

HYDROTHERMAL FORMATION AND OXIDATION OF A CALCITE-MARCASITE VUG AT THE HAUGHTON IMPACT STRUCTURE: MAPPING OF ALTERATION ASSEMBLAGES WITH HYPERSPECTRAL IMAGING. R. N. Greenberger¹, J. F. Mustard¹, G. R. Osinski^{2,3}, L. L. Tornabene^{2,4}, A. Pon-trefract², C. L. Marion², R. L. Flemming², J. H. Wilson⁵, and E. A. Cloutis⁶, ¹Dept. of Earth, Environmental, and Planetary Sciences, Brown University, Providence, RI, 02912, Rebecca_Greenberger@brown.edu, ²Dept. of Earth Sciences & Centre for Planetary Science and Exploration, University of Western Ontario, London, ON, N6A 5B7, Canada, ³Dept. Physics & Astronomy, University of Western Ontario, London, ON, N6A 5B7, Canada, ⁴SETI Institute, Mountain View, CA 94043, USA, ⁵Headwall Photonics, Inc., Fitchburg, MA, 01420, ⁶Dept. of Geography, University of Winnipeg, Winnipeg, MB R3B 2E9, Canada.

Introduction: Hydrothermal systems generated by meteorite impacts may explain some deposits of secondary minerals on Mars and are important in understanding prospects for habitable environments [e.g., 1-6]. As such, hydrothermal deposits on Mars have been identified as prime targets for future landed and sample return missions [7].

Studies of terrestrial impact-driven hydrothermal systems provide insights into these geological processes on other planets and their potential for habitability. Hyperspectral imaging can be used in the field and laboratory to better understand these systems and to develop exploration criteria. To explore this application, we used hyperspectral imaging to map a hydrothermal calcite-marcasite vug within the impact melt rocks at the Haughton impact structure, Devon Island, Canadian High Arctic (75.37°N, 89.68°W, ~23 Ma, 23 km apparent diameter) [8-13]. The vug has been oxidized and altered at low temperatures to sulfate and oxide minerals [9, 12]. This site was selected for its fantastic exposures of hydrothermal mineralization [8, 9, 12]. The goals of this work are to characterize and map spatially the hydrothermal mineralization and later weathering products, to understand the evolution in fluid chemistry and mineralogy through time, and to identify the most habitable locations.

Methods: The outcrop was imaged during the 2013 field season with a Channel Systems near infrared (NIR) imager covering wavelengths 0.65-1.1 μm (10 nm spectral resolution and sampling) and calibrated to reflectance using a dark object subtraction and ratio to Spectralon[®] panel imaged next to the outcrop. Samples that were representative of the major phases at the outcrop were collected, stored on ice, and measured with an Analytical Spectral Devices, Inc. (ASD) point spectrometer in the field to minimize changes in hydration state or mineralogy before analysis. This abstract focuses on five samples collected within the hyperspectral images of the outcrop. Samples were imaged in the laboratory at Headwall Photonics, Inc. with their high efficiency visible-near infrared (0.4-1.0 μm , 1.785 nm spectral resolution) and shortwave infrared (1.0-2.5 μm , 12.0656 nm spectral resolution) imagers. Spectrally-similar units were mapped in field

and laboratory imaging data with spectral parameters [e.g., 14]. Mineralogy was determined for powdered samples with XRD and coatings with μXRD [15]. Interpretation of these XRD data is ongoing. Major element chemistry was determined with elemental analyses for C and N and ICP-AES following a flux fusion sample preparation for other elements [16].

Results: ASD spectra enable identification of spectrally-dominant mineralogies [see 17-21 for spectral features assignments], and sampling locations are shown in Figure 1. APDI-13-14a is a popcorn-textured mixed sulfate with likely copiapite or ferricopiapite and possible fibroferrite and is dominated chemically by Fe with little Ca. Hyperspectral imaging also shows small patches of gypsum within the sample. APDI-13-14b is a dark red coating on the calcite rock and is a mixture of gypsum and an Fe^{3+} oxide or sulfate. Chemically, it has high Ca and Fe. APDI-13-14c is the unaltered marcasite. APDI-13-14h is a blue-gray phase that is a mixture of an Fe^{2+} -bearing sulfate or other mineral and calcite, possibly with some clay. APDI-13-14j is a red-colored oxidized marcasite with spectral features indicating hydration and a minor sulfate component. These mineral identifications are consistent with Izawa et al. [12] for different samples from this site.

