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# Revision 1

## Discovery of zinc-rich mineral on the surface of lunar orange pyroclastic beads

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## ABSTRACT

We present the first discovery of a Zn-rich mineral on the pristine surface of orange pyroclastic beads from Apollo sample 74220. This Zn-rich mineral is wide occurring, trigonal or hexagonal shaped, with a normalized composition of ~59 wt% Zn, ~26 wt% O (calculated), ~6 wt % S, ~5 wt % Na, and ~4 wt % Cl. The crystal morphology, homogeneity, and chemistry of individual grains are most consistent with gordaite, a zinc chlorohydroxosulfate mineral, showing an empirical formula of $Na_{1.02}Zn_{3.98}[(SO_4)_{0.84}(OH)_{0.30}](OH)_6[Cl_{0.50}(OH)_{0.50}]\bullet nH_2O$, albeit the exact amounts of OH and $H_2O$ are uncertain. The pristine 74220 sample used in this study was only exposed directly to air for a cumulative period of 16 days before our study. The same Zn-rich crystals, examined 12 to 15 months apart, show no visible physical and chemical changes. Thus, 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. The composition of zinc-rich mineral indicates that the vapor condensates consist of metallic Zn and metallic Na with either ZnS or native S, 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 lunar volcanic gas may be under higher pressure than previously thought, and the gas composition may be different than previously inferred. Our study is also relevant to collection, handling, curation, and sample preparation of returned samples from other planetary bodies.

**Keywords**: Lunar orange beads, volcanic gas, vapor condensates, the Moon, zinc-rich mineral, gordaite

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## INTRODUCTION

Lunar pyroclastic beads were produced in fire-fountain eruptions powered by gas exsolved from partial melts of the deep lunar mantle (>250 km, e.g., Delano 1986; Meyer et al. 1975). These primitive basaltic beads were reported to contain H and C residues after significant degassing (Saal et al. 2008; 2013; Wetzel et al. 2015) and a surface coat rich in volatile elements condensed from the gas (e.g., S, Zn, Cl), among which S and Zn are the most abundant (e.g., Meyer et al. 1975). One of the key unanswered questions is how volatiles and volatile elements are lost from lunar melts. The condensable species of Zn, S, and Cl depend on chemical compositions and physical conditions of the volcanic gas, which major components are H, C, and S species (Renggli et al. 2017). As such, condensed S and Zn species on the surface of the beads would provide constraints on chemical and physical conditions of the volcanic gas, and hence offer us the best opportunity to study volatiles in the deep lunar interior. However, a host phase of condensable volatile elements has never been revealed, despite of considerable surface analyses of pyroclastic beads in 1973-1993 (Butler 1978; McKay et al. 1973; Heiken and McKay 1974; Heiken et al. 1974; Chou et al. 1975; Meyer et al. 1975; Butler and Meyer 1976; Goldberg et al. 1976; Wasson et al. 1976; Tera and Wasserburg 1976; Clanton et al. 1978; Cirlin et al. 1978; Cirlin and Housley 1979; Housley et al. 1979; McKay and Wentworth 1992). Here, we report the first observation of a host mineral for Zn, S, Cl, and Na on the surface of orange beads from Apollo 17 soil 74220, using advanced analytical field-emission scanning electron microscopy.

## HISTORY OF THE SAMPLE

A small portion (~0.058 g) of pristine Apollo 17 soil 74220 was allocated for this work. Unlike other lunar soils with light gray to dark gray color, soil 74220 is orange as it is nearly made of pure orange glass (90 vol% of the soil is made of glass, Lunar Sample Compendium,

https://curator.jsc.nasa.gov/lunar/lsc/74220.pdf). A detailed process history of the allocated sample was kindly provided by the Apollo Sample Curation Office at JSC (R. Zeigler, L. Watt, Pers. Comm. on Sept. 11, 2018). Soil sample 74220 was collected in a Documented Bag (DB) 12E and placed into Sample Collection Bag (SCB) 8 carried by the astronauts on the lunar surface. SCB 8 was put into a containment bag to protect the command module. The containment bag was a beta cloth duffle bag with a draw-string mouth. The samples inside these bags were exposed to air inside the lunar and command modules (pure $O_2$ with moisture from respiration) from five to seven days with two to four depressurization-repressurization cycles on the Moon. On the recovery ship in an isolated work area with filtered air, all of the SCBs were removed from the containment bags, and all the returned containers (including DB 12E containing 74220) were individually bagged in two Teflon bags and one polyethylene bag, all heat sealed (Dec. 1972). During this step, samples were exposed to filtered air for nine to thirteen hours on the recovery ship, and then were sealed in filtered air for about one and one-half days before being introduced into nitrogen environment at the Lunar Receiving Laboratory (LRL), where these sealed bags were unsealed in the nitrogen processing lines (cabinets). The parent sample (74220, 2) of our sample was allocated to J.J. Katz on September 4, 1974 in a Pristine Sample Laboratory (PSL) Poly Vial container, which was further sealed in two Teflon bags. This parent sample was returned unopened on August 7, 1976. When returned, the sealed package (the original container and the sealed two Teflon bags) was stored in the Returned Sample Storage in air until November 25, 2009 when it was transferred into a PSL gas $N_2$ cabinet and split. The split sample was put in a plastic container, which was again sealed in dry $N_2$ by two Teflon bags. This sealed package was then stored in the Pristine Sample Vault (nitrogen) until it was shipped in May 2017. In summary, all pristine 74220

samples were directly exposed to 5-7 days in nearly pure $O_2$ and ~2 days in filtered air before processing in the $N_2$ atmosphere in the LRL.

After we opened the double bags and sample container and prepared samples in 2017, the first scanning electron microscope (SEM) session was performed within ~9 days. The remaining sample stayed in the container in terrestrial air and used for additional SEM studies in 2017 and in September 2018. Therefore, samples used in our first SEM session have been exposed directly to pure $O_2$ and the terrestrial air for less than 18 days.

