Experimental investigation of Apollo 16 “Rusty Rock” formation by a lunar fumarolic gas

Christian J. Renggli¹,¹ and Stephan Klemme²,²

¹Institut für Mineralogie, Universität Münster
²University of Muenster

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Abstract

The Apollo 16 sample 66095, named “rusty rock”, is uniquely enriched in volatile and moderately volatile elements. The impact melt breccia is characterized by the abundant occurrence of Fe-rich sulfide and chloride alteration phases, including FeS, ZnS and FeCl. These phases have previously been interpreted to be the result of fumarolic alteration of the breccia. Here we present the results of two different experimental approaches, which aim to constrain the temperature conditions and the process under which the “rusty rock” alteration formed. The first experimental set-up assumes that the metals Zn, Cu and Fe were introduced into the rock by a C-O-S-Cl gas phase, and that the Fe-rich sulfides and chlorides were deposited from this gas phase. This “gas deposition” experiment suggests that the alteration assemblage formed over the temperature range of 538-638 °C. The second experimental set-up simulates a scenario, where Fe metal particles in the lunar rock react with a Zn-C-O-S-Cl gas phase at six different temperatures between 396 °C and 1005 °C. This latter “metal reaction” experiment resulted in the formation of sulfide and chloride coatings on the Fe metal chips. The “rusty rock” alteration phases FeCl and (Zn,Fe)S were abundantly present in the coating of the Fe metal chip reacted at 580 °C. Both experiments lead to results which are in agreement, providing a temperature of 580 ± 50 °C for the fumarolic alteration on the Moon, as observed in the Apollo 16 “rusty rock”.

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Experimental investigation of Apollo 16 “Rusty Rock” alteration by a lunar fumarolic gas

C. J. Renggli\textsuperscript{1}, S. Klemme\textsuperscript{1}

\textsuperscript{1} Institut für Mineralogie, Universität Münster, Münster, 48149, Deutschland

Corresponding author: Christian Renggli (renggli@uni-muenster.de)

ORCID: Renggli 0000-0001-8913-4176

ORCID: Klemme 0000-0001-7859-9779

Key points

- Experiments constrain the temperature of fumarolic Apollo 16 “Rusty Rock” alteration to 580 ± 50 °C.
- Gas deposition and gas-solid metal reaction experiments reproduce the „Rusty Rock” alteration phases FeCl\textsubscript{2} and (Zn,Fe)S
Abstract

The Apollo 16 sample 66095, named „Rusty Rock”, is enriched in volatile and moderately volatile elements. The impact melt breccia is characterized by the abundant occurrence of Fe-rich sulfide and chloride alteration phases, including FeS, ZnS and FeCl₂. These phases have previously been interpreted to be the result of fumarolic alteration of the breccia. Here we present the results of two different experimental approaches, which aim to constrain the temperature conditions and the process under which the „Rusty Rock” alteration formed. The first experimental set-up assumes that the metals Zn, Cu and Fe were introduced into the rock by a C-O-S-Cl gas phase, and that the Fe-rich sulfides and chlorides were deposited from this gas phase. This “gas deposition” experiment suggests that the alteration assemblage formed over the temperature range of 538-638 ± 5 °C. The second experimental set-up simulates a scenario, where Fe metal particles in the lunar rock react with a Zn-C-O-S-Cl gas phase at six different temperatures between 396 ± 5 °C and 1005 ± 5 °C. This latter “metal reaction” experiment resulted in the formation of sulfide and chloride coatings on the Fe metal chips. The „Rusty Rock” alteration phases FeCl₂ and (Zn,Fe)S were abundantly present in the coating of the Fe metal chip reacted at 580 ± 5 °C. Both experiments lead to results which are in agreement, providing a temperature of 580 ± 50 °C for the fumarolic alteration on the Moon, as observed in the Apollo 16 „Rusty Rock”.

Plain Language Summary

The Apollo 16 sample 66095, colloquially named „Rusty Rock”, is an unusual lunar rock which is enriched in volatile elements such as sulfur and chlorine. We investigate two processes by which sulfides and chlorides may form in a lunar fumarolic system, by conducting experiments in evacuated silica glass tubes at reducing conditions. First, we assume that metals and volatiles (Zn, Cu, Fe, S and Cl) are all deposited from a gas phase (gas deposition experiments), and second, we assume that Fe metal is already present in the rock and that the Fe altered by the introduction of a Zn-S-Cl-bearing gas phase (metal reaction experiment). In both experimental setups we observe the formation of „Rusty Rock” alteration phases FeCl₂ and (Zn,Fe)S at 580 ± 50 °C, constraining the temperature of
fumarolic alteration recorded in the Apollo 16 sample 66095. Hence, our experiments confirm that the characteristic S- and Cl-rich minerals found in the lunar “Rusty Rock” were formed by a lunar fumarole. More broadly, lunar metal deposits may be associated with ancient fumarolic processes.

1. Introduction

The Apollo 16 „Rusty Rock” 66095 is a unique lunar sample which is highly enriched in the volatile elements S and Cl and in moderately volatile trace metals such as Tl, Br, Cd, Sn, Zn, Pb, Rb, Cs, Ga, B and Li (Krähenbühl et al., 1973; Taylor et al., 1973; Shearer et al., 2014; Day et al., 2017; Day et al., 2019). This volatile element enrichment of the „Rusty Rock” is in contrast to the vast majority of lunar samples which are generally very volatile depleted relative to terrestrial magmatic rocks (e.g. McCubbin et al., 2015).

Sample 66095 is a fine-grained impact melt breccia with lithic clasts, including anorthosite, troctolite, basalt and a minor KREEP-like component. The lithic clasts further contain metallic iron-nickel grains. These grains are commonly altered on the rims to (Fe,Ni)Cl₂, FeO(OH,Cl), FeS and occasional ZnS (Taylor et al., 1973; El Goresy et al., 1973; Taylor et al., 1974; Hunter and Taylor, 1981a; Hunter and Taylor, 1981b; Shearer et al., 2014). The alteration occurs on the surface of the rocks as well as the interior, suggesting that it was not a secondary process that occurred after sampling, in the spacecraft or on Earth (Meyer, 2009). Similar alteration features were observed in more than 20 different Apollo 16 samples (Taylor et al., 1973; Jean et al., 2016). This suggests that the alteration is a regional lunar process, rather than limited to sample 66095. Sulfidation (sulfide formation via gas-solid reactions) is not only associated with FeNi grains, but it also occurs disseminated in veins and replacement textures of olivine and pyroxene in Apollo 16 rocks (Norman, 1981; Colson, 1992; Norman et al., 1995; Shearer et al., 2012). This underlines the broader importance of the „Rusty Rock”, which provides a unique insight into the transport of volatile elements in the lunar crust.

