

**CONTRASTING ABUNDANCE OF EXTRATERRESTRIAL AND TERRESTRIAL ALTERATION PRODUCTS IN THE MILLER RANGE NAKHLITE METEORITES.** Z. T. Eriksen<sup>1</sup> (eriksenz@msu.edu), S. M. Dorfman<sup>1</sup>, M. A. Velbel<sup>1,2</sup>, and J. Li<sup>3</sup>; <sup>1</sup>Michigan State University, East Lansing, MI; <sup>2</sup>Smithsonian Institution, Washington, DC; <sup>3</sup>University of Michigan, Ann Arbor, MI.

**Introduction:** The spatial and temporal distribution of aqueous alteration products in Martian rocks has potential to elucidate the history of the Martian climate. A key indicator of acidic aqueous environments is jarosite, a hydrated iron sulfate mineral with a chemical formula of  $KFe_3(SO_4)_2(OH)_6$  where Na and  $H_3O$  commonly substitute for K. Jarosite was identified in situ at Meridiani Planum [1] and has been identified and texturally and compositionally described in several Martian meteorites [1-12; 15]. Orbital observations have identified geomorphological features on the surface of Mars analogous to terrestrial fluvial environments, supporting the hypothesis that the Martian surface was altered by periods of aqueous activity [2]. The presence of jarosite at Meridiani Planum supports orbital observations and further constrains the composition/pH of the paleofluids affecting the geochemistry of the Martian surface [2]. However, until Mars sample return, Martian meteorites represent our only sampling of Mars [7].

The four Miller Range (MIL) nakhlites (cumulate clinopyroxenite SNC meteorites) are presently understood to be paired [8]. The petrography and primary/secondary mineralogy of MIL 03346 have been extensively analyzed [1-12; 15]; however, characterization of the secondary mineralogy of the remaining three nakhlites (MIL 090030, 090032, 090136) remains limited. In particular, terrestrially-derived secondary jarosite has been identified in several allocations of MIL 03346 and in MIL 090032 [10; 11]. Secondary jarosite identified within a breached olivine melt inclusion in MIL 090136,21 may be pre-terrestrial in origin [11]; however, confirmation remains difficult. Quantifying differences between spatial distribution, composition and abundance of secondary minerals within the MIL nakhlites is critical to understanding pre-terrestrial and terrestrial chemical weathering.

Here, we report sharp contrasts in abundance of secondary K-sulfates between MIL 03346 and MIL 090136. Secondary jarosite was structurally identified and chemically described in the exterior olivine crystal (truncated by outer edge) and provisionally identified in the interior olivine crystal (~500 microns perpendicular to outer edge) in MIL 03346,171, while completely absent from MIL 090136,26. Non-destructive identification and compositional and textural characterization of alteration phases were accomplished through application of scanning electron microscopy – energy dispersive X-ray spectroscopy (SEM-EDS) and Raman spectroscopic analytical techniques. Complementary application of SEM-EDS and Raman

spectroscopy allowed for textural, structural and chemical classification of secondary sulfates.

**Samples and Methods:** Two polished thin sections were examined for the purposes of this study: MIL 03346,171 and MIL 090136,26. Both thin sections contain portions of fusion crust preserving the exposed outer edge of the meteorite, allowing for approximate spatial determination of secondary phases relative to the terrestrially exposed surface. MIL 03346,171 contains a significantly lower modal abundance of olivine relative to MIL 090136,26 [13]. Optical petrography was used to identify secondary alteration prior to application of other analytical techniques.

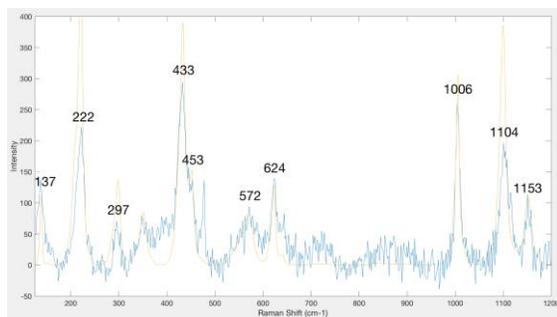
Combined SEM-EDS analysis was performed at the Center for Advanced Microscopy at Michigan State University. Carbon-coated samples were examined and imaged with a JEOL 7500F (field emission) SEM, and EDS was conducted on an Oxford Instruments Aztec system using a 150 mm<sup>2</sup> silicon drift detector and an ultra-thin window. Following image acquisition and EDS mapping, spectra were acquired from areas within secondary phases featuring co-localized regions of K and S. Areas of interest displaying K/S wt% ratios comparable to ideal jarosite ratios were analyzed with Raman spectroscopy.

The Renishaw inVia confocal Raman microscope in the Mineral Science Research Laboratory at the University of Michigan was used to further structurally and compositionally describe and identify secondary K-sulfates. The Raman microscope is equipped with a depolarized 532 nm green laser with 50 mW maximum power and an 1800 line per mm grating. Point counts were acquired with an acquisition time of 25 seconds and a spot size of 2 μm<sup>2</sup>. The confocal mode was applied to improve the axial spatial resolution and therefore increase the signal:noise ratio, and a beam filter was used to minimize oxidation/damage of secondary alteration phases.

**Results:** In sample MIL 03346,171, the presence of secondary jarosite was found to be independent of distance from the terrestrially exposed outer edge. Complementary SEM-EDS and Raman spectroscopic analyses confirm the presence of secondary terrestrial jarosite in the exterior olivine [14] in MIL 03346,171. Jarosite was identified on the basis of its diagnostic peaks at 138, 223, 299, 353, 434, 452, 573, 623, 1006, 1101, and 1152 cm<sup>-1</sup>, and characteristic fluorescence between 3410 and 3420 cm<sup>-1</sup> indicative of OH-stretching [15] (Fig. 1). SEM elemental abundances and Raman peak positions indicate a composition similar to the potassic endmember [15]. SEM-EDS analysis of the

interior olivine [14] in MIL 03346,171 (Fig. 2) identified several phases similar in composition to K-jarosite filling cracks associated with incipiently altered olivine [10; 14]; the structure and composition of these phases will be further discussed.