## METHODS

We conducted analyses in three different sessions. In the first session in 2017, we opened the double bags and container, picked 17 grains and placed them on a piece of carbon tape on one SEM stub (~10 mm diameter, stub 1) around May 30$^{th}$, 2017. The stub was carbon coated and was examined on June 9$^{th}$, 2017 using a Zeiss 1550 VP FE-SEM with an Oxford X-Max SDD Electron Dispersive Spectrometer (EDS) system and a HKL electron back-scatter diffraction (EBSD) system. A second SEM stub (stub 2) was prepared with 76 additional grains from the open container, uncoated, and examined with the SEM in September 2017. Among the 93 grains in the 2017 sessions, two are soil grains (aggregates), four are rock fragments, and the rest are rounded beads (53) or broken glass shards (34). Only the outmost surfaces of 35 beads are visible, whereas the remaining beads only display interior surfaces.

In the third SEM session in 2018, 19 beads were picked from the opened container, and were pressed on a clean indium mount on September 12, 2018. In order to check carbon contents, the indium mount was cleaned in the order of acetone, ethanol, and dichloromethane for 5-10 minutes, and then baked in vacuum (~6.7 x $10^3$ Pa) at 105 °C for ~7 days to remove organic contamination. We performed SEM observations in 2018 on two beads in the indium mount and

two beads from the 2017 mounts (one from stub 1 and one from stub 2) to examine the changes of the Zn-rich phase after they were exposed directly to terrestrial atmosphere for ~15 months. In summary, in samples prepared for the SEM study, there are 54 beads with visible outer surfaces and six soil grains.

In all SEM sessions, back-scatter electron imaging (BSE) was carried out in both high vacuum and variable pressure (25 Pa) modes. EDS was used in high vacuum mode for quantitative elemental analysis of the Zn-rich phase and other minerals on the lunar beads. These EDS data were processed using the XPP correction procedure with Oxford factory internal standards. EBSD analyses were performed on several large crystals of the Zn-rich mineral in 2017 and in 2018. Owing to the rough curved surface of the beads, we did not attempt electron probe analysis of the Zn-rich phase. Raman analysis was attempted with a Renishaw inVia$^{TM}$ Qontor Raman Spectrometer with a green laser (512 nm) at 1 mW power.

## RESULTS

We observed a Zn-rich mineral in the first SEM session of 2017. Further examination showed that Zn-rich mineral occurs on the outer surface of 15 beads out of 37 beads studied, but did not occur on the fractured interior surfaces nor on the surface of non-bead, soil or rock grains (Figs. 1 and 2). Nanometer-sized dendritic pyroxene, metallic Fe ($Fe^0$), and skeletal chromium-bearing ulvöspinel are visible on and near the surface of beads, and often lie underneath the Zn-rich phase (Figs. 1 and 2). The same zinc chlorohydroxosulfate grains did not display visible changes after exposed to the ambient air for 15 months (Figs. 2 and S3).

The Zn-rich crystals appear to be a single phase (uniform brightness in BSE images) with a trigonal or hexagonal shape, and are typically <3 μm in the largest dimension and <1 μm in thickness (Figs. 1, 2, S1, and S2). These Zn-rich crystals are highly electron beam sensitive. As

a result, we were not able to obtain any EBSD pattern. Raman analysis of several Zn-rich minerals also did not yield any Raman feature, although Raman analysis of glass suggests presence of olivine and pyroxene. The EDS analysis of the Zn-rich mineral on all examined beads showed that it contains Zn, O, S, Cl, and Na with variable amounts of contamination from the underlying glass. The ~1 μm thick aggregates in Figure S2 display the least contamination from the glass (Fig. 3). The normalized composition from a representative EDS analysis of this aggregates is: ~59 wt% Zn, ~26 wt% O (calculated), ~6 wt % S, ~5 wt % Na, ~4 wt % Cl , and 0.4 wt% Mg (Table 1). The Mg is possibly derived from the underneath glass. Glass without the trigonal/hexagonal Zn-rich mineral contains ~0.1 wt% S and 0.5-1 wt% Na with no detectable Zn and Cl (e.g., Fig. 3). The atomic ratios of Zn/Na (~4) and Zn/S/Cl (~8/~1.7/1) of the Zn-rich aggregates remain unchanged at different excitation voltages of 15, 10, and 6 kV. These results confirm that the Zn-rich mineral is a single phase. Further, EDS analysis of beads mounted in indium shows no detectable carbon (Fig. 3). Therefore, the most likely mineral is gordaite, $NaZn_4(SO_4)(OH)_6Cl•6H_2O$, which is the only known zinc salt containing all the observed elements and is also hexagonal. By charge balance of the observed elements with oxygen and OH, we calculated an empirical formula of the Zn-rich mineral as $Na_{1.02}Zn_{3.98}[(SO_4)_{0.84}(OH)_{0.30}](OH)_6[Cl_{0.50}(OH)_{0.50}]•nH_2O$, which contains significant deficiencies at $SO_4^{2-}$ and $Cl^-$ sites than the ideal gordaite. Without direct identification of its crystal structure, we will refer to this Zn-rich mineral as zinc chlorohydroxosulfate in the following text. Among all the beads studied, we did not observe ZnS, NaCl, $FeCl_2$, or native S ($S^0$).