Recent work has highlighted unique isotopic signatures of the Apollo 16 „Rusty Rock” 66095, providing insights into the origin of enriched volatile elements (Shearer et al., 2014; Day et al.,
The „Rusty Rock” is one of the most S-rich Apollo 16 samples, and with \( \delta^{34}\text{S} = +1.9\text{%} \) one of the most isotopically light lunar samples (Kerridge et al., 1975). Other lunar samples with light \( \delta^{34}\text{S} \) compositions include volatile coatings on Apollo 17 pyroclastic glass beads and troilite replacement veins in Apollo 16 breccias (Shearer et al., 2012). Because the light S isotopes preferentially partition into a gas phase, isotopically light \( \delta^{34}\text{S} \) in 66095 sulfides indicate that they deposited from a volcanic or fumarolic gas (Shearer et al., 2012; Shearer et al., 2014). The Cl isotopic composition of 66095, on the other hand, is heavy with respect to lunar igneous rocks, with \( \delta^{37}\text{Cl} \) ranging from +14.0\text{%} to +15.6\text{%} (Sharp et al., 2010; Shearer et al., 2014; Gargano et al., 2020). Apart from lunar apatites (Wang et al., 2012; Ustunisik et al., 2015), these are the heaviest Cl isotopic compositions measured in lunar samples (Shearer et al., 2014). As the overall Cl isotopic composition of the Moon was inferred to be similar to that of the Earth, the occurrence of much heavier isotopic compositions was attributed to the volatilization of metal halides (Sharp et al., 2010; Shearer et al., 2014; Gargano et al., 2020). These metal halides were deposited from the gas phase on pyroclastic glass beads, and in altered regolith and breccia such as 66095 (Shearer et al., 2014). The isotopic composition of Zn supports the interpretation of S and Cl isotopic compositions and the \( \delta^{66}\text{Zn} \) composition of the „Rusty Rock” reveals the lightest isotopic signature of Zn recorded in any sample analyzed, with \( \delta^{66}\text{Zn} = -13.7\text{%} \) (Day et al., 2017). This light isotopic signature was interpreted to be caused by degassing from a volatile-depleted Moon and condensation in the lunar regolith and on the Moon’s surface (Day et al., 2017; Day et al., 2019). Note that Cu and Fe isotopic compositions of 66095 are not fractionated and are within the range of normal lunar mare basalts \( \delta^{65}\text{Cu} = 0.9\text{%}, \delta^{56}\text{Fe} = 0.1\text{%} \) (Day et al., 2019). Iron is considered a non-volatile element but Cu is moderately volatile (Lodders, 2003; Norris and Wood, 2017; Sossi and Fegley, 2018; Sossi et al., 2019) so that stable Cu isotopes should have been fractionated if Cu had been deposited from a gas phase in the „Rusty Rock”. In a lunar volcanic gas at 1 bar and 1200 °C Zn is two orders of magnitude more volatile than Cu, and four orders of magnitude more volatile than Fe (Renggli et al., 2017).

Two different mechanisms are conceivable for the formation of the observed sulfide and chloride alteration in the „Rusty Rock” samples. In the first scenario, all metals (i.e., Zn, Cu and Fe),
together with S and Cl, were introduced into the rock by a fumarolic gas phase, and this caused deposition of metal sulfides and chlorides (gas deposition process). For example, in such a process lawrencite could be introduced into the „Rusty Rock” as a gas according to the reaction FeCl$_2$(g)=FeCl$_2$(s) (Colson, 1992). Similarly, Zn and Cu could be introduced as chloride, sulfide or elemental gas species and deposited under the same conditions as FeCl$_2$. This process would be recorded in the „Rusty Rock” by light isotopic signatures of the metals and the isotopically light Zn isotopes support this process (Day et al., 2017). However, the Cu and Fe isotopes are not isotopically light (Day et al., 2019) and hence this process does not account for the Cu and Fe isotopic signatures of 66095. In a second scenario, the metals Fe and Cu were not introduced by the gas phase, but instead, they were present in the rock prior to gas metasomatism, and hence the metals Cu and Fe reacted with a gas phase to form sulfides and chlorides (metal reaction process). Based on the isotopic composition, the latter mechanism was proposed to explain the alteration of Cu and Fe in the „Rusty Rock” (Day et al., 2019).

In both mechanisms a S- and Cl-bearing gas phase causes the alteration, either by introducing the metals, or by reacting with the metals in the rock to cause the sulfidation and chlorination. The gas-solid reactions may have occurred in ejecta blankets (Haskin and Warren, 1991) with volatiles sourced from comets or meteorites, or mobilized from the crust (El Goresy et al., 1973; Papike et al., 1991). Norman et al. (1995) first proposed that the source of sulfidation in Apollo 16 ferroan noritic anorthosites was driven by anhydrous C-O-S-Cl vapors, derived from shallow magmatic sources in the lunar crust. The role of a S-rich and H-poor gas phase was supported by Shearer et al. (2012). Similarly, Shearer et al. (2014) suggested that FeCl$_2$, FeS and ZnS in the „Rusty Rock” formed by a H-poor C-O-S-Cl gas, without a major extra-lunar contribution. Consequently, we conduct our experiments in a H-free system.

Our aim is to investigate these gas deposition and metal reaction processes proposed for the „Rusty Rock” alteration experimentally, and constrain the temperature conditions under which the „Rusty Rock” alteration (FeCl$_2$, FeS, ZnS) formed. Furthermore, we aim to put constraints on the fumarolic gas composition and test if the two mechanisms discussed above (deposition of Fe from the
gas phase vs. in-situ reaction with a C-O-S-Cl gas) are viable. For this purpose we used two different experimental approaches, simulating the different proposed alteration mechanisms, where the first approach assumes that all major elements of the alteration assemblage (i.e., Zn, Fe, Cu, Cl and S) were transported by a gas phase to form deposits along a temperature gradient (gas deposition experiment), essentially identical to the formation of mineral deposits from fumarolic gases (Renggli and Klemme, 2020). The second approach assumes that the Fe metal was already present in the rock and reacted with a C-O-S-Cl gas phase (metal reaction experiment). In this experiment we also include Zn in the gas phase due to the evidence from light δ⁶⁶Zn in the „Rusty Rock”, suggesting deposition from a gas phase (Day et al., 2017).

2. Methods

2.1 Experimental Rationale

We conducted two different gas-solid reaction experiments in evacuated silica glass tubes (Fig. 1). We adopted the experimental setup from Renggli & Klemme (2020), where we showed that these types of experiments can reproduce sulfide and chloride deposits in observed in terrestrial fumaroles. The experimental set-up follows, in principle, Nekvasil et al. (2019), where a volatile element-rich source material is placed in an evacuated silica glass tube in the hot zone of a furnace. The volatile and moderately volatile elements are mobilized and transported in the gas phase, and minerals are deposited in colder parts along the furnace temperature gradient. The ~30 cm long silica glass tube (Fig. 1) is placed in a vertical furnace so that the starting material is in the hot zone of the furnace. The furnace has a strong temperature gradient from the hot zone to the top of the furnace (Fig. 1) and hence temperatures within the long glass tubes range from 1240 °C, to 316 °C at the top of the glass tube (Supplement 1; Renggli and Klemme, 2020). Overall, the experimental set-up, which is used to simulate the transport of metals in fumarolic gases on the Moon, is similar to natural fumaroles, characterized by large gradients in temperature and variations in redox conditions, and gas composition with time.
Our set-up does not allow precise control of the redox conditions in our experiments, as in conventional gas-mixing furnaces. However, our experimental results allow us to constrain the dynamic evolution of the gas phase and the redox conditions during the runs. As our starting material is placed in a graphite cup, the system in the hot zone (at 1240 °C) is graphite saturated so that \( f_{O_2} \) cannot exceed the C-CO buffer (\( \log f_{O_2} = -16.9 \) at 1240 °C and 1 bar). This buffer assemblage is only operational if oxygen is present. In colder parts of the experimental glass tubes the system remains reducing. Our results below show that metallic phases (e.g. Cu-whisker or Fe-metal chips) and no metal oxides are present, which constrains the redox conditions at lower temperatures to below the iron-wüstite buffer (see 4.1 Constraints on the gas phase composition).

All experiments were conducted using evacuated and sealed silica glass tubes at an initial internal pressure of 10^-5 bar. The silica glass tubes were suspended in a vertical tube furnace (Gero GmbH, Germany), so that the starting material was placed in the hot zone of the furnace, i.e. 1240 °C. The furnace had a temperature gradient of 900 °C from the hot zone to the top of the silica glass tube (Fig. 1, Supplement 1), measured at 1 cm steps with a type B thermocouple. The temperature gradient is not linear along the tube, such that the 1 cm tube segments cover temperature ranges from 15 °C at the high and low temperature ends, to 65 °C where the gradient is steep around 700 °C (see Renggli and Klemme 2020 for more details). We conservatively estimate a temperature error associated with the preparation of the experiments of ±5. All experiments were run for 24 h. The starting material mixtures reacted at high temperature (1240 °C) to form a gas phase that subsequently moved upwards along the temperature gradient over the duration of the run (Nekvasil et al., 2019). The amount of starting materials in the pellets was limited to 0.05 g. This quantity was chosen to avoid an overpressurization of the ampules (\( P < 3 \) bar), assuming that the entire pellet material was in the gas phase at 1250 °C and give the inner volume of the sealed ampules (4 mm inner diameter, \( \approx 3770 \) mm³, see Renggli and Klemme 2020). The pressure in the experiments is not constant and evolves with time. Initially, as the volatile elements form a gas phase the pressure increases and rapidly equilibrates throughout the ampule, and gas species move along the temperature gradient by Soret diffusion.
(Nekvasil et al., 2019). As the solid phases begin to deposit from the gas phase on the silica glass tube wall the pressure decreases again (Renggli and Klemme, 2020).

