1	Experimental constraints on metal transport in fumarolic gases									
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12	Highlights									
13	• New experimental method allows exploration of otherwise inaccessible metal transport									
14	processes in fumarolic gases									
15	• Fumarolic metal transport experiments reproduce observations from nature									

16 • Thermodynamic calculations fail to reproduce experimental results

17 Abstract

Metals are efficiently transported in a gas phase and the gas composition strongly affects 18 19 transport rates of these metals in the gas phase. Here we present a new approach to systematically 20 investigate metal transport and deposition from volcanic gases of different compositions: We test the 21 effect of sulfur and chlorine on the volatilization of 30 metal oxides and the phases deposited along a 22 temperature gradient of 1250-300 °C in evacuated silica glass tubes in water-free systems. In total, we 23 observe 30 different deposited phases, including oxides, sulfides and chlorides. The experimental 24 results are compared with closed system and open system thermochemical equilibrium calculations. 25 The closed system calculations provide insights into the metal speciation in the gas phase, and the 26 open system calculations provide thermodynamic predictions of the temperature ranges over which 27 metals deposited from the gas phase. Both approaches only partially reproduce the experimental 28 observations of the deposited phases in the silica glass tubes. However, when we compare our 29 experimental results with records from fumaroles on three different volcanoes (Kudriavy volcano, 30 Russia, La Fossa crater on Vulcano, Italy, and Momotombo, Nicaragua), we find that our experiments 31 agree very well with natural observations. We suggest that similar experimental investigations are powerful tools in the study of metal transport in ore forming systems involving gas phases, and results 32 33 may be applied to various processes in terrestrial and planetary environments.

34 Keywords

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Volcanic gas; Fumarole; Metal transport; Metal deposition; Experimental volcanology

36 **1. Introduction**

Volcanic degassing plays a major role in the global cycling of volatile and moderately volatile elements (Halmer et al., 2002). Volcanic gases transport metals from high-temperature magmatic sources to shallower depths with lower temperatures and pressures where the metals deposit. Some metals are enriched in volcanic gases by up to a factor of 10⁵ relative to the magmatic source, and quiescently degassing volcanoes emit kilograms to tons of metals per day (Calabrese et al., 2011; 42 Mather et al., 2012; Zelenski et al., 2013). Metal emissions in arc volcanic plumes range from 1-100 43 kg/day (Ag, Au, U, Te, W), over 100-1000 kg/day (Mo, As, Bi, In, Cs) to 1000-10'000 kg/day (Zn, 44 Cu Pb, Tl, Cd, Se, Sn), whereas emissions from hotspot volcanic plumes are up to three orders of 45 magnitude lower (Edmonds et al., 2018). In addition to the emissions at the surfaces of volcanoes, 46 large quantities of metals deposit below the surface, where they can form hydrothermal ore deposits 47 (Henley and Seward, 2018; Mernagh et al., 2020).

The behavior of metals in high-density hydrothermal fluids and brines ($\rho > 0.5$ gcm⁻³, T < 48 49 400 °C) has been studied extensively (e.g., Brugger et al., 2016; Louvel et al., 2017), but experimental 50 investigations of metal transport in low-density vapor and gas phases ($\rho < 0.2 \text{ gcm}^{-3}$) are more limited 51 (e.g., Williams-Jones and Heinrich, 2005; Pokrovski et al., 2013). Instead, knowledge of the metal 52 behavior in low density volcanic gases is largely based on thermodynamic modeling (e.g., Symonds et 53 al., 1987; Symonds and Reed, 1993) and sampling of natural fumarole condensates from active 54 volcanoes (e.g., Symonds et al., 1990; Hedenquist et al., 1994; Taran et al., 1995; Zelenski et al., 55 2013; Zelenski et al., 2014).

56 Metals transported in hydrothermal fluids occur as a diverse range of species, coordinated by ligands including Cl, S, F, OH-groups, as oxides, and in their elemental form. Many of these species 57 58 are ionic and require charge balancing in the fluid, and vary as a function of oxygen fugacity (fO_2) , 59 pH, temperature, and pressure (Brugger et al., 2016). In contrast, metal species in volcanic gases are not charged, but they also include chloride, fluoride, sulfide, oxide, iodide, hydroxide and elemental 60 61 species (Symonds and Reed, 1993; Henley and Seward, 2018). The availability of these ligands, in 62 particular Cl and S, has a strong control on the transport of metals and the temperature and pressure 63 conditions where they deposit from the gas phase (e.g., Symonds et al., 1987; Symonds and Reed, 64 1993; Renggli et al., 2017).

Metal emission rates from volcanoes are commonly assessed by directly probing fumaroles using silica glass tube setups (e.g., Giggenbach, 1975; Le Guern and Bernard, 1982). Gaps in our understanding of volcanic degassing originate from the inherent dangers associated with sampling of toxic gases in fumarolic environments. Major volatile species in volcanic gas (H₂O, CO₂, SO₂, H₂S,

69 HCl) are monitored and measured remotely by spectral means, but trace metal emissions require 70 direct sampling on the volcano, or aerosol sampling. In order to account for the metal emissions from 71 magmatic sources, reactions with sub-volcanic rocks (Henley et al., 2015; Henley et al., 2017) and the 72 interaction with meteoric fluids (Giggenbach, 1984; Benavente et al., 2013) must be considered. Only 73 few fumaroles have been sampled at near magmatic temperatures (> 900 °C), where these secondary 74 processes played a minor role (Henley and Seward, 2018). The hottest gases sampled to our knowledge, are on Kudriavy, Russia (940 °C, Taran et al., 1995), Erta Ale, Ethiopia (1084 °C, 75 76 Zelenski et al., 2013) and Tolbachik, Russia (1020-1135 °C, Zelenski et al., 2014). Kudriavy volcano 77 will serve us as the main case study to which we will compare our experimental results.

78 In addition to direct sampling of deposits from fumarolic degassing, metal transport and 79 speciation in volcanic gases is commonly assessed by computational means, using Gibbs free energy 80 minimization calculations (Symonds and Reed, 1993). This approach has been applied to multiple 81 volcanic systems, including Kudriavy volcano, Iturup, Kurile Islands, Russia (Wahrenberger et al., 82 2002). Where direct sampling is too dangerous, such as on explosively erupting volcanoes (Symonds 83 et al., 1987; Symonds and Reed, 1993), or not possible, such as in the study of extraterrestrial 84 volcanism and magma ocean degassing on the early Earth, or on exoplanets (Schaefer and Fegley, 85 2004; Schaefer and Fegley, 2007; Schaefer and Fegley, 2017; Renggli et al., 2017), thermodynamic 86 modeling is the primary method to study volcanic degassing. However, direct comparison of deposits 87 sampled at active fumaroles and thermochemical equilibrium calculations showed significant 88 discrepancies (Wahrenberger et al., 2002).

