Direct evidence of volcanic outgassing of Na and K on the Moon from Apollo orange beads

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ABSTRACT

We report the first discovery of a pervasive Na-K-sulfate formed from vapor condensed Na-K-S on the surface of Apollo 74220 orange beads. The molar (Na + K)/S values (A) of different grains range between 1.3 and 2.3, indicating that the original condensates comprise Na-K-sulfides with possible excess native S (for A < 2) or excess Na and K (for A > 2). Together with the previous report of the Zn-Na-S-Cl condensates that contain mostly metallic Zn, our observations show that Na A and K B condense as sulfides before Zn A condenses in its native state. Both thermochemical calculations of lunar volcanic gas and direct observations are inconsistent with the common assumption that moderately volatile elements vaporize and condense as chlorides. The textural relationship of Na-K-S condensates underlying Zn-Na-S-Cl condensates suggests Na-K-S was deposited before Zn-Na-S-Cl, which depleted sulfur from volcanic gas and inhibited the formation of ZnS. These forms of condensates require the volcanic gas that carried 74220 orange beads to be highly reducing (made of mostly H2) with a sufficient partial pressure of S2(g) or H2S(g) to enable interactions between Na and K with S.

1. Introduction

Lunar volcanic beads are the best samples to study volatile loss mechanisms during lunar magmatic activities. These beads are products of volcanic eruptions at 3.3 to 3.6 Ga (Taylor et al., 1991). Chemistry of these beads shows that their parent melts only experienced a small degree of fractional crystallization after forming in the mantle at a depth of 300 km or deeper (Taylor et al., 1991). Parent melts of beads contain abundant volatiles (Saal et al., 2008; Hauri et al., 2011). Although it was suggested that pyroclastic beads were derived from the localized water-rich mantle (Paniello et al., 2012; Albarède et al., 2015), additional studies of melt inclusions in mare basalts showed that enrichment of volatiles in the mantle sources is not unique to pyroclastic beads, the parent melts of pyroclastic beads are less outgassed than those of mare basalts (Chen et al., 2015; Ni et al., 2019; Saal and Hauri, 2021). It is well known that the surfaces of rapidly quenched beads contain enriched moderately volatile elements (MVEs) (Meyer Jr. et al., 1975) with the MVEs traditionally defined under conditions for the Solar Nebula gas (Lodders, 2003; additional discussion in the Supplementary Materials). Recent models show the condensed species of MVEs are closely related to chemical compositions (gas species of H, C, S, and MVEs) and physical conditions (pressure and oxygen fugacity) of the volcanic gas (e.g., Renggli et al., 2017; Zolotov and Liu, 2021). Therefore, the condensed species of MVEs on the surface of volcanic beads can be used to understand the gas species of MVEs and physical conditions of the gas (Ma and Liu, 2019a). However, despite the considerable effort to study the coatings on the outer portions of volcanic beads from 1973 to 1993 (McKay et al., 1973; Heiken and McKay, 1974; Heiken et al., 1974; Chou et al., 1975; Meyer Jr. et al., 1975; Butler Jr. and Meyer Jr., 1976; Goldberg et al., 1976; Tera and Wasserburg, 1976; Wasson et al., 1976; Butler Jr., 1978; Cirilin et al., 1978; Clanton et al., 1978; Cirilin and Housley, 1979; McKay and Wentworth, 1992), how the MVEs condense from the gas had remained largely undiscovered except for one report of NaCl on a bead from soil 74002 (Clanton et al., 1978). With modern technology, Ross et al. (2011) reported Zn-S, Zn, and S on the surface of a green bead from soil 15401. In 2019, we reported a zinc chlorohydroxosulfate that was formed from condensed Zn-Na-S-Cl phases on the surface of 74220 orange beads (Ma and Liu, 2019a). The chemistry of the Zn-Na-S-Cl mixture was used to show that Zn and Na degassed as Zn A and Na B, which subsequently condensed mainly in their native states with minor amounts of Zn- and Na-sulfides or chlorides. As discussed in Ma and Liu (2019a), this finding differs from the results of the...
thermochemical model of a C-H-O-S gas with minor F, Cl, Zn, Cu, other metal volatiles by Renggli et al. (2017), where \( \text{ZnS}_2 \) is the dominant solid species for \( \text{ZnS}_2 \). For this discrepancy, Ma and Liu (2019a) proposed possible causes are higher gas pressures, different gas compositions, and decoupled degassing of Zn, Na, and S (Ma and Liu, 2019a).

Here, we report the discovery of a second condensate-derived phase, Na-K-sulfate, during our examination of 74220 orange beads. This new discovery reveals direct evidence of volcanic outgassing of Na and K, helps to explain the aforementioned discrepancy, and provides further insights on the volcanic gas associated with the 74220 eruption.

2. Materials and methods

The 74220 orange beads used in this study are the same as those in Ma and Liu (2019a), which were prepared without any fluid treatment. A detailed history of the sample was presented in Ma and Liu (2019a) and a brief summary is included here. The sample was collected and stored in unsealed sample bags. After collection, the sample bags hosting Apollo 17 soil 74220 were directly exposed to 5–7 days of nearly pure \( \text{O}_2 \) atmosphere in the lunar module and to ~2 days of filtered air before being processed in the Lunar Receiving Laboratory. From the allocated pristine sample, about 87 orange beads (54 with visible outer surfaces, 45 were examined), two soil grains (one aggregate), and four rock/mineral fragments were handpicked in a clean lab in 2017, 2018, 2019, and 2020. The elemental compositions of secondary electron (SE) and backscattered electron (BSE) modes in high vacuum were obtained with an XPP correction procedure calibrated with Oxford factory internal standards (albite-Na, feldspar-K, FeS) and our first Scanning Electron Microscope (SEM) session in 2017, the sample was exposed to Pasadena air for ~9 days. Combining the time the samples were exposed in the lunar module and the receiving ship, samples used in our first SEM session were directly exposed to air (pure \( \text{O}_2 \) and the terrestrial air) for less than 18 days (Ma and Liu, 2019a).

A ZEISS 1550VP field-emission SEM was used for surface imaging and elemental analyses. Surfaces of samples were imaged using secondary electron (SE) and backscattered electron (BSE) modes in high vacuum in 2017, 2018, 2019, and 2020. The elemental compositions of the Na-phase and the surface of beads were measured with an Oxford X-Max SDD Energy Dispersive Spectrometer (EDS) system attached to the SEM and obtained with an XPP correction procedure calibrated with Oxford factory internal standards (albite-Na, feldspar-K, FeS, wollastonite-Ca, SiO\(_2\)-Si, MgO-Mg, Al\(_2\)O\(_3\)-Al, pure metals for Ti, Cr, Mn, Fe and Zn). To evaluate the XPP correction procedure of the SEM-EDS, several electron probe standards (anhydrite, anorthite, fayalite, basaltic glasses) were analyzed with the EDS system at 15 kV and 10 kV, respectively. Results show excellent agreement for most elements except that FeO displays 15–18% relative differences at 10 kV (Fig. S8). An accelerating voltage of 15 kV was used to evaluate the presence of heavier elements such as Zn or Cu. The interior glass and the surface of beads were analyzed at a 10 kV voltage. The Na-phase and nearby regions were analyzed under 10 kV and 7 kV voltages, respectively. The chemistry of the Na-phase was derived from EDS data at 7 kV since the interference from the underlying glass at this voltage is relatively small.

We obtained a more quantitative analysis of the Na-phase and the surface of beads, using a JEOL JXA-8200 electron probe micro-analyzer (EPMA). Although these beads were not polished, the top of spherical beads has a small curvature and thus the area under the electron beam is nearly flat with respect to the source and Wavelength Dispersive Spectrometers in the EPMA. We performed such analyses of carbon-coated SEM stubs in two sessions. In the first session, Na, Mg, Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, and Zn were measured on the surfaces of two orange beads from 742220 Stub 1 at 15 kV and 10 nA with a focused beam. The excitation volume of X-ray generation by the electron beam at 15 kV was ~3 μm in diameter, estimated using the Casino (version 2.42) Monte Carlo simulation of electron trajectory (Drouin et al., 2007). We located a large Na-phase (~0.7 μm wide and ~6 μm long) on an orange bead from 742220 Stub 2 (Fig. S10) and positioned the beam so that the Na-phase lies on the top of the bead. In the second session, we analyzed this Na-phase grain and nearby surface, and the same two orange beads from 742220 Stub 1, using a focused beam of 10 kV and 5 nA, which excited X-rays on a sample to ~1.5 μm depth. Na, Mg, Al, Si, S, K, Ca, Ti, Cr, Mn, and Fe were measured, except for Zn owing to its low abundances in the Na-K-sulfate. A Faraday cup was used to measure beam current. For calibration, natural and synthetic standards are used, including microcline (K\(_2\)O), albite (Na\(_2\)O), forsterite (Mg\(_2\)O), anorthite (Al\(_2\)O\(_3\)), anhydrite (CaSO\(_4\)), sodalite (Ca\(_4\)O\(_4\)), TiO\(_2\) (Ti\(_2\)O\(_3\)), Cr\(_2\)O\(_3\) (Cr\(_2\)O\(_3\)), Mn\(_2\)SiO\(_4\) (Mn\(_2\)O\(_4\)), fayalite (Fe\(_2\)O\(_4\)), and ZnO (ZnO). All analyses were processed using the CITZAF correction procedure. All elements were counted for 20 s at peak positions, and Na was measured first to limit Na loss. The mean atomic number method (Donovan and Tingle, 1996) was used for the background correction of each element.

3. Results

We report the discovery of a Na-rich phase on the surface of orange beads, in addition to previously reported zinc chlorohydroxosulfate. This Na-rich phase was present in our first SEM session in 2017 but was overlooked owing to its nearly transparent appearance in BSE images. These grains remain unchanged after the sample was exposed to Pasadena air for longer than three years (Figs. S1, S1-S6, and S10). The Na-phase is present in a high number density as discrete laths or rods with a width of <0.7 μm and a length of ~6 μm (Figs. 1, 5, 5-S4, S6, and S10). The Na-phase occurs on the outside surface of beads of different shapes and sizes. About 80% of the 45 orange beads studied contain this Na-phase, whereas they are absent on the surfaces of the agglutinate and broken mineral grains. In comparison, previously reported zinc chlorohydroxosulfate only occurs on the surface of about 50% of the beads studied, typically as a few larger, equant, hexagonal or trigonal grains (Figs. S1-S6, and Ma and Liu, 2019a). On several occasions, when both phases are in contact with each other, the Na-phase lies beneath the zinc chlorohydroxosulfate, suggesting that the Na-phase formed before the zinc chlorohydroxosulfate (Figs. 1 and S6). Underneath Na-phase and zinc chlorohydroxosulfate, the surface of orange beads appears to be devitrified with abundant nanocrystals of pyroxene and metallic iron (Figs. 1 and S2-S5, Ma and Liu, 2019b). However, underneath this layer, the interior of the beads is still vitreous as seen on the broken surfaces of the same beads (Figs. S1-S4).

The SEM-EDS analyses revealed that the Na-phase contains distinctively higher Na, K, and S than the Na-phase-free surface but contains no detectable Zn and Cl (Figs. 2 and S7). Intensities of O, Na, K, and S\(_2\)O\(_3\) peaks increase relative to Si, Mg, and Al with decreasing beam voltages. This suggests the Na-phase is composed of mainly Na, K, and O. The small grain size of Na-phase on unpolished beads presents a challenge to the precise quantification of its compositions since excitation volumes of electron beams at 15 kV or 10 kV (~3.0 or 1.5 μm in diameter, respectively) invariably included the underlying materials.

We used two approaches to determine the chemical composition of the Na-phase. First, we derived the composition of the Na-phase, using the correlations of Na, K, and S with Si, Al, Ca, and Mg from the SEM-EDS data obtained at 7 kV on multiple Na-phase grains (the Supplementary Materials, Fig. S9 and Table S1). Based on the assumption that the variations in the data are due to variable degrees of mixing between the Na-phase and the underlying glass, fittings of different element trends show that the pure Na-phase contains 18.3 mol% Na, 4.7 mol% K, 15.6 mol% S, and 61.5 mol% O. This result suggests the Na-phase is a Na-K-sulfate with a molar (Na + K)/S of ~1.5 and a molar Na:K: S ratio of ~2.4: ~0.6: 2. Second, the EPMA data of the Na-phase grain (Fig. S10) show that Na\(_2\)O, K\(_2\)O, and SO\(_3\) range from 2.69–7.24 wt%, 0.79–2.58 wt%, 6.22–10.2 wt%, respectively (Table 1). Although these analyses were still contaminated by the underlying and surrounding materials, the effect is uniform for Na, K, and S in the Na-phase since the bead contains very low concentrations of these elements. Therefore, the molar (Na + K)/S values reflect that of the Na-phase, which are ~1.3 to
contain higher concentrations of Na. The Na-phase approaches confirm that the Na-phase is a Na-K-sulfate. Similar to the value inferred from SEM-EDS data and to the interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.

2.3, similar to the value inferred from SEM-EDS data and to the individual SEM-EDS point on the same grain (Table 1). In summary, both approaches confirm that the Na-phase is a Na-K-sulfate.

The EPMA data also show that the surfaces of 74220 orange beads contain higher concentrations of Na$_2$O, K$_2$O, and S than those in the interiors of orange beads, suggesting that a thin surface coating comprises MVEs in addition to discrete phases (Fig. 4). The EPMA results show large variations as some points may include small Na-phases of $<$1 μm.

4. Discussion

4.1. Formation of Na-K-sulfate through in situ alteration of Na-K-S condensates

We can exclude the possibility that Na-K-sulfate is terrestrial contamination because the sample is pristine and has never come in contact with terrestrial Na-sulfates during sample transport and handling.

Sulfates are frequently found as gas-solid reaction products in terrestrial fumaroles, with Na-sulfates found in high temperature ($>$400 °C) ones (Balic-Zunic et al., 2016). Among different Na-sulfates, ivsite, Na$_3$H(SO$_4$)$_2$, displaying a similar crystal shape to the Na-sulfate on 74220 orange beads, is a rare mineral in terrestrial fumaroles. The type of sulfates produced through gas-solid reactions depends on the solid chemistry and Na-sulfates are less common and only produced when the solid is enriched in Na (Renggli and King, 2018). However, gas-solid reactions unlikely produce the Na-K-sulfate on lunar orange beads. In contrast to SO$_2$-rich gas in terrestrial eruptions, S species in lunar volcanic gas are dominated by reduced species, with S$_2$(O) and H$_2$SO$_4$ at high temperature and possibly COS(O) at low temperatures and high pressures (Renggli et al., 2017). Thus, the reaction product with the reduced gas is not expected to be sulfate.

From the above discussion, the most likely origin of the Na-K-sulfate on the surface of 74220 orange beads is terrestrial alteration of lunar Na-K-S condensates on the surface of these beads. Because the 74220 sample was not sealed in vacuum after its collection on the Moon, original Na-K-S phases (alkali-sulfides or native elements) are highly reactive and could be easily altered upon their exposure to cabin air (mostly O$_2$) in the lunar module, the terrestrial air (O$_2$ and H$_2$O) on the retrieval ship, and the trace quantity of other gases (O$_2$ and H$_2$O) in N$_2$ in curation for the last 50 years (Ma and Liu, 2019a). The product from these reactions would take the crystal shape typical of the Na-K-sulfate.

Several mechanisms could form Na-K-S condensates on the surface of the beads, including gas-solid reaction, micrometeorite impact, and vapor condensation. One possibility is that S$_2$(O) and H$_2$SO$_4$ could react with Na and K at the surface of the beads, enriched through the rapid diffusion of Na and K (e.g., Su et al., 2021). However, we discard such an origin for the following reasons. First, the Na-K-S grains lack elements of similar diffusivity, e.g., Cu (Ni and Zhang, 2016). Second, diffusivity of Zn is about three orders of magnitude less than Na (Ni and Zhang, 2016). One would expect that this mechanism is inefficient to generate overlying Zn-Na-S-Cl condensates. Third, despite enrichment of Na and K by diffusion, Ca and Mg would still be the dominant cations. However, below the Na-K-S condensates lies a thin, volatile-rich, nano-crystalline coating of the glass beads without any Ca- or Mg-S phases. Last and more importantly, recent studies of individual orange beads discovered in-gassing of Na into otherwise degassed beads (Su et al., 2021). If gas-solid reaction were the formation mechanism for the Na-K-S grains, an in-gassing profile would not have been present.

We also evaluate if Na-K-S and previously reported Zn-Na-S-Cl could be derived from impact vapor from micrometeorites since 74220 is a soil sample. Micrometeorite impacts can melt and vaporize surface materials resulting in thin, amorphous glass coatings with nanometer-sized metallic iron and depleted in Na and K (Keller and McKay, 1993). Impact vaporized Na and K reside for ~45–90 days in the lunar environment before some escape in the solar wind and the rest permanently lock into glass coatings or impact glass spheres (Keller and McKay, 1993; Colaprete et al., 2016). However, owing to low quantities (<1 wt%) of Na, K, Cl, S, and Zn in lunar rocks and soils (Haskin and Warren, 1991), the chance is slim for Na, K, Cl, S, and Zn in the lunar exosphere to recombine and form Na-K-sulfate and zinc chlorohydroxosulfate minerals. The absence of these phases on soil and mineral grains in the 74220 sample further supports that Na-K-S and Zn-Na-S-Cl mixtures are volcanic vapor condensates.

The discrete and frequent occurrence and the position of the Na-K-S above the volatile-rich coating but below the Zn-Na-S-Cl condensates are most consistent with condensation of Na-K-S from the volcanic gas associated with the 74220 eruption that produced the orange beads. Because the oxidation and hydration of the original condensates involved only moisture in the atmosphere, the terrestrial alteration did not affect the relative proportions of Na, K, and S in the original condensate. The molar (Na + K)/S values (~1.3–2.3) of the Na-K-sulfate indicate that the original condensate is not pure sulfides, but likely a mixture of Na$_2$S + K$_2$S with excess S (<2) or with excess Na and K (>2).
4.2. Causes for absences in previous studies of 74220 orange beads

The lack of reports of Na-K-sulfate and zinc chlorohydroxosulfate in early studies of 74220 orange beads is likely caused by the sample preparation methods used in these studies. Many previous studies cleaned, sieved, and fixed samples for observations using fluid. The inferred metallic Zn and Na in the Zn-Na-S-Cl condensates are highly reactive to fluids, whereas the inferred Na$_2$S and K$_2$S in the Na-K-S condensates may be less reactive with alcohols but are highly reactive with water or moisture. Thus, depending on the cleaning or separation procedure, such as the type of fluid and the duration of sonication or sieving, MVEs in the condensates could be partially or totally removed by the fluid treatment in the previous studies. This is confirmed by our re-examination of 74220 orange beads sonicated with ethanol and then fixed using isopropanol-graphite suspension (Liu et al., 2020). A Zn-Na-S residue was observed due to the partial dissolution of zinc chlorohydroxosulfate (Fig. 3), suggesting the alcohol treatment removed Cl (Liu et al., 2020). However, the Na-K-sulfate appears to survive alcohol treatments although the shape of these grains differs from that on our pristine samples (Fig. 3). Similar evidence of sample preparation effects was shown by measurable Pb in water washes (26–120 ppb) of green beads and acid washes (53–455 ppb) of green and orange beads (Tatsumoto et al., 1987). Considering the reactivity of MVEs and solubility of the hydrated and oxidized mineral forms, studies using acetone, water, or weak acid for cleaning likely removed most if not all MVEs from the surfaces. Therefore, cautions need to be exercised when using abundances and isotope data of MVEs of bulk samples or of leachates from these studies (Thode and Rees, 1971; Grant et al., 1974; Tera and Wasserburg, 1976; Thode and Rees, 1976; Wasson et al., 1976; Krahenbuehl, 1980; Ding et al., 1983; Tatsumoto et al., 1987; Korotev and Kemmer, 1992; Moynier et al., 2006; Herzog et al., 2009; Paniello et al., 2012).

4.3. Comparison with green beads

Surface minerals from condensed MVEs are not unique to 74220 orange beads. The surfaces of green beads also contain higher MVEs concentrations (Zn, S, Na, K) than the interiors (Meyer Jr. et al., 1975; Gurlin and Housley, 1979; Table 1). Examination of green beads from Apollo soil 15401 and clod 15366 showed the presence of Zn-S, Zn, and S condensates on the surface (Ross et al., 2011; Liu et al., 2020). Compared to the 74220 orange beads, the Zn-S phases on the surface of Apollo 15366 green beads are much smaller (<0.1 µm) (Liu et al., 2020). The Zn phase on the 15401 green bead (Ross et al., 2011) has a shape similar to the zinc chlorohydroxosulfate on orange beads (Ma and Liu, 2019a) but is also much smaller (~1 µm). The different sizes of surface minerals between green and orange can be explained by the different abundances of Na, K, Zn, and S in the source melts, which lead to different outgassing paths. Based on lower H$_2$O/Ce values of 74220 melt inclusions than the inferred value in the parent melt of Apollo 15 green beads, Hauri et al., 2017 suggested that the 74220 magma experienced more degassing. However, the 74220 source contains higher abundances of H$_2$O, S, Zn, Na, K, and incompatible elements than the source melt of Apollo 15 green beads (Chen et al., 2015; Hauri et al., 2015; Ni et al., 2019). Therefore, upon ascending, volatiles in the 74220 melt can reach solubility limits at deeper depths than those in Apollo 15 green beads. The lower abundances of volatiles in the source of green beads imply a shallower degassing depth of volatiles in Apollo green-bead melts, which further indicates that the volcanic gas may not contain the pressure and abundances of the gas species needed to condense large grains of Na-K-S and Zn-Na-S-Cl phases.

4.4. Outgassing and condensation of MVEs in lunar volcanic eruptions

The observed vapor condensates shed light on the outgassing and condensation mechanisms of volatiles and MVEs from lunar magmas. Thermochemical models of lunar volcanic gas, using the inferred H$_2$O, CO$_2$, S, and Cl contents in the pre-eruptive melt, showed that Cl gas is a minor component in the volcanic gas, and ZnCl$_2$ and NaCl are not major gas species or condensed phases (Renggli et al., 2017; Zolotov and Liu, 2021). This is supported by the absence of metal-chlorides on the surface of beads, implying MVEs are not outgassed from lunar magma in the form of metal-chlorides as implied by isotope studies (Sharp et al., 2010; Paniello et al., 2012; Kato et al., 2015). Reactions of metal-chlorides and S$_2$ in the gas may produce Na-K-S solids. However, Cl concentration in the gas, relative to that of Na, K, and S, is insignificant. Such reactions are not expected to produce the large number of Na-K-S grains observed on the surface of many beads.

Since oxygen is the most abundant element, dissolved MVEs in silicate melts are expected to form covalent bonds with oxygen. The
Table 1
Electron probe data of surface of 74220 orange and 15366 green beads and one Na-sulfate grain, in comparison to SEM-EDS dat of the Na-sulfate grain.

| 74220-2 (Figs. 1 & S1) | 74220-S1-b8 | 15366-S1-b2 | 15366-S1-b6 | 15366-S1-b4 | 74220-S2-b10 Na-phase (Fig. S10) |
|------------------------|------------|-------------|-------------|-------------|----------------------------------|
| d.l.                   | N          | 1           | 2           | 3           | 1                                 |
| kV                     | kV         | wt%         | kV          | kV          | kV                                |
| O                      | 59.6       | 59.8        | 59.6        | 59.3        | 59.4                              |
| Ti                     | 15.3       | 15.3        | 15.2        | 14.5        | 16.9                              |
| Fe                     | 2.67       | 2.67        | 2.67        | 2.67        | 2.67                              |
| Cr                     | 0.44       | 0.44        | 0.44        | 0.44        | 0.44                              |
| Mn                     | 0.11       | 0.09        | 0.09        | 0.12        | 0.12                              |
| Mg                     | 8.39       | 7.85        | 7.82        | 7.77        | 10.0                              |
| Na                     | 3.35       | 2.99        | 3.10        | 3.17        | 3.17                              |
| K                      | 0.05       | 0.05        | 0.05        | 0.06        | 0.06                              |
| S                      | 0.12       | 0.24        | 0.05        | 0.17        | 0.19                              |
| Zn                     | 0.09       | 0.06        | 0.02        | 0.00        | 0.10                              |
| Cl                     | 0.01       | 0.01        | 0.01        | 0.01        | 0.01                              |
| Na atom/2S             | 1.3        | 2.0         | 2.3         | 2.0         | 2.3                               |
| molar (Na + K)/S       | 0.4        | 0.8         | 0.5         | 0.8         | 0.5                               |

* All analyses are mixtures of the surface or the Na-sulfate with the underlying glass. d.l.: detection limits of electron probes at two analytical conditions: 15 kV and 10 nA, and 10 kV and 5 nA, respectively. All elements were counted for 20 s. n.d.: not determined. b.d.: below detection limits. N: number of analyses. When N > 3, the average values and 1 standard deviation (1σ) of the average are listed. For single-point analyses, 1σ precision was estimated from counting statistics.
observations of condensates in the form of Na-K-sulfides from this study and native elements from Ma and Liu (2019a) indicate that Na, K, and Zn are likely outgassed in their native states (Na\(_{\text{d}}\), K\(_{\text{d}}\), Zn\(_{\text{d}}\)) through congruent dissociative evaporation reactions:

