NANOMINERALOGY OF LUNAR BEADS: DISCOVERY OF ZINC SULFIDE (ZnS) NANOCRYSTALS ON A YELLOW BEAD FRAGMENT, CONDENSED FROM VOLCANIC VAPORS 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 are being discovered at nanoscales [2,3].

During our ongoing nanomineralogy investigation of lunar pyroclastic beads (green, orange and yellow) in Apollo regolith samples, we have identified new phases derived from volcanic condensates, including a zinc chlorohydroxosulfate mineral and a Na-K-sulfate on orange beads in Apollo 74220 [4,5] and possible Zn-S deposits on green beads in Apollo 15366 [6]. Here, we present the discovery of nano-sized zinc sulfide (ZnS) condensate on the pristine surface of a yellow bead fragment from Apollo sample 15426 (Figs. 1-4) and discuss its origin and significance for lunar science research. We characterized its composition, structure and texture using field-emission scanning electron microscope (SEM) with low-voltage X-ray energy-dispersive spectroscopy (EDS) and electron back-scatter diffraction (EBSD).

Occurrence, chemistry, and crystallography: We observed that a thin layer of zinc sulfide (ZnS) nanocrystals fully covers the surface of a yellow bead fragment, over both the darker and brighter regions (Figs. 1-4). Native iron is scattered on the surface at nanoscales, underneath the ZnS layer. Dendritic pyroxene, chromite, and olivine, which are common on the orange beads [4], are not found on this yellow bead. The zinc chlorohydroxosulfate mineral and Na-K-sulfate are also absent on this yellow bead fragment.

The ZnS phase occurs as more-or-less spherical crystals, ~ 30 to 50 nm in diameter (Fig. 4). Its composition by SEM-EDS at low-voltages gives rise to a formula of ~ZnS.

We have attempted EBSD but were unable to acquire structural information on the ZnS due to its small size. This ZnS phase with a spherical shape does not show any hexagonal feature so it is most likely sphalerite with a cubic structure. ZnS with a hexagonal structure is wurtzite.

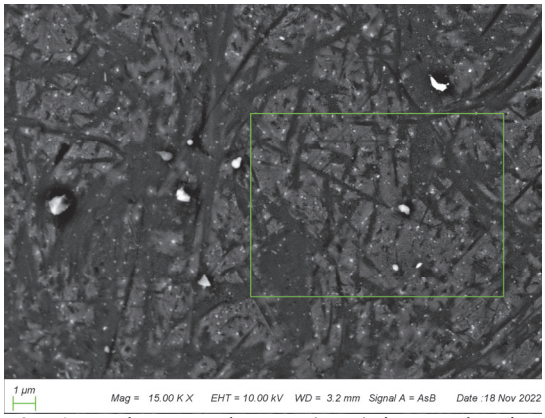

Fig. 1. Backscatter electron (BSE) image showing the surface of a yellow bead fragment from Apollo 15426. Rectangle outlines region shown in Fig. 2.

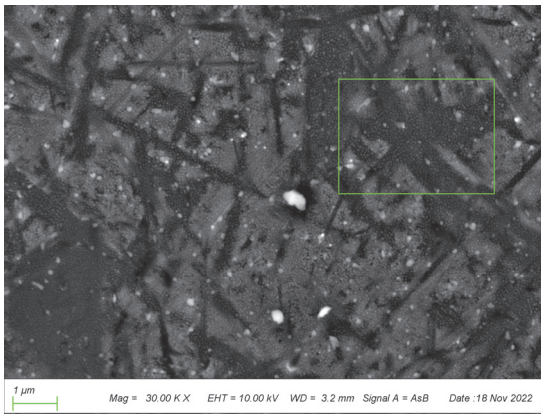

Fig. 2. Enlarged BSE image showing a layer of ZnS nanocrystals on the bead surface. Rectangle outlines region shown in Fig. 3

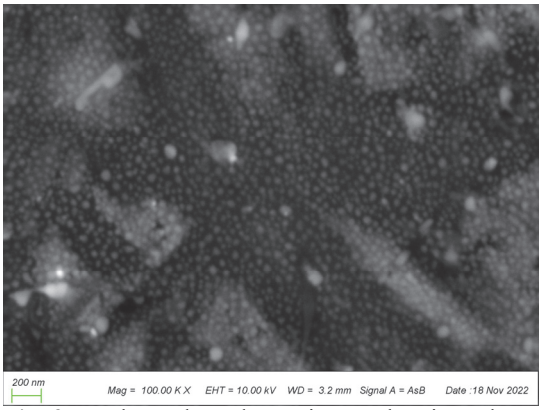

Fig. 3. Further enlarged BSE image showing a layer of ZnS nanocrystals on the bead surface.