In this study, we investigate the effect of the ligand elements S and Cl on the transport of metals under controlled laboratory conditions in water-free systems, and compare the experimental results to thermochemical equilibrium calculations and observations from Kudriavy, La Fossa and Momotombo volcano. The experimental setup is conceptually based on the setup used on natural volcanoes, when silica glass tubes are inserted directly into the fumaroles and precipitates from the gas phase are sampled (Le Guern and Bernard, 1982). Previous experimental studies used an open system experimental approach at oxidizing conditions, where a silica glass tube was installed in a box 96 furnace above a Pt crucible containing a degassing silicate melt (Scholtysik and Canil, 2018;
97 Scholtysik and Canil, 2020). Our approach is different as we use a closed system setup with an
98 evacuated and sealed silica glass tube (Nekvasil et al. 2019).

99 **2. Methods**

100

2.1 Experimental setup

101 We adapted the experimental setup of Nekvasil et al. (2019), but instead of synthetic silicate 102 melts as the volatile and metal sources, we use pellets consisting of metal oxides and volatile elements 103 (S and Cl). A similar setup has previously been used to simulate volcanic degassing and metal 104 transport on the Moon and on Mars (Ustunisik et al., 2011; Ustunisik et al., 2015; King et al., 2018; 105 Nekvasil et al., 2019). The starting materials consisted of mixtures of 30 metal oxides (Table 1) and 106 varied amounts of S and NaCl (source of Cl). To test the effect of S and Cl on the transport of metals 107 in a gas phase we prepared four different mixtures, all using the same metal oxide mix. The metal 108 oxide mixture was prepared for equal molar abundances of all metals, accounting for different metal 109 oxidation states, in order to allow a better comparison between the behaviors of the metals 110 investigated (Table 1). Whilst other experimental studies used silicate melts as a source of volatile 111 metals, we found that metal oxide powders together with S and Cl as starting materials resulted in 112 larger quantities of deposited phases, which enabled us to better characterize the deposits. The first 113 starting material mixture contained both elemental S and NaCl (MO-S-Cl), the second mixture only 114 contained the metal oxide mix (MO), the third mixture contained elemental S as the sole ligand (MO-115 S) and the fourth mixture contained Cl as the sole ligand (MO-Cl), added as NaCl to the mixture 116 (Table 1).

The starting materials were pelletized, and the pellets (24-40 mg, Table 1) were placed at the bottom of silica glass tubes. The tubes typically had inner diameters of 4 mm, a wall thickness of 1 mm and a length of 30 cm. The tubes were evacuated at 10^{-5} bar and sealed over a H₂-O₂ flame, and were suspended into the top part of a vertical tube furnace (Gero GmbH, Germany) (Fig. 1). Temperatures within the furnace were carefully measured with Type S thermocouples. The starting material pellets were placed in the hot zone of the furnace with a temperature of 1250 °C. The furnace has a strong temperature gradient from the hot zone to the top of the furnace (Fig. 2) and hence temperatures within the long glass tubes range from 1238 °C to 320 °C at the top of the glass tube. Note that the temperature gradient in the furnace is not constant over the entire range (Fig. 2). The experiments were run over 24 hours. However, a preliminary experiment, which was run for only one hour, showed the same distribution of mineral deposits. We noticed that runs for 24 hours produced larger crystals, facilitating the mineralogical identification.

129 The pressure in the silica glass tube during the experiments is a function of pellet size, the 130 imposed vacuum during sealing of the tube (10^{-5} bar) , temperature and time. As the source material 131 volatilizes the pressure increases and as the phases deposit along the temperature gradient the pressure decreases again. The sealed tubes (4 mm inner diameter, 300 mm length) have an inner volume of 132 3770 mm³. Assuming S and Cl are entirely in the gas phase at 1250 °C forming metal sulfide (MS) 133 134 and metal chloride (MCl) species, the maximum pressures in the tubes are 10.9 (MO-S-Cl), 17.8 135 (MO-S) and 3.6 bar (MO-Cl). These first-order estimates do not account for the formation of metal 136 oxides, elemental metal or sulfur gas species such as S_2 , nor do they account for the lower 137 temperatures along the tube, providing first order maximum pressure estimates.

138 At the end of the experiments, the silica tubes were lifted out of the furnace and quenched in 139 water. They were then cut in 1 cm long segments using a slow speed diamond blade saw. Due to the 140 temperature gradient of the furnace (Fig. 2) each centimeter long segment encompasses a temperature range from 15 °C at the low and high temperature end of the furnace, where the temperature gradient 141 of the furnace is relatively flat, to 65 °C around 700 °C, where the temperature gradient in the furnace 142 143 is steep. The temperature gradient in the furnace was measured repeatedly and remained constant within less than 5 °C over more than 6 months. This is less than the temperature variability within the 144 145 1 cm tube segments over which we average our observations. The 1 cm tube segments were broken 146 into 2-5 mm sized shards and mounted on aluminum stubs with the inside of the tube walls facing 147 upwards. Care was taken to minimize the exposure of the samples to ambient air. The products of gassolid reactions are often easily modified by the exposure to humidity in the air (Dalby et al., 2018),
which is why the samples were immediately placed in an evacuated desiccator until analysis.

150 Direct control of gas fugacities such as fO_2 is not possible in evacuated and sealed silica glass 151 tubes with large temperature gradients of 1000 °C. Redox conditions vary with temperature along the silica glass tube, but also with time as phases such as sulfides, chlorides and oxides deposited from the 152 153 gas phase. For example, the deposition of native metals and sulfides will result in an increase of fO_2 in 154 the remaining gas. In gas mixtures, redox conditions and metal transport along a temperature gradient 155 are further affected by Soret thermal diffusion (Nekvasil et al. 2019). However, our observations of 156 different phase assemblages including sulfides, chlorides, oxides and native metals enable us to put 157 some first order constraints on redox conditions at selected temperatures (see 3.5 Estimation of redox conditions). These considerations restrict the $\log fO_2$ between the Magnetite-Wüstite and Mangetite-158 159 Hematite buffers.