Extensive complementary SEM-EDS/Raman spectroscopic examination of areas of secondary alteration in 15 olivines in MIL 090136,26 yielded no significant co-localization of K and S, and thus little promise for jarosite. This negative result is in sharp contrast to MIL 03346,171, despite their presumed pairing. Excluding areas of co-localized K, S, and Ca (MIL 03346,171), olivine alteration veins in both meteorites have similar bulk chemistry, yielding enrichments in SiO<sub>2</sub> and FeO and depletions in MgO, relative to unaltered olivine.

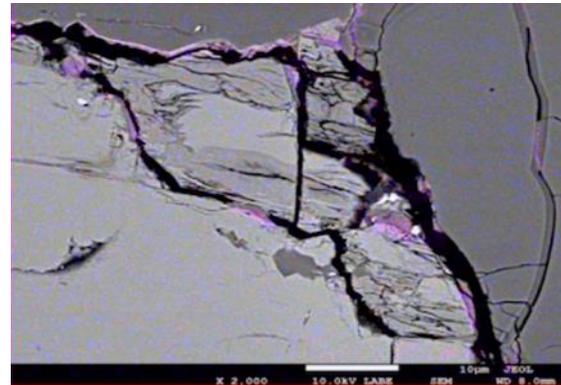


**Figure 1.** Raman spectra of terrestrial K-jarosite obtained from MIL 03346, 171. Blue – spectrum obtained from MIL 03346, 171; yellow – reference jarosite spectrum retrieved from ruff.

**Discussion:** Jarosite had been previously reported in exterior olivine alteration veins in MIL 03346,171 based on stoichiometric elemental abundances [10], but was not definitively identified. Applying complementary methods of SEM-EDS and Raman spectroscopy, we structurally identified and compositionally characterized this phase. Our estimated K-rich composition is in agreement with several published compositional analyses from other allocations of MIL 03346 [9,11]. These jarosite-hosting alteration veins crosscut the fusion crust, confirming their terrestrial origin [10]. Interior crack-filling phases associated with incipiently altered olivine (possible jarosite) in MIL 03346,171 (Fig. 2) appear compositionally similar to confirmed jarosite adjacent to the terrestrially exposed surface. Previously reported terrestrial jarosite in MIL 03346 is primarily found near the terrestrially exposed outer edge [6,16]. Although the jarosite shown in Figure 2 is located ~5 mm perpendicular to the fusion crust, its origin is likely terrestrial, considering the network of cracks penetrating the sample.

The relative abundance of terrestrial jarosite in MIL 03346 sharply contrasts with paired meteorite MIL 090136. Our negative result agrees with previous work

on this meteorite, which found no secondary jarosite by electron microprobe and SEM analysis of exterior allocation MIL 090136,25 [11]. Similar to the MIL nakhilites, the Yamato paired nakhilites have also demonstrated variability in secondary mineralogy [17]. This difference in terrestrially-derived secondary mineralogy may be the result of differing degrees of chemical weathering following delivery to Earth. Scenarios resulting in varying degrees of terrestrial aqueous alteration will be discussed.



**Figure 2.** SEM image of interior olivine (MIL 03346,171) overlain by false color EDS map of K (blue) and S (red). Putative jarosite represented by co-localized K and S (purple).

**Acknowledgements:** Special thanks to Amy Albin and Abigail Vanderberg at the MSU Center for Advanced Microscopy. Samples were allocated by the Antarctic Meteorite Working Group (MWG), and this work was supported by funds disbursed by the Michigan Space Grant Consortium Undergraduate Research Fellowship.

**References:** [1] Klingelhöfer G. et al. (2004) *Science*, 306(5702), 1740-1745. [2] Baker V.R. (2001) *Nature*, 412 (6843), 228-236. [3] Vicenzi E.P. et al. (2007) *LPSC Abstract #2335*. [4] Fries M. et al. (2007) *LPSC Abstract #2195*. [5] McCubbin N.J. et al. (2009) *Geochim. Cosmochim. Acta*, 73(16), 4907-4917. [6] Hallis L.J. & Taylor G.J. (2011) *Meteorit. Planet. Sci.*, 46(12), 1787-1803. [7] Velbel M.A. (2012) *SEPM SP (102)*, 97-117. [8] Udry A. et al. (2012) *Meteorit. Planet. Sci.*, 47(10), 1575-1589. [9] Kuebler K.E. et al. (2013) *J. Geophys. Res-Planets*, 118(3), 347-368. [10] Stopar J.D. et al. (2013) *Geochim. Cosmochim. Acta*, 112, 208-225. [11] Hallis L.J. (2013) *Meteorit. Planet. Sci.*, 48(2), 165-179. [12] Hallis L.J. et al. (2014) *Geochim. Cosmochim. Acta*, 134, 275-288. [13] Corrigan C.M. et al. (2015) *Meteorit. Planet. Sci.*, 50(9), 1497-1511. [14] Velbel M.A. (2016) *Geochim. Cosmochim. Acta*, 180, 126-145. [15] Sasaki K. et al. (1998) *Can. Mineral.*, 36, 1225-1235. [16] Velbel M.A. et al. (2010) *LPSC Abstract #2223*. [17] Noguchi T. (2009) *J. Geophys. Res-Planets*, 114(E10).