### 2.2 Experiments

Our starting material mixtures consisted of reagent grade oxides, sulfides and chlorides as the volatile sources for the experiments, instead of synthetic silicate melts (Ustunisik et al., 2015; Nekvasil et al., 2019), to produce larger amounts of transported metals (Renggli and Klemme, 2020). The reagents were pressed into pellets (2 mm diameter) in a pellet press and at room temperature. The pellets were subsequently dried at 50 °C over night and placed in graphite crucibles at the bottom of the silica glass tubes.

The first type of experiments, which we call “gas deposition experiments”, simulates the transport of Zn, Cu and Fe in a C-O-S-Cl gas and the resulting deposition of sulfide and chloride phases (Renggli and Klemme, 2020). The starting material was a mixture of ZnO, FeS, CuS, MgCl₂ and C in the relative molar abundances of 1-1-1-3-4 (Table 1), pressed into a 50 mg pellet and placed in an open graphite crucible, which was then placed at the bottom of a 30 cm long evacuated silica glass tube. Upon heating, the volatile reagents in the pellet form a gas (at 1240 °C) with equal molar concentrations of Zn, Fe and Cu, and equal molar concentrations of S and Cl. MgO was the only solid that remained in the graphite crucible after the experiment (Supplement 2).

In the second type of experiments, which we call “metal reaction experiments”, we investigated the reaction of Fe metal with a Zn-C-O-S-Cl gas phase at 396±5, 496±5, 580±5, 708±5, 825±5 and 1005±5 °C. These temperatures reflect the positions of the metal chips relative to the temperature gradient in the tube furnace at 7, 11, 13, 15, and 21 cm from the top of the furnace respectively (Table 2, Supplement 1), with a ±5 °C temperature uncertainty resulting from the positioning of the tube in the furnace. As the source of volatiles, a pellet containing a mixture of ZnO, MgCl₂, S and C in the relative molar abundances of 1-1-1-4 (Table 1) was pressed and placed in an open graphite crucible in the evacuated silica glass tube. In this experiment, volatilization of the starting material pellet forms a gas with relative abundances of Zn:S:Cl = 1:1:2. After the experiment the remaining pellet only consisted of MgO (Supplement 2), which is evidence for complete
volatilization of Zn, S and Cl. Iron metal chips with diameters of ~ 1 mm were placed on silica glass wool spacers along the tube prior to the evacuation of the tube. The contact of the Fe metal chips with the silica glass wool resulted in the formation of minor amounts of Fe$_2$SiO$_4$.

The silica glass tubes were lifted out of the furnace and quenched in cold water. The quenched tubes were cold within less than 10 seconds, minimizing secondary alteration within the tubes. The tubes were then cut in 1cm long segments, corresponding to the position of the tubes relative to the temperature gradient in the furnace (Supplement 1). The samples were immediately placed in an evacuated desiccator in order to avoid alteration by exposure to the humidity in the air (Dalby et al., 2018). Aliquots of the reacted Fe metal chips were embedded in epoxy resin and prepared as polished cross-sections. The mounts were polished dry without water to avoid hydration of the samples, however the chlorides partially hydrated during sample preparation.

All samples were characterized with a JSM-6610 Series Scanning Electron Microscope (SEM). The silica tube segments with the sulfide and chloride deposits on the inner silica glass tube wall were analyzed without carbon coating using the low-vacuum capability of the SEM at 50 Pa. This allowed a minimization of sample exposure to ambient air and modification during sample preparation. The cross-sectioned samples were carbon coated and analyzed and imaged at high-vacuum using the Back-Scattered Electron (BSE) detector. All EDS analysis (both of the reacted surfaces and the cross-sectioned samples) were done at an acceleration voltage of 20 kV and a working distance of 10 mm, using the JEOL EDS analysis station with a dry silicon drift detector. The JEOL software performs and automated EDS peak identification and integrates the spectra to provide semi-quantitative atomic abundances. Due to the chemical simplicity of our experimental system no significant peak overlap is observed in the EDS spectra, allowing the integration of the spectra and the extraction of the compositions of the experimental phases. We analyzed each observed phase 5-10 times and provide standard deviations. We report the results of the EDS analysis as atomic% (Table 3 and Table 4).
3. Results

3.1 Gas deposition experiments

We observe eight different phases deposited on the inner wall of the silica glass tube, over the entire temperature range from 330-1240 °C (Fig. 2, Table 3). With the exception of forsterite (Mg$_2$SiO$_4$), which forms as the product of a reaction of the starting material with the silica glass tube, the phases were deposited from the Zn-Fe-Cu-C-O-S-Cl gas. We observe forsterite only at high temperatures (T > 698±5 °C) with grain sizes of up to 20 μm. This suggests that minor amounts of the MgCl$_2$ in the starting material were transported in the gas phase and reacted with the hot silica glass tube wall. The only chemical compound remaining in the graphite crucible after the experiment is MgO, suggesting that gas phase transport of Mg was a minor process. The MgO forms a dense pellet with grain sizes of up to 20 μm (Supplement 2). Phases deposited from the gas phase are spread over almost the entire silica tube from 330-1140±5 °C, with little overlap of different phases (Fig. 3).

Chalcocite (Cu$_2$S) occurs between 878±5-1140±5 °C and forms tabular grains often deposited in patches or groups of multiple single crystals (Fig. 2a & b). Below 1000 °C the crystals form increasingly well-developed crystal faces, whereas the typical habit of chalcocite crystals is more rounded at higher temperatures, especially in the case of crystals deposited near the melting point of Cu$_2$S at 1130 °C. The crystals have diameters of up to 60 μm and are commonly associated with higher abundances of forsterite on the tube wall. All chalcocite crystals show the growth of Cu-metal whiskers extruding from their surface (Fig. 2b). The whiskers have lengths of up to 10 μm and are composites of copper fibers with sub-micron diameters. At 698±5-830±5 °C (Fig. 3) we observe an unidentified Fe-Cu-S-Cl phase. These rare crystals have diameters of ~40 μm and well-developed triangular crystal faces.

The largest quantities of metal sulfide and chloride deposits occur over the relatively narrow temperature range of 540±5-700±5 °C (Fig. 3). In this narrow temperature range we observe the phases described in the Apollo „Rusty Rock”, including FeS, lawrencite (FeCl$_2$) and wurtzite (ZnS). FeS (presumed troilite) (638±5-698±5 °C) forms platy crystals and occurs together with lawrencite...
The FeS plates have diameters of up to 200 μm. Lawrencite occurs over a wider temperature range of 538±5-698±5 °C (Fig. 2). Where lawrencite coexists with FeS (Fig. 2d) the crystals are small, with prismatic grains up to 10 μm in length. At slightly lower temperature (>638±5 °C) the lawrencite forms large platy grains (Fig. 2e). Between 538±5 and 587±5 °C we observe a sharp boundary between a lawrencite and wurtzite dominated section (Fig. 2f). In the wurtzite dominated section we observe occasional triangular, platy FeCl₂ grains (Fig. 2g). The occurrence of wurtzite is limited to a narrow temperature range of 538±5-587±5 °C (Fig. 3). The typical hexagonal shape of wurtzite is only occasionally observed, but here we find that it forms dense aggregations of intergrown ZnS crystals (Fig. 2g). Below 538±5 °C we only observe Zn-phases and no Cu- or Fe-bearing minerals. Below 498±5 °C the only phase observed is ZnCl₂ (Fig. 3). ZnCl₂ is highly deliquescent and rapidly absorbs enough water from the atmosphere to form an aqueous solution, once exposed to air. This process occurs within less than 5 minutes in the relatively humid air of Münster in the summer, apparent in all samples where ZnCl₂ is present (Fig. 2i). Finally, in the transitional temperature range between 498±5 and 538±5 °C (Fig. 3) we observe an unidentified Zn-phase containing both S and Cl (Fig. 2h).

