WHY IS BLOOD FALLS RED? THE HUNT FOR IRON (HYDR)OXIDES AT THE TERMINUS OF TAYLOR GLACIER. J. A. Mikucki1, E. C. Sklute2, A. Jarratt3, M. D. Dyar2,3, and P. A. Lee4, 1Department of Microbiology, University of Tennessee, 1311 Cumberland Ave. Knoxville, TN 37996, jmkucki@utk.edu, 2Planetary Science Institute, 1700 E. Fort Lowell Rd. Ste. 106, Tucson, AZ. 85719, 3Department of Astronomy, Mount Holyoke College, 50 College St., South Hadley, MA. 01075, 4Hollings Marine Lab, 331 Fort Johnson Rd, Charleston, SC 29412.

Introduction: The enigmatic rust color of Blood Falls against its glacially monochromatic backdrop has caught attention since its discovery over 100 years ago [1]. Early in the study of this site, the iron-rich effluent emanating from the snout of Taylor Glacier at Lake Bonney was reported in 1962 to produce the hydrated iron oxide concretion, limonite, among other precipitates [2]. This was followed closely by a 1965 report of goethite seen in laboratory samples [3], and reports of iron-stained minerals in 1979 and 1980 [4,5]. At the time, the reportedly x-ray amorphous iron hydroxides were identified by microscopy using morphology and color analysis, and inferred from iron content in the sediment coupled with known weathering processes [5]. Experiments that reprecipitated iron hydroxides upon HCl dissolution and NH₂OH neutralization were used as further evidence to support this initial identification [2]. Until recently, there has been no reason to question these early analyses. So the idea that the reddish-orange color of the ice apron is due to iron-oxides has persisted for over 50 years. [6-8]. However, because the McMurdo Dry Valleys in general, and Blood Falls in particular are enticing Mars and ocean worlds analogue sites for both mineralogical and astrobiological studies, a re-examination of the characterization of surface sediments was apropos. In doing so on a selection of four samples, we have not found the iron (hydr)oxides we expected to be coating every sample. Here we discuss results of those analyses and how the mystery of the mineralogy of Blood Falls can inform our exploration of Mars and other Solar System bodies.

Methods: Sample ES25 was collected 11-22-06, a non-outflow year, from the ice apron’s “upper mush” (Fig. 1A,B). The other three samples were collected during 2018 when evidence for recent discharge existed. ES24 (moraine sediment) and ES26 (colored sediment) were collected on 11-19-18 (Fig. 1C), and ES27 (colored sediment) was collected 11-28-18 (Fig. 1D). Samples were shipped frozen to the US. Prior to analyses, ES24 and ES25 were stored oxically at room temperature and samples ES26 and ES27 were stored oxically at 4°C. ES24, ES26, and ES27 are glacial moraine sediments in colored colloidal suspensions (ES24) or ice matrix (ES26 and ES27). ES25 is a gray moraine sediment in fluid. The orange-red colloidal portion of the sample was pipetted from thawed, agitated samples and oxically dried for analysis.

X-ray diffraction (XRD) analysis was performed on a Rigaku Smartlab II SE (Cu Ka radiation, Bragg-Brentano geometry, 5-80 2θ). Baseline corrections and mineral identifications were made using Rigaku Smartlab software. Fourier transform infrared (FTIR) spectra were obtained on a Bruker Alpha FTIR spectrometer with a diamond attenuated total reflectance (ATR) attachment (360-4000 cm⁻¹, 4 cm⁻¹ resolutions, 128 scans). Continuum removal was performed with OPUS using a concave rubberband correction. Raman spectra (300-3200 cm⁻¹) were obtained with a Bruker BRAVO spectrometer (758 and 852 nm excitation lasers 100, 1000ms integrations). Spectra were baseline corrected using the rubberband algorithm using tools available at: http://nemo.cs.umass.edu:54321/

Scanning electron microscopy (SEM) was performed on a Carl Zeiss EVO50 in secondary and backscattered electron modes, and included qualitative compositional surveys using a Bruker SDD EDS system. Electron probe micro analysis (EPMA) was done using a Cameca SX100 electron probe with four WDS spectrometers and Bruker SDD EDS (15kV, 15nA, with a 2 µm beam diameter). Samples were analyzed for Na, Al, Si Ca, Fe, Mg, Mn, Ti, and S using silicate
and oxide standards for calibration. Mössbauer spectra were collected on a Web Research (now See-Co) W302 Mössbauer spectrometer at 295, 220, 150, 80, and 4K using a Janus closed cycle He compressor.

**Results:** XRD of Blood Falls samples (Fig. 2) shows no sign of iron oxide, which is not surprising because those phases are reported to be XRD amorphous. ES24 is predominantly calcite, alkali feldspar, quartz, and hedenbergite, ES25 is aragonite and minor calcite and covellite, ES26 is calcite with minor quartz and anorthite, and ES27 is calcite, albite, and quartz. Raman analyses (data not shown) support these identifications and show no evidence for iron (hydr)oxides.

FTIR spectra (Fig. 3), which can be used to detect trace amounts of (hydr)oxides, do not show goethite (nor lepidocrocite; not shown). Possible hematite features are seen in spectra for ES24, ES26, and ES27, but the Mössbauer data only support minor hematite in ES27. Mössbauer fits for the other two samples are only consistent with ferricyanide, which is not apparent in FTIR data. Almost no FTIR or Mössbauer digital data exist for surface-sorbed iron that could shed light on this perplexing problem, and published plots lack the resolution to assess additional clarity.

SEM images (not shown) do not reveal crystal morphologies consistent with iron (hydr)oxides, only calcite and aragonite crystals with nanoparticulate, iron-bearing debris. SEM and EPMA elemental analysis both indicate that Fe correlates with Si, and in some cases Ca, but does not appear as (hydr)oxides.

**Conclusions:** While Blood Falls is an interesting (bio)geochemical Mars analogue, it also mirrors some of the analytical challenges associated with planetary exploration. Blood Falls has been observed for over 100 years, but, like Mars, relatively few sample points are available. Also, collected samples present similar analytical challenges due to their amorphous and ephemeral nature. Blood Falls effluents produce a range of iron concentration, with a recent discharge analyses showing 476 μM Fe [10]. Past data suggest the presence of iron (hydr)oxides, however, data from the sample set described here suggest that Fe is incorporating into calcite and aragonite. Understanding the tools needed to study this variable and enigmatic environment will be invaluable in planetary science.

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**References:**