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

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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 $FeCl_2$ 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 $FeCl_2$. 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 $FeCl_2$ 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 $FeCl_2$ 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 $(Fe,Ni)Cl_2$, 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.,

2017; Day et al., 2019). The „Rusty Rock" is one of the most S-rich Apollo 16 samples, and with $\delta^{34}S$=+1.9‰ one of the most isotopically light lunar samples (Kerridge et al., 1975). Other lunar samples with light $\delta^{34}S$ 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 $\delta^{34}S$ 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 $\delta^{37}Cl$ ranging from +14.0‰ to +15.6‰ (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 $\delta^{66}Zn$ composition of the „Rusty Rock" reveals the lightest isotopic signature of Zn recorded in any sample analyzed, with $\delta^{66}Zn$ = -13.7‰ (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 ($\delta^{65}Cu$ = 0.9‰, $\delta^{56}Fe$ = 0.1‰) (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),

93 together with S and Cl, were introduced into the rock by a fumarolic gas phase, and this caused
94 deposition of metal sulfides and chlorides (gas deposition process). For example, in such a process
95 lawrencite could be introduced into the „Rusty Rock" as a gas according to the reaction
96 $FeCl_{2(g)}$=$FeCl_{2(s)}$ (Colson, 1992). Similarly, Zn and Cu could be introduced as chloride, sulfide or
97 elemental gas species and deposited under the same conditions as $FeCl_2$. This process would be
98 recorded in the „Rusty Rock" by light isotopic signatures of the metals and the isotopically light Zn
99 isotopes support this process (Day et al., 2017). However, the Cu and Fe isotopes are not isotopically
100 light (Day et al., 2019) and hence this process does not account for the Cu and Fe isotopic signatures
101 of 66095. In a second scenario, the metals Fe and Cu were not introduced by the gas phase, but
102 instead, they were present in the rock prior to gas metasomatism, and hence the metals Cu and Fe
103 reacted with a gas phase to form sulfides and chlorides (metal reaction process). Based on the isotopic
104 composition, the latter mechanism was proposed to explain the alteration of Cu and Fe in the „Rusty
105 Rock" (Day et al., 2019).

106 In both mechanisms a S- and Cl-bearing gas phase causes the alteration, either by introducing
107 the metals, or by reacting with the metals in the rock to cause the sulfidation and chlorination. The
108 gas-solid reactions may have occurred in ejecta blankets (Haskin and Warren, 1991) with volatiles
109 sourced from comets or meteorites, or mobilized from the crust (El Goresy et al., 1973; Papike et al.,
110 1991). Norman et al. (1995) first proposed that the source of sulfidation in Apollo 16 ferroan noritic
111 anorthosites was driven by anhydrous C-O-S-Cl vapors, derived from shallow magmatic sources in
112 the lunar crust. The role of a S-rich and H-poor gas phase was supported by Shearer et al. (2012).
113 Similarly, Shearer et al. (2014) suggested that $FeCl_2$, FeS and ZnS in the „Rusty Rock" formed by a
114 H-poor C-O-S-Cl gas, without a major extra-lunar contribution. Consequently, we conduct our
115 experiments in a H-free system.

116 Our aim is to investigate these gas deposition and metal reaction processes proposed for the
117 „Rusty Rock" alteration experimentally, and constrain the temperature conditions under which the
118 „Rusty Rock" alteration ($FeCl_2$, FeS, ZnS) formed. Furthermore, we aim to put constraints on the
119 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 δ^{66}Zn 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 fO_2 cannot exceed the C-CO buffer ($\log fO_2$ = -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, ~3770 mm^3, 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, $MgCl_2$ 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, $MgCl_2$, 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

198 volatilization of Zn, S and Cl. Iron metal chips with diameters of ~ 1 mm were placed on silica glass
199 wool spacers along the tube prior to the evacuation of the tube. The contact of the Fe metal chips with
200 the silica glass wool resulted in the formation of minor amounts of Fe_2SiO_4.

201 .