3.2 Metal reaction experiments

The Fe metal chips reacted with a C-O-S-Cl-Zn gas at 396±5, 496±5, 580±5, 708±5, 825±5 and 1005±5 °C, and the run products show that the reaction resulted in extensive reaction coatings with variable amounts of FeCl₂, (Zn,Fe)S and FeS (Table 4). In Figures 4 and 5 we show backscattered electron images of the surface coatings on the metal chips and polished cross-sections of the coated Fe metal chips. With increasing temperature, the coatings become thicker and coarser grained (Fig. 5). This proved to be problematic during the sample polishing of the cross-sections for SEM analysis, as the sulfide coatings partially decoupled from the underlying Fe metal chips.

At 396±5 °C the coating almost exclusively contains FeCl₂ (lawrencite) which crystallized as prismatic crystals with lengths of up to 200 μm and thicknesses of up to 40 μm (Fig. 4a). On the surface coatings we did not observe any sulfide phase. In cross-section it’s evident that the coatings
are thin with thicknesses of up to 20 μm (Fig. 4a & b). In addition to lawrencite we also detected traces of S by EDS. However, we could not observe individual grains.

At 496±5 °C lawrencite forms a dense and fine-grained coating on the reacted Fe metal (Fig. 4d). Individual grains are small with diameters of less than 5 μm. In cross-section we observe that the coating is much thicker than at 396±5 °C, measuring up to 80 μm (Fig. 4e & f). We also observe reaction between the lawrencite and the epoxy resin in which the sample is embedded (Fig. 4f). This secondary alteration of the coating likely occurred during embedding in the liquid resin as it did not change once the resin hardened.

At 580±5 °C we observe FeCl₂ and (Zn,Fe)S in the coating of the Fe metal chip (Fig. 4g). The coating is fine-grained with individual (Zn,Fe)S crystals with diameters of up to 8 μm. The coating has partially engulfed silica glass fibers on which the Fe metal chip was placed (Fig. 4g). In cross-section we observe that the coating with a thickness of up to 150 μm partially detached from the metal, suggesting a poor cohesion (Fig. 4h & i). The coating appears to be layered, with the FeCl₂ on the metal chip and the sulfide on the surface (Fig. 4i).

At 708±5 °C (Zn,Fe)S dominates the coating and only traces of FeCl₂ are observed in cross-section (Fig. 5 a-c). The sulfide grains have diameters of up to 40 μm (Fig. 5a), with a total coating thickness of ~100 μm (Fig. 5b). Traces of FeCl₂ were detected in the coating by EDS, but individual grains could not be identified unambiguously, suggesting grain sizes of less than 2 μm.

At 825±5 °C the coating only contains sulfides. It is the only sample where pure FeS could be distinguished from (Zn,Fe)S. At the surface of the coating grains have diameters of up to 60 μm (Fig. 5d). The coating is dense and the individual sulfide crystals are euhe dral. The coating is partially detached from the underlying Fe metal chip (Fig. 5e), but in some sections the contact is observed. The pure FeS is in direct contact with the metal chip and forms an undulatory interface (Fig. 5f). The (Zn,Fe)S occurs on the surface of the coating.

Finally, at 1005±5 °C the coating mainly consists of (Fe,Zn)S (Fig. 5 g-i). The sulfide grains have diameters of up to 50 μm. The coating thickness exceeds 200 μm and was mostly lost during
preparation of the cross-sections (Fig. 5h). The surface of the reacted Fe metal chip is highly undulatory and porosity is observed to a depth of 200 μm (Fig. 5h & i). The pore space formed during the reaction with the C-O-S-Cl-Zn gas and suggests a mobilization of Fe at 1005±5 °C. Indeed, apart from (Fe,Zn)S we also observe fayalite (Fe₂SiO₄) in the coating (Fig. 5g & i). The fayalite is primarily located where the Fe metal chip was in contact with the silica glass wool or the wall of the silica glass tube, facilitating the reaction.

In summary, 580±5 °C is the only temperature at which both FeCl₂ and (Zn,Fe)S could be observed abundantly in the coatings. At lower temperatures only traces of sulfide could be detected in the coatings, whereas at 708±5 °C only traces of FeCl₂ were detected. At even higher temperatures (825±5, 1005±5 °C) chlorides are absent from the coatings.

4. Discussion

Both the “gas deposition experiments” and the “metal reaction experiments” result in the formation of mineral assemblages containing sulfides and chlorides, and both experimental approaches reproduce the fumarolic alteration products observed in the lunar Apollo 16 „Rusty Rock” 66095. In the gas deposition experiments FeS, FeCl₂ and ZnS occur over the temperature range of 538-638±5 °C. In the metal reaction experiment the most extensive reaction and formation of both (Zn,Fe)S and FeCl₂ occurred at 580±5 °C, which is an almost identical temperature range as the gas deposition experiment. The two experiments suggest that 580 ± 50 °C is the temperature condition under which fumarolic alteration occurred on the Moon, as recorded in the „Rusty Rock” samples.

In our dry high temperature experiments we did not observe any oxyhydroxides and oxides that have been reported in the Apollo „Rusty Rock” samples, such as akaganéite (β-FeO(OH,Cl)), goethite (α-FeO(OH)) or hematite (α-Fe₂O₃) (Shearer et al., 2014). We conducted our experiments with water free, dried reagents, following the proposed H-poor nature of the C-O-S-Cl gas phase (Norman et al., 1995; Shearer et al., 2012; Shearer et al., 2014). Our experiments have consistently reproduced the dry alteration phases observed in the „Rust Rock”. This suggests, that the oxyhydroxides are a secondary alteration product of the primary FeCl₂ formed at high temperature.
The textural evidence from the Apollo 16 sample suggests that oxyhydration did not form upon exposure to a terrestrial atmosphere, but that akaganéite did replace lawrencite, based on the Cl-isotopes (Shearer et al., 2014). This suggests that the initial fumarolic alteration phase at 580 ± 50 °C was followed by a secondary alteration phase at lower temperatures and with a gas at higher $f$H$_2$ and $f$H$_2$O.

We performed our experiments in sealed and evacuated silica tubes with a 900 °C temperature range. In such an experimental setup the direct control of gas fugacities (e.g. $f$O$_2$ and $f$S$_2$) is not possible in the same way as in a conventional gas mixing furnace. Furthermore, the gas fugacities may vary along the temperature gradient, as well as over time as phases are deposited from the gas phase or gas species are bound to solids via chemisorption (King et al., 2018; Nekvasil et al., 2019). In addition, gas-solid reaction experiments may be kinetically limited (Renggli and King, 2018), as they are in nature (King et al., 2018). However, the large temperature gradient, variations in gas fugacities with temperature and time, as well as pressure increase with volatilization of elements at high temperature, followed by a pressure degrease as phases deposit from the gas at lower temperatures, are analogous to natural fumarolic processes (Henley and Seward, 2018). We argue that our experimental approach adequately represents these natural systems (Renggli and Klemme, 2020). Furthermore, some first order estimates on the gas composition can be made based on the phases observed in the experiments and in the lunar „Rusty Rock”.

