Supplementary Information: Trace Metals as Indicators of Microbially-Induced Weathering in Water-Limited Systems: The Snake River Plain as an Analog for Post-Noachian

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Figures and Tables

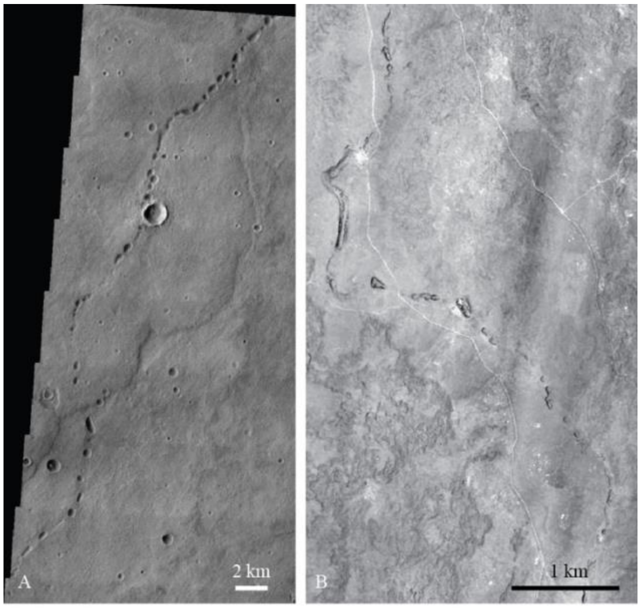
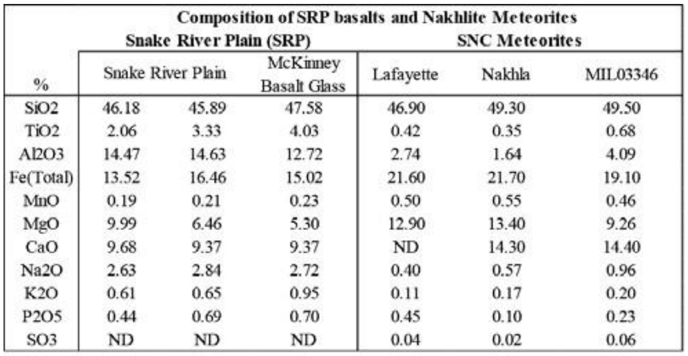


Figure 1: Lava tubes/caves are observed both on Mars (A, Mars Odessey/ THEMIS image of flows from Hadriaca Patera, PIA07055, NASA/CalTech JPL, ASU) and at CROM (B, NPS photo credit) in Idaho.



Composition of SRP basalts and Nakhlite Meteorites

%	Snake River Plain (SRP)			SNC Meteorites		
	Snake River Plain		McKinney Basalt Glass	Lafayette	Nakhla	MIL03346
SiO2	46.18	45.89	47.58	46.90	49.30	49.50
TiO2	2.06	3.33	4.03	0.42	0.35	0.68
Al2O3	14.47	14.63	12.72	2.74	1.64	4.09
Fe(Total)	13.52	16.46	15.02	21.60	21.70	19.10
MnO	0.19	0.21	0.23	0.50	0.55	0.46
MgO	9.99	6.46	5.30	12.90	13.40	9.26
CaO	9.68	9.37	9.37	ND	14.30	14.40
Na2O	2.63	2.84	2.72	0.40	0.57	0.96
K2O	0.61	0.65	0.95	0.11	0.17	0.20
P2O5	0.44	0.69	0.70	0.45	0.10	0.23
SO3	ND	ND	ND	0.04	0.02	0.06