## DISCUSSION

This is the first report of Zn, Cl, Na, S, and O occurring as one mineral phase, a zinc chlorohydroxosulfate (likely gordaite), on lunar orange beads. Sulfate was indicated in two early

studies (Cirlin et al. 1978; McKay and Wentworth 1992). A third study by Clanton et al. (1978) reported Na-Zn-Cl or Na-Zn-S in surface coating and euhedral NaCl grains on 74001/2 beads. However, the SEM-EDS instrument used in Clanton et al. (1978) was incapable to detect oxygen. McKay and Wentworth (1992) observed Zn (± Na)-S-O association on 74220 and 74001/2 beads. Although Zn and Na were suspected to occur together, the instrumentation used in the 1992 study cannot distinguish Zn *L* and Na *K* peaks. The X-ray photoemission spectroscopy of 74001 orange beads by Cirlin et al. (1978) showed that a portion of sulfur was in oxidized form, but it is unclear what is associated with $SO_4^{2-}$. The observation of zinc chlorohydroxosulfate on the surface of 74220 beads in this study is rather unexpected, considering our sample likely experienced the shortest exposure to terrestrial air than those in previous two studies. The samples studied by McKay and Wentworth (1992) had been exposed to the ambient air since 1978. Although these authors reported secular changes on the samples, a phase containing Zn, Na, S, and Cl was not observed. The study by Cirlin et al. (1978) published ~6 years after Apollo 17 samples returned to Earth, although it is unclear if the samples were sealed in $N_2$ before their measurements. Our sample and those in early studies experienced the same exposure history before they arrived at the Lunar Receiving Lab at JSC, but our sample was directly exposed to the terrestrial air for <9 days before observing the zinc chlorohydroxosulfate in the first SEM session. We exclude the possibility that the zinc chlorohydroxosulfate is terrestrial contamination. Natural occurrences of gordaite on Earth have only been confirmed in sulfide chimneys from Juan de Fuca ridge and the Edmond hydrothermal field, Central Indian Ridge, via reactions between discharging hydrothermal fluids and sea water (Brett et al. 1987; Nasada et al. 1998; Wu et al. 2016), or in a hydrothermal vein in San Francisco Mine, Chile (Schlüter et al. 1997). Gordaite is a common

product of Zn corrosion in Marine environments (e.g., Odnevall and Leygraf 1993). However, based on the lunar sample record, our sample never came in contact with Zn metal.

Zinc chlorohydroxosulfate in our study, however, is likely an alteration product of vapor-deposited Zn, Cl, S, and Na-bearing solids clustered on the surface of volcanic beads. Although the mantle source of 74220 beads is more water rich among Apollo basalts (Hauri et al. 2011; Chen et al. 2015), the amount of water in zinc chlorohydroxosulfate is unlikely sourced from the volcanic gas in lunar fire-fountain eruptions, especially when $H_2$ is the dominant H species in the volcanic gas (e.g., Renggli et al. 2017). Because the zinc chlorohydroxosulfate in our sample did not show visible changes after being exposed in the terrestrial air for ~15 months, we further suggest zinc chlorohydroxosulfate formed within the 18 days exposure to ambient air. The formation of zinc chlorohydroxosulfate probably started when the samples were exposed to the atmosphere in command and surface modules (pure $O_2$ with some moisture), or to the filtered marine air before they were sealed in dry $N_2$. The rapid reaction with terrestrial air is supported by a terrestrial-like hydrogen isotope signature of 74220 samples measured in 1973 (Epstein and Taylor 1973). Moreover, after sealing in dry $N_2$, the reaction could have continued with trace moisture diffused into the container while the sealed-double bag was sitting in the air. Terrestrial experiments show that formation of zinc chlorohydroxosulfate is rapid, within days of exposure of metal Zn to marine environments with Na, Cl, and $SO_4$ derived from sea water (Odnevall and Leygraf 1993; Coles et al. 2008; Diler et al. 2014). Since sample 74220 had never been in direct contact with sea water or its spray, Na, Cl, and S in the zinc-rich mineral are not terrestrial. Moreover, the alteration of vapor condensates appears to be complete, because of the lack of Zn and Cl in areas without the Zn-rich mineral and the absence of additional Zn, Na, Cl, and S species

on multiple beads. Therefore, from the composition of the zinc-rich mineral, we derive that vapor condensates on 74220 beads are composed of Zn, Na, S, and Cl in an atomic ratio of ~8:~2:~1.7:1.

The solid species of these elements in the vapor condensates can be assessed using the composition of the vapor condensates. Because the atomic abundances of Zn and Na are in excess with respect to S and Cl, the vapor condensates would contain metallic Zn ($Zn^0$) and metallic Na ($Na^0$), as previously hypothesized by Cirlin et al. (1978). The solid phases of S and Cl may be present as $S^0$ or ZnS, and $ZnCl_2$ or NaCl, respectively. Differentiating between $S^0$ versus ZnS and $ZnCl_2$ versus NaCl will require samples that have not seen any type of terrestrial air. Considering the hydration and oxidation required to form zinc chlorohydroxosulfate, $S^0$ and $ZnCl_2$ are the most likely candidates. Among all possible reactions of different species, the extreme hygroscopic nature of $ZnCl_2$, the reactivity of $S^0$ and $Na^0$, and the lowest Gibbs free energy make the following reaction most likely:

$$3.73Zn + 0.84S + 0.25ZnCl_2 + 1.02Na + (3.4+n)\,H_2O + 3.38O_2 =$$

$$Na_{1.02}Zn_{3.98}[(SO_4)_{0.84}(OH)_{0.30}](OH)_6[Cl_{0.50}(OH)_{0.50}]\bullet nH_2O.$$

Although S is one of the major volatile components of lunar volcanic gas, most of S is likely lost as $S_{2(g)}$ or $H_2S_{(g)}$, and only a small mount was deposited as native $S^0$ or ZnS on the surface of lunar beads (Renggli et al. 2017).