160

2.2 Analytical methods

161 We used a JSM-6610 Series Scanning Electron Microscope (SEM) to image and analyze the 162 phases on the inner tube walls of the tube segments. In initial test experiments, we noticed that many of the precipitated phases are subject to alteration in air. To minimize sample handling and exposure 163 164 of the samples to air we did not coat the samples. Instead, we used the low-vacuum capability of the 165 SEM. Under these analytical conditions, the SEM provides high contrast Back-Scattered Electron (BSE) images and Energy Dispersive Spectroscopy (EDS) measurements for qualitative chemical 166 analysis of the phases. The low-vacuum analyses were done at a pressure of 50 Pa and an acceleration 167 voltage of 20 kV, at a working distance of 10 mm. We used the JEOL EDS analysis station with a dry 168 169 silicon drift detector. In addition to JEOL's automated EDS peak identification, we inspected each 170 spectrum manually and extracted atomic abundances of the identified elements from the quantified spectra. We analyzed each observed phase 3-10 times and identified them using the averages of the 171 172 atomic abundances, calculating the respective stoichiometries.

2.3 Thermodynamic modeling

Each experiment was thermodynamically modeled using a Gibbs free energy minimization approach. For this purpose, we used the commercial software package HSC chemistry 9 by Outotec (Roine, 2015). The data on which the calculations are based largely originate from the NIST-JANAF thermochemical database (Chase, 1998) with additional sources (e.g. Robie and Hemingway, 1995).

We limited the calculations to a subset of elements, including Cu, Zn, Ga, Ge, Mo, Ag, Cd, In, Te, Re, Tl, Pb, S, Cl and O (Table 1). A total of 211 solid and 185 gas species were included in the calculations. Calculations were conducted in 50 °C steps over the experimental temperature range of 300-1250 °C at atmospheric pressure. The atmospheric pressure of the calculations falls in the range estimated for the experiments with maximum pressures in the silica glass tubes of up to 18 bar.

183 Note that a number of factors limit Gibbs free energy minimization calculations, used to 184 model the speciation of metals in the gas and solid phase. The results of the calculations are strongly 185 dependent on the choice of the chemical system, and missing species or other missing thermodynamic 186 parameters in the thermodynamic database (Roine, 2015) may have a substantial effect on the 187 outcome of the calculations. For example, thermodynamic data is largely limited to end-member compositions in systems forming solid solutions (e.g. Ag₂S-Cu₂S), and the thermodynamics of 188 189 sometimes complex solid solutions are unknown, and hence not incorporated in the database of the 190 thermodynamic model (Roine, 2015). Moreover, using a commercially available thermodynamic 191 software, it is challenging to ascertain the accuracy of the modeling results. Nevertheless, the models 192 we used in our study, and similar models, are commonly applied to interpret observations from natural 193 systems (e.g., Symonds and Reed, 1993; Henley and Seward, 2018). One of the main aims of this 194 study is to test whether thermodynamic models, such as the one used in our study, give results that are 195 similar to natural observations or our experimental results. For these reasons, we limit the discussion 196 of the results of our thermodynamic calculations to the well-known metals Cu, Zn, Ge, Ag, Cd and Pb 197 and their compounds. The complete results of the calculations are available in the electronic 198 supplement.

3. Experimental results

200 In all four experiments, we observe deposits along the entire silica glass tubes with distinct 201 zonations (Fig. 2). Most deposits contain crystals in the range of tens to hundreds of microns, with 202 rare crystals extending up to a millimeter in diameter. Only rare crystals are large enough to be 203 identified visually without magnification. At the high temperature end (> 800 °C), the silica glass 204 tubes are milky and deposited phases are not visible from the outside. The milky appearance is due to 205 partial re-crystallization of the SiO₂-glass on the inner tube wall. The pellets placed in the hot end of 206 the tube corrode the silica glass, react and result in crystallization upon quench of the tube. We 207 observe this process in all experiments as quench textures with a melt mainly enriched in Ga, with 208 additional Ba, Zn and Co (Fig. 3a, 4a, 5a and 6a). We do not take the alteration of the silica glass tube 209 into consideration when assessing metal transport and in comparison with thermodynamic modeling 210 and natural fumarole deposits. We only consider phases in the discussion that deposited from the gas, 211 based on their textures.

212 Below we only describe metal-bearing mineral phases that were transported in the gas phase 213 from the source. The transported metals include Cu, Zn, Ga, Ge, Ag, Cd, In, Te, Ba, Re Tl and Pb, 214 which deposited as sulfides, chlorides, oxides and native metals. As mentioned above, some metals 215 were deposited during reactions with the silica glass tube, primarily as melts, including Ga, Ba, Co, Cr 216 and Ni. In addition, 14 of the 30 metals included in the experiments were not transported from the 217 source at all. The oxides of Sc, V, Y, Zr, Nb, La, Pr, Nd, Sm, Eu, Gd, Lu, Hf and Ta remained in the 218 source pellet. These refractory elements include high-field-strength elements (i.e., Zr, Nb, Hf and Ta) 219 and the rare earth elements, which are not mobilized in a dry, S and Cl bearing gas phase. Sulfur and 220 Cl could no longer be detected in the pellets after the experiments, suggesting complete volatilization 221 of these elements.

3.1 Experiment MO-S-Cl

The experiment with a starting material mixture of metal oxides, S and NaCl resulted in the most mineralogically diverse deposits in the silica glass tube compared to the other experiments. The deposits include 13 identified and 3 unidentified phases.

A solid solution of Ag₂S and Cu₂S is the first phase to deposit in the high temperature range of 760-1200 °C. At 1100-1200 °C the deposits are Cu₂S-dominated, whereas at lower temperatures the deposits are Ag₂S-rich. The largest quantities of (Ag,Cu)₂S deposited around 1000 °C and all deposits are spherical and appear as droplets with diameters of 2-10 μ m (Fig. 3b). With decreasing temperatures the droplet diameters decrease to < 2 μ m. This textural observation suggests that (Ag,Cu)₂S condensed as a liquid. The melting points in the system (Ag,Cu)₂S are 842 °C (Ag₂S) and 1130 °C (Cu₂S), with an eutectic temperature of 640 °C (Effenberg and Ilyenko, 2006).

233 Rheniite (ReS₂) (Korzhinsky et al., 1994) occurs at 760-1040 °C. The sulfide forms thin 234 plates that occur as clusters and occasionally form rosette assemblages. The plates have diameters of 235 up to 200 μ m and are so thin that they are partially transparent to the electron beam (Fig. 3b).