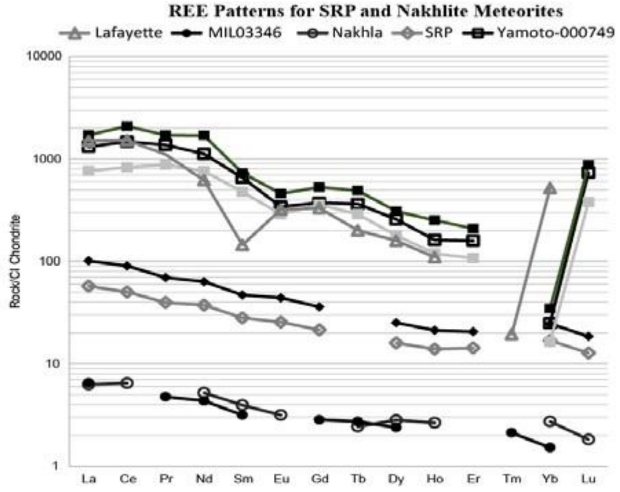


Figure 2: Composition and LREE Patterns for SRP basalts in comparison to SNC meteorites. SRP basalts in comparison to SNC meteorites. Preliminary analyses of the McKinney Basalt glass, which will is used in this study, are also shown. Gaps indicate values in the basalt or meteorite data that were below detection limits or not measured. SRP basalts fall between the low and high ranges of SNC meteorites, suggesting SRP basalts are useful analogs of potential Martian weathering biosignatures (Wilson et al., 1996; Thompson, 1983; Phillips-Lander et al., unpublished data; Day et al., 2006; Dreibus et al., 2003; Dreibus et al, 1982; Boctor et al., 1976).

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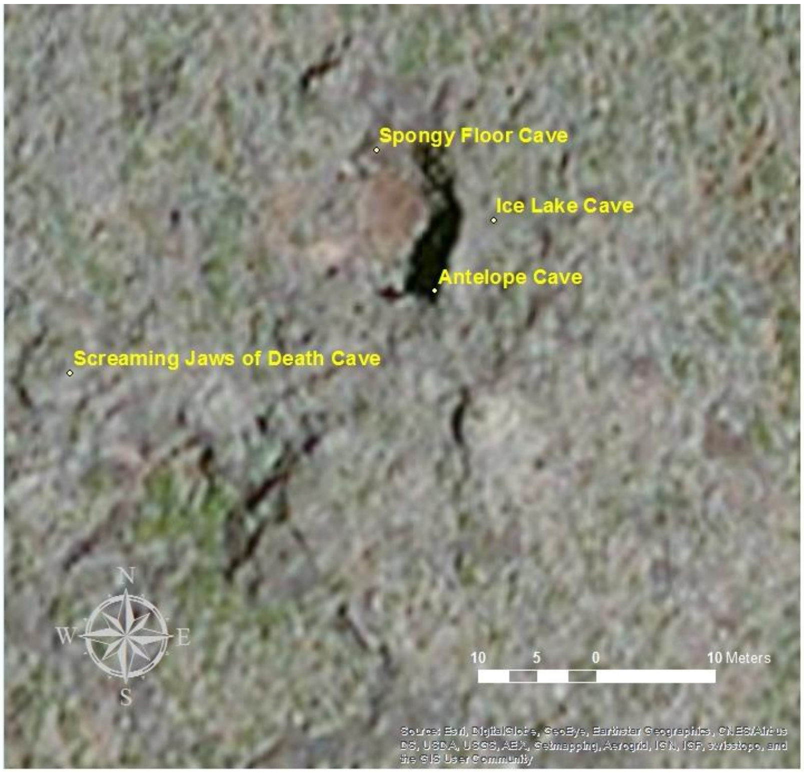

Source: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS User Community

Figure 3: Cave locations within Grassy Flow, north of the Visitor's Center at CROM. All caves are within a <1.6 km distance from each other, which minimizes decontamination requirements for White Nose Syndrome and highlights the environmental (T, pH, water phase) diversity of spatially co-located lava caves. (Map courtesy NPS)

