

Driving fumarole activity on the Moon 2. Nano-Scale textural and chemical analysis of alteration in “rusty rock” 66095. P.P. Provencio¹, C.K. Shearer^{1,2}, and A.J. Brearley². ¹Institute of Meteoritics, University of New Mexico, Albuquerque, New Mexico 87131 (cshearer@unm.edu), ²Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, New Mexico 87131.

Introduction: “Rusty Rock” 66095 has produced significant debate concerning its origin, yet it has and will continue to reveal significant insights into the behavior of volatiles on the Moon. Sample 66095 consists of a fine-grained, subophitic to ophitic impact melt-rock surrounding a wide variety of lithic clasts [1,2]. Alteration is found in the interior as well as on the surface of 66095. A brownish colored alteration extends from margins of Fe-Ni metal grains into the adjacent silicates and consists of a variety of identified to potential low-temperature minerals [1-6]. The origin of this alteration and its hydrogen and oxygen isotopic signatures have been attributed to alteration on the Moon [7,8], as well as to “terrestrial” alteration during or following transport to Earth [4,9]. Another interesting aspect of 66095 is its enrichment in ²⁰⁴Pb, Cd, Bi, Br, I, Ge, Sb, Tl, Zn, and Cl indicating that portions of this sample contain a volatile-derived component [eg.10-14]. Similar enrichments have also been observed in Apollo 16 (A-16) soils [8,11-14]. The origins of these enrichments have been attributed to fumarolic-hydrothermal [14], magmatic, or impact processes [11,12]. However, the mineralogical carriers of this volatile-rich component have not been fully identified or characterized [5, 8]. This is particularly true of the Cl-bearing mineralogy. Here, we examine the nano-scale mineralogy and geochemistry of the alteration in 66095 to gain additional insights into the petrogenesis of the rusty rock, the origin of the “rusty” alteration, and transport of volatiles in the lunar crust and on the lunar surface.

Analytical approach: Splits from three “Rusty Rock” 66095 subsamples were powdered and analyzed in this study using an FEI Quanta 3D Field Emission Gun FIB/SEM/EDS (focused ion beam for extracting site specific areas of the sample, scanning electron microscopy for imaging microtexture, and energy dispersive spectroscopy for identifying Cl- and Zn-rich areas for extraction and conducting chemical analysis), and TEM/STEM/ EFTEM (transmission electron microscopy for nano-scale imaging, scanning TEM for chemical contrast, and energy filtered TEM for imaging specific chemical species). In addition, four FIB sections of iron-rich grain boundaries were prepared for a TEM/EDS study from a thin section of “Rusty Rock” 66095, in order to examine the nano-structure, chemistry, and crystal diffraction. Two sample splits were analyzed with SEM/EDS/FIB to map the iron-rich

grain/alteration boundaries by cutting down into the boundaries. To minimize terrestrial alteration, after cutting TEM mounts, samples were analyzed within hours of preparation and/or stored under vacuum until analysis.

Nano-scale alteration mineralogy: Taylor et al. [6] concluded that β FeO(OH,Cl) (akaganéite) was the dominant iron hydroxide in 66095. They postulated that this phase was a product of oxyhydration of Fe-Ni metal and lawrencite (FeCl₂). However, lawrencite was not identified in these previous studies [1-14].

In the course of this multi-prong study, our group has made numerous observations related to the alteration of this lithology, as follows: (1) Cl has a fractionated isotopic signature which is enriched in ³⁷Cl [15,16]. (2) Stanfieldite (Ca₄(Mg,Fe²⁺,Mn)₅(PO₄)₆) is closely associated with Fe-Ni metal and Ca-bearing silicates (plagioclase, high-Ca pyroxene) [16]. This is the first documented occurrence of this phosphate in lunar samples. Stanfieldite is also found in pallasites and some of these occurrences have been attributed to oxidation of Fe-Ni metal [17]. (3) SEM observations show that akaganéite occurs adjacent to Fe-Ni metal and troilite grains and within the finer-grained matrix making up 66095, consistent with the previous observations of Taylor et al. [6]. The akaganéite is Cl-rich (1-4 wt.% Cl) and consists of elongate, somatoidal crystal shapes (Fig. 1). (4) The interface between the akaganéite and Fe-Ni metal is complex consisting of numerous Fe-hydroxides and oxides. In addition to akaganéite we have identified goethite, hematite, and feroxyhyte (δ Fe³⁺O(OH)) using electron diffraction (Fig. 2). The identification of hematite and goethite is consistent with micro-Raman observations [16]. These two phases have a distinctly different morphology from the akaganéite (Fig. 1 and 2). (5) Lawrencite was identified adjacent to Fe-Ni metal using EDS and electron diffraction analysis in 66095 (Fig. 2 and 3). The lawrencite reaches a grain size of up to 1 μ m. (6) With continued exposure to the relatively low humidity of New Mexico, the lawrencite in the FIB sections became increasingly hydrated over several weeks. Over this period of time, the phase reacted to an intergrowth of an Fe-rich amorphous phase, goethite and hematite. These phases have a considerably different morphology than the akaganéite (Fig. 1 and 3). (7) Even after extensive study of individual fragments prepared without water, no other alkali or transition metal chlorides

(i.e. NaCl, KCl, MgCl₂, ZnCl₂, PbCl₂) were identified in 66095. The apparent absence of these chloride phases may simply reflect the fact that they are present in very low abundances and are distributed heterogeneously within the sample. Alternatively, the conditions of lunar fumarolic activity (gas composition and temperature) may have been outside the stability field for these chlorides. For example, these conditions may have favored the formation of Zn and Pb sulfides rather than chlorides. Textural evidence indicates Zn sulfide-bearing gas reacted with primary troilite to produce sphalerite.

Conclusions: Cl isotopes and the occurrence of volatile-bearing phases such as lawrencite strongly support a lunar origin for the volatile component in 66095 and A16 soils. The rusty rock itself may represent a portion of a lunar fumarole system that is analogous to ejecta blanket volatile transfer systems proposed by [18]. Other observations indicate some of the oxidation and perhaps the hydration is lunar in origin. As shown in pallasites by [17], the occurrence of stanfieldite indicates 66095 was partially oxidized on the Moon. The contrasting nano-scale morphology of the akaganéite compared to terrestrial alteration of lawrencite indicates that much of the akaganéite was not produced by terrestrial alteration of FeCl₂. The contrast between chloride assemblages in fumarole deposits represented by 66095 (FeCl₂) and pyroclastic deposits represented by Apollo 15 and 17 (NaCl) may reflect both gas composition and temperature of deposition.

References: [1]Garrison, J.R. and Taylor, L.A. (1980) In Proc. Conf. Lunar Highland Crust (ed. Papike and Merrill). 395-417. GCA Supp. 12, Lunar Planetary Institute, Houston. [2]Hunter, R.H. and Taylor, L.A. (1981a) Proc. 12th LPSC 253-259. [3]Hunter, R.H. and Taylor, L.A. (1981b) Proc. 12th LPSC 261-280. [4]Taylor, L.A. et al. (1974) *Geology* 2, 429-432. [5]El Goresy, A. et al. (1973) Proc. 4th LSC 733-750. [6]Taylor, L.A. et al. (1973) Proc. 4th LSC 829-839. [7]Freidman, I. et al. (1974) *Science* 185, 346-349.[8] Lunar Sample Compendium. <http://curator.jsc.nasa.gov/lunar/lsc/66095.pdf>. [9]Epstein, S. and Taylor, H.P. (1974) Proc. 5th Lunar Sci. Conf. 1839-1854. [10]Nunes, P.D. and Tatsumoto, M. (1973) *Science* 182, 916-920. [11]Allen, R.O. et al. (1973) Proc. 6th LSC 2271-2279. [12]Hughes, T.C. et al. (1973) *Lunar Sci. IV* 400-402. [13]Jovanovic, S. and Reed, G.W. (1981) Proc. 12th LPSC 2271-2279. [14]Krahenbuhl, U. et al. (1973) Proc. 4th LSC 1325-1348. [15]Sharp, Z.D. et al. (2010) *Science* 329, 1050-1053. [16] Shearer, C.K. et al. (2013) *Geochimica et Cosmochimica Acta*. In review. [17]Davis, A. M. and Olsen, J.E. (1991) *Nature* 353, 637-639. [18]McKay, D.S. et al. (1972) Proc. Lunar Sci. Conf. 3rd, 739-752.

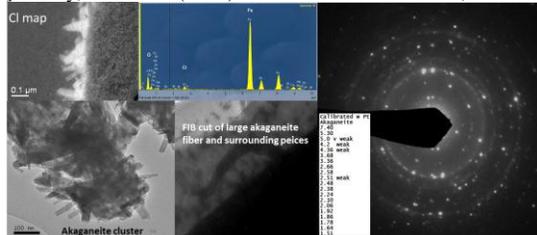


Figure 1. On the left are transmission electron microscope (TEM) images of akaganéite crystal clusters from a loose powder sample.

The lower left shows individual crystal fibers that appear somotoidal in shape. The upper left is a energy filtered TEM Cl map showing the presence of a Cl-rich phase (akaganéite) extending from a troilite surface (right) into a void (left). In the lower center is a TEM image of a FIB-prepared thin section (~50 nm thick). One large akaganéite fiber and surrounding smaller akaganéite grains were observed adjacent to Fe-Ni-metal interface. The energy dispersive X-ray spectrum (EDS) of this area is shown at the upper center. The spectrum is dominated by the intense Fe peak with minor Ni, Cl, O, and Zn (Cu peak is from the sample grid). The intensity of the O peak varies with the relative proportion of Fe-Ni metal and akaganéite in the section. At the right is the akaganéite electron diffraction ring pattern of the FIB section area shown at the lower center.

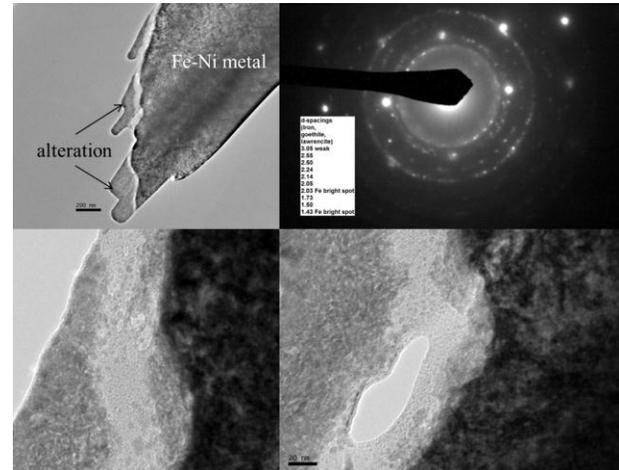


Figure 2. The top left diagram is a FIB prepared section of the grain boundary between Fe-Ni- metal and alteration. The electron diffraction and magnified TEM images illustrate that this alteration is fairly complex. The outer edge of the alteration consists of goethite, hematite and ferroxyhyte ($\delta\text{Fe}^{3+}\text{O}(\text{OH})$). The alteration zone immediately adjacent to the body-centered Fe-Ni metal (kamacite) consists of lawrencite, face-centered Fe-Ni metal (taenite) and possibly goethite. Taenite appears to have reacted more readily than kamacite.

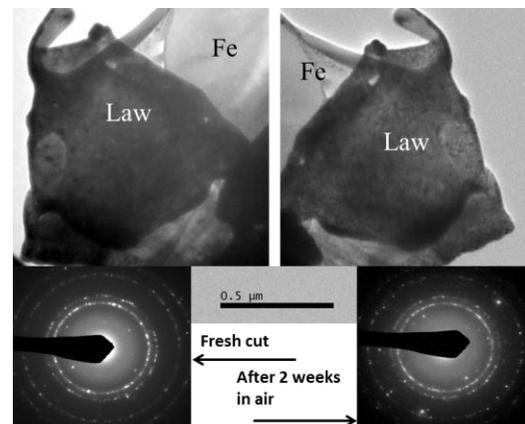


Figure 3. Upper images show bright field TEM images of the interface between lawrencite (Law) and fcc Fe-Ni metal (Fe) identified by EDS and electron diffraction (lower left and right images). After two weeks in air, nano-crystalline hematite and possibly goethite appear to be replacing lawrencite.