## IMPLICATIONS

Our results have several implications, from volcanic degassing on the Moon to processing of returned planetary samples on Earth. First, our results provide new insights in lunar volcanic degassing inferred from Zn and Cl isotope signatures (Moynier et al. 2006; Herzog et al. 2009; Sharp et al. 2010; Paniello et al. 2012; Kato et al. 2015). The Zn and Cl isotope compositions of lunar basalts and pyroclastic beads indicate that the Moon experienced significant loss of volatiles

and volatile elements, and Zn and Cl were likely lost in the form of $ZnCl_2$, $FeCl_2$, and NaCl (Moynier et al. 2006; Herzog et al. 2009; Sharp et al. 2010; Paniello et al. 2012; Kato et al. 2015). However, the absence of $FeCl_2$ or NaCl on samples studied, the deficiency of Cl relative to Na and Zn, and our inferred composition of vapor condensate imply that $ZnCl_2$ (and other metal chlorides) is a minor vapor and solid phase compared to metallic forms of Zn and Na in the volcanic gas associated with lunar fire-fountain eruptions, which further suggests the Zn and Cl degassing is likely decoupled. Detailed examination of Zn and Cl isotope data of 74220 samples reveal some interesting issues. Depletion of heavy Zn isotopes of bulk 74220 sample ($\delta^{66}Zn$ = -3.37 and -3.83 ‰) was explained by the presence of $ZnCl_2$ condensates in the sample (Paniello et al. 2012), whereas enriched chlorine isotopes of bulk 74220 sample ($\delta^{37}Cl$ = +8.6 and +9.3 ‰) are proposed to be caused by significant degassing of $ZnCl_2$, $FeCl_2$, and NaCl (Sharp et al. 2010). If bulk 74220 sample contains condensed $ZnCl_2$, we would expect that Zn and Cl isotopes show similar enrichment or depletion of heavy isotopes. The opposite trend of the Zn and Cl isotope compositions of bulk 74220 sample implies either the effects of other non-volcanic processes such as impact volatilization or sample preparation (see below), or Zn and Cl degassing is decoupled. However, whether Zn and Cl degassing is decoupled for 74220 cannot be fully ascertained from the available data, because isotope measurements on pure beads from sample 74220 are needed. Moreover, all Zn measurements of sample 74220 did not analyze leachates (Moynier et al. 2006; Herzog et al. 2009; Paniello et al. 2012), whereas some of the surface Zn, if not all, are likely dissolved. In fact, this possibility is supported by the work of Day et al. (2017), the leachates using water of two lunar rocks contain much higher Zn than the residues (Table S2 in Day et al. 2017).

Second, recent discoveries of residual H in pyroclastic beads and melt inclusions suggest that mantle sources for these primitive magmas are likely water rich (Saal et al. 2008; 2013; Hauri

et al. 2011; Chen et al. 2015). This inference appears to contradict dry conditions required for degassing of metal chlorides (Sharp et al. 2010). Decouple of Zn and Cl degassing from other volatile elements, high Zn and Cl abundances in pyroclastic beads with directly measured high H contents in melt inclusions (Hauri et al. 2011), and the loss of H as $H_2$*(g)* other than $H_2O$*(g)* (e.g., Renggli et al. 2017) would indicate that a water-rich mantle source for pyroclastic beads does not prohibit degassing of Zn and Cl.

Third, our results can be used to evaluate the thermochemical model of volcanic gas by Renggli et al. (2017). The model by Renggli et al. (2017) assumed that the melt contains volatiles similar to those reported in Saal et al. (2008) and Wetzel et al. (2015). Based on thermodynamics, Renggli et al. (2017) calculated the stable gas and solid condensate species at different conditions (IW-2, IW, $10^{-6}$ bar, 1 bar). Their results show that zinc exists in the gas in the native form ($Zn_{(g)}$), but condenses dominantly as ZnS via reaction with $S_{2(g)}$ under all calculated conditions (IW-2, IW, $10^{-6}$ bar, 1 bar). At the higher gas pressure (1 bar), metallic Zn appears as a minor solid species. Contrast to the model predictions, our results imply that zinc condenses dominantly as $Zn^0$. The difference between model predication and our observation implies revisions of the assumptions in the model: lunar melt contains significantly less sulfur and hence less $S_{2(g)}$ in the volcanic gas, or most sulfur was lost before Zn condensed, or lunar volcanic gas had higher pressures. Presence of a hot gaseous cloud during the fire-fountain eruption was also indicated based on the heat capacity and cooling rate of 74220 beads (Hui et al. 2018). Therefore, metal Zn as the main species of zinc condensed from the vapor is consistent with a gas cloud that facilitates separation of $S_2$ (and Cl species) from Zn.

Fourth, our results also suggest that sample preparation techniques used in bulk sample analysis, especially for volatile elements, need to pay special attention to the soluble condensates.

Considering the rapid reaction with ambient air, exposure durations of pristine samples to ambient air before analyses need to be documented and reported. Moreover, leachates of samples will need to be analyzed for volatile elements (e.g., Zn, Pb, Cu). As shown above, sample preparation in Zn analysis involved cleaning of samples in HCl (Moynier et al. 2006; Herzog et al. 2009) or double-distilled water (Paniello et al. 2012), but the leachates were not analyzed in these studies. As a result, the reported 140-254 ppm values in these studies likely underestimate the concentrations of the vapor condensed Zn in bulk 74220 sample. Using the chlorine concentration in the leachate of bulk 74220 sample (50 ppm, Sharp et al. 2010), and the inferred atomic Zn/Cl ratio of 8 from our study, we inferred the surface Zn in bulk 74220 to be ~737 ppm. Furthermore, for vapor condensates from the volcanic gas, measurements of pure glass beads from 74220 for both Zn and Cl concentrations and isotopic values are needed.