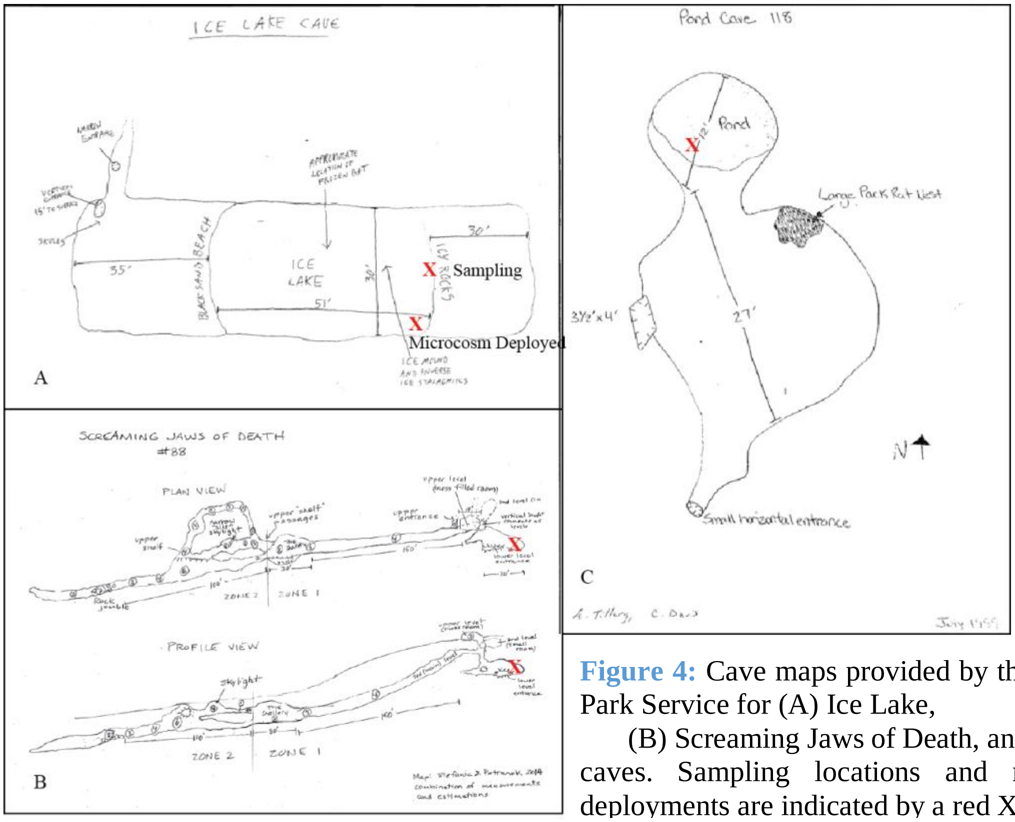

Figure 4: Cave maps provided by the National Park Service for (A) Ice Lake, (B) Screaming Jaws of Death, and (C) Pond caves. Sampling locations and microcosm deployments are indicated by a red X.

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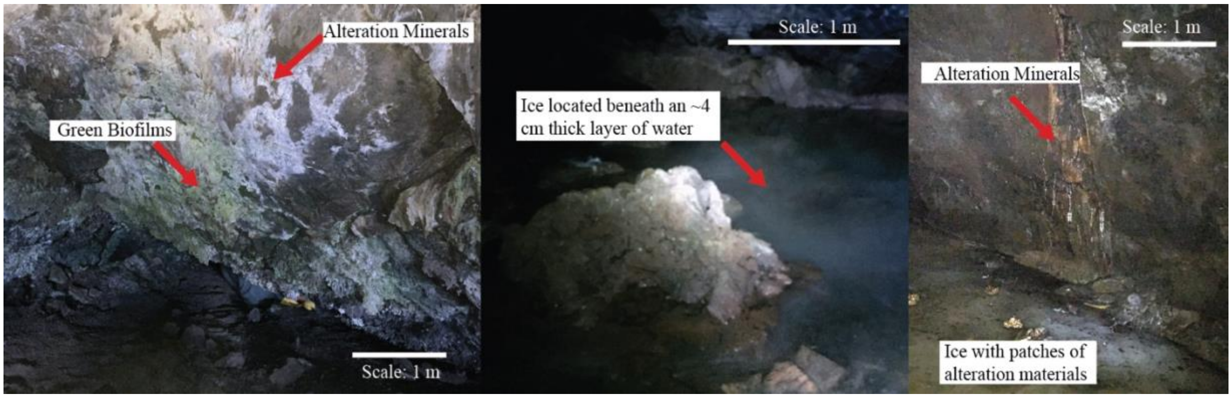

Figure 5: Site Selection for Field Experiments. *Left:* Screaming Jaws of Death has liquid water dripping into the cave year round (water:rock condition); *Center:* Pond Cave alternates between seasonal ice and liquid water (water/ice:rock) and is shown here as the ice begins to melt; *Right:* Ice Lake is perennially frozen. Water freezes as it enters the cave, creating a permanent ice lake that entrains patch alteration minerals (dark spots in the ice).