NIR hyperspectral imaging of the outcrop was used to map the units representative of these samples (Fig. 1). The primary marcasite (green) is seen dominantly on the ceiling or vertical walls of the outcrop where water is unlikely to collect. Patches of oxidized marcasite (brown) occur within the unaltered marcasite. The copiapite and fibroferrite phase (yellow) often is present directly below the marcasite, and the red coatings of gypsum and an Fe^{3+} oxide or sulfate (red) are seen below the copiapite and fibroferrite phases. There is one small patch of the blue-gray material that occurs below the red coating.

Discussion: The spatial relationships among the secondary mineral assemblages suggest a progression from marcasite to mixed valence Fe-sulfates to Fe^{3+} -oxides or sulfates and gypsum as hot, reducing fluids evolved to oxidizing, more neutral fluids with a more complex chemistry (Fig. 2). Primary marcasite formed from post-impact hydrothermal systems at tempera-

tures of ~100-240°C and pH <5 [10] and then weathered at low temperatures [12] to intermediate phases such as the oxidized marcasite. These altering fluids were likely acidic and at least mildly oxidizing, and water/rock ratios were probably relatively low. As the marcasite dissolved and oxidized, very acidic, somewhat oxidizing fluids likely resulted and led to precipitation of the copiapite and fibroferrite, which only have Fe²⁺ and Fe³⁺ cations [e.g., 22-23]. This suggests little interaction between the fluids and surrounding calcite-rich rock, which would have neutralized the fluids somewhat and contributed Ca. Minor gypsum mixed with the Fe-sulfates suggests that there was limited dissolution of calcite. The red coatings then formed from completely oxidized, less acidic fluids that had interacted with the calcite host rock and likely dissolved the copiapite-bearing assemblage [e.g., 22, 24].

From these results, a wide range in fluid compositions (T, pH, Eh, and composition) is mapped and inferred in these types of deposits, and the phases present are similar to those reported in oxidized massive sulfide deposits [e.g., 22-23]. Izawa et al. [12] characterized individual samples from this site but did not study their spatial distributions or spectral signatures. They argued that Fe and S oxidation are important microbial processes at the Haughton impact structure and could

also be operating on Mars, and the boundaries that we map here between marcasite and copiapite/fibroferrite and between copiapite/fibroferrite and gypsum/Fe³⁺ sulfate or oxide would be prime locations for further work in the search for evidence of microbial processes.

References: [1] Newsom H. E. (1980), *Icarus*, 1, 207-216. [2] Osinski G. R. et al. (2013), *Icarus*, 2, 347-363. [3] Tornabene L. L. et al. (2009), *LPS XL*, Abstract# 1766. [4] Schwenzer S. P. and Kring D. A. (2009), *Geol.*, 37, 1091-1094. [5] Marzo G. A. et al. (2011), *Icarus*, 2, 667-683. [6] Tornabene L. L. et al. (2013), *JGR*, 5, 994-1012. [7] MEPAG E2E-iSAG (2011), *Astrobiology*, 12, 175-230. [8] Osinski G. R. et al. (2001), *Meteoritics & Planet. Sci.*, 36, 731-745. [9] Osinski G. R. et al. (2005), *Meteoritics & Planet. Sci.*, 40, 1859-1877. [10] Osinski G. R. et al. (2005), *Meteoritics & Planet. Sci.*, 40, 1759-1776. [11] Tornabene L. L. et al. (2005), *Meteoritics & Planet. Sci.*, 40, 1-19. [12] Izawa M. R. M. (2011), *Astrobiology*, 11, 537-550. [13] Young K. E. et al. (2013), *GRL*, 40, 3836-3840. [14] Pelkey S. M. et al. (2007), *JGR*, 112, 18 pp. [15] Flemming R. L. (2007), *Can. J. Earth Sci.*, 44, 1333-1346. [16] Murray R. W. et al. (2000), *ODP Tech. Note*, 29, 1-27. [17] Hunt G. R. et al. (1971), *Modern Geol.*, 3, 1-14. [18] Hunt G. R. and Salisbury J. W. (1971), *Modern Geol.*, 2, 23-30. [19] Clark R. N. et al. (1990), *JGR*, 95, 12653-12680. [20] Burns R. G. (1993), *Cambridge Univ. Press*, 2nd ed., 578 pp. [21] Cloutis E. A. et al. (2006), *Icarus*, 184, 121-157. [22] Jambor J. L. et al. (2000), *Rev. in Min. and Geochem.*, 40, 303-350. [23] Jerz J. K. and J. D. Rimstidt (2003), *Am. Min.*, 88, 1919-1932. [24] Chou I. M. et al. (2013), *J. of Asian Earth Sci.*, 62, 734-758.

