DISCOVERY OF LUNAR HALITE NANOCRYSTALS ON THE SURFACE OF A BLACK BEAD FROM APOLLO 73001, 226. Yang Liu[1] and Chi Ma[2], [1]Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, USA (yang.liu@jpl.nasa.gov); [2]Division of Geology and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, USA (chima@caltech.edu).

Introduction: Apollo sample 73001 in its original drive tube was placed in a secondary stainless-steel tube that had a metal knife edge seal (known as a core sample vacuum container, CSVC). The tube in this CSVC was sealed on the Moon and had remained unopened until gas extraction, XCT, and then extrusion/dissection in March of 2022 [1]. After opening, Apollo 73001 always resided in clean environment in dry N_2 gas. Thus, Apollo 73001 among all available Apollo samples has the shortest residence time in a terrestrial environment. Here, we report the discovery of numerous NaCl nanocrystals on the surface of one black bead.

Sample and Methods: We examined black beads (subsample 681, 1 mg) from 73001, 227, which are loose pieces broken off the parent sample, 73001, 226, a black bead clod, identified by Computed X-ray Topography [2].

The subsample 681, was allocated inside an unsealed Teflon bag, which was placed inside a metal container covered with a Teflon cap. The capped stainless container was then sealed in N_2 gas in two Teflon bags. These bags maintain positive pressure until cut open in the lab. It took ~30 minutes from opening the bags to placing the sample mount in a carbon coater, which was vacuumed to ~$4x10^{-4}$ torr. After carbon coating, the reaction of bead surface with terrestrial air significantly slowed.

We placed 5 full beads, 4 partial beads, and 1 angular fragment on a piece of carbon tape. All beads have visible, original outside surface. The diameters of the full beads range from 70 µm to 184 µm. After carbon coating, the samples were immediately characterized using a ZEISS 1550VP field emission scanning electron microscope (FE-SEM). About 7 hours later, we re-examined the same features observed in the first SEM session and observed no changes. Minerals and glass on this black bead were analyzed with an Oxford X-Max 80 mm^2 SDD Energy Dispersive Spectrometer (EDS) system attached to the SEM and the chemistry was obtained with an XPP correction procedure calibrated using Oxford factory internal standards. Variable excitation voltages were used to constrain contamination in the EDS analysis by other phases underneath nanocrystals.

Results: Black beads from 73001, 226 are mostly devitrified as shown by the crystallinity in the interior exposed on the fracture surface.

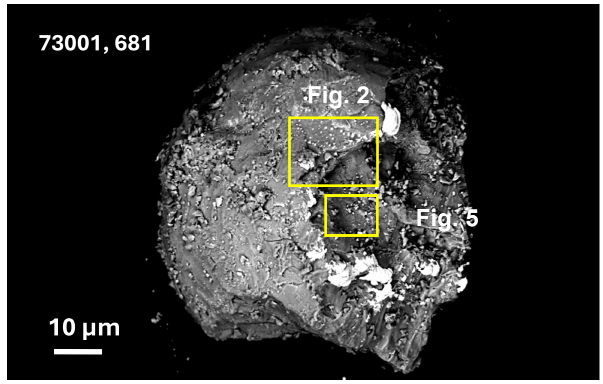

Fig. 1. Back Scattered Electron (BSE) image showing the NaCl-bearing black bead from clod 73001,227/226.

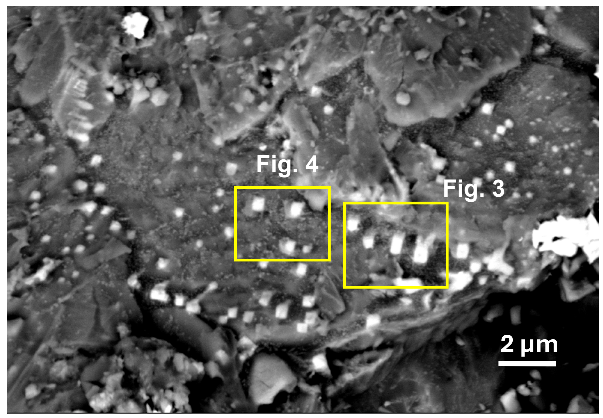

Fig. 2. BSE image of the depression area containing NaCl. Boxes show locations of Figs. 3 and 4. Bright cubic grains are ilmenite ($FeTiO_3$).

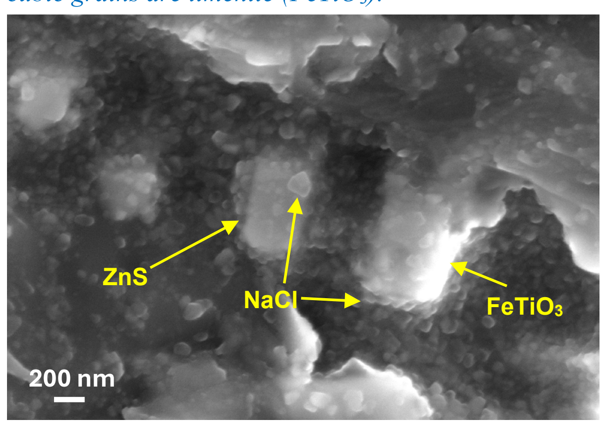

Fig. 3. Secondary electron (SE) image showing NaCl lying on top of ZnS, which covers ilmenite grains and then surface of the bead.

We observed occurrence of NaCl (most likely halite) only on one small bead of 70 µm diameter (Fig. 1).