Results from this study are also highly relevant to collection, handling, and curation of returned samples from other planetary bodies. Surface mineralogy, chemistry, and reactivity of returned samples are not only interesting to science (volcanic or impact processes) but also important for future human explorations. The rapid alteration of vapor condensates as reported in this study 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). Investigations of surface mineralogy, chemistry, and reactivity need to be performed as soon as sample containers are open to the 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. NASA's plan to open these samples offers an excellent opportunity to resolve uncertainties caused by terrestrial alteration. Maintaining the pristine states of these vacuum-

sealed samples during sample handling and processing is critical to the study of vapor condensates on volcanic beads in these samples. The development of sampling handling approaches will be highly beneficial to samples that will be returned from asteroids and Mars.

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## REFERENCES CITED

Brett, R., Evans, H.T., Gibson, E.K., Hedenquist, J.W., Wandless, M.V., and Sommer, M.A. (1987) Mineralogical studies of sulfide samples and volatile concentrations of basalt glasses from the southern Juan de Fuca Ridge. Journal of Geophysical Research: Solid Earth, 92(B11), 11373-11379.

Butler, P., Jr. (1978) Recognition of lunar glass droplets produced directly from endogenous liquids: The evidence from S-Zn coatings. In: Lunar and Planetary Science Conference, 9th, Houston, Tex., March 13-17, 1978, Proceedings. Volume 2. (A79-39176 16-91) New York, Pergamon Press, Inc., 1978, p. 1459-1471.

Butler, J., Jr., and Meyer, C., Jr. (1976) Sulfur prevails in coatings on glass droplets: Apollo 15 green and brown glasses and Apollo 17 orange and black (devitrified) glasses. In: Lunar Science Conference, 7th, Houston, Tex., March 15-19, 1976, Proceedings. Volume 2. (A77-34651 15-91) New York, Pergamon Press, Inc., 1976, p. 1561-1581.

Chen, Y., Zhang, Y., Liu, Y., Guan, Y., Eiler, J., and Stolper, E.M. (2015) Water, fluorine, and sulfur concentrations in the lunar mantle. Earth and Planetary Science Letters, 427, 37-46.

Chou, C.L., Boynton, W.V., Sundberg, L.L., and Wasson, J.T. (1975) Volatiles on the surface of Apollo 15 green glass and trace-element distributions among Apollo 15 soils. In: Lunar Science Conference, 6th, Houston, Tex., March 17-21, 1975, Proceedings. Volume 2. (A78-46668 21-91) New York, Pergamon Press, Inc., 1975, p. 1701-1727.

Cirlin, E.H., and Housley, R.M. (1979) Scanning Auger microprobe and atomic absorption studies of lunar volcanic volatiles. In: Lunar and Planetary Science Conference, 10th, Houston, Tex., March 19-23, 1979, Proceedings. Volume 1. (A80-23557 08-91) New York, Pergamon Press, Inc., 1979, p. 341-354.

Cirlin, E.H., Housley, R.M., and Grant, R.W. (1978) Studies of volatiles in Apollo 17 samples and their implication to vapor transport processes. In: Lunar and Planetary Science Conference, 9th, Houston, Tex., March 13-17, 1978, Proceedings. Volume 2. (A79-39176 16-91) New York, Pergamon Press, Inc., 1978, p. 2049-2063.

Clanton, U.S., McKay, D.S., Waits, G., and Fuhrman, R. (1978) Sublimate morphology on 74001 and 74002 orange and black glassy droplets. In: Lunar and Planetary Science Conference, 9th, Houston, Tex., March 13-17, 1978, Proceedings. Volume 2. (A79-39176 16-91) New York, Pergamon Press, Inc., 1978, p. 1945-1957.

Cole, I.S., Muster, T.H., Furman, S.A., Wright, N., and Bradbury, A. (2008) Products Formed during the Interaction of Seawater Droplets with Zinc Surfaces: I. Results from 1- and 2.5-Day Exposures. Journal of The Electrochemical Society, 155(5), C244-C255.

Day, J.M.D., Moynier, F., and Shearer, C.K. (2017) Late-stage magmatic outgassing from a volatile-depleted Moon. Proceedings of the National Academy of Sciences. DOI:10.1073/pnas.1708236114

Delano, J.W. (1986) Pristine lunar glasses: Criteria, data and implications. Journal of Geophysical Research 91, D201-D213.

Diler, E., Rouvellou, B., Rioual, S., Lescop, B., Nguyen Vien, G., and Thierry, D. (2014) Characterization of corrosion products of Zn and Zn–Mg–Al coated steel in a marine atmosphere. Corrosion Science, 87, 111-117.

Ding, T.P., Thode, H.G., and Rees, C.E. (1983) Sulphur content and sulphur isotope composition of orange and black glasses in Apollo 17 drive tube 74002/1. Geochimica et Cosmochimica Acta, 47, 491-496.

Epstein, S., and Taylor, H.P., Jr. (1973) The isotope composition and concentration of water, hydrogen and carbon in some Apollo 15 and 16 soils and in the Apollo 17 orange soil. Proceedings of the Fourth Lunar Science Conference, Supplement 4, Geochimica et Cosmochimica Acta, 2, 1559-1575.

Goldberg, R.H., Tombrello, T.A., and Burnett, D.S. (1976) Fluorine as a constituent in lunar magmatic gases. In: Lunar Science Conference, 7th, Houston, Tex., March 15-19, 1976, Proceedings. Volume 2. (A77-34651 15-91) New York, Pergamon Press, Inc., p. 1597-1613.

Hauri, E.H., Weinreich, T., Saal, A.E., Rutherford, M.C., and Van Orman, J.A. (2011) High Pre-Eruptive Water Contents Preserved in Lunar Melt Inclusions. Science 333, 213-215.

Heiken, G., and McKay, D.S. (1974) Petrography of Apollo 17 soils. In: Lunar Science Conference, 5th, Houston, Tex., March 18-22, 1974, Proceedings. Volume 1. (A75-39540 19-91) New York, Pergamon Press, Inc., 1974, p. 843-860.