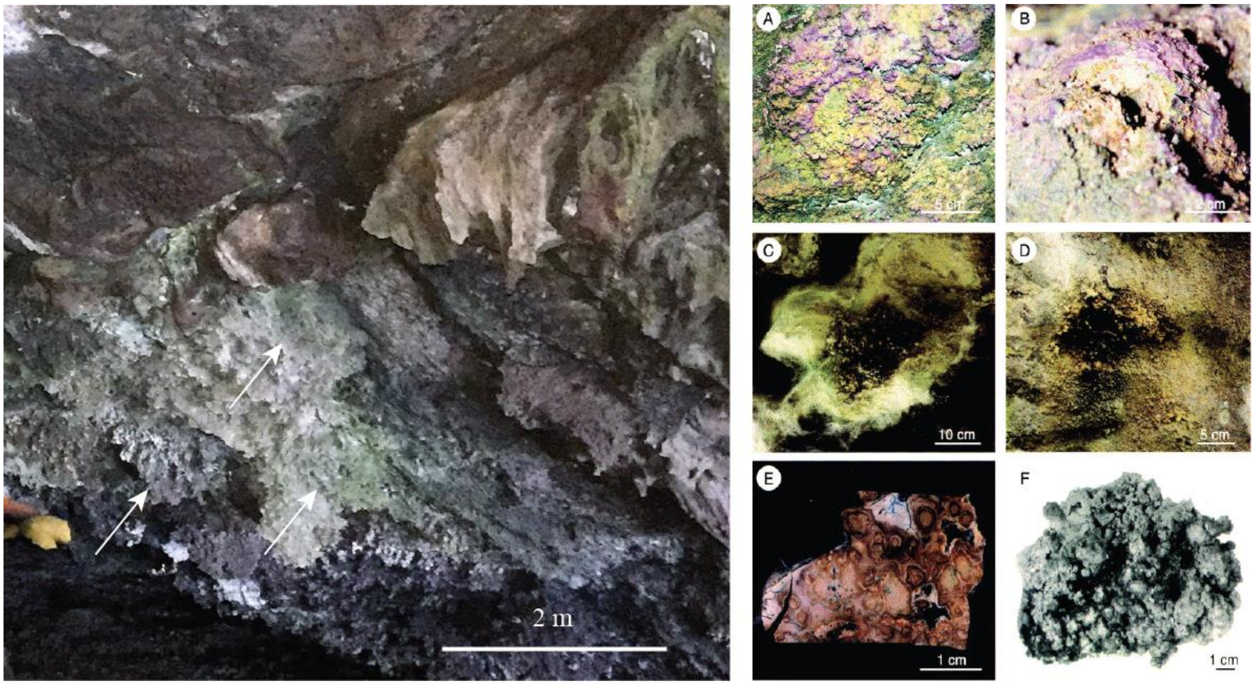

Figure 7: Cave wall in Screaming Jaws of Death, covered in green biofilms and a similar popcorn type texture (highlighted with arrows) as observed in Lèveillè et al.'s (2000) study of Hawaiian lava caves (A-F on the right).

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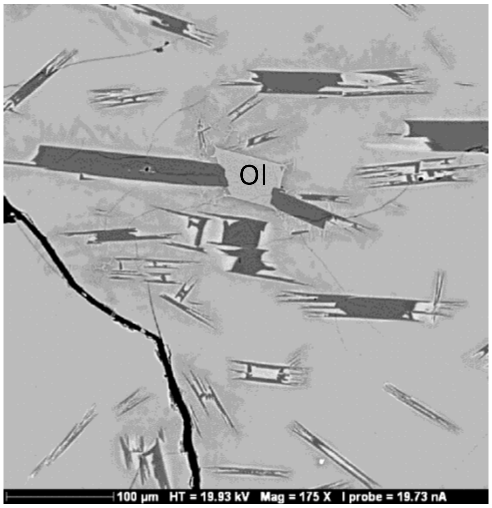

Figure 7: Backscatter image of McKinney Basalt, SRP displays olivine (ol) and plagioclase phenocrysts (dark crystals) in glass.

Figure 8: (A) Cartoon of how field microcosms work; (B) field microcosms deployed in Pond Cave (top right), Screaming Jaws of Death (bottom left) and Ice Lake (bottom right) in May 2016.