Halite (NaCl) occurs over the largest temperature range of 500-1040 °C (Fig. 7a). The halite textures change distinctly over this temperature range, as it is deposited as a melt above its liquidus temperature (801 °C), forming droplet patches with diameters of up to 1 mm (Fig. 3d) at 820 °C, and euhedral crystals below the liquidus temperature (Figs. 3e-g).

We observe cadmoindite (CdIn₂S₄) (Chaplygin et al., 2004) from 650 to 1040 °C. The sulfide forms needles with thicknesses of less than 50 μ m and lengths of up to 500 μ m (Fig. 3f). The needles are commonly intergrown with halite cubes suggesting simultaneous deposition.

Argutite (GeO₂) is the only oxide in this experiment (Fig. 7a) and occurs with NaCl, CadIn₂S₄ and (Cd,Zn)S at 580 to 760 °C. The small crystals (< 10 μ m) form dense accumulations, which are often intergrown with NaCl and (Cd,Zn)S (Fig. 3e).

Zink-bearing greenockite (Cd,Zn)S and Cd-bearing wurtzite (ZnS) (Fig. 7a) occur in an intermediate temperature range with greenockite at higher temperatures (650-760 °C) followed by wurtzite at lower temperatures (435-650 °C). We can further identify both minerals based on their
euhedral hexagonal appearance (Fig. 3e-h). Greenockite additionally exhibits its typical orangeyellow color.

251 Lead is the predominant element in four different phases at lower temperatures. These include 252 an unidentified In-Pb-S phase (535-650 °C), galena (PbS, 435-580 °C), cotunnite (PbCl₂, 420-500 °C) and hephaistosite (TlPb₂Cl₅, 420-440 °C). The unidentified In-Pb-S phase occurs as needles, with 253 254 diameters of up to 100 µm and lengths of up to 2 mm (Fig. 3g), and is associated with NaCl and ZnS. 255 Galena is easily identified in SEM images due to its cubic habit, with crystal sizes of 50 µm (Figs. 3h 256 & i). Cotunnite occurs mostly together with galena and forms spherical assemblages of crystals with 257 diameters of $< 5 \,\mu$ m. Hephastosite occurs over the most limited temperature range and forms crystals 258 with diameters of up to $50 \,\mu m$ (Fig. 3j).

Below 400 °C, we only observe three phases. These include lafossaite (TICl, Roberts et al. 2016), elemental S and Te. Lafossaite occurs at 340-420 °C and forms droplet-like deposits with grain diameters of 10-20 μ m (Fig. 3k). Elemental S occurs at 300-380 °C and forms droplets with diameters of up to 500 μ m. Tellurium is limited to the lowest temperatures at 300-340 °C and occurs in droplets together with S (Fig. 3l). Both elements may be transported to lower temperatures and their transport is limited by the experimental setup.

265 **3.2 Experiment MO**

In the absence of S and Cl, metal transport is limited and the diversity of deposited phases is small, with four identified phases and five additional unidentified deposits (Fig. 7b). We observe In oxide (In₂O₃) crystals at temperatures between 1040 and 1220 °C with crystal diameters of 20-50 μ m (Fig. 4b & c). Native silver occurs at 1000-1040 °C, and it condensed into liquid just above the melting point (T_m = 961.78 °C), apparent from the droplet texture (Fig. 4c).

271 Reaction products of metals with the silica glass tube wall are more abundant in the MO 272 experiment, compared to the S- and Cl-bearing experiments. In addition to quench textures above 273 1200 °C, with a melt rich in Ga, Zn and Co (Fig. 4a), reaction textures occur at 880-1040 °C (Fig. 4d).

274 The SiO₂ crystallites are surrounded by a melt that is enriched in Pb, Ag, Cd, Zr and Tl.

At 930-1000 °C, CdO deposited in areas of several mm² of the tube wall, forming a coating with a fibrous texture (Fig. 4e). At slightly lower temperatures (700-930 °C), a Cd-bearing phase occurs with the stoichiometric formula $3CdO-2TeO_2-MoO_3$. Individual crystals of this phase have sizes of up to 8 µm (Fig. 4f) and form a dendritic network.

Below 700 °C, the only deposited elements are Tl, Re and Te (Fig. 7b). Tl₂O occurs over the largest temperature range (300-700 °C), both above and below its melting point ($T_m = 579$ °C). Below the melting point, we observed the trigonal Tl₂O plates (Fig. 4i). Thallium also occurs associated with Te (500-580 °C) and Re (300-500 °C) as a melt above 460-500 °C (Fig. 4g), which reacted with the silica glass tube. Below 460 °C, the Re-Tl-oxide and Tl₂O are entirely crystalline (Fig. 4h & i).

284

3.3 Experiment MO-S

In the experiment MO-S, we identified ten different phases deposited along the silica tube. At 760-1200 °C abundant (Ag,Cu)₂(S,Te) melt droplets condensed (Fig. 5b-e). The droplet diameters decrease with decreasing temperature from 50 μ m to < 5 μ m. The droplet shapes suggest that these phases condensed as a melt over the entire temperature range. Overall, the Te concentration is higher than in the (Ag,Cu)₂S melt droplets observed in the experiment MO-S-Cl.

Two oxide phases are identified in the deposits, including $(In,Ge,Zn)_2O_3$ (760-1100 °C) and GeO₂ (650-890 °C). $(In,Ge,Zn)_2O_3$ forms deposits with diameters of up to 50 µm, and in the overlapping temperature range (760-1100 °C) it is always texturally associated with $(Ag,Cu)_2(S,Te)$ droplets (Fig. 5d). Furthermore, $(In,Ge,Zn)_2O_3$ and GeO₂ are intergrown where they occur together (Fig. 5e).

Lead appears as altaite (PbTe, 540-890 °C, Fig. 5f) and galena (PbS, 540-760 °C, Fig. 5g) and the two phases are associated and intergrown in some cases (Fig. 5i). Furthermore, we observe a Terich solid solution (Pb(Te,S)) at 535-580 °C. The Pb-bearing phases deposited alongside greenockite 298 (CdS, 535-650, Fig. g-i). Grain sizes decrease from 10 μ m towards lower temperatures to > 2 μ m. 299 Greenockite is further identified visually based on the orange color of the deposits.

300 Rheniite deposits are smaller than in the MO-S-Cl experiment and occur at lower 301 temperatures (435-580 °C, Fig. 5j). Rhenium is further incorporated as a minor element in Tl_2S 302 (carlinite, 380-580 °C, Fig. 5k). At the lowest temperatures (300-400 °C) we observe elemental S and 303 Te (Fig. 5l).