4.1 Constraints on the gas phase composition

As mentioned above, the starting material used in our experiments contained graphite powder (Table 1) and it was placed in graphite crucibles. Graphite acts as a strong reducing agent and limits the $f$O$_2$ at the source at 1240 °C, as any free oxygen will react with the excess graphite to form CO gas. This is in analogy to the formation of CO-rich lunar volcanic gas that was argued to have formed by the oxidation of graphite (Fogel and Rutherford, 1995; Nicholis and Rutherford, 2009). The CO-bearing gas includes gaseous Zn and O due to the decomposition of ZnO and reaction with graphite. A second decomposition process follows the equations $ZnO + MgCl_2 = ZnCl_2(g) + MgO$ or $ZnO + MgCl_2 = Zn(g) + Cl_2(g) + MgO$, but these do not directly impinge on the oxygen fugacity.
At lower temperatures gas compositions, or gas fugacities, are assessed based on the phase assemblages observed in the experiments and the lunar „Rusty Rock”. First, we discuss the “gas deposition experiments”. All chalcocite crystals deposited between 880-1140 °C show the growth of Cu metal whiskers on the surface (Fig. 2a &b). Metal whiskers on sulfides are an indication of a decrease in \(f_{S_2}\) after the formation of the sulfides in a low pressure environment (Wagner, 1952; Nicolle and Rist, 1979). For example, iron whiskers were observed on sulfide grains in samples from asteroid 25143 Itokawa, sampled by Hayabusa (Matsumoto et al., 2020). The observation of Cu metal whiskers on the Cu\(_2\)S grains illustrates that the gas fugacities in our runs are not constant over time. Initially, the Zn-Cu-Fe-C-O-S-Cl compounds in the source volatilize rapidly which results in increasing gas pressure in the silica glass tube. As sulfides and chlorides deposit from the gas phase along the temperature gradient the gas pressure decreases again. The sole species remaining abundantly in the gas phase is CO, controlled by the reaction of excess graphite with any available oxygen in the source at 1240 °C. We therefore assume that \(\log f_O^2\) remains constant with time, but \(\log f_{S_2}\) decreases as the sulfides are deposited. The formation of the Cu metal whiskers suggests that \(\log f_{S_2}\) drops to the phase boundary of Cu\(_2\)S and Cu in the \(\log f_{S_2}\)-\(\log f_O^2\) space, as indicated by the arrow in Figure 6a.

The occurrence of FeS and FeCl\(_2\) together in both experimental approaches in the temperature range 580 ± 50 °C, which we identified as the temperature condition forming the „Rusty Rock” alteration on the Moon, allows further constraints of \(\log f_{S_2}\) and \(\log f_{Cl_2}\) in the experiment and for the lunar „Rusty Rock”. The presence of both FeS and FeCl\(_2\) (Fig. 2d for the gas deposition experiment and Fig. 4i for the metal reaction experiment) constrains the two variables to the univariate line indicated in Figure 6b. At 600 °C \(\log f_{S_2}\) is in the range of -13.2 to -10.5 and \(\log f_{Cl_2}\) is in the range of -13.9 to -12.5 (Fig. 6b).

Finally, in the Fe “metal reaction experiments” the redox state, at least in the colder parts of the tube, is further constrained by the Fe metal chips at 396±5, 496±5, 580±5, 708±5, 825±5 and 1005±5 °C. As we did not observe any oxidized iron in the experiments, we conclude that the \(\log f_O^2\)
remained below the iron-wüstite (IW) buffer at all temperatures and for the entire duration of the experiment.

Recent calculations of a lunar volcanic gas phase revealed that main gas species are S, CO and H$_2$ at 1200 °C, 10$^{-6}$ bar and reducing conditions of IW-2 (Renggli et al., 2017). This model was based on measurements of the volatiles H, S, Cl, F and C in partially degassed lunar pyroclastic glass beads (Saal et al., 2008; Wetzel et al., 2015). In such a volcanic gas composition the metals primarily deposit as sulfides with only minor abundances of elemental metal. Zink, Fe, Ni and Cu were observed as sulfides in coatings on the pyroclastic glass beads and the only chloride that was observed was NaCl (Butler and Meyer, 1976; Wasson et al., 1976; Clanton et al., 1978; Cirlin and Housley, 1979). Iron and Zn-chlorides, as observed in the Apollo 16 „Rusty Rock”, and in our experiments, are not predicted as deposited solids in the thermodynamic model and were not observed in pyroclastic glass bead coatings (Renggli et al., 2017). As a consequence, we suggest that the gas composition forming the „Rusty Rock” alteration had a different composition than the volcanic gas driving pyroclastic eruptions. Specifically, the logCl$_2$ must have been orders of magnitude higher in the „Rusty Rock” alteration environment, compared to the pyroclastic gas, allowing the deposition of metal chlorides from the gas phase and the reaction of Fe metal in the host rock to chloride. Commonly used 50% condensation temperatures (Lodders, 2003) suggest deposition of Fe above 1300 °C (Day et al., 2019). However, our experimental results showed that FeCl$_2$ are deposited from a gas phase at temperatures as low as 540 °C. This underlines the importance of experimental exploration of a broader range of gas compositions from which metals deposit and condensate in planetary environments. Finally, in our experiments, the relative abundances of Fe-, Zn-, and Cu-phases were limited by the addition of these metals to the starting materials in equal molar abundances (Table 1). These abundances do not represent those in the lunar samples, but were chosen to allow a better comparison of the behavior of these metals in our experiments.

Note that the sulfide mineralization was not just observed in the Apollo 16 „Rusty Rock” but sulfides have been observed in other Apollo 16 samples, including 67016 (Norman, 1981; Norman et al., 1995; Shearer et al., 2012), as well as Apollo 11, 14 and 17 rocks (McKay et al., 1972; Ramdohr,
172; Elardo et al., 2012). However, these rocks do not show chloride alteration and the predominant
sulfide phase is troilite (Shearer et al., 2012). In our experiment FeS was deposited from the gas phase
at 638±5-698±5 °C (Fig. 3). In addition to sulfide veins, likely deposited from a reducing S-rich gas,
troilite also occurs in metasomatic replacement textures of olivine to troilite and low-Ca pyroxene
(Colson, 1992; Norman et al., 1995; Shearer et al., 2012). In an ongoing study we will further
investigate the conditions under which these metasomatic replacement reactions occurred. At more
oxidizing conditions sulfates rapidly form when SO₂ reacts with basaltic glasses and minerals (King et
al., 2018; Renggli et al., 2019a). At reducing conditions relevant to the Moon and Mercury (Blewett et
al., 2013; Nittler et al., 2014) sulfides are predicted to form in a S-rich environment. At 700 °C and an
oxygen fugacity <IW additional sulfides may form including Na-, Ca- and Mg-sulfides (Renggli et al.,
2019b).

5. Conclusions

We conducted gas deposition and metal reaction experiments to simulate fumarolic alteration
in the Apollo 16 „Rusty Rock” 66095. The silica glass tube experiments are a useful tool to explore
metal transport processes and gas-solid reactions, such as sulfidation processes. Our experiments
indicate that the observed mineral assemblage of the rusty rock was formed at 580 ± 50 °C. In this
temperature range we observed the deposition of FeCl₂, ZnS and FeS in the gas deposition
experiment, and the formation of FeCl₂ and (Zn,Fe)S coatings on Fe metal grains reacted with a Zn-
C-O-S-Cl gas. The gas deposition experiments also showed that Cu₂S was deposited at higher
temperatures above 880 °C. Consequently, if Cu was carried in the lunar fumarolic gas, it must have
been deposited at higher temperatures and therefore likely at greater depths in the lunar crust
compared to the „Rusty Rock” alteration. This result supports the hypothesis that Cu was not
introduced into the „Rusty Rock” by a fumarolic gas, but was already present in the host rock, as
suggested by the normal lunar mare basalt δ⁶⁵Cu composition (Day et al., 2019). Our experiments do
not allow us to discriminate between the deposition of FeCl₂ and FeS from the fumarolic gas vs. the
in-situ reaction of metallic iron with a C-O-S-Cl gas. Both processes result in the formation of FeCl₂
and FeS in the temperature range of 580 ± 50 °C. The observed assemblage of FeCl₂ and FeS, and the
absence of oxidized iron, allowed us to constrain sulfur and chlorine fugacities in the gas phase at reducing conditions below the IW buffer. At 600 °C log$_{10} f_{S_2}$ is at -13.5 to -10.5 and log$_{10} f_{Cl_2}$ is at -13.9 to -12.5.

