associated mineralization via bat guano unlikely. The results presented here further refute the prospect that mammals influence mineral precipitation in the COM caves. Nevertheless, such deposits could record evidence of any organic compounds or organisms associated with them or influencing their formation. Terrestrial thenardite has been shown to harbor biological and/or organic compounds (Richardson et al., 2008) and even facilitate detection of such compounds (Richardson et al., 2009a, b).

7. Conclusion

Secondary precipitates in basaltic caves of the Holocene COM basaltic flows were dominated by Na-sulfates (thenardite, mirabilite) with minor concentrations of Na-carbonates (trona, natron). The deposits are found in cavities along cave ceilings and walls as well as localized efflorescent mounds on the cave floors. The occurrence of Na-sulfate and Na-carbonate minerals in the subsurface of COM suggests that similar mineral assemblages could occur in the subsurface of Mars. Secondary sulfate minerals were modeled to form as a result of leaching of overlying basalt. The formation of sodium heptahydrate was invoked in order to achieve saturation with respect to sodium sulfate phases. This phase may have implications for the formation of sodium sulfate salts in cold, humid terrestrial and extraterrestrial environments (Hall and Hamilton, 2008). The presence of these secondary minerals in caves on Mars offers a highly promising target for finding signs of life because the caves would also protect the biomolecules from the destructive solar radiation, increasing the likelihood of preservation.

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