304 3.4 Experiment MO-Cl

In the experiment MO-Cl we identified eight phases with an additional four unidentified phases (Fig. 7d). At high temperatures (>1000 °C) these include deposits and reaction textures of oxides (Figs. 6a-d), whereas at lower temperatures chlorides are prevalent, mainly condensed as melts (Figs. 6e-i). The In-Ge-Na-oxide (825-1080 °C) occurs as large deposits with diameters of up to 500 μ m (Fig. 6b) and as fibrous deposits (Fig. 6c). Very finely dispersed Mo-rich oxides (1100-1180 °C) appear in reaction textures with the silica tube (Fig. 6d).

Halite appears over the largest temperature range (535-1080 °C, Fig. 6e), but is mostly associated with other chlorides. Mixed chloride melts appear to have separated during quench, resulting in complex textures containing NaCl, CdCl₂, ReCl₃, CuCl₂ and PbCl₂ (420-825 °C, Fig. 6fi). Lafossaite is the only chloride at lower temperatures (300-435 °C, Fig. 6j & k). An additional Te-In-Pb-chloride phase forms hexagonal plates (535-580 °C, Fig. 6g). Finally, elemental Te occurs at 300-435 °C (Fig. 6l).

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3.5 Estimation of redox conditions

Our observations of sulfides, chlorides, oxides and native metals allow some first order constraints on redox conditions at selected temperatures. We use the HSC9 software to calculate $\log fO_2$ for the systems discussed here. In the experiments MO-S-Cl and MO-S, we observe GeO₂ at 700 °C (Fig. 7). As the GeO₂-Ge buffer at 700 °C is at $\log fO_2 = -21.1$, which is above the Iron-Wüstite buffer (IW, $\log fO_2 = -21.6$), this information provides a minimum value of the $\log fO_2$. In the experiment MO-S we can further constrain an upper limit for $\log fO_2$ at 700 °C, based on the presence

of PbS and its reaction to PbSO₄ at $log/O_2 = -12.8$, which is just below the Magnetite-Hematite buffer 324 (MH, $\log fO_2 = -11.6$). The $\log fO_2$ relative to the Magnetite-Wüstite buffer (MW, $\log fO_2 = -20.6$) of 325 the experiment MO-S at 700 °C can therefore be constrained to MW-1 to MW+7.8, which falls 326 largely in the magnetite stability field. For the experiment MO-S-Cl at 700 °C we cannot constrain an 327 328 upper logfO₂ limit. In₂O₃ is present at 1050 °C in the experiments MO-S, MO-Cl and MO and provides an additional constraint on log fO_2 . At 1050 °C the In₂O₃-In buffer is at log fO_2 = -13.2, which 329 330 equates to MW-1.1 (MW, $\log fO_2 = -12.1$ at 1050 °C) and is hence a lower limit. MO is the most 331 oxidized experiment with the lower \log/O_2 limit constrained by the CdO-Cd buffer at 1000 °C 332 $(\log fO_2 = -10.6)$ which equates to MW+2.4 (MW, $\log fO_2 = -13.0$ at 1000 °C).

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4. Comparison of our results to previous experimental studies

334 Nekvasil et al. (2019) conducted similar silica glass tube metal transport experiments to investigate vapor deposition of minerals on the surface of Mars, using Fe-bearing volatile-doped 335 336 silicate melts as the source at high temperatures. They used oxygen monitor assemblages to constrain the redox conditions in their experiments, which fall in the stability field of magnetite. This is in the 337 338 same stability range as our experiments, which are also above the MW-buffer, as discussed above. 339 Nekvasil et al. (2019) let their experiments cool slowly to simulate the cooling of deposits on Mars 340 and observed secondary oxidation and hydration. The main deposits they observe include chlorides 341 (halite, sylvite below 800 °C), partially overlapping with our observations (Fig. 7) and Fe-bearing 342 phases including sulfides, oxides and chlorides (Nekvasil et al., 2019).

Scholtysik and Canil (2018) developed an open system experimental setup to simulate the volatilization and deposition of trace metals from melts in the simplified chemical systems Na₂O-Al₂O₃-SiO₂ and Na₂O-Fe₂O₃-SiO₂ melts at 900 °C. In their experimental setup, the melts were placed in Pt crucibles, above which silica glass tubes were suspended, extending out of the box furnace to room temperature in air. As Scholtysik and Canil's (2018) experiments did not include complexing agents such as S and Cl, we can compare their results only to our S- and Cl-free experiment MO (Fig. 6b). Here we compare the deposition temperatures of Cd, Ag, Cu and Tl, which we observed in our 350 MO experiment, with the results from Scholtysik and Canil (2018). Note that Scholtysik and Canil 351 (2018) determined the bulk chemistry of the condensates, whereas we identified the respective phases without bulk analysis. In our experiment MO, Cd deposits occur at high temperatures (700-1000 °C), 352 353 whereas Scholtysik and Canil (2018) observed Cd deposition at much lower temperatures 354 (125-425 °C). Similarly, we observed Ag only at high temperatures (880-1040 °C) in the MO 355 experiment, whereas Scholtysik and Canil (2018) observed a peak in Ag deposition at only 400 °C. 356 Furthermore, we did not observe any Cu deposits in the MO experiment, but Scholtysik and Canil 357 (2018) observed Cu deposition at low temperatures (below 400 °C). As mentioned above, Cu 358 remained in the source pellet in our run MO and was not transported in the gas phase, which is 359 supported by the low volatility of Cu in the Cl-free thermodynamic calculations (see discussion under 360 5.2). Only Tl formed abundant deposits at lower temperatures in our runs (300-700 $^{\circ}$ C), which 361 primarily condensed below 400 °C in the experiments of Scholtysik and Canil (2018).