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

210 All samples were characterized with a JSM-6610 Series Scanning Electron Microscope
211 (SEM). The silica tube segments with the sulfide and chloride deposits on the inner silica glass tube
212 wall were analyzed without carbon coating using the low-vacuum capability of the SEM at 50 Pa.
213 This allowed a minimization of sample exposure to ambient air and modification during sample
214 preparation. The cross-sectioned samples were carbon coated and analyzed and imaged at high-
215 vacuum using the Back-Scattered Electron (BSE) detector. All EDS analysis (both of the reacted
216 surfaces and the cross-sectioned samples) were done at an acceleration voltage of 20 kV and a
217 working distance of 10 mm, using the JEOL EDS analysis station with a dry silicon drift detector. The
218 JEOL software performs and automated EDS peak identification and integrates the spectra to provide
219 semi-quantitative atomic abundances. Due to the chemical simplicity of our experimental system no
220 significant peak overlap is observed in the EDS spectra, allowing the integration of the spectra and the
221 extraction of the compositions of the experimental phases. We analyzed each observed phase 5-10
222 times and provide standard deviations. We report the results of the EDS analysis as atomic% (Table 3
223 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_2SiO_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_2S) 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_2S 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

(Fig. 3d). 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 $FeCl_2$ 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 $ZnCl_2$ (Fig. 3). $ZnCl_2$ 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 $ZnCl_2$ 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 $FeCl_2$, (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 $FeCl_2$ (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

276 are thin with thicknesses of up to 20 μm (Fig. 4a & b). In addition to lawrencite we also detected
277 traces of S by EDS. However, we could not observe individual grains.

278 At 496±5 °C lawrencite forms a dense and fine-grained coating on the reacted Fe metal (Fig.
279 4d). Individual grains are small with diameters of less than 5 μm. In cross-section we observe that the
280 coating is much thicker than at 396±5 °C, measuring up to 80 μm (Fig. 4e & f). We also observe
281 reaction between the lawrencite and the epoxy resin in which the sample is embedded (Fig. 4f). This
282 secondary alteration of the coating likely occurred during embedding in the liquid resin as it did not
283 change once the resin hardened.

284 At 580±5 °C we observe $FeCl_2$ and (Zn,Fe)S in the coating of the Fe metal chip (Fig. 4g). The
285 coating is fine-grained with individual (Zn,Fe)S crystals with diameters of up to 8 μm. The coating
286 has partially engulfed silica glass fibers on which the Fe metal chip was placed (Fig. 4g). In cross-
287 section we observe that the coating with a thickness of up to 150 μm partially detached from the
288 metal, suggesting a poor cohesion (Fig. 4h & i). The coating appears to be layered, with the $FeCl_2$ on
289 the metal chip and the sulfide on the surface (Fig. 4i).

290 At 708±5 °C (Zn,Fe)S dominates the coating and only traces of $FeCl_2$ are observed in cross-
291 section (Fig. 5 a-c). The sulfide grains have diameters of up to 40 μm (Fig. 5a), with a total coating
292 thickness of ~100 μm (Fig. 5b). Traces of $FeCl_2$ were detected in the coating by EDS, but individual
293 grains could not be identified unambiguously, suggesting grain sizes of less than 2 μm.

294 At 825±5 °C the coating only contains sulfides. It is the only sample where pure FeS could be
295 distinguished from (Zn,Fe)S. At the surface of the coating grains have diameters of up to 60 μm (Fig.
296 5d). The coating is dense and the individual sulfide crystals are euhedral. The coating is partially
297 detached from the underlying Fe metal chip (Fig. 5e), but in some sections the contact is observed.
298 The pure FeS is in direct contact with the metal chip and forms an undulatory interface (Fig. 5f). The
299 (Zn,Fe)S occurs on the surface of the coating.