Halite nanocrystals occur mainly in a depression on the original surface (Fig. 2). Some halite nanocrystals are present on the broken surface immediately below the depression (Fig. 1) but appear in fewer numbers than in the depression. The halite grains range from ~30 nm to 100 nm in size and sit on top of ZnS (Figs. 3-4). Underneath the ZnS, part of the depression also contains euhedral ilmenite grains of ~500 nm size (Fig. 2). All black beads from 73001, 226 contain a coating made of ZnS of 30-50 nm sizes.

Halite has only been found rarely in lunar samples, only on three beads out of 400 ones studied by [3]. Halite nanocrystals, also occurring on the depression on a black bead from drill core 74002, are larger than those observed in this study, ranging from 100-300 nm [3]. Other deposits on the same 74002 bead include an unidentified S-rich feature with minor amounts of Na and K. Clanton et al. [3] interpreted NaCl formed through volcanic vapor deposits.

Discussion

Lunar origin of halite: Sample 73001 has never been processed using water or other liquid, thus eliminating the possibility that halite formed through lab-liquid-solid reaction. Thus, halite on the 73001, 226 black bead formed on the Moon.

Formation of halite: We question that halite was deposited by the volcanic gas powered the eruption of black beads in the 73001, 226 clod. Deposition/condensation from volcanic gas, i.e., solid directly formed from the gas phase is not a selective process, it coats any surfaces. This is supported from our studies of 74220 orange beads or the 15426/15366 green glass clods [4-7]. In contrast, halite is rare and has only occurred in depressions on black beads ([3] and this study). Previous studies of orange and green beads showed that lunar volcanic gas in these eruptions are Cl poor [4,5] so Na bonded with S during the gas deposition on orange beads [5]. The 73001, 226 black bead and 74002 black beads are similar to 74220 orange beads in TiO_2 contents, implying they likely formed by the same eruption [8]. Therefore, the lack of wide-spread NaCl on the surface of black and orange beads indicates halite is less likely a direct product from the volcanic gas erupting with these beads.

Although 73001, 226 is a clod like green bead clods, the lack of NaCl on green beads suggests the formation of halite may be unique to black beads. Black beads are crystallized, suggesting a slower cooling rate than orange beads [8,9], likely due to burial by hot pyroclastics near the vent [8]. The confinement of NaCl on surface depressions indicates topography control in its formation, possibly through post-deposition processes. One possibility is fumarolic activity from outgassing magma underneath the pyroclastic deposit. Another possibility is impact-induced remobilization of Cl and fumarolic processes. Similar processes were proposed for $FeCl_2$ formation in lunar regolith breccia (Rusty Rock, 66095) based on Zn and Cu isotopes [10]. 73001 clod is also a loosely consolidated regolith breccia.

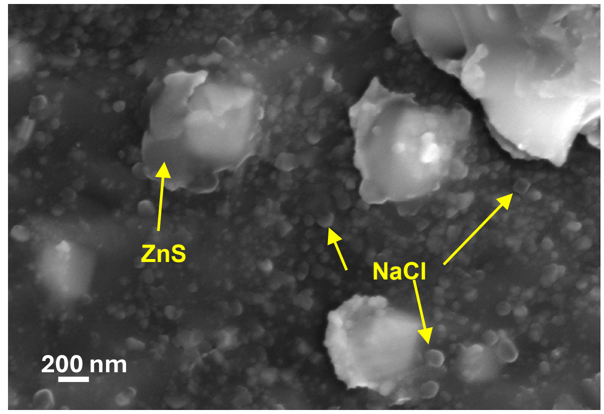

Fig. 4. SE image showing NaCl grains above ZnS coating in another location of the NaCl-containing area of the original bead surface of the bead in Fig. 1.

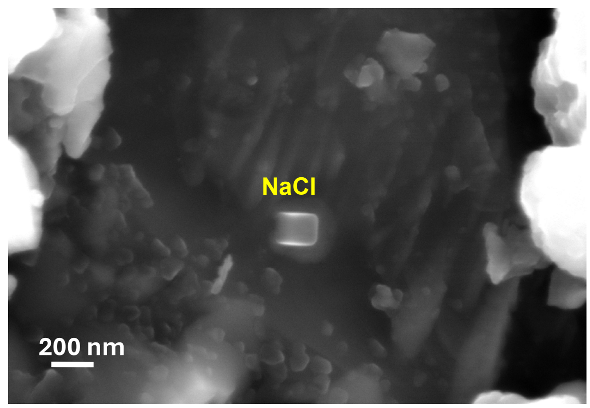

Fig. 5. SE image showing a well-formed NaCl crystal on the broken surface of the bead in Fig. 1.

Summary: Our discovery of lunar halite nanocrystals on a black bead shows additional volatile movement on the surface of the Moon, possibly unique to black beads.

References: [1] Gross, J., et al. (2023) Preliminary Catalog for Double Drive Tube Samples 73001 and 73002. https://curator.jsc.nasa.gov/lunar/angsa_catalog.cfm. [2] Shearer, C.K. et al. (2023) *54th LPSC*, 1773. [3] Clanton, U.S. et al. (1978) *LPSC., 9th*, 1945-1957. [4] Ma, C. & Liu, Y. (2019) *Am. Min., 104*, 447-452. [5] Liu, Y. & Ma, C. (2022) *Icarus*, *382*, 115044. [6] Ma, C.& Liu, Y. (2023) *54th LPSC*, 1420. [7] Ma, C.& Liu, Y. (2024) 55th LPSC, #1347. [8] Weitz, C.M. et al. (1999) *MAPs, 34*, 527-540. [9] Arndt, J. & von Engelhardt, W. (1987) *JGR, 92,* E372-E376. [10] Day, J.M.D. et al. (2019) *GCA*, *266*, 131-143.