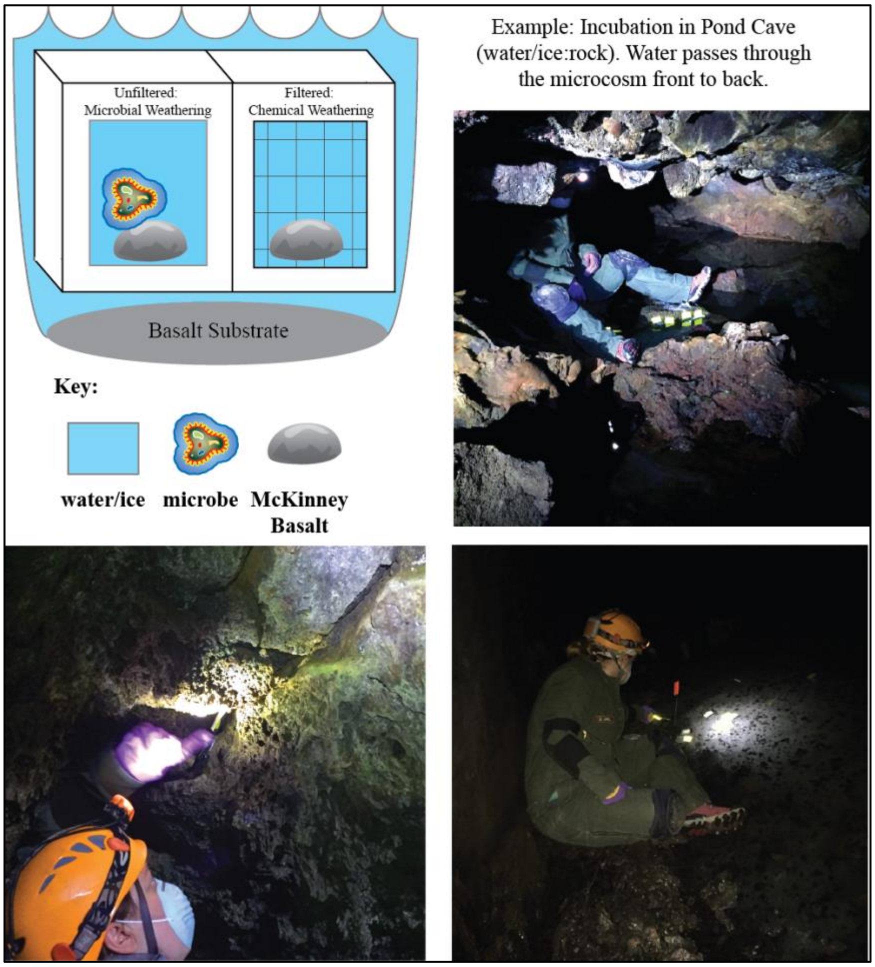

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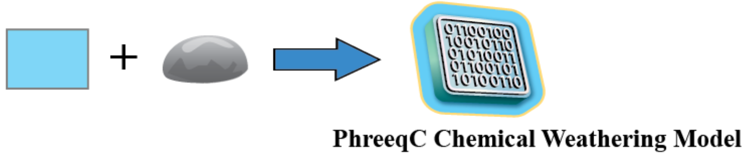
Figure 9: Work Flow: Characterize microbial colonization, weathering, and biosignatures in each lava cave environment.

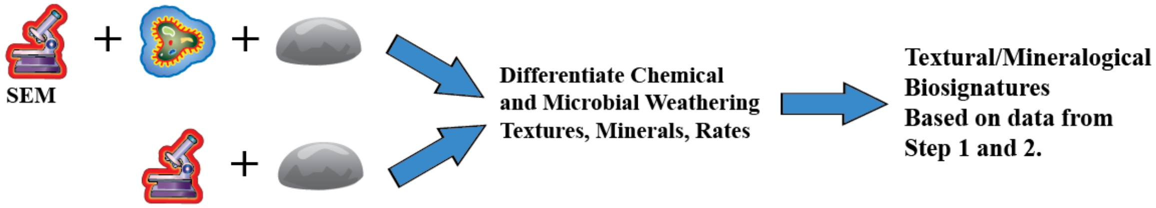
1. Characterize chemical weathering processes: Use analyses of water (ICP-OES) and reacted rock billets (XRD/Raman) from abiotic conditions to create a geochemical model for chemical weathering.