300 Finally, at 1005±5 °C the coating mainly consists of (Fe,Zn)S (Fig. 5 g-i). The sulfide grains
301 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 (Fe_2SiO_4) 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 $FeCl_2$ 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 $FeCl_2$ 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, $FeCl_2$ 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 $FeCl_2$ 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-Fe_2O_3) (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 „Rusty Rock". This suggests, that the oxyhydroxides are a secondary alteration product of the primary $FeCl_2$ 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 fH_2 and fH_2O.

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. fO_2 and fS_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 fO_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 fS_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_2S 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 $\log fO_2$ remains constant with time, but $\log fS_2$ decreases as the sulfides are deposited. The formation of the Cu metal whiskers suggests that $\log fS_2$ drops to the phase boundary of Cu_2S and Cu in the $\log fS_2$-$\log fO_2$ 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 $\log fS_2$ and $\log fCl_2$ 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 $\log fS_2$ is in the range of -13.2 to -10.5 and $\log fCl_2$ 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 $\log fO_2$

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_2, 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 $\log fCl_2$ 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,

1972; 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 SO_2 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 $FeCl_2$, ZnS and FeS in the gas deposition experiment, and the formation of $FeCl_2$ 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 Cu_2S 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 δ^{65}Cu composition (Day et al., 2019). Our experiments do not allow us to discriminate between the deposition of $FeCl_2$ 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 $FeCl_2$ and FeS in the temperature range of 580 ± 50 °C. The observed assemblage of $FeCl_2$ 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 logfS_2 is at -13.5 to -10.5 and logfCl_2 is at -13.9 to -12.5.

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588

589

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)	-	-
$MgCl_2$	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
	cm	°C
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

603

604 *Table 3: EDS analysis of the observed phases in the "gas deposition experiment" given in*
605 *atomic %. Standard deviations of the analyses are given in brackets. Backscattered electron images of*
606 *the analyzed phases are shown in Fig. 2.*

Temperature °C	Phase	S atomic %	Cl atomic %	Fe atomic %	Cu atomic %	Zn atomic %
300-538	$ZnCl_2$	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	$FeCl_2$	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	Cu_2S	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.

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

608

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

Temperature °C	Phase	S atomic %	Cl atomic %	Fe atomic %	Zn atomic %
396	$FeCl_2$	n.d.	65.3(2.2)	34.1(2.1)	n.d.
496	$FeCl_2$	3.4(2.2)	59.9(6.4)	19.8(3.9)	16.9(1.6)
580	$FeCl_2$	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	$FeCl_2$	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)