The interior of this yellow bead contains 4.8 wt.% TiO_2, in contrast to <0.5 wt.% TiO_2 in Apollo 15 green glass beads from the same Apollo sample. Apollo 15 yellow beads fall in the low-Ti basalt classification of lunar mare basalts. In comparison with vapor condensates on other beads, our measurements of yellow beads are still in progress. In addition to this yellow bead fragment, we have studied one more yellow bead, which does not contain ZnS nanocrystals. Additional studies are planned to determine the frequency of its occurrence.

The spherical ZnS nanocrystal on the yellow bead fragment is absent on Apollo 15 green beads (Fig. 5). Rather the Zn-S deposit, with a molar Zn/S ≈ 1, on Apollo 15366 green beads [6] is more angular. [6] estimated the grain sizes are also <50 nm but cannot confirm the presence of Zn-sulfide crystals. A previous study of a green bead from Apollo 15 soil 15401 also reported Zn-S materials of similar size but irregular shape [7].

Such ZnS nanocrystals have not been observed on the surface of lunar Apollo 74220 orange beads [4-5]. Rather, on the orange beads, Zn was deposited as metallic Zn with small amounts of metallic Na or Na_2S or NaCl, and ZnS or $ZnCl_2$ [4]. Where it is present, we observed that $(Na,K)_2S$ was deposited before the Zn metal [5].

Origin and significance: This ZnS phase is direct evidence of condensation from vapors during the volcanic eruption that formed the yellow and green beads on the Moon. Such a finding is consistent with the thermochemical modeling in [8], suggesting the volcanic gases in these eruptions may have similar properties as those used in [8]. However, the vapor deposits on orange beads differ from the model in [8] or those formed in experiments in [9]. Based on the superposition relationship of the condensates, we proposed that S in volcanic gas of the orange bead eruption was depleted by the formation of $(Na,K)_2S$ [5]. Additionally, current model [8] and starting gas compositions in [9] did not include Na and K and overestimated $Cl_{(g)}$.

The different vapor condensates between green, yellow, and orange beads could reflect some fundamental differences in their gas properties. Although Na-K condensates are yet to be located on green beads, in-gassing of Na, K, Cu and Zn is present for both green and orange beads [10-11]. Potential causes could be gas pressure and gas chemistry between different eruptions. Further studies will help to distinguish different causes. Our ongoing nanomineralogy investigation of lunar samples has revealed exciting discoveries. These studies together with recent discoveries of in-gassing of moderately volatile elements (Na, K, Zn, Cu) [10,11] are reshaping our understanding of the lunar volcanic gas. We are going to examine more Apollo samples.

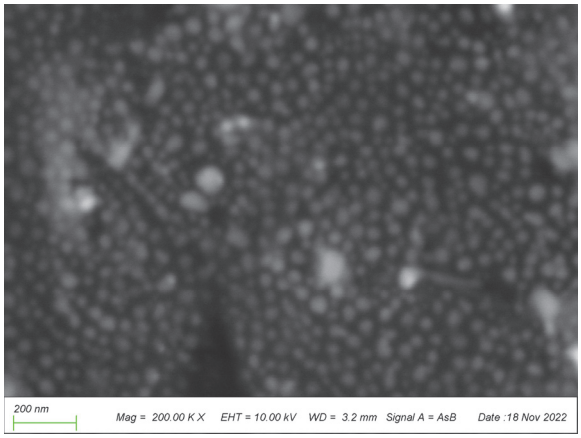

Fig. 4. High-magnification BSE image showing ZnS nanocrystals on the surface of the yellow bead.

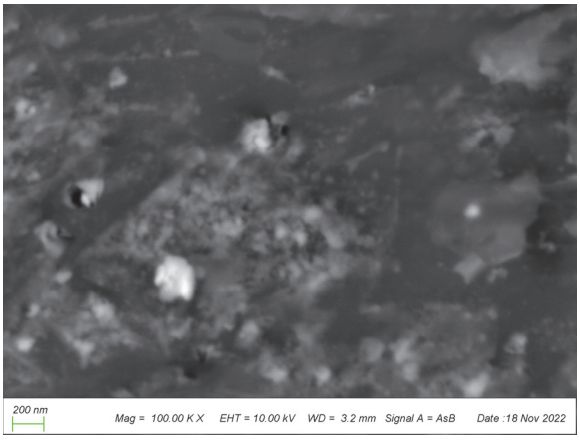

Fig. 5. BSE image showing the surface of a green bead from the same Apollo sample 15426. ZnS nanocrystals are not observed here.

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