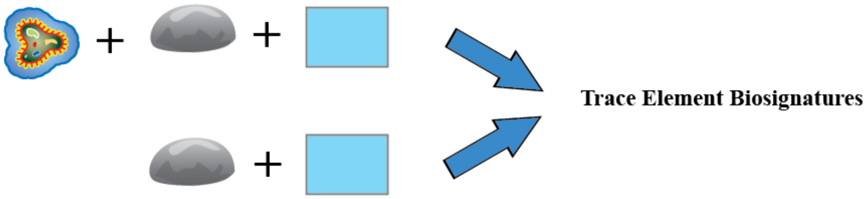
2. Characterize microbial colonization and weathering:

   a. Use XRD/Raman to characterize weathering products.

   b. Use SEM (preparation after Gorby et al, 2006) to assess microbial colonization, EPS coverage, and association between microorganisms/EPS and weathering textures/minerals.



3. Determine trace element biosignatures



4. Determine microbial diversity/community structure present and their potential metabolisms using DNA analysis and GC of dissolved gases.

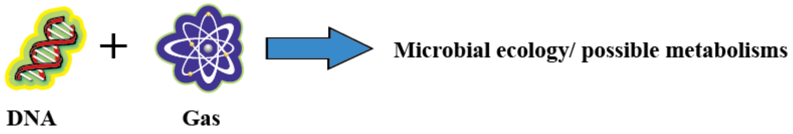


Figure 9: Field microcosms will be constructed based on Phillips-Lander et al. (2014) and adapted for the pH and T conditions expected to be encountered. All microcosms and basalt billets will be sterilized using ethanol and UV to prevent microbial contamination. One half of batch experiments for each time point will have 0.45 μm filters attached to the tubes to prevent microbial colonization and represent chemical weathering. The filter choice extends the life of the microcosm, while preventing microbial incursion. Reactors without filters will allow basalt chips to be colonized and weathered by native microbial consortia.

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Table 1: Aqueous Geochemistry mg/L

Site	Spongy Floor	Ice Lake	Pond	Screaming Jaws of Death
T (oC)	0.5	0.2	0.1	10.6
pH	6.5	7.6	6.42	nd
Anions				
Alkalinity	2.56	42.6	17.7	nd
F-	0.5	0.1	nd	nd
Cl-	1.6	1.83	12.2	nd
NO3-	0.7	0.2	1.9	nd
SO42-	2.11	3.93	1.83	nd
Cations				
Na	3.3	3.95	3.12	nd
K	1.28	7.44	1.69	nd
Mg	1.1	4.04	0.99	nd
Ca	3.22	34.4	3.9	nd
Fe	0.02	19.05	bdl	nd
Mn	0.8	0.87	bdl	nd

nd= not determined
bdl=below detection limits

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Methods

Field Methods

We utilized coupled field and laboratory methods to determine the degree of chemically and microbially induced weathering in different lava cave environments present at CROM. Background geochemical sampling of weathered rock faces and fluid samples were collected from four cave locations located within a 1.6 km diameter area in the Grassy Flow (7,360±60 year; Kuntz et al., 2007). These cave sites included Screaming Jaws of Death, Pond Cave, Ice Lake Cave, and Spongy Floor Cave, which represent warm/dry, cold/wet, icy/wet, and cold/dry conditions, respectively.

We measured pH in the field utilizing pH paper. Temperatures of the aqueous phase and rock surfaces were measured using a Etekcity 774 Infrared Thermometer.

Laboratory Methods

Polystyrene syringe filters were utilized to field filter water samples. We allowed frozen samples to equilibrate to room temperature before filtration. We utilized trace metal grade nitric acid to acidify filtered samples for cation analysis. Upon collection and filtration, we placed all samples on ice in a cooler, where they remained at or below 4°C during transport to the laboratory. Samples sent out for analysis were shipped on cold packs to maintain <4°C temperatures during transport.

Major and trace elements were analyzed using inductively coupled plasma optical emission spectroscopy on a Perkin Elmer ICP-OES Optima 5300DV at the University of Kansas (KU). We are currently waiting for KU to certify the trace element data. Filtered, unacidified samples for anion analysis were analyzed using a Microdrill Ion Chromatograph at KU. Alkalinity was determined in the laboratory using filtered unacidified samples. Dissolved gases will be analyzed using gas chromatography at KU.