\[
\begin{align*}
\text{NaO}_{0.5}, & \quad (\text{i}) = \text{Na}_{\text{d}} + \frac{1}{2} \text{O}_2, \\
\text{KO}_{0.5}, & \quad (\text{i}) = \text{K}_{\text{d}} + \frac{1}{2} \text{O}_2, \\
\text{ZnO}_{0.5} & = \text{Zn}_{\text{d}} + \frac{1}{2} \text{O}_2,
\end{align*}
\]

as suggested by the thermodynamic models (Sossi and Fegley Jr., 2018; Sossi et al., 2019). Once in the gas, MVEs condense in different phases depending on the species of major volatiles (C-H-O-S species) and the gas conditions (T, P, and f\(_{\text{O}_2}\)). Observations from this study suggest there are sufficient amounts of S gas species (H\(_2\)S\(_{\text{d}}\) or S\(_{\text{d}}\)) to react with Na\(_{\text{d}}\) and K\(_{\text{d}}\) to form NaS\(_{\text{d}}\) and K\(_{\text{d}}\)S or (Na,K)\(_{\text{d}}\)S, whereas the chemistry of zinc chlorohydrosulfate in Ma and Liu (2019a) indicates Zn\(_{\text{d}}\) mainly condenses as metallic Zn. The textural relationship observed in this study further indicates that Na\(_{\text{d}}\) and K\(_{\text{d}}\) condensed from the gas before Zn\(_{\text{d}}\).

Decoupled degassing between S and Zn and higher gas pressure are proposed to explain the discrepancy between the observation of metallic-Zn-rich condensates and the prediction of ZnS condensate by the thermochemical model (Ma and Liu, 2019a). The texture relationship (Figs. 1 and S6) and the fact that Na is more abundant than Zn support the decoupling degassing hypothesis, in that the condensation of Na-K-S depleted S in the volcanic gas, leaving insufficient S to react with Zn\(_{\text{d}}\). An implication from the observed Na-K-S and Zn-Na-S-Cl condensates is that the volcanic gas has sufficient density (pressure) that enables interaction between S gas species and Na\(_{\text{d}}\) and K\(_{\text{d}}\) to form Na\(_{\text{d}}\)S and K\(_{\text{d}}\)S or (Na,K)\(_{\text{d}}\)S, whereas the chemistry of zinc chlorohydrosulfate in Ma and Liu (2019a) indicates Zn\(_{\text{d}}\) mainly condenses as metallic Zn. The textural relationship observed in this study further indicates that Na\(_{\text{d}}\) and K\(_{\text{d}}\) condensed from the gas before Zn\(_{\text{d}}\).

The post-eruptive contents are those measured in the interior of the beads. It is noted that the concentration profiles of volatile elements in the glass bead can be used to estimate the amount of volatile loss. However, albeit the presence of the profiles, the center of volcanic beads shows extensive volatile loss (Saal et al., 2008). For example, orange beads appear to be more extensively degassed with the volatile contents in the center much lower than those in the olivine-hosted melt inclusions (Hauri et al., 2011). Moreover, the volcanic loss history is more complicated than previously thought, as shown by the U-shaped Na concentration profiles in orange beads (Su et al., 2021).

Two approaches were used to estimate the pre-eruptive volatile contents in the 74220 parent melt. First, because Zn in melt inclusions was not measured, Hauri et al. (2015) estimated pre-eruptive Na and Zn contents by adding surface concentrations in the literature to those in the bead interiors, corrected using sulfur concentrations in the surface coat, bead interior, and the least-degassed melt inclusion. This approach assumes Na and Zn condenses in the same proportion to S as those in the melt. From this approach, Hauri et al. (2015) showed that 42% of Na, 97% of Zn, and 63% of S were lost during the 74220 eruption. There are several issues with the approach by Hauri et al. (2015). First, the S concentration of the surface coat from Thode and Rees (1976) used in the estimation is likely a minimum value, because some of the S is lost during the sample preparation using acetone. A higher S content in the surface coat will lead to a smaller degree of loss. Second, elements/S values during vaporization and condensation could differ from those in the melt. Thus, correction using S could lead to over- or under-estimation depending on the volatility of the element relative to S. Third, although the S concentration of the surface coat was likely underestimated, the value in bulk sample (1143 ppm) is already larger than the difference between the average bead interior (325 ppm) and the melt inclusion (884 ppm), suggesting the addition of S in the surface coat by possible subsequent eruptions. Second approach uses volatiles in olivine-hosted melt inclusions after correcting for post-entrapment effects. Using Na, Zn, and other MVEs directly measured from a melt inclusion and a 74220 orange bead, Ni et al. (2019) estimated that 11% Na and 78% Zn were lost by degassing during the 74220 eruption. Uncertainty arises from imperfect correction of the amount of post-entrapment crystallization and measurements of devitrified inclusions comprising different mineral phases.

Among Na, K, and Zn, the extent of K loss is least constrained. Using the K concentration in an orange bead from Hauri et al. (2015) and one melt inclusion, Ni et al. (2019) showed that K did not outgas. However, Na-K-S condensates prove that K indeed outgassed during the volcanic eruption. The discrepancy is likely due to the use of only one bead and one melt inclusion in the calculation by Ni et al. (2019). As shown in Fig. 4, Na\(_{\text{o}}\), K\(_{\text{o}}\), and S data of volcanic beads display considerable scattering. To estimate the amount of K loss, we used the average K concentrations (0.063 wt% K\(_{\text{o}}\)) in the interiors of orange beads measured with SIMS from Hauri et al. (2015) and the average value (0.08 wt%) of bulk 74220 in the literature after excluding data for samples processed in liquid (Wänke et al., 1973; Duncan et al., 1974; Nava, 1974; Rhodes et al., 1974). The ratio between these two numbers is 78%, suggesting ~22% loss of K by the eruption.

Outgassing experiments of mafic melts showed rapid loss of Na, K, and Zn at magmatic temperatures (Storey, 1973; Sossi et al., 2019). Vaporization experiments of a basalt, similar to Apollo 12 basalt, showed that 50% of original Na\(_{\text{o}}\) and 25% of original K\(_{\text{o}}\) were lost.

### 4.5. Extents of Na, K, Zn, and S loss during the 74220 eruption

The extents of volatile loss during 74220 eruption are estimated by comparing pre-eruptive and post-eruptive volatile contents (Table 2).

| %degassed | Zn | S | Ga | Ge | Pb | Na | K |
|-----------|----|---|----|----|----|----|----|
| Hauri et al. (2015) | 97 | 63 | 36 | 100 | 93 | 42 | n.d. |
| Ni et al. (2019) | 78 | n.d. | 41 | n.d. | 20 | 11 | Not degassed |
| This study | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 21 |

See text for detailed discussion.

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**Table 2**

Estimates of the extent of volatile loss of the 74220 eruption.
after 1 h of heating at 1200 °C in a vacuum (≪10⁻⁹ bar) (Storey, 1973). Experiments of synthetic ultramafic materials at ~1 bar showed ~67% and ~96% loss of Na₂O and K₂O, respectively, within 1 h of heating at 1400 °C and IW + 1.7 (Sossi et al., 2019). The average composition of orange beads mostly resembles that of the ultramafic material in Sossi et al. (2019) (Table S2). Comparison between experimental results and the estimated loss (Table 2) suggests volatile loss occurred <10 min at 1400 °C (longer at lower temperature), which is consistent to the duration (~7.5 min) estimated to cool the melt from an initial temperature of ~1450 °C to glass transition temperature (~700 °C) with a cooling rate of ~100 °C/min using values by Hui et al. (2018). More importantly, the above comparison shows that volatile loss from lunar magma is rapid and volcanic activities after the Moon formed can lead to additional volatile loss from the lunar interior.

5. Conclusions

We report the first discovery of a Na-K-sulfate, originated by alteration of Na-K-S condensates from lunar volcanic gas onto the surface of Apollo 74220 orange beads. Chemistry of the Na-K-sulfate suggests that Na and K in volcanic gas condensed as Na₂S + K₂S (± S or Na + K). The Na-K-sulfate lies underneath the previously reported zinc chlorohydr质地, suggesting the deposition of Na-K-S condensate before the Zn-Na-S-Cl condensates. These observations suggest that Na, K, Zn are outgassed from lunar magma in native species, and subsequently Na and K condensed as Na-K-sulfide and depleted the gas of S so that Zn condensed mostly in metal form. The incongruent degassing and condensation suggest that isotopic fractionations of these elements are more complicated than previously thought. Additionally, the fact that moderately volatile Na, K, and Zn outgassed and re-condensed in lunar volcanic eruptions at ~3.5 Ga suggests that volcanic activities redistribute these elements from the mantle to the crust, and most of these elements did not reach the escape velocity during volcanic events after the Moon stratified into crust, mantle and core.

Declaration of Competing Interest

None.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.icarus.2022.115044.

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