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References

Blewett D. T., Vaughan W. M., Xiao Z., Chabot N. L., Denevi B. W., Ernst C. M., Helbert J., D’Amore M., Maturilli A., Head J. W. and Solomon S. C. (2013) Mercury’s hollows: Constraints on formation and composition from analysis of geological setting and spectral reflectance. J. Geophys. Res. Planets 118, 1013–1032.

Butler P. and Meyer C. (1976) Sulfur prevails in coatings on glass droplets - Apollo 15 green and brown glasses and Apollo 17 orange and black (devitrified) glasses. Proc. Lunar Sci. Conf. 7, 1561–1581.

Chase M. W. (1998) NIST-JANAF Thermochemical Tables. 4th ed., Physical and Chemical Reference Data.

Cirlin E. H. and Housley R. M. (1979) Scanning Auger Microprobe and atomic absorption studies of lunar volcanic volatiles. In Planetary Science Conference Proceedings. pp. 341–354.

Clanton U. S., McKay D. S., Waits G. and Fuhrman R. (1978) Sublimate morphology on 74001 and 74002 orange and black glassy droplets. Lunar Planet. Sci. Conf. 9, 1945–1957.

Colson R. O. (1992) Mineralization on the Moon?: Theoretical Considerations of Apollo 16 “Rusty Rocks,” Sulfide Replacement in 67016, and Surface-Correlated Volatiles on Lunar Volcanic Glass. Proc. Lunar Planet. Sci. 22, 427–436.

Dalby K. N., Berger J. A., Brand H. E. A., Cairney J. M., Eder K., Eggins S. M., Herring A., Hervig R. L., Krieder P. B., Mernagh T. P., Palm A. B., Renggli C. J., Troitzsch U., Yue L. and King P. L. (2018) Analytical Techniques for Probing Small-Scale Layers that Preserve Information on Gas–Solid Interactions. Rev. Mineral. Geochem. 84, 103–175.
Day J. M. D., Moynier F. and Shearer C. K. (2017) Late-stage magmatic outgassing from a volatile-depleted Moon. *Proc. Natl. Acad. Sci.*, 201708236.

Day J. M. D., Sossi P. A., Shearer C. K. and Moynier F. (2019) Volatile distributions in and on the Moon revealed by Cu and Fe isotopes in the ‘Rusty Rock’ 66095. *Geochem. Cosmochim. Acta*, S0016703719301218.

El Goresy A., Ramdohr P., Pavićević M., Medenbach O., Müller O. and Gentner W. (1973) Zinc, lead, chlorine and FeOOH-bearing assemblages in the Apollo 16 sample 66095: Origin by impact of a comet or a carbonaceous chondrite? *Earth Planet. Sci. Lett.* 18, 411–419.

Elardo S. M., McCubbin F. M. and Shearer C. K. (2012) Chromite symplectites in Mg-suite troctolite 76535 as evidence for infiltration metasomatism of a lunar layered intrusion. *Geochem. Cosmochim. Acta* 87, 154–177.

Fogel R. A. and Rutherford M. J. (1995) Magmatic volatiles in primitive lunar glasses: I. FTIR and EPMA analyses of Apollo 15 green and yellow glasses and revision of the volatile-assisted fire-fountain theory. *Geochem. Cosmochim. Acta* 59, 201–215.

Gargano A., Sharp Z., Shearer C., Simon J. I., Halliday A. and Buckley W. (2020) The Cl isotope composition and halogen contents of Apollo-return samples. *Proc. Natl. Acad. Sci.*, 202014503.

Haskin L. A. and Warren P. (1991) Lunar Chemistry. In *Lunar source book* (eds. G. H. Heiken, D. T. Vaniman, and B. V. French). Cambridge University Press, New York. pp. 357–474.

Henley R. W. and Seward T. M. (2018) Gas–Solid Reactions in Arc Volcanoes: Ancient and Modern. *Rev. Mineral. Geochem.* 84, 309–349.

Hunter R. H. and Taylor L. A. (1981a) Rust and schreibersite in Apollo 16 highland rocks: Manifestations of volatile-element mobility. In *Lunar and Planetary Science Conference Proceedings* 253-259.

Hunter R. H. and Taylor L. A. (1981b) Rusty Rock 66095: A paradigm for volatile-element mobility in highland rocks. In *Lunar and Planetary Science Conference Proceedings*.

Jean M. M., Bonder B., Farley C. and Taylor L. A. (2016) “Rusty Rocks” from the Moon: Volatile-Element Contributions from Meteorites. In Lunar and Planetary Science Conference. p. 2498. Available at: http://adsabs.harvard.edu/abs/2016LPI....47.2498J [Accessed August 7, 2019].

Kerridge J. F., Kaplan I. R., Petrowski C. and Chang S. (1975) Light element geochemistry of the Apollo 16 site. *Geochem. Cosmochim. Acta* 39, 137–162.

King P. L., Wheeler V. M., Renfgli C. J., Palm A. B., Wilson S. A., Harrison A. L., Morgan B., Nekvasil H., Troitzsch U., Mernagh T., Yue L., Bayon A., DiFrancesco N. J., Baile R., Kreider P. and Lipi W. (2018) Gas–Solid Reactions: Theory, Experiments and Case Studies Relevant to Earth and Planetary Processes. *Rev. Mineral. Geochem.* 84, 1–56.

Krähenbühl U., Ganapathy R., Morgan J. A. and Anders E. (1973) Volatile elements in Apollo 16 samples: implications for highland volcanism and accretion history of the moon. In *Proceedings of the 4th Lunar Science Conference*. Pergamon Press, New York. pp. 1325–1348.

Lodders K. (2003) Solar System Abundances and Condensation Temperatures of the Elements. *Astrophys. J.* 591, 1220.
Matsumoto T., Harries D., Langenhorst F., Miyake A. and Noguchi T. (2020) Iron whiskers on asteroid Itokawa indicate sulfide destruction by space weathering. *Nat. Commun.* **11**, 1–8.

McCubbin F. M., Kaaden K. E. V., Tartèse R., Klima R. L., Liu Y., Mortimer J., Barnes J. J., Shearer C. K., Treiman A. H., Lawrence D. J., Elardo S. M., Hurley D. M., Boyce J. W. and Anand M. (2015) Magmatic volatiles (H, C, N, F, S, Cl) in the lunar mantle, crust, and regolith: Abundances, distributions, processes, and reservoirs. *Am. Mineral.* **100**, 1668–1707.

McKay D. S., Clanton U. S., Morrison D. A. and Ladle, G.H. (1972) Vapor phase crystallization in Apollo 14 breccia. In *Proceedings of the Third Lunar Science Conference* pp. 739–752.

Meyer C. (2009) 66095 “Rusty Rock.” *Lunar Sample Compend.*, 22.

Nekvasil H., DiFrancesco N. J., Rogers A. D., Coraor A. E. and King P. L. (2019) Vapor-Deposited Minerals Contributed to the Martian Surface During Magmatic Degassing. *J. Geophys. Res. Planets* **124**, 1592–1617.

Nichols M. G. and Rutherford M. J. (2009) Graphite oxidation in the Apollo 17 orange glass magma: Implications for the generation of a lunar volcanic gas phase. *Geochim. Cosmochim. Acta* **73**, 5905–5917.

Niccolle R. and Rist A. (1979) The mechanism of whisker growth in the reduction of wüstit. *Metall. Trans. B* **10**, 429–438.

Renggli C. J. and Klemme S. (2020) Experimental constraints on metal transport in fumarolic gases. *J. Volcanol. Geotherm. Res.* **400**, 106929.
Renggli, King P. L., Henley R. W., Guagliardo P., McMorrow L., Middleton J. P. and Turner M. (2019a) An experimental study of SO2 reactions with silicate glasses and supercooled melts in the system anorthite–diopside–albite at high temperature. *Contrib. Mineral. Petrol.* **174**, 3.