Microbial colonization and weathering will be analyzed using X-ray diffraction (XRD), Raman spectroscopy, and scanning electron microscopy (SEM). SEM analysis is scheduled for August 3rd 2016. XRD and Raman analysis is in progress and will be completed by August 2, 2016.

Microbial diversity and community structure will be determined using background rock samples from each of the caves. These samples were sent to Amanda Stockton at Georgia Institute of Technology for metagenomics. This work is being contributed by the Stockton laboratory at no cost to the project.

Field Incubation Experiments

We deployed field microcosm experiments in order to differentiate *in situ* chemical and microbial weathering rates. Field microcosms have been employed successfully in groundwater, sulfuric acid caves, and hydrothermal systems to detect and differentiate microbial weathering processes and rates (Heibert and Bennett, 1992; Rogers et al., 1998; Rogers and Bennett, 2004; Engel et al., 2004; Bennett et al., 2006; Kandianis et al., 2008; Phillips-Lander et al., 2014). However, short-term field microcosms may show enhanced weathering and trace element biosignatures that may not be maintained over longer-times scales due to passivation of weathering surfaces, either as a result of secondary mineral precipitation or EPS coverage. At the same time, long-term microcosms may be limited by clogging of filters in chemical weathering controls, which could lead to dramatically different results between chemical and microbial weathering experiments. In order to address these potential issues, we are conducting nested short-term (6 month intervals) and long-term (1 year) microcosm experiments to allow us to break down and track changes that occur over time. Comparison between long-term and short-term experiments will aid in the recognition of preserved seasonal weathering signals in chemical and microbial weathering. This will allow us to determine both seasonal and long-term weathering rates for abiotic and biological systems.

Microcosms were built out of HDPE boxes, which we drilled holes into in order to allow for the passage of water into and out of the microcosm. Filters (0.45 μm) were attached to the interiors of one half of microcosms to prevent microbial incursion into the experimental apparatus, while allowing for the passage of water. The other half of microcosms had no filters, in order to allow microbial colonization and weathering. Each microcosm was loaded with a 2.5 cm^2 McKinney Basalt billet. Billets and microcosms had been previously UV and ethanol (90%) sterilized and were assembled in a sterile, UV hood. One set, one control (chemical weathering), and one microbial weathering microcosm were deployed for each cave for each time point (6 mo and 1 year).

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Upon retrieval from the caves in September 2016 and May 2017, basalt billets will be immediately placed in sterile, wide-mouth HDPE bottles with 2.5% glutaraldehyde solution in order to fix samples and preserve fine-scale microbe-mineral surface interactions (e.g. Gorby et al., 2006).

Field Experimental Design and Apparatus

The temperature and aqueous geochemistry within each cave are collected using field measurements at sampling intervals. Upon completion of each microcosm experiment, reacted basalt billets are collected in sterile bags. Sample billets from microcosm experiments will be analyzed using the workflow in Figure 9 to determine the potential microbial influence on secondary weathering products and trace element biosignatures using a (1) OU's Renishaw InVia Raman microscope with 532 and 785 nm laser lines and mapping capability as well as a (2) Rigaku Ultima IV X-ray diffractometer with MDI Jade(2010), (3) OU's Zeiss NEON FEG-SEM with energy dispersive X-ray spectroscopy and a secondary ion beam (FIB) to determine microbial associations with weathering textures and secondary minerals FIB (Bennett et al., 2006; Templeton et al., 2009; Phillips-Lander et al., 2014), and (4) Comparison between chemical and microbial weathering end members. A billet subsection will be preserved in OU's -80ºC freezer at the terminus of each microcosm experiment. This sample may be utilized in the future for phylogenetic analysis to determine if microbial community shifts occurred over the course of the experiments, as changes microbial succession in the microcosms may influence organic, textural, mineralogical, and elemental biosignatures. Results from field microcosm experiments will determine what role microorganisms play in weathering and textural (SEM), mineralogical (Raman/XRD), and trace element (based on comparison between data from chemical and microbial weathering) biosignature formation in each cave climate type and whether these biosignatures differ between cave climates.

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