

DISCOVERY OF A Na-K-SULFATE ON APOLLO 74220 ORANGE BEADS: DIRECT EVIDENCE OF VOLCANIC OUTGASSING OF Na AND K ON THE MOON. Yang Liu¹ and Chi Ma², ¹Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, USA (yang.liu@jpl.nasa.gov), ²Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, USA.

Introduction: Lunar volcanic beads offer the best opportunities to study volcanic degassing on the Moon, given that they are rapidly quenched from the melt that experienced the least differentiation from the primitive melt. Despite the well-known fact that moderately volatile elements (MVEs) are enriched on the surface of volcanic beads [1], condensed mineral species of MVEs have never been revealed until recently [2]. Our previous study reported a zinc chlorohydroxosulfate, containing condensed Zn, Na, S, and Cl in decreasing abundances [2]. We showed that the ratios between Zn/Na/S/Cl can be used to constrain the condensate chemistry and to infer the volcanic gas conditions. Here, we report a new discovery of Na-K-sulfate that is made of condensed Na, K, and S on the surface of Apollo 74220 orange beads [3].

Methods: Samples in this study are the same as in Ma and Liu [2]. Three different mounts of 87 beads, 2 soil grains, and 4 rock/mineral fragments were prepared without any fluids from a pristine allocation of Apollo 74220 sample [2]. These mounts were examined using a Zeiss 1550 VP field emission (FE)-SEM and elemental compositions were semi-quantitatively determined with an Oxford X-Max SDD Energy Dispersive Spectrometer (EDS) system. Secondary electron (SE) imaging, backscattered electron (BSE) imaging, and EDS analyses were conducted in high vacuum mode at different voltages (15 kV, 10 kV, 7 kV, and 6 kV) in 2017, 2018, 2019, and 2020, respectively. After counting sample preparation in our lab together with the time the samples spent in the lunar module and the receiving ship, we estimated that samples studied in our first SEM session in [2] were directly exposed to air (pure O₂ and the terrestrial atmosphere) for less than 18 days.

Results: A Na-phase was observed in our first SEM session in 2017 (Fig. 1). The Na-phase remains unchanged after the sample was exposed to air for more than three years. The Na-phase occurs in a high number density as discrete laths or rods with a width of <0.4 μm and a length <3 μm (e.g., Fig. 1). About 80% of the beads studied contains the Na-phase, whereas the surfaces of the agglutinate and broken mineral grains do not contain this phase. In comparison, previously reported zinc chlorohydroxosulfate only occurs on the surface of ~50% of the beads studied, typically as a few equant, larger, hexagonal, or trigonal grains [2] (Fig. 1). On several occasions that both phases are in contact with each other, the Na-phase lies beneath the

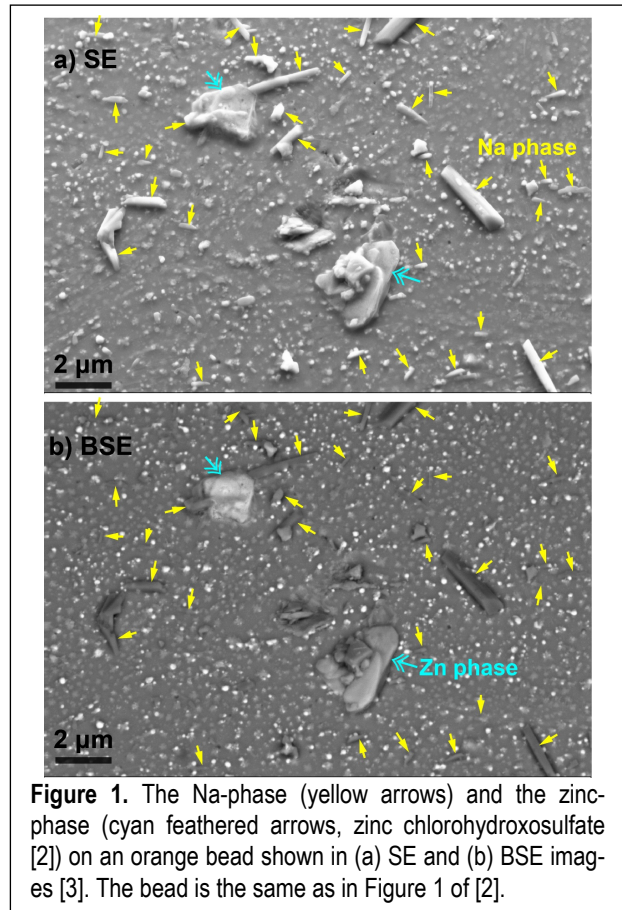


Figure 1. The Na-phase (yellow arrows) and the zinc-phase (cyan feathered arrows, zinc chlorohydroxosulfate [2]) on an orange bead shown in (a) SE and (b) BSE images [3]. The bead is the same as in Figure 1 of [2].

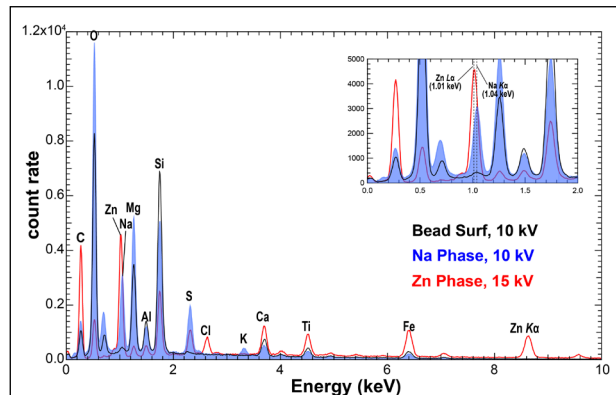


Figure 2. EDS spectra of the Na-phase (filled spectrum), the Zn-phase (red line), and orange bead (black line). Note that the Zn La (1.01 keV) and Na Ka (1.04 keV) are distinctive between two phases (the inset).

zinc chlorohydroxosulfate (Fig. 1), suggesting that the Na-phase formed before the zinc chlorohydroxosulfate.

The Na-phase contains no detectable Zn and Cl, but has distinctively higher Na, K, and S than the Na-phase-free surface (Fig. 2), with Na₂O, K₂O, and SO₃ up to 17.0 wt.%, 6.86 wt.%, and 39.9 wt.% in individual EDS analyses, respectively. Owing to the small sizes of the Na-phase, EDS analyses contain interference from the underlying glass. Based on anti-correlations of Na, K, and S with Si using data obtained at 7 kV, the molar composition of the pure Na-phase is 19 mol% Na, 5 mol% K, 16 mol% S with the rest being O. This composition indicates that the Na-phase is a sulfate with oxide contents as ~28 wt.% Na₂O, 11 wt.% K₂O, and 61 wt.% SO₃. Although the composition and morphology resemble mineral ivsite [Na₃H(SO₄)₂], given the lack of definitive structure identification, we refer to the Na-phase as Na-K-sulfate in the following text.

Discussion: We exclude the possibility of the Na-K-sulfate being terrestrial contamination because the sample is pristine and has never come in contact with terrestrial Na-sulfates during sample transport and handling. Moreover, the Na-K-sulfate is unlikely to be directly condensed from lunar volcanic gas. Although Na-sulfates occur in terrestrial fumaroles [4], the solid condensates are expected to be metal-sulfides given the reduced nature of lunar volcanic gas (H_{2(g)}, S_{2(g)}, H₂S_(g), and COS_(g)) [5, 6].

Because Apollo sample 74220 was not sealed in the vacuum, the original condensates (sulfides or native species) are highly reactive and can be easily altered during their exposure to pure O₂ in the lunar module, the terrestrial air (O₂ and H₂O) on the retrieval ship, and the trace quantity of other gases in N₂ in curation for the last 50 years [2]. However, since fluids were not used in sample preparation we expect the alteration by air occurred *in situ* without modification of the chemistry of the original condensates. Therefore, *the molar ratios of Na, K, and S in the Na-K-sulfate (~2.4:~0.6:2) represent that of the original condensates*, which further implies the condensates contain mixed Na₂S, K₂S, and S.

Reexamination of green beads from Apollo 15 green glass clods is ongoing. Our preliminary results [7] and that by Ross et al. [8] showed that green beads also contain Zn-S condensates of a much smaller size and a lesser density than those on orange beads. The Na-K-condensates were not observed in this study; they might be present but below the limit of detection for SEM-EDS.

The difference between green and orange beads likely reflects different abundances of Na, K, Zn, and S in the source melts. The 74220 source melt contains higher abundances of H₂O, S, Zn, Na, K, and incompatible elements than the source melt of Apollo 15 green beads [1, 9-11]. Therefore, volatiles in the 74220

source melt can reach solubility limits at deeper depths than those in Apollo 15 green beads, which implies 74220 parent melt has lost more volatiles than Apollo 15 green beads. In addition, the lower abundances and a shallower degassing of volatiles in Apollo green beads indicate that the volcanic gas may not contain the pressure and abundances of the gas species needed to condense abundant Na-K-S and Zn-Na-S-Cl phases. This explanation is supported by the estimated, lower H₂O/Ce ratio of the 74220 source melt, which indicated more degassing of 74220 melt [11, 12].

Implications: Discovery of Na and K in volcanic vapor condensates shows that K was actively outgassed with H, F, Cl, S, Na, and Zn during the pyroclastic eruption that formed the orange beads. This finding suggests that enriched K isotopes in lunar rocks do not require conditions only available in the giant impact [13] but can be adequately explained by their source rocks experienced degassing in the lunar magma ocean.

Direct observation of vapor condensates offers insights on mechanisms of volatile degassing from lunar magma. The lack of Na, K, and Zn chlorides on the surface of beads suggests these elements are not outgassed from lunar magma in the form of metal-chlorides as implied by isotope studies [14, 15]. Rather, our results support that Na, K, and Zn devolatilized in their native states (Na_(g), K_(g), Zn_(g)) through dissociation of metal-oxygen bonds, which is consistent with the thermodynamic models [5, 16, 17]. Once in the gas, Na_(g) and K_(g) subsequently reacted with the S gas species (H₂S_(g), S_{2(g)}) to form Na₂S and K₂S. In contrast, Zn_(g) condensed dominantly as Zn_(s) [2], which differs from ZnS_(s) predicted by the thermochemical model [5]. Based on the textural relationship that Na-K-S deposited before Zn-Na-S-Cl, a likely explanation is that the condensation of Na-K-S depleted S in the gas thus leaving insufficient S to form ZnS.

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