Heiken, G.H., McKay, D.S., and Brown, R.W. (1974) Lunar deposits of possible pyroclastic origin. Geochimica et Cosmochimica Acta, 38, 1703-1718.

Herzog, G.F., Moynier, F., Albarède, F., and Berezhnoy, A.A. (2009) Isotopic and elemental abundances of copper and zinc in lunar samples, Zagami, Pele's hairs, and a terrestrial basalt. Geochimica et Cosmochimica Acta, 73, 5884-5904.

Housley, R.M., Grant, R.W., and Cirlin, E.H. (1979) XPS and SAM studies of the surface chemistry of lunar impact glasses including 12054. In: Lunar and Planetary Science Conference, 10th, Houston, Tex., March 19-23, 1979, Proceedings. Volume 2. (A80-23617 08-91) New York, Pergamon Press, Inc., 1979, p. 1483-1490.

Hui, H., Hess, K.-U., Zhang, Y., Nichols, A.R.L., Peslier, A.H., Lange, R.A., Dingwell, D.B., and Neal, C.R. (2018) Cooling rates of lunar orange glass beads. Earth and Planetary Science Letters, 503, 88-94.

Kato, C., Moynier, F., Valdes, M.C., Dhaliwal, J.K., and Day, J.M.D. (2015) Extensive volatile loss during formation and differentiation of the Moon. Nature Communications 6, 7617.

McKay, D.S., and Wentworth, S.J. (1992) Morphology and Composition of Condensates on Apollo 17 Orange and Black Glass. In G. Ryder, H.H. Schmitt, and P.D. Spudis, Eds. Workshop on Geology of the Apollo 17 Landing Site, Part 1. LPI Technical Report 92-09, Part 1, p. 31. Lunar and Planetary Institute, Houston, Texas.

McKay, D.S., Clanton, U.S., and Ladle, G.H. (1973) Scanning electron microscope study of Apollo 15 green glass. Proceedings of the 4$^{th}$ Lunar Science Conference. Suppl. 4, Geochimica et Cosmochimica Acta, 1, 225-238.

Meyer, C., Jr., McKay, D.S., Anderson, D.H., and Butler, P., Jr. (1975) The source of sublimates on the Apollo 15 green and Apollo 17 orange glass samples. In: Lunar Science Conference, 6th, Houston, Tex., March 17-21, 1975, Proceedings. Volume 2. (A78-46668 21-91) New York, Pergamon Press, Inc., 1975, p. 1673-1699. 2, 1673-1699.

Moynier, F., Albarède, F., and Herzog, G.F. (2006) Isotopic composition of zinc, copper, and iron in lunar samples. Geochimica et Cosmochimica Acta, 70, 6103-6117.

Nasdala, L., Witzke, T., Ullrich, B., and Brett, R. (1998) Gordaite [$Zn_4Na(OH)_6(SO_4)Cl{\cdot}6H_2O$]: Second occurrence in the Juan de Fuca Ridge, and new data. American Mineralogist, 83, p. 1111.

Odnevall, I., and Leygraf, C. (1993) Formation of NaZn4Cl(OH)6SO4 · 6H2O in a marine atmosphere. Corrosion Science, 34(8), 1213-1229.

Paniello, R.C., Day, J.M.D., and Moynier, F. (2012) Zinc isotopic evidence for the origin of the Moon. Nature, 490, 376.

Renggli, C.J., King, P.L., Henley, R.W., and Norman, M.D. (2017) Volcanic gas composition, metal dispersion and deposition during explosive volcanic eruptions on the Moon. Geochimica et Cosmochimica Acta, 206, 296-311.

Saal, A.E., Hauri, E.H., Lo Cascio, M., Van Orman, J.A., Rutherford, M.C., and Cooper, R.F. (2008) Volatile content of lunar volcanic glasses and the presence of water in the Moon's interior. Nature, 454, 192-196.

Saal, A.E., Hauri, E.H., Van Orman, J.A., and Rutherford, M.J. (2013) Hydrogen Isotopes in Lunar Volcanic Glasses and Melt Inclusions Reveal a Carbonaceous Chondrite Heritage. Science, 340, 1317-1320.

Schlüter, J., Klaska, K.H., Friese, K., Adiwidjaja, G., and Gebhard, G. (1997) Gordaite, $NaZn_4(SO_4)(OH)_6Cl \bullet 6H_2O$, a new mineral from the San Francisco Mine, Antofagasta, Chile. Neues Jahrbuch Fur Mineralogie-Monatshefte(4), 155-162.

Sharp, Z.D., Shearer, C.K., McKeegan, K.D., Barnes, J.D., and Wang, Y.Q. (2010) The chlorine isotope composition of the Moon and implications for an anhydrous mantle. Science, 329, 1050-1053.

Tera, F., and Wasserburg, G.J. (1976) Lunar ball games and other sports. Lunar and Planetary Science Conference, 7, p. 858.

Wasson, J.T., Boynton, W.V., Kallemeyn, G.W., Sundberg, L.L., and Wai, C.M. (1976) Volatile compounds released during lunar lava fountaining. In: Lunar Science Conference, 7th, Houston, Tex., March 15-19, 1976, Proceedings. Volume 2. (A77-34651 15-91) New York, Pergamon Press, Inc., 1976, p. 1583-1595.

Wetzel, D.T., Hauri, E.H., Saal, A.E., and Rutherford, M.J. (2015) Carbon content and degassing history of the lunar volcanic glasses. Nature Geoscience, 8, 755-758.

Wu, Z., Sun, X., Xu, H., Konishi, H., Wang, Y., Wang, C., Dai, Y., Deng, X., and Yu, M. (2016) Occurrences and distribution of “invisible” precious metals in sulfide deposits from the Edmond hydrothermal field, Central Indian Ridge. Ore Geology Reviews, 79, 105-132.