362 Scholtysik and Canil (2020) used the same experimental setup and melt compositions as 363 Scholtysik and Canil (2018) to investigate the effect of Cl on metal transport by adding NaCl to the 364 melt at oxidizing conditions in air. Here we compare results of these Cl-bearing experiments with our 365 experiment MO-Cl (Fig. 7d). The mineralogy of the described phased deposited by the gas phase 366 differs considerably between our experiment and those of Scholtysik and Canil (2020). Most notably, 367 they observed a range of silicate phases, including quartz, suggesting volatilization of silica from the 368 melt source. Furthermore, as the experiments by Scholtysik and Canil (2018 & 2020) were much 369 more oxidized, oxychlorides were deposited and some deposited phases were subjected to secondary 370 hydration. A direct comparison of the deposited phases is, therefore, difficult. However, we can 371 compare the results of our experiment MO-Cl with the temperature ranges over which Scholtysik and 372 Canil (2020) observed significant metal deposits, and the deposition of NaCl. In our experiment MO-373 Cl we identified NaCl at high temperatures (535-1080 °C), whereas Scholtysik and Canil (2020) 374 observed NaCl at much lower temperatures below 550 °C. Note that NaCl in natural fumarolic 375 systems is observed over a much larger temperature range, i.e. from 200 to 850 °C (see discussion in 376 section 6). Scholtysik and Canil (2020) observed peaks in the amount of Cu, Pb and Cd between 500377 600 °C, which agrees well with our identification of CuCl₂, PbCl₂ and CdCl₂ over the same temperature range. They also observed significant amounts of deposited Ag at 600 and 200 °C, whereas we observed Ag-deposits in the experiment MO-Cl only at 950 °C as Ag₂Te. Finally, we observed most of the Zn and Tl deposits below 400 °C, which is in agreement with the observations of Scholtysik and Canil (2020).

382 In summary, the comparison of our experimental results with previous experimental metal transport and deposition studies shows limited agreement. There are a number of important 383 384 differences between our experiments and earlier studies, which result in the discrepancies. First, we 385 did not investigate the volatilization of metals from silicate melts, but used mixtures of metal oxides 386 as the starting materials to which we added the volatiles S and Cl, to study the deposition of sulfide, chloride, oxide and native metals from the gas phase. In contrast, Scholtysik and Canil (2018, 2020) 387 388 used Na₂O-Al₂O₃-SiO₂ and Na₂O-Fe₂O₃-SiO₂ melts as the sources from which the metals volatilized. 389 Second, our experiments were more reduced at a fO_2 below the MH and above the MW buffers, 390 whereas the experiments of Scholtysik and Canil (2018, 2020) were conducted in air. Third, we used 391 evacuated and sealed silica glass tubes allowing at least partial equilibration, but Scholtysik and 392 Canil's (2018, 2020) experiments were in an open system. The open glass tube setup used by 393 Scholtysik and Canil (2018, 2020) is affected by a chimney effect, whereby hot air from the box 394 furnace advects upwards through the tube, dragging the metal-bearing gas species to cooler sections 395 of the tube and into the exhaust funnel. Such a chimney effect does not operate in evacuated and 396 sealed silica glass tubes and explains the systematically lower deposition temperatures reported by 397 Scholtysik and Canil (2018, 2020), compared to our experimental results. Finally, in respect to points 398 two and three, our experiments are more similar to those of Nekvasil et al. (2019). However, Nekvasil 399 et al. (2019) used a Fe-bearing melt source with no added trace metals, limiting the comparability.

400 5. Thermodynamic calculations and comparison with experimental 401 results

402 We simulated the experimental metal transport systems using two approaches, which both 403 employ thermochemical Gibbs free energy minimization techniques (Symonds and Reed, 1993). Both 404 approaches include calculations over the experimental temperature range of 300-1250 °C, with 50 °C 405 temperature steps, and at atmospheric pressure. The first approach assumes a closed system and 406 calculates the equilibrium speciation of solids and metals at each temperature and pressure for each 407 bulk composition. This is the most commonly used method in the calculation of metal speciation in 408 volcanic gases (Symonds et al., 1987; Symonds and Reed, 1993; Wahrenberger et al., 2002; Renggli 409 et al., 2017; Henley and Seward, 2018).

The second approach accounts for the deposition of condensed phases along a temperature gradient, and the resulting change in the chemical composition of the gas phase, as the metal content of the gas-phase decreases with decreasing temperature. At each incremental step towards lower temperatures, equilibrium speciation is calculated for the pertinent bulk composition of the gas phase from the incrementally higher temperature step (Wahrenberger et al., 2002).

Figures 8-11 show the results of the closed-system equilibrium speciation calculations for the systems MO-S-Cl, MO, MO-S and MO-Cl. The results are presented as normalized mole fractions of the selected metals Cu, Zn, Ge, Ag, Cd and Pb down to 10⁻⁴ mole fractions. Solid lines denote solid phases and stippled lines denote gas species.

419

5.1 Calculations MO-S-Cl and comparison with experimental results in this system

420 The calculations in the system MO-S-Cl produce the most complex speciations of the four 421 investigated systems, due to the presence of both S and Cl available as ligands for solid and gas 422 species, which is in agreement with the experimental results (Fig. 8). In this composition, the 423 calculations show that Ge is the most volatile element followed by Pb, Cd, Ag, Zn and Cu. Above 424 900 °C, Ge is predominantly in the gas phase as GeS_(g), whereas at lower temperatures the predicted solids are GeO₂ and GeS₂. At low temperature (500 °C) the volatility of Ge increases again as GeCl_{4(g)} 425 becomes stable (Fig. 8c). Germanium is the only element that is predicted to occur abundantly as an 426 oxide in the presence of S and Cl. This is in agreement with the experimental observations where 427

428 Ge₂O deposited at 580-760 °C (Fig. 7a). However, we did not observe GeS₂ in the experiments as 429 predicted by the calculations.

The models show that the main solid Cu phases should be Cu₂S and Cu (> 1000 °C) and CuS (< 1000 °) (Fig. 8a). The only gas species with abundances > 10⁻⁴ mole fractions over the investigated temperature range is CuCl_(g) at T > 1150 °C. However, a Cu₂S-Ag₂S solid solution phase, which we observed in the experiments (Fig. 3b), cannot be predicted by the model due to the lack of thermochemical data in the thermodynamic database, and hence Cu₂S and Ag₂S were calculated as two independent phases. However, the calculations reasonably agree with the observation of Ag₂S-Cu₂S at high temperatures (Fig. 7a) with decreasing abundance to 750 °C.

The model predicts Zn to occur as ZnS above 600 °C, and additional abundant phases at low temperatures are ZnIn₂S₄ and ZnGa₂S₄ (Fig. 8b). We observed ZnS in the experiments, forming a solid solution with CdS, but not the phases ZnIn₂S₄ and ZnGa₂S₄. Furthermore, the calculated and observed temperature ranges are not in agreement, as we observed ZnS at 435-650 °C. The most abundant gas species are Zn_(g) and ZnCl_{2(g)}.

Silver is calculated to form abundant phases other than sulfides (Fig. 8d). These include native Ag (> 1050 °) and AgTe. Sulfides have abundances of 0.01 to 0.2 mole fractions and include Ag_{1.64}S and Ag₂S. Finally, AgCl becomes increasingly abundant below 500 °C. These calculations do not reproduce the observations from the experiment, where we observed Ag₂S-Cu₂S at 760-1200 °C (Fig. 7a). This is likely due to the lack of heat capacity data for the solid solution in the model.