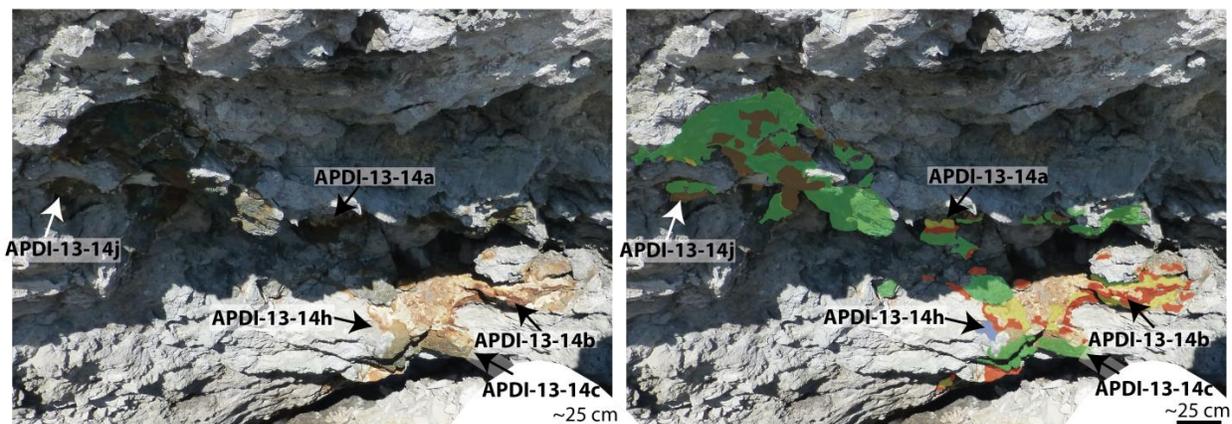


Fig. 1: (left) Photograph of calcite-marcasite vug with sampling locations labeled. (right) Units with assemblages similar to the collected samples mapped using the NIR imager data and overlain on a photograph. Green: marcasite, brown: oxidized marcasite, yellow: popcorn-textured copiapite/fibroferrite-bearing mixed sulfates, red: dark red gypsum + Fe³⁺ oxide or sulfate coating, blue: Fe²⁺ sulfate or other mineral + calcite.

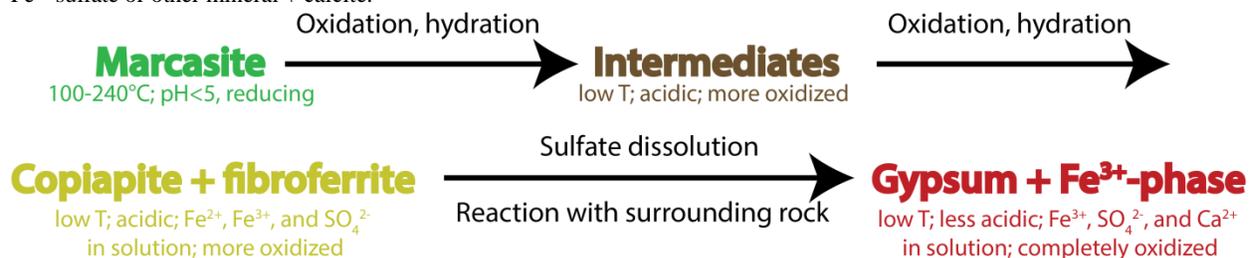


Fig. 2: Inferred alteration sequence based on spatial relations determined through NIR mapping (Fig. 1) and laboratory analyses. See explanation and references in the text.