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

613

Figures

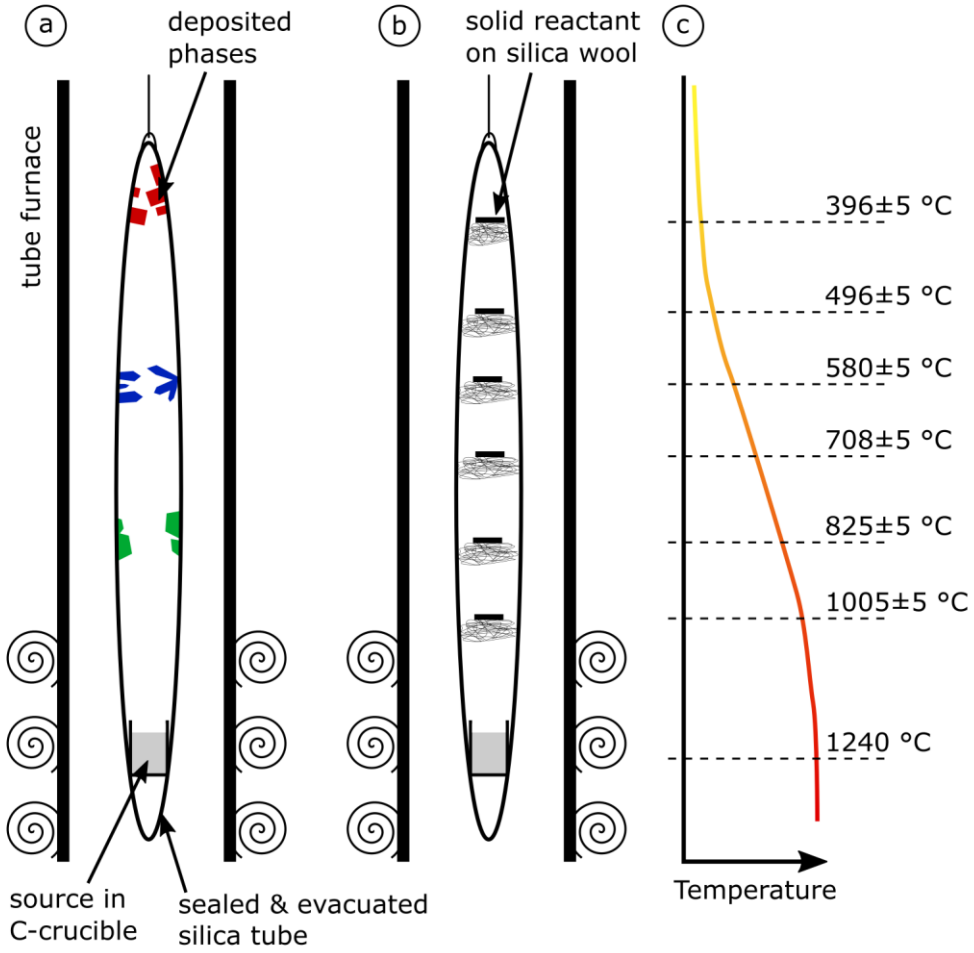


Figure 1: Illustration of the experimental setup in a vertical tube furnace. a) Gas deposition experiment. The source in the hot zone of the furnace volatilizes and different phases are deposited along the temperature gradient within the silica glass tube.; b) Metal reaction experiment. The Fe metal chips were placed on SiO_2 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.