The thermodynamic model predicts Cd to be stable as CdS over the entire temperature range together with increasingly abundant CdCl₂ below 500 °C (Fig 8e). The predominant gas species is Cd_(g), followed by CdS_(g) and CdCl_(g). Cadmium is a representative example of the discrepancies between calculations and experimental observations. The predicted dominant solid phase is in agreement (CdS in this case). However, the closed system equilibrium approach does not reliably predict the observed temperature range of the deposited phase (Fig. 7a). 453 Lead occurs as PbS above 400 °C, whereas $PbCl_2$ predominates below (Fig. 8f). This is in fair 454 agreement with the experimental observations, where we observed both phases concurrently at 496-455 535 °C (Fig. 3i). The main gas species are $PbS_{(g)}$ followed by $PbCl_{(g)}$, $PbTe_{(g)}$, $Pb_{(g)}$ and $PbCl_{2(g)}$, with 456 the latter becoming increasingly important towards lower temperatures (Fig. 8f).

457

5.2 Calculations MO and comparison with experimental results in this system

458 Copper and Zn are both predicted by the model to be stable as oxides (CuO, Cu₂O and ZnO) 459 in the absence of the ligands S and Cl (Fig. 9a & b). Gas species of these two metals have abundances 460 of $< 10^{-4}$ mole fractions over the entire temperature range. In the given system, the most abundant gas 461 species are Cu_(g) and Zn_(g). The low volatility is reflected in the absence of deposits of these metals <462 1200 °C in the experiment (Fig. 7b).

Germanium is only slightly more volatile than Cu and Zn. GeO_2 is stable over the entire temperature range and $GeO_{(g)}$ occurs above 10^{-4} mole fractions only at T > 1200 °C (Fig. 9c). In comparison, we did not observe any Ge-deposits in the experiment MO.

The calculations for Ag and Cd correctly predict the stability of native Ag at T > 600 °C and CdO. Additional AgReO₄ at lower temperatures and CdO*Ge₂O₃ did not form in the experiment (Fig. 9d & e). Both metals occur in their elemental form in the gas phase (Ag_(g) and Cd_(g)). Note that the database does not contain thermochemical data for the experimentally observed 3CdO-2TeO₂-MoO₃ phase, and hence the model does not predict such a phase.

The model predicts PbMoO₄ (wulfenite) to be the most stable Pb phase, with only minor amounts of PbO (Fig. 9f). In the experiment, no distinct Pb-phase could be observed (Fig. 7b) as Pb, along with Ag, Cd, Zr and Tl occurs in reaction textures with the silica tube (Fig. 4d).

474

5.3 Calculations MO-S and comparison with experimental results in this system

The metal speciation in the system MO-S only differs in the absence of chloride species from the system MO-S-Cl. The relative abundances of sulfides, oxides, tellurides and native metals remains broadly the same (Fig. 10). A detailed comparison of Figs. 8 and 10 shows minor differences in some sulfide species. For example, the calculated abundance of Cu₂S relative to CuS is slightly lower in the 479 system MO-S, compared to MO-S-Cl. GeS and GeS₂ also have lower abundances compared to GeO₂. 480 These minor differences suggest that fS_2 may be slightly lower in the MO-S system, compared to the 481 MO-S system. A lower f_{S_2} in the MO-S system is also suggested by the experimental results where 482 the phases CdIn₂S₄ and ZnS are absent. Instead, In and Zn are incorporated in an oxide phase in the 483 experiment (Fig. 7c).

484

5.4 Calculations MO-Cl and comparison with experimental results in this system

The calculated speciation of metals in the MO-Cl system is markedly different from the other 485 486 experiments. In addition to the presence of chloride species, the metals are overall more volatile, with 487 gas species abundant at lower temperatures compared to the other systems (Fig. 11). However, Cu is 488 the only metal where a chloride species (CuCl, Fig. 11a) is the dominant species, followed by native 489 Cu, CuO and Cu₂O. Zink, Ge and Cd are predicted to occur as oxides (ZnO, GeO₂ and CdO), and lead 490 as a molybdate (PbMoO₄). This is in strong contrast to the observations from the experiment MO-Cl 491 where Cd, Cu and Pb deposited as chlorides (Fig. 7d). Gaseous chloride species with abundances >10⁻⁴ mole fractions include CuCl_(g), CuCl_{2g)}, ZnCl_{2(g)}, AgCl_(g), CdCl_{2(g)}, CdCl_(g), PbCl_{2(g)} and PbCl_(g). 492

493

5.5 Open system calculations and comparison with experimental results

Closed system equilibrium calculations predict at which temperature certain phases and 494 495 gaseous species are stable. However, they do not account for a change in the gas composition as 496 phases deposit and condense with decreasing temperatures. To address this issue, we conducted a set 497 of open system calculations with the same initial conditions and species as in the closed system models. Starting at 1250 °C, at each 50 °C incremental step the solid phases were removed from the 498 499 bulk composition of the next temperature step, resulting in the removal of the "deposited" phases. The 500 overall speciation of the metals remains the same as in the closed system models (Figs. 8-11) and 501 details are not given here. The results of these calculations are available in the electronic supplement.

502 The predicted temperature ranges over which the metals Cu, Zn, Ge, Ag, Cd and Pb deposit as solids are shown in Figure 12. Presence of solids was limited to phases with abundances of $> 10^{-9}$ 503 504 mole fractions in the calculations. In Figure 12, we compare the modeling results with the temperature 505 ranges over which we observed solid phases of the selected metals in the experiments (Fig. 7). It is 506 apparent that the open system calculations do not reliably reproduce the experimental results. Overall, 507 the calculations predict that the metals should deposit at higher temperatures than observed in the 508 experiments. This implies that the calculated volatility of the metals is systematically underestimated 509 for most metals and investigated systems. Note that the limitations of thermochemical equilibrium 510 calculations to model natural fumarolic processes have previously been pointed out by Wahrenberger 511 et al. (2002), who showed that open and closed system calculations could not fully reproduce 512 observations from fumaroles sampled on Kudriavy volcano. Consequently, in the following section 513 we will compare our experimental results with data from natural fumaroles.