Zhu, L., Seff, K., Witzke, T., and Nasdala, L. (1997) Crystal structure of $Zn_4Na(OH)_6SO_4Cl{\cdot}6H_2O$. Journal of Chemical Crystallography, 27(5), 325-329.

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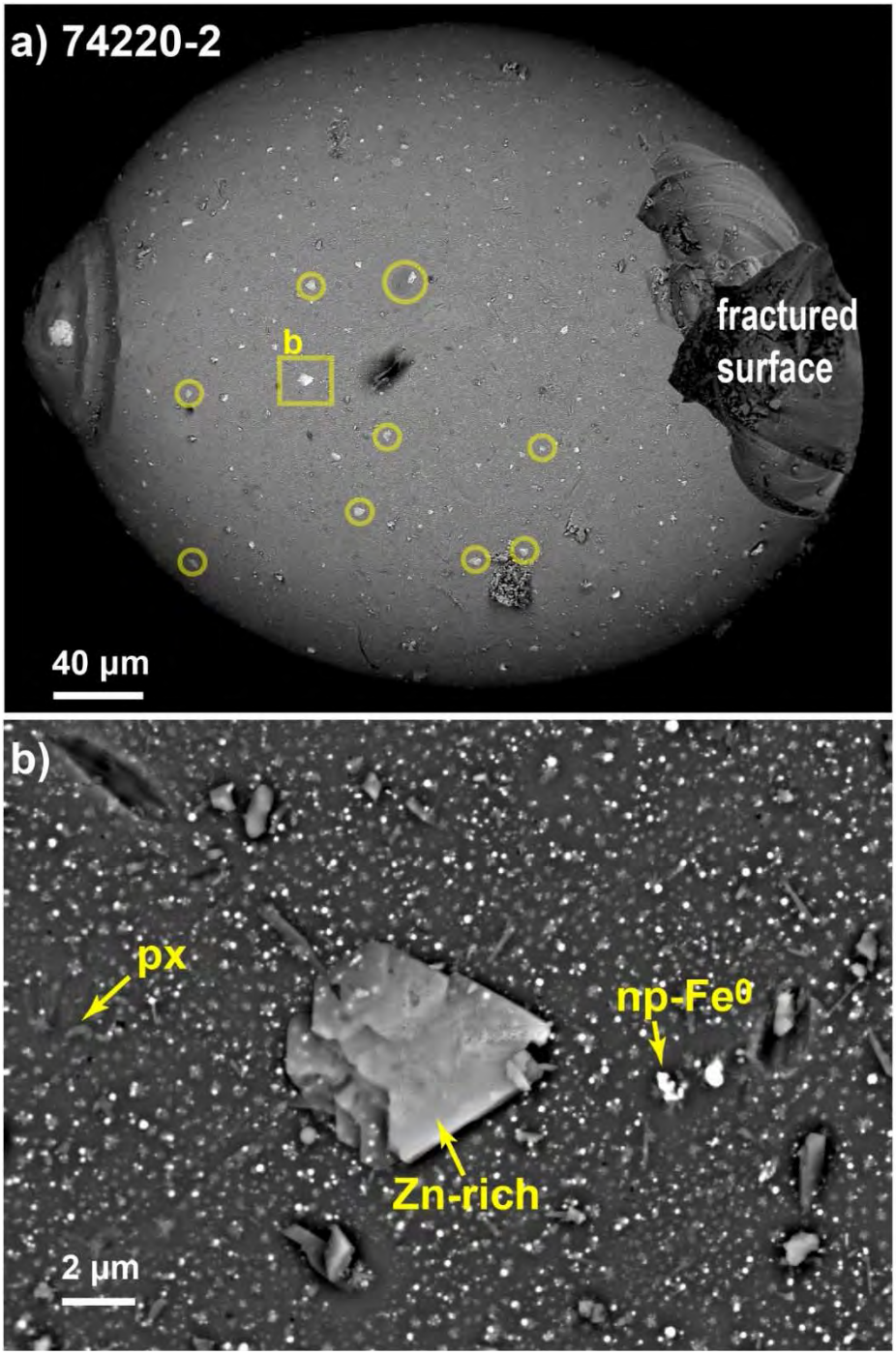


**Figure 1**. An example of the Zn-rich mineral on the surface of an orange bead from Stub 1 of 2017 sample mounts (imaged within ~9 days after original container was opened). (a) Backscattered electron image (BSE) of the bead showing the occurrences of the Zn-rich mineral (circles). (b) High magnification BSE image of the Zn-rich mineral (Zn-rich) showing platy crystals of a trigonal or hexagonal form. Nanometer pyroxene (px) and native iron (np-$Fe^0$) are also present near the surface of the bead, which are likely quench crystals. The Zn-rich mineral lies above px and np-$Fe^0$. This bead was imaged 15 months later and surface Zn-rich minerals show no changes (Fig. S3).