Renggli, Palm A. B., King P. L. and Guagliardo P. (2019b) Implications of Reactions Between SO2 and Basaltic Glasses for the Mineralogy of Planetary Crusts. *J. Geophys. Res. Planets* **124**, 2563–2582.

Roine A. (2015) *Outotec HSC Chemistry 8.1.*, Outotec Research Center, Finland.

Saal A. E., Hauri E. H., Cascio M. L., 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**, 192–195.

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.

Shearer C. K., Burger P. V., Guan Y., Papike J. J., Sutton S. R. and Atudorei N.-V. (2012) Origin of sulfide replacement textures in lunar breccias. Implications for vapor element transport in the lunar crust. *Geochim. Cosmochim. Acta* **83**, 138–158.

Shearer C. K., Sharp Z. D., Burger P. V., McCubbin F. M., Provencio P. P., Brearley A. J. and Steele A. (2014) Chlorine distribution and its isotopic composition in “rusty rock” 66095. Implications for volatile element enrichments of “rusty rock” and lunar soils, origin of “rusty” alteration, and volatile element behavior on the Moon. *Geochim. Cosmochim. Acta* **139**, 411–433.

Sossi P. A. and Fegley B. (2018) Thermodynamics of Element Volatility and its Application to Planetary Processes. *Rev. Mineral. Geochem.* **84**, 393–459.

Sossi P. A., Klemme S., O’Neill H. St. C., Berndt J. and Moynier F. (2019) Evaporation of moderately volatile elements from silicate melts: experiments and theory. *Geochim. Cosmochim. Acta* **260**, 204–231.

Taylor L. A., Mao H. K. and Bell P. M. (1974) Identification of the Hydrated Iron Oxide Mineral Akaganéite in Apollo 16 Lunar Rocks. *Geology* **2**, 429–432.

Taylor L. A., Mao H. K. and Bell P. M. (1973) “Rust” in the Apollo 16 rocks. In *Proc. 4th Lunar Sci. Conf.* pp. 829–839.

Ustunisik G., Nekvasil H., Lindsley D. H. and McCubbin F. M. (2015) Degassing pathways of Cl-, F-, H-, and S-bearing magmas near the lunar surface: Implications for the composition and Cl isotopic values of lunar apatite. *Am. Mineral.* **100**, 1717–1727.

Wagner C. (1952) Mechanism of the Reduction of Oxides and Sulphides to Metals. *JOM* **4**, 214–216.

Wang Y., Guan Y., Hsu W. and Eiler J. M. (2012) Water Content, Chlorine and Hydrogen Isotope Compositions of Lunar Apatite. *Meteorit. Planet. Sci. Suppl.* **75**, 5170.

Wasson J. T., Boynton W. V., Kallemeyn G. W., Sundberg L. L. and Wai C. M. (1976) Volatile compounds released during lunar lava fountaining. *Proc. Lunar Sci. Conf.* **7**, 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. *Nat. Geosci.* **8**, 755–758.
Tables

Table 1: Composition of the experimental charges of the gas deposition and metal reaction experiments. The table shows nominal molar concentrations of the reagent mixtures and weighed-in values.

|                     | Gas deposition experiment | Metal reaction experiment |
|---------------------|---------------------------|---------------------------|
|                     | Molar abundances | Weight g | Molar abundances | Weight g |
| ZnO                 | 1                         | 0.0068(1)             | 1                         | 0.0158(1)             |
| FeS                 | 1                         | 0.0073(1)             | -                         | -                   |
| CuS                 | 1                         | 0.0080(1)             | -                         | -                   |
| MgCl₂               | 3                         | 0.0239(1)             | 1                         | 0.0185(1)             |
| S                   | -                         | -                     | 1                         | 0.0062(1)             |
| C                   | 4                         | 0.0040(1)             | 4                         | 0.0094(1)             |
| Total               |                           | 0.05                  |                           | 0.05                 |

Table 2: Experimental conditions and positions of Fe metal chips along the silica tube in the metal reaction experiment. Temperatures were measured with a type B thermocouple in the vertical tube furnace in 1 cm steps prior to the experiments.

| Distance from top of tube | Temperature °C |
|---------------------------|----------------|
| cm                        |                |
| a                         | 7              | 396±5            |
| b                         | 11             | 496±5            |
| c                         | 13             | 580±5            |
| d                         | 15             | 708±5            |
| e                         | 17             | 825±5            |
| f                         | 21             | 1005±5           |
| Volatile source           | 31             | 1240±5           |
| Tube length               | 28 cm          |
| Duration                  | 24h            |
Table 3: EDS analysis of the observed phases in the "gas deposition experiment" given in atomic %. Standard deviations of the analyses are given in brackets. Backscattered electron images of the analyzed phases are shown in Fig. 2.

| Temperature °C | Phase       | S atomic % | Cl atomic % | Fe atomic % | Cu atomic % | Zn atomic % |
|---------------|-------------|------------|-------------|-------------|-------------|-------------|
| 300-538       | ZnCl₂       | n.d.       | 59.0(1.7)   | 0.9(0.7)    | n.d.        | 39.9(1.9)   |
| 498-538       | Zn-Cl-S     | 22.8(1.3)  | 30.8(6.3)   | 0.5(0.2)    | n.d.        | 45.9(7.3)   |
| 538-587       | ZnS         | 43.0(2.1)  | 6.5(0.7)    | 3.7(0.4)    | 0.8(0.1)    | 46.0(2.1)   |
| 538-698       | FeCl₂       | 1.9(2.2)   | 61.1(3.5)   | 36.6(1.3)   | n.d.        | 0.3(0.1)    |
| 638-698       | FeS         | 44.4(1.9)  | 4.5(2.2)    | 50.0(2.7)   | 0.9(0.3)    | n.d.        |
| 698-830       | Cu-Fe-Cl-S  | 31.5(3.0)  | 20.5(3.2)   | 16.2(3.9)   | 31.6(3.5)   | n.d.        |
| 878-1140      | CuS         | 35.0(2.5)  | 2.8(1.0)    | 6.4(0.8)    | 55.7(2.0)   | n.d.        |
| 878-1140      | Cu (whiskers)| 5.1(2.7)  | 2.0(1.3)    | 2.4(1.4)    | 90.5(3.7)   | n.d.        |

n.d. = not detected, i.e., below the detection limit

Table 4: EDS analysis of the observed mineral phases in the "metal reaction experiment" given in atomic %. Standard deviations of the analyses are given in brackets. Backscattered electron images of the analyzed phases are shown in Figs. 3 and 4.

| Temperature °C | Phase       | S atomic % | Cl atomic % | Fe atomic % | Zn atomic % |
|---------------|-------------|------------|-------------|-------------|-------------|
| 396           | FeCl₂       | n.d.       | 65.3(2.2)   | 34.1(2.1)   | n.d.        |
| 496           | FeCl₂       | 3.4(2.2)   | 59.9(6.4)   | 19.8(3.9)   | 16.9(1.6)   |
| 580           | FeCl₂       | 0.9(0.6)   | 61.1(3.8)   | 28.4(5.2)   | 9.6(1.9)    |
| 580           | (Zn,Fe)S    | 49.5(0.3)  | 4.4(1.1)    | 2.7(0.2)    | 43.4(1.0)   |
| 708           | FeCl₂       | 1.2(0.7)   | 62.8(13.3)  | 28.4(15.7)  | 7.8(2.6)    |
| 708           | (Zn,Fe)S    | 50.3(0.8)  | n.d.        | 22.6(3.2)   | 26.9(3.2)   |
| 825           | (Zn,Fe)S    | 50.7(0.2)  | n.d.        | 18.3(1.4)   | 31.0(1.2)   |
| 825           | (Fe,Zn)S    | 50.2(0.3)  | n.d.        | 28.3(0.5)   | 21.5(0.3)   |
| 825           | FeS         | 50.8(0.5)  | n.d.        | 48.7(0.6)   | 0.4(0.1)    |
| 1005          | (Zn,Fe)S    | 50.4(0.3)  | n.d.        | 14.7(0.9)   | 34.8(0.6)   |
| 1005          | (Fe,Zn)S    | 50.1(0.2)  | n.d.        | 22.1(0.8)   | 27.8(1.0)   |