514

6. Comparison of our results to natural fumarolic metal deposits

515 Our experiments were to simulate metal transport and deposition in fumarolic systems. To 516 assess the validity of this approach we compare our experimental results (Fig. 7) to records of metal 517 deposits sampled at natural fumaroles. We primarily compare our experiments with deposits sampled 518 in silica glass tubes at Kudriavy volcano (Wahrenberger et al., 2002; Africano et al., 2003; Chaplygin et al., 2004; Yudovskaya et al., 2006). Additionally, we include fumarole records from La Fossa on 519 Vulcano, Italy (Garavelli et al., 1997; Roberts et al., 2006; Campostrini et al., 2008) and Momotombo 520 521 volcano in Nicaragua (Quisefit et al., 1989). In Figure 13, we present a comparison of the results from 522 experiment MO-S-Cl with these observations. The comparison is limited to phases observed in the 523 experiment (Fig. 7a) and to phases described in the three natural settings, including Ag₂S-Cu₂S, NaCl, 524 ReS₂, CdIn₂S₄, (Cd,Zn)S, PbS, PbCl₂, TlPb₂Cl₅, TlCl and S. We do not compare data from natural 525 fumaroles with the other experiments, as they do not include both S and Cl.

First, we consider the phases (Cd,Zn)S, PbS, PbCl₂, TlPb₂Cl₅, TlCl and S. The observed temperature ranges of these phases in the experiment fall within the conditions recorded on the volcanoes. For some phases, this agreement is excellent (Fig. 13). For example, TlPb₂Cl₅, TlCl, PbCl₂ and PbS were all observed on La Fossa crater on Vulcano, within the temperature range of 400-500 °C (Garavelli et al., 1997; Roberts et al., 2006; Campostrini et al., 2008). Galena (PbS) occurs over a wide range of temperatures in natural fumaroles. The deposition temperatures vary between 532 different volcanoes. For example, PbS is reported on La Fossa in the temperature range of 420-520 °C (Garavelli et al., 1997), on Momotombo in the range of 100-220 °C (Quisefit et al., 1989), and on 533 Mutnovsky over 240-400 °C (Zelenski and Bortnikova, 2005). Reported temperature ranges also vary 534 535 on a single volcano between different sampling expeditions, such as in the case of Kudriavy. Wahrenberger et al. (2002) reported a temperature range of 620-680 °C, Yudovskaya et al. (2006) 536 reported lower temperatures of 490-650 °C, and Africano et al. (2003) observed intermediate 537 temperatures of 625-650 °C for the deposition of PbS. These differences are explained by variations 538 539 in the composition and temperature of the emitted gases, different sampling procedures, and analytical resolution. 540

541 Second, for some phases there is poorer agreement between our experiments and the natural data (Fig. 13). These include Ag₂S-Cu₂S, NaCl, ReS₂ and CdIn₂S₄. Some of the discrepancies are 542 explained based on variations of the natural fumarolic system. For example on Kudriavy, Cu₂S is 543 544 reported at 800-850 °C by Wahrenberger et al. (2002) and at 490-550 by Yudovskaya et al. (2006). NaCl shows considerable overlap between the experiment and the natural observations. In the 545 546 experiment, NaCl is observed at higher temperatures than on any volcano, but there is a complete overlap with NaCl observations on Kudriavy (550-720 °C, Yudovskaya et al. 2006). On Momotombo, 547 548 NaCl deposits were observed over a large temperature range of 200-850 °C (Quisefit et al., 1989). 549 Phases that show no overlap between experiment and volcanoes are ReS₂ and CdIn₂S4. Both phases 550 deposited at higher temperatures in the experiment compared to Kudriavy, where these minerals have 551 been observed (Korzhinsky et al., 1994; Chaplygin et al., 2004; Tessalina et al., 2008).

552

7. Summary and conclusions

553 Overall, we observe 30 different phases in four experimental systems (MO-S-Cl, MO, MO-S, 554 MO-Cl). Although the starting material contained 32 different chemical elements (Table 1), we found 555 that the diversity of the deposited phases is surprisingly limited. 14 metal oxides were not mobilized 556 in our experiments, including high field strength and rare earth elements (Sc, V, Y, Zr, Nb, La, Pr, Nd, 557 Sm, Eu, Gd, Lu, Hf and Ta). In comparison, natural fossil and active fumaroles belong to the most 558 mineralogically diverse systems with hundreds of different minerals, many of which have only 559 recently been observed in nature (e.g., Balić-Žunić et al., 2016; Henley and Seward, 2018). One reason for the low mineral diversity in our experiments is, that our experiments only cover a limited 560 range of redox conditions (between the MW and MH buffers), and were water free. However, natural 561 562 fumarole deposits commonly include more varied oxidized phases such as sulfates. Another limitation 563 to the mineralogical diversity of the deposited phases is the selection of metals in the experiments. We 564 did not include iron in the starting material to avoid the reaction with the silica tube wall and the 565 formation of fayalite. We also excluded a range of elements that form diverse deposits in fumaroles, 566 namely F, As, Se, Br, Sb and I. Furthermore, we excluded noble metals such as Au, which may be 567 deposited in fumaroles and in the subvolcanic environment in considerable quantities. Water in 568 fumarolic systems is often of meteoric origin. Similarly, fumarolic gases and fluids entrain oxidizing 569 air when emitted at the surface, which can lead to disequilibrium processes. In our discussion above, 570 we disregarded disequilibrium processes both in the experiments and in nature, which is a challenge 571 for future studies. Finally, a major difference between our experiments and natural processes is that 572 we used oxide powders as the metal source in our experiments. This is in contrast to nature, where 573 metals are emitted from a magmatic silicate melt source, or scavenged from sub-volcanic rocks 574 through which the gases pass.

575 Our experimental approach provides an additional instrument to direct sampling of toxic 576 gases and their deposits on active volcanoes, to investigate metal transport and deposition in fumarolic 577 systems. The comparison of the experimental results with thermochemical equilibrium calculations 578 and natural observations show that the experiments simulate the natural process much better than 579 thermodynamic models. This is because equilibrium model calculations predict at which temperature 580 gas or mineral phases are stable, but our results show that the models cannot reliably predict the 581 temperatures where these phases deposited, as deposition in nature occurs in a transport process more 582 akin to the experiments.

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731 Tables

732Table 1: Nominal molar composition of the starting material pellets and weighed-in quantities of733reagents in g. MO-S-Cl: Starting material that contains metal oxides (O), S and Cl, M-O: Starting material that734contains only metal oxides and no S or Cl, MO-S: Starting material that only contains metal oxides and S but no735Cl, MO-Cl: Starting material that only contains metal oxides and Cl but no S. