NANOMINERALOGY OF LUNAR ORANGE BEADS: DISCOVERY OF A ZINC-RICH MINERAL (PROBABLY GORDAITE), DERIVED FROM VOLCANIC VAPOR CONDENSATES ON THE MOON.

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Introduction: Nanomineralogy is the study of Earth and planetary materials at nanoscales, focused on characterizing nanofeatures (such as inclusions, exsolution, zonation, coatings, pores) in minerals and rocks, and revealing nanominerals and nanoparticles [1]. With advanced high-resolution analytical scanning electron microscopy, we are now capable to characterize geomaterials down to nanoscales easier and faster. Nanofeatures, new minerals and new occurrences of minerals with important geological significance at micron and nanoscales are being discovered [2,3].

During a nanomineralogy investigation of lunar orange beads in Apollo sample 74220, we identified a zinc chlorohydroxosulfate mineral, likely gordaite, with an empirical formula of $Na_{1.02}Zn_{3.98}[(SO_4)_{0.84}(OH)_{0.30}](OH)_6[Cl_{0.50}(OH)_{0.50}]\bullet nH_2O$, on the pristine surface of orange pyroclastic beads (Figs. 1-4) [4]. We characterized its composition, structure and petrography using field-emission scanning electron microscope (SEM), low-voltage X-ray energy-dispersive spectroscopy (EDS), electron backscatter diffraction (EBSD), and micro-Raman. Here, we present more data on this Zn-rich mineral and discuss its origin and implication for lunar science and future sample-return method.

Occurrence, chemistry, and crystallography: In Apollo sample 74220, this Zn-rich mineral occurs as single-crystal or cluster on the very surface of 15 orange beads out of 37 we examined (Figs. 1-4). Other minerals observed in the surface of orange beads, also underneath the Zn-rich phase, are dendritic Ti-rich pyroxene, native iron, and Ti-rich chromite at submicron to nanoscales (Figs. 2-4). Olivine was found in the surface of several beads.

The Zn-rich mineral occurs as euhedral, hexagonal or trigonal-shaped, platy crystals, ~ 1 to 6 μm in plate diameter and < 1 μm in thickness. Its composition (Table 1) by SEM-EDS gives rise to a normalized composition of ~59 wt% Zn, ~26 wt% O, ~6 wt % S, ~5 wt % Na, and ~4 wt % Cl, showing an empirical formula of $Na_{1.02}Zn_{3.98}[(SO_4)_{0.84}(OH)_{0.30}](OH)_6[Cl_{0.50}(OH)_{0.50}]\bullet nH_2O$, although the exact amounts of (OH) and H_2O are uncertain. It is a zinc chlorohydroxosulfate mineral, probably gordaite. The same Zn-rich crystals, examined ~15 months apart, show no visible physical and chemical changes. We attempted EBSD and micro-Raman but

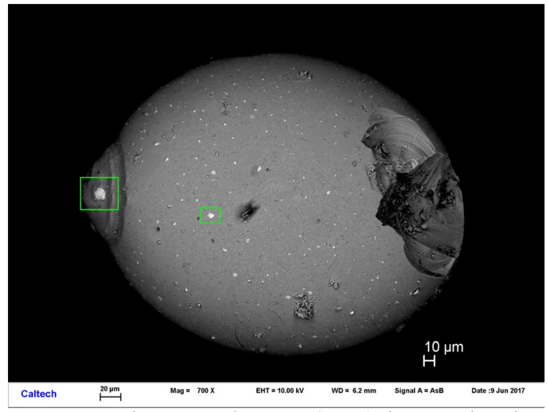


Fig. 1. Backscatter electron (BSE) image showing one orange bead with a Zn-rich mineral. Rectangles outline regions shown in Figs. 2-3.

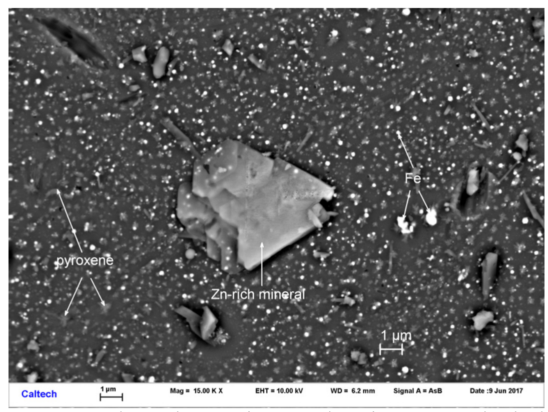


Fig. 2. Enlarged BSE image showing one euhedral crystal of the Zn-rich mineral on the bead surface.

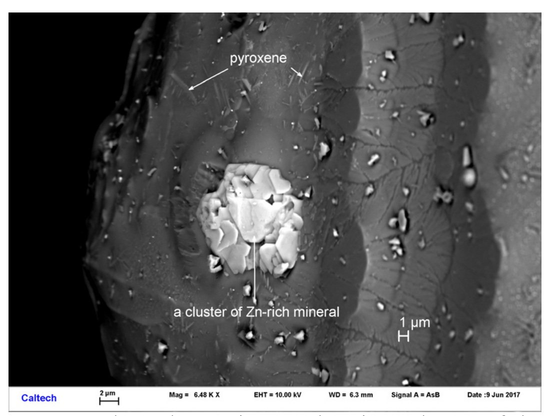


Fig. 3. Enlarged BSE image showing a luster of the Zn-rich mineral on the bead surface.

were unable to acquire structural information on the Zn phase due to electron or laser beam damage.

Origin and significance: This Zn-rich phase is the first observation of a host mineral for Zn, S, Cl, and Na on the surface of orange beads from Apollo 17 soil 74220. The 74220 sample used in this study is pristine and was only exposed directly to air for a cumulative period of 16 days before our study. We observed the Zn-rich phase in the first SEM session, excluding the possibility that the zinc phase is terrestrial contamination.

This zinc-rich mineral likely formed through rapid alteration (oxidation and hydration) by terrestrial air of the original vapor-deposited Zn, Cl, S, and Na-bearing solids [4], likely via the following reaction:

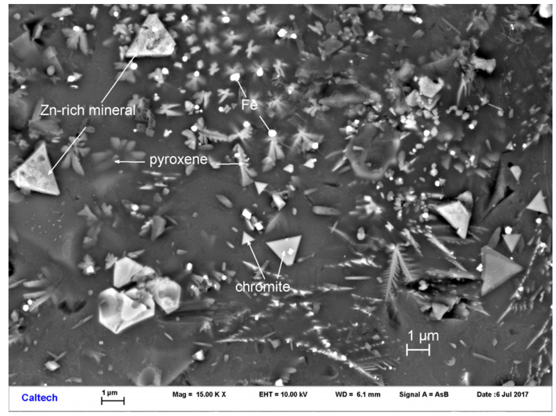
$$3.73Zn+0.84S + 0.25ZnCl_2 + 1.02Na + (3.4+n)\ H_2O+3.38O_2 = Na_{1.02}Zn_{3.98}[(SO_4)_{0.84}(OH)_{0.30}](OH)_6[Cl_{0.50}(OH)_{0.50}]\bullet nH_2O.$$

The composition of the zinc-rich mineral indicates that the vapor condensates consist of metallic Zn and metallic Na with either ZnS or native S or Na_2S, and either $ZnCl_2$ or NaCl. This is the first direct evidence that metallic Zn and Na are key components in the vapor condensates of lunar volcanic gas, which implies compositions and pressures of lunar volcanic gas are different from previous thoughts [4].

Results from this study are also highly relevant to collection, handling, and curation of returned samples from other planetary bodies. The rapid alteration of vapor condensates on the surface of 74220 beads with terrestrial atmosphere indicates that samples need to be kept in the state they are collected in (e.g., in vacuum for the Moon and asteroids, or similar atmosphere they are collected on Mars) [4]. Investigations of surface mineralogy, chemistry, and reactivity need to be performed as soon as sample containers are open to terrestrial air. Moreover, samples stored for future analysis need to be kept in an environment similar to their host bodies. To fully resolve the solid species in the vapor condensates, we will need to study pristine samples sealed under vacuum since their collection on the Moon.

Nanomineralogy of Apollo samples is leading to exciting discoveries. We plan to study green beads next.

References: [1] Ma C. (2008) Eos Trans. AGU 89th, Abstract MR12A-01. [2] Ma C. (2015) Microscopy and Microanalysis 21(S3):2353-2354. [3] Ma C. (2018) *American Mineralogist* 103:1521-1522. [4] Ma C. and Liu Y. (2019) *American Mineralogist* 104: in press.



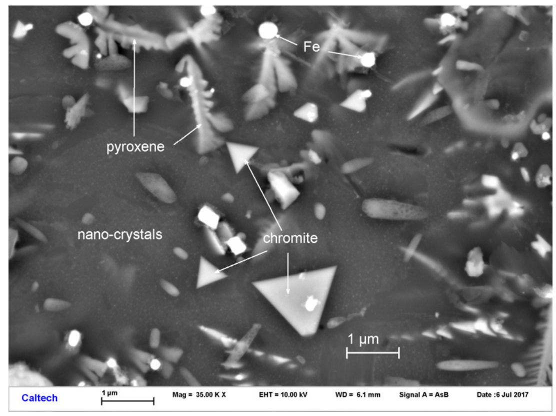


Fig. 4. BSE images showing the Zn-rich mineral on the surface of one other orange bead, where pyroxene, native Fe and chromite occur on and near the surface.

Table 1. Normalized EDS composition for the Zr-rich mineral, from [4].

Element	wt%	atom%
O calculated	*26*	*53*
Zn	58.3 ± 0.3	29.1
Na	5.2 ± 0.2	7.5
Mg	0.4 ± 0.1	0.6
S	6.1 ± 0.1	6.2
Cl	4.0 ± 0.1	3.7