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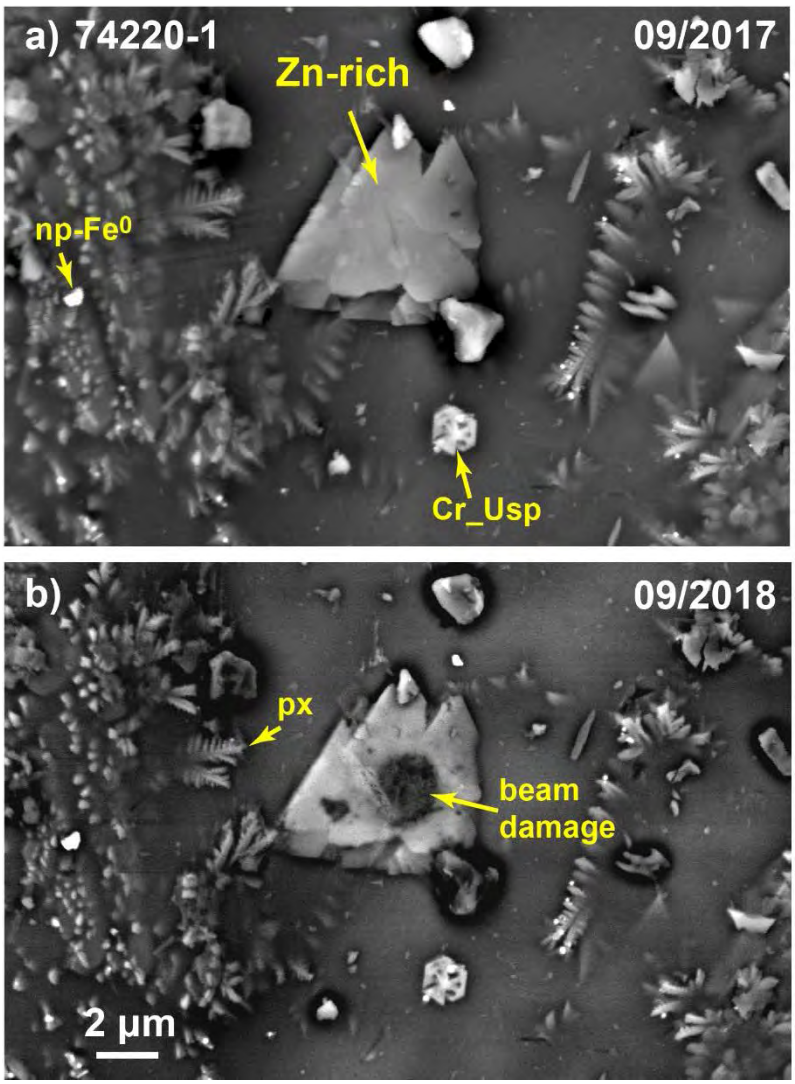


**Figure 2**. Comparison of Zn-rich grains imaged 12 months apart. a) A cluster of the Zn-rich mineral each with a trigonal or hexagonal crystal shape on a volcanic bead (Fig. S1) that was studied after exposing to the ambient air for ~3 months. b) The same cluster imaged after 15 months in the terrestrial air. Except for electron beam damages (dark regions on the cluster), other regions of the cluster display no morphological and chemical changes. Other phases near the surface are nanometer native Fe (np-$Fe^0$), pyroxene (px), and chromian ulvöspinel (Cr_Usp), which are likely quench crystals. Note that the isometric mineral (Cr-Usp) exhibits a different form (skeletal) from the Zn-rich grains.

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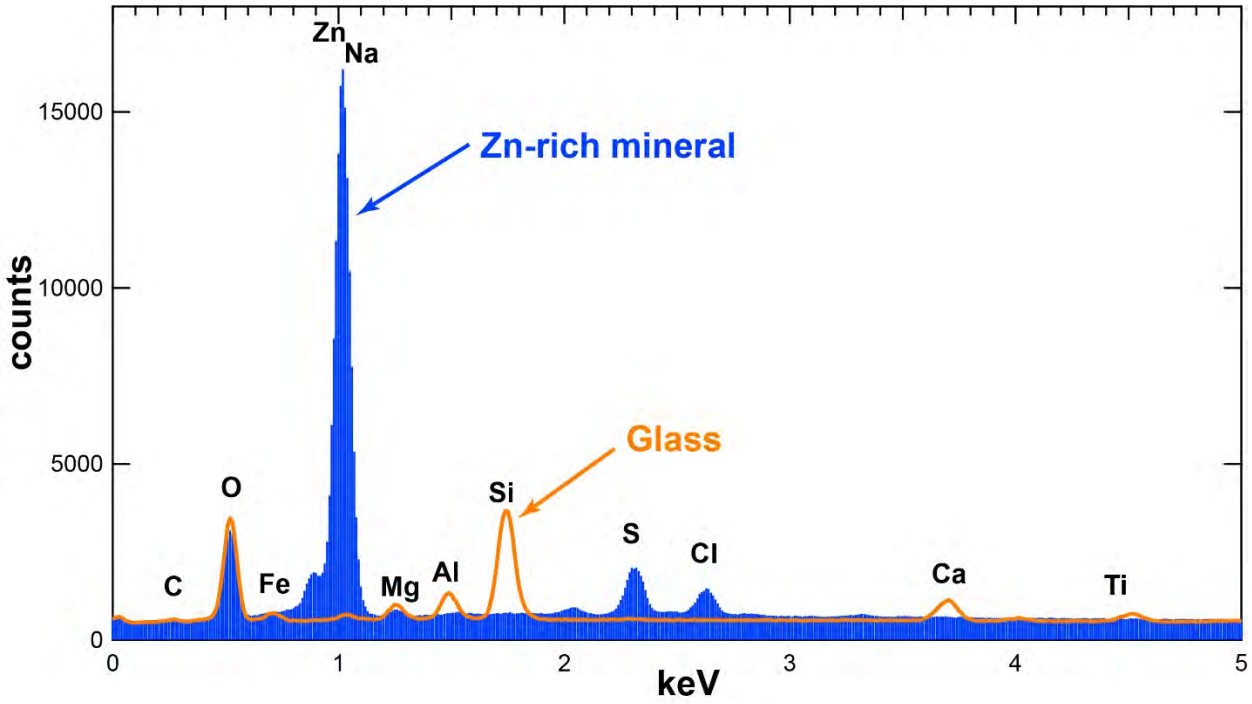


426

427 **Figure 3**. EDS spectra of the Zn-rich mineral and the glass substrate (see Fig. S2 of EDS locations).

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428 **Table 1.** Representative composition of the Zn-rich mineral.*

| **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 |

429 *Uncertainties are one sigma values based on counting statistics.