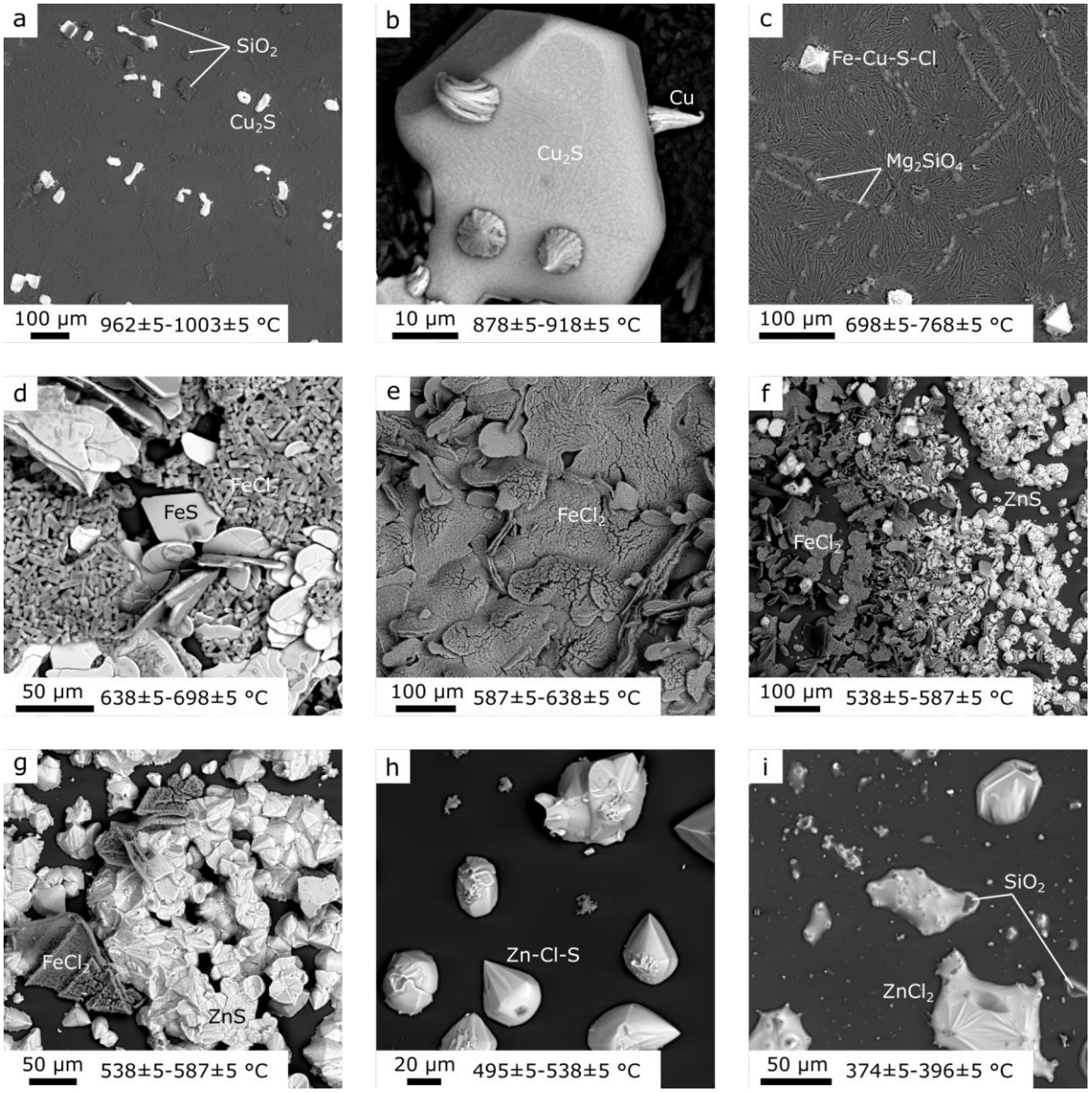
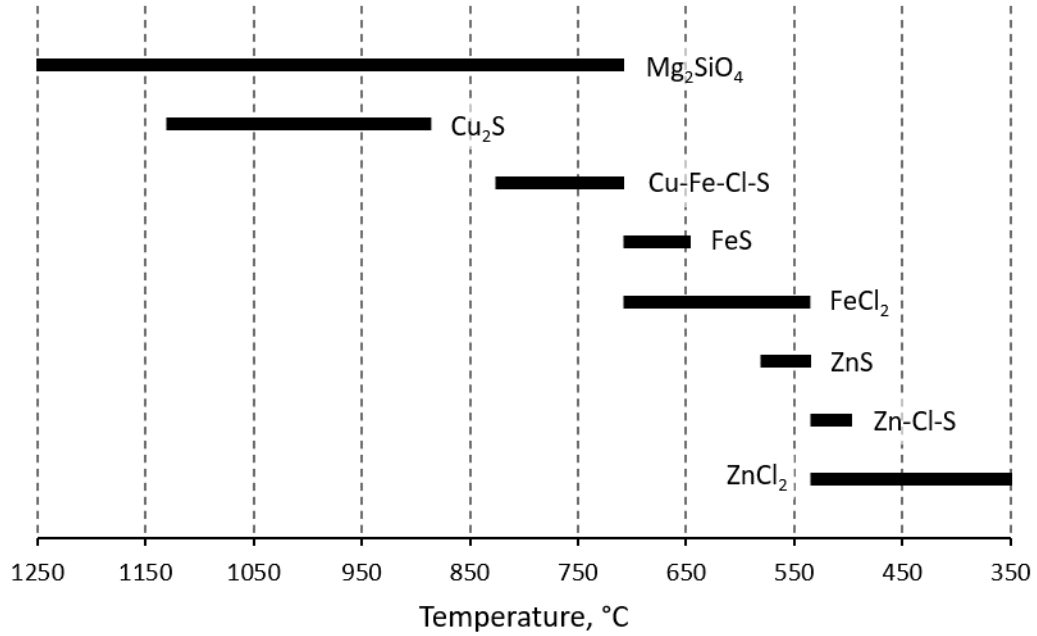


Figure 2: Backscattered electron images of phases deposited on the inner silica tube wall ("gas deposition experiment"). a) Cu_2S grains and SiO_2 glass dust which was formed during opening of the tube, 962±5-1003±5 °C; b) Cu_2S grain with Cu metal whiskers, 878±5-918±5 °C; c) Unidentified Fe-Cu-S-Cl phase and Mg_2SiO_4, the reaction product of MgO with the silica glass tube wall, 698±5-768±5 °C; d) FeS and $FeCl_2$, 638±5-698±5 °C; e) $FeCl_2$, 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.