n.d. = not detected, i.e., below the detection limit
Figure 1: Illustration of the experimental setup in a vertical tube furnace. a) Gas deposition experiment. The source in the hot zone of the furnace volatilizes and different phases are deposited along the temperature gradient within the silica glass tube.; b) Metal reaction experiment. The Fe metal chips were placed on SiO₂ glass wool spacers at 396±5, 496±5, 580±5, 708±5, 825±5 and 1005±5 °C; c) schematic of the furnace temperature gradient with temperatures at which the Fe metal chips were placed within the tube.
Figure 2: Backscattered electron images of phases deposited on the inner silica tube wall ("gas deposition experiment"). a) Cu$_2$S grains and SiO$_2$ glass dust which was formed during opening of the tube, 962±5-1003±5 °C; b) Cu$_2$S grain with Cu metal whiskers, 878±5-918±5 °C; c) Unidentified Fe-Cu-S-Cl phase and Mg$_2$SiO$_4$, the reaction product of MgO with the silica glass tube wall, 698±5-768±5 °C; d) FeS and FeCl$_3$, 638±5-698±5 °C; e) FeCl$_3$, 587±5-638±5 °C; f) FeCl$_2$ and ZnS, 538±5-587±5 °C; g) FeCl$_2$ and ZnS, 538±5-587±5 °C; h) Unidentified Zn-Cl-S phase, 495±5-538±5 °C; i) Liquidized and hydrated ZnCl$_2$ due to its deliquescence, SiO$_2$ glass shards, 374±5-396±5 °C.
Figure 3: Distribution of phases deposited along the temperature gradient in the silica tube summarizing the observations shown in Fig. 2 from the gas deposition experiment. The solid bars show the temperature ranges over which the respective phases were observed in the silica glass tube by investigation of the inner tube wall with back-scattered electron microscopy and EDS analysis. „Rusty Rock” phases are observed over the temperature range 538±5-638±5 °C.
Figure 4: Backscattered electron images of the Fe metal reaction experiment. Images a, d and c show the surfaces of the coatings and images b, e, f, h and i show cross-sections of the samples. The rows indicate the temperatures, 396±5 °C (a-c), 496±5 °C (d-f) and 580±5 °C (g-h).
Figure 5: Backscattered electron images of the Fe metal reaction experiment. Images a, d and c show the surfaces of the coatings and images b, e, f, h and I show cross-sections of the samples. The rows indicate the temperatures, 708±5 °C (a-c), 825±5 °C (d-f) and 1005±5 °C (g-h).
Figure 6: a) Phase stability diagram of the system Cu-S-O as a function of logfS_2 and logfO_2 at 900 °C, 1 bar. The univariate line in brown shows the condition for coexistence of Cu and Cu_2S as observed in the metal transport experiment and the formation of Cu whiskers on the Cu_2S crystal. The brown arrow indicates a decrease in logfS_2 with experimental duration resulting in the growth of Cu whiskers. b) Phase stability diagram of the system Fe-S-Cl as a function of log fS_2 and logfCl_2 at 600 °C, 1 bar. The univariate line shows the co-stability of FeCl_2 and FeS as observed in the metal transport experiment at 638±5-698±5 °C (Fig. 2d) and the Fe metal-gas reaction experiment at 580±5 °C (Fig. 4g-i). Calculations were made with the program HSC9 by Outotec, largely based on data from the NIST-JANAF thermochemical data base (Chase, 1998; Roine, 2015).
Supplement to:

Experimental investigation of Apollo 16 “Rusty Rock” alteration by a lunar fumarolic gas

C. J. Renggli¹, S. Klemme¹

¹ Institut für Mineralogie, Universität Münster, Münster, 48149, Deutschland

Corresponding author: Christian Renggli (renggli@uni-muenster.de)

ORCID: Renggli 0000-0001-8913-4176

ORCID: Klemme 0000-0001-7859-9779
Supplement 1: Temperature gradient in the vertical tube furnace

Table 1: Temperature gradient in the vertical tube furnace (Gero GmbH, Germany) measured with a type B thermocouple at 1 cm intervals. The thermocouple was equilibrated for 10 minutes at each step. Small temperature variations were likely due to thermal convection in the furnace.

| Distance (cm) | Temperature (°C) | Min | Avg. | Max |
|---------------|------------------|-----|------|-----|
| 1             |                  | 304 | 304.5| 305 |
| 2             |                  | 311 | 311.5| 312 |
| 3             |                  | 315 | 315.5| 316 |
| 4             |                  | 321 | 322  | 323 |
| 5             |                  | 329 | 330  | 331 |
| 6             |                  | 342 | 343  | 344 |
| 7             |                  | 357 | 358  | 359 |
| 8             |                  | 373 | 374  | 375 |
| 9             |                  | 395 | 396.5| 398 |
| 10            |                  | 421 | 422  | 423 |
| 11            |                  | 460 | 461.5| 463 |
| 12            |                  | 497 | 498.5| 500 |
| 13            |                  | 537 | 538.5| 540 |
| 14            |                  | 585 | 587  | 589 |
| 15            |                  | 637 | 638.5| 640 |
| 16            |                  | 695 | 697.5| 700 |
| 17            |                  | 767 | 768.5| 770 |
| 18            |                  | 828 | 829.5| 831 |
| 19            |                  | 877 | 878.5| 880 |
| 20            |                  | 916 | 918  | 920 |
| 21            |                  | 960 | 962  | 964 |
| 22            |                  | 1001| 1003 | 1005|
| 23            |                  | 1042| 1043.5|1045|
| 24            |                  | 1079| 1080 | 1081|
| 25            |                  | 1106| 1107 | 1108|
| 26            |                  | 1139| 1140 | 1141|
| 27            |                  | 1162| 1163 | 1164|
| 28            |                  | 1187| 1188 | 1189|
| 29            |                  | 1210| 1211 | 1212|
| 30            |                  | 1228| 1228.5|1229|
| 31            |                  | 1240| 1240.5|1241|
| 32            |                  | 1251| 1251 | 1251|
| 33            |                  | 1260| 1260 | 1260|
| 34            |                  | 1265| 1265 | 1265|
| 35            |                  | 1269| 1269 | 1269|
| 36            |                  | 1272| 1272 | 1272|
| 37            |                  | 1275| 1275 | 1275|
| 38            |                  | 1277| 1277 | 1277|
| 39            |                  | 1278| 1278 | 1278|
| 40            |                  | 1280| 1280 | 1280|
| 41            |                  | 1281| 1281 | 1281|
| 42            |                  | 1281| 1281 | 1281|
| 43            |                  | 1280| 1280 | 1280|
| 44            |                  | 1278| 1278 | 1278|
| 45            |                  | 1275| 1275 | 1275|
Figure 1: the solid line depict the temperature gradient in the vertical tube furnace measured with type B thermocouple from the top of the alumina furnace tube. The colored range indicates the length and position of the evacuated silica glass tube relative to the thermal gradient in the furnace. The stippled lines a, b, c, d, e and f indicate the positions of the Fe-metal chips placed in the silica glass tube of the metal reaction experiment. The corresponding temperatures at these positions are $396\pm5$, $496\pm5$, $580\pm5$, $708\pm5$, $825\pm5$ and $1005\pm5$ °C.
Supplement 2: Devolatilized pellets

Figure 2: Back-scattered electron image of the devolatilized starting material pellet from the metal reaction experiment. The devolatilized pellet consists entirely of MgO and has lost all Zn, S and Cl to the gas phase. This suggests that the Zn-volatilization reactions $\text{ZnO} + \text{MgCl}_2 = \text{ZnCl}_2(\text{g}) + \text{MgO}$ or $\text{ZnO} + \text{MgCl}_2 = \text{Zn}(\text{g}) + \text{Cl}_2(\text{g}) + \text{MgO}$ were completed, leaving only MgO.