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631 *Figure 3: Distribution of phases deposited along the temperature gradient in the silica tube*
632 *summarizing the observations shown in Fig. 2 from the gas deposition experiment. The solid bars*
633 *show the temperature ranges over which the respective phases were observed in the silica glass tube*
634 *by investigation of the inner tube wall with back-scattered electron microscopy and EDS analysis.*
635 *„Rusty Rock" phases are observed over the temperature range 538±5-638±5 °C.*

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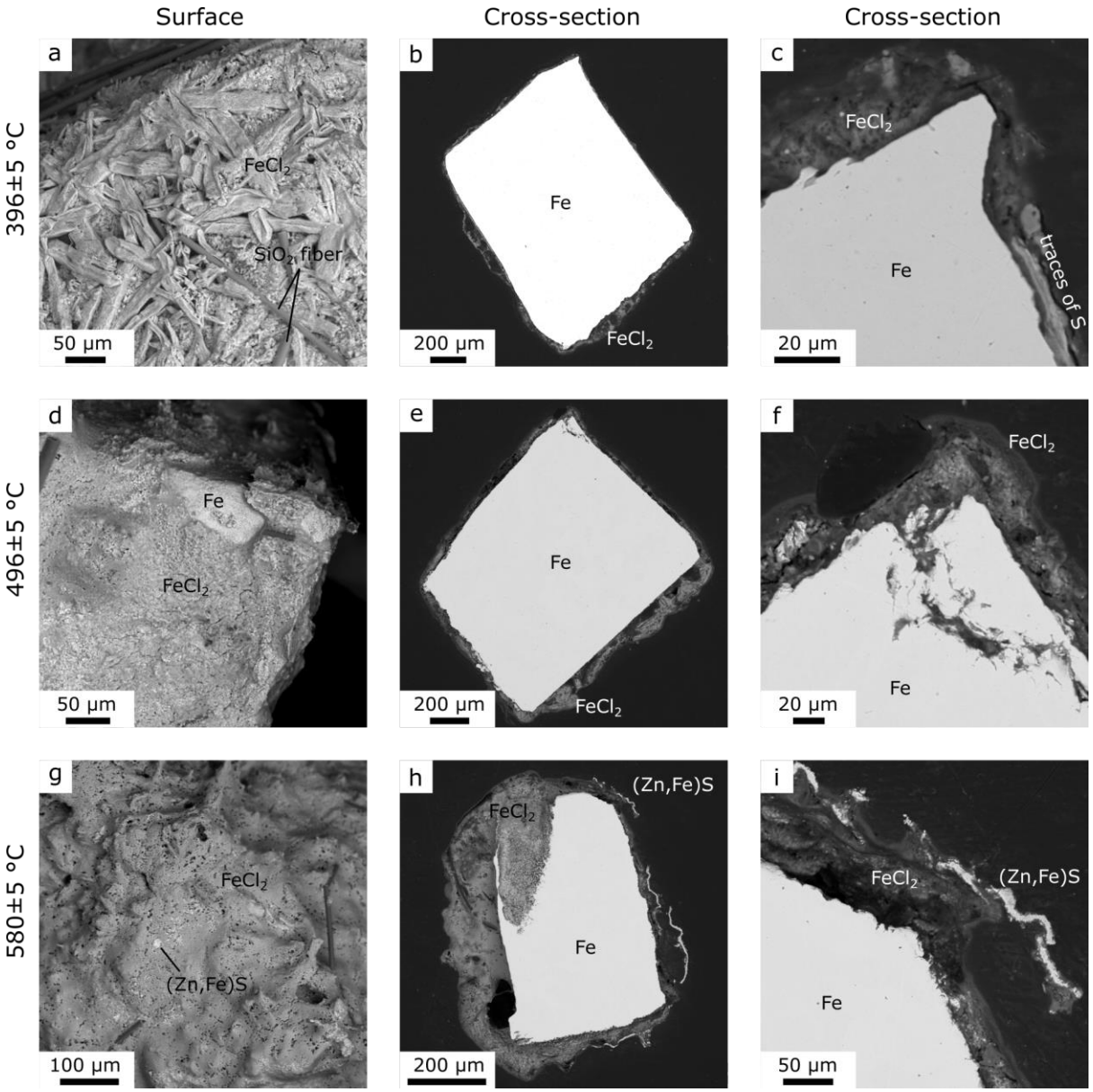
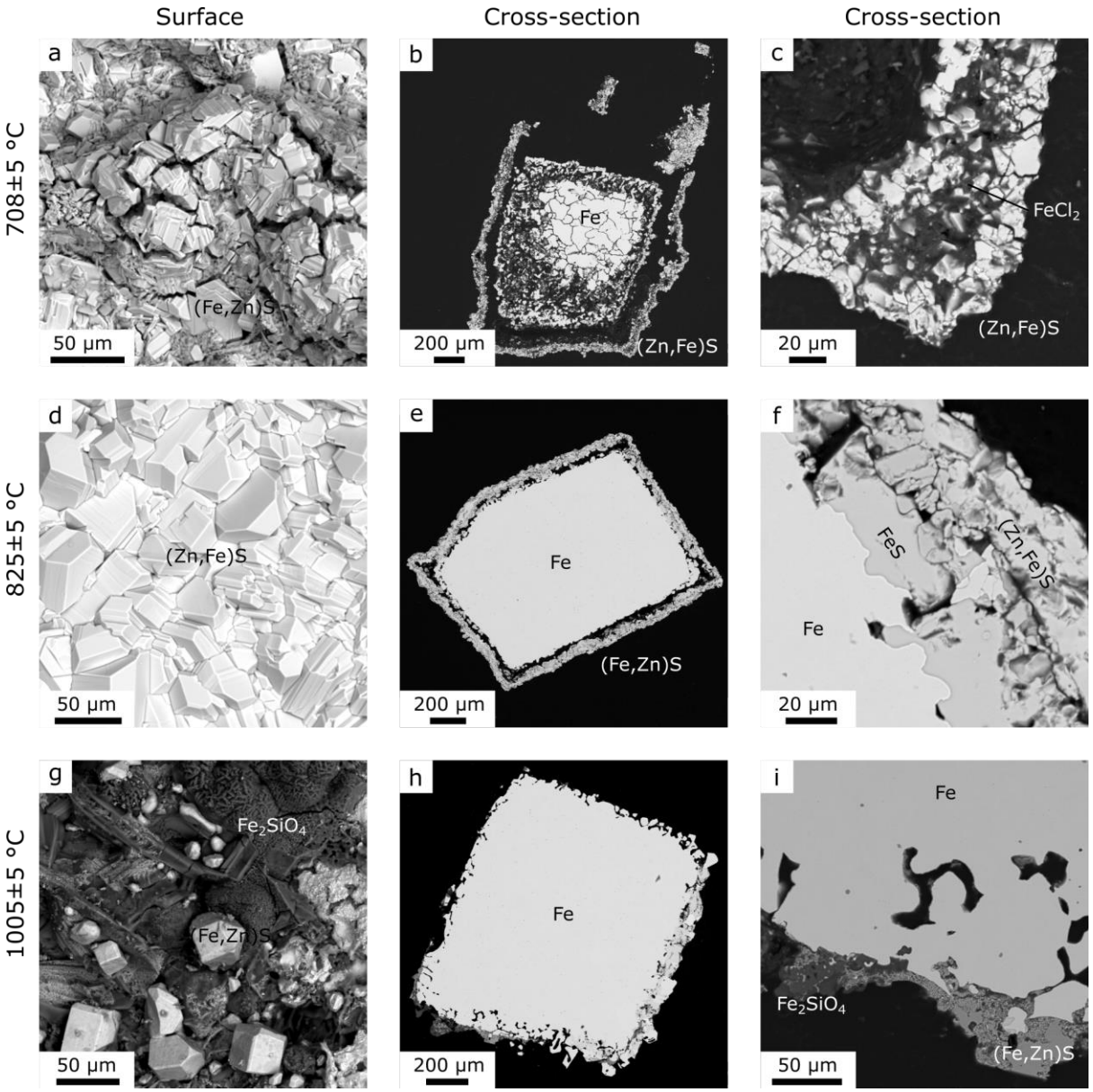


Figure 4: Backscattered electron images of the Fe metal reaction experiment. Images a, d and c show the surfaces of the coatings and images b, c, e, f, h and I show cross-sections of the samples. The rows indicate the temperatures, 396±5 °C (a-c), 496±5 °C (d-f) and 580±5 °C (g-h).



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643 *Figure 5: Backscattered electron images of the Fe metal reaction experiment. Images a, d and c show*
644 *the surfaces of the coatings and images b, c, e, f, h and I show cross-sections of the samples. The rows*
645 *indicate the temperatures, 708±5 °C (a-c), 825±5 °C (d-f) and 1005±5 °C (g-h).*

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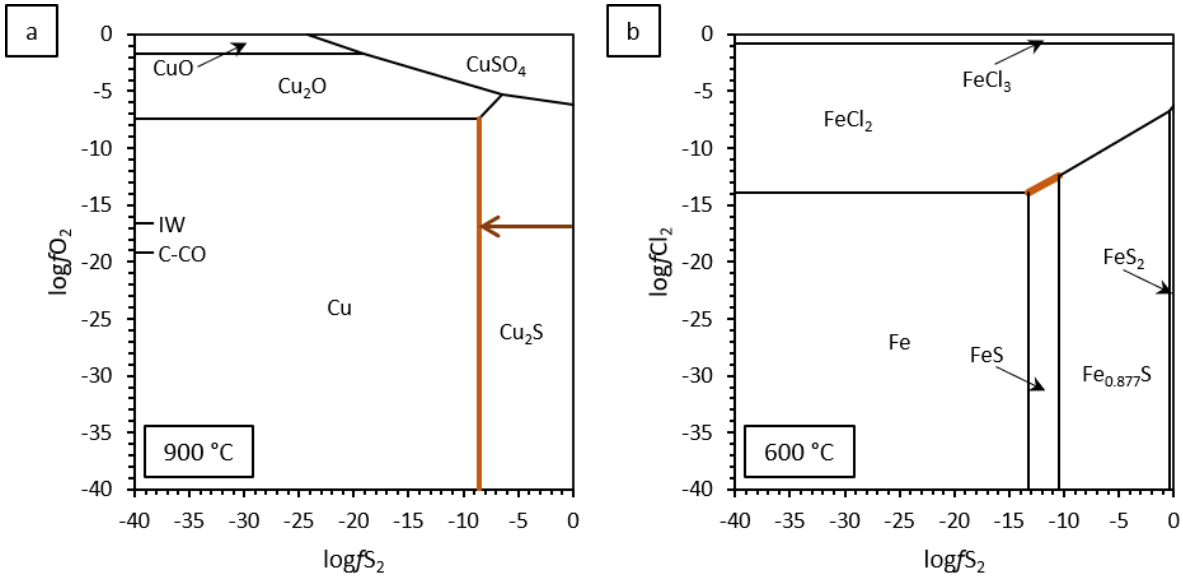

Figure 6: a) Phase stability diagram of the system Cu-S-O as a function of logfS_2 and logfO_2 at 900 °C, 1 bar. The univariate line in brown shows the condition for coexistence of Cu and Cu_2S as observed in the metal transport experiment and the formation of Cu whiskers on the Cu_2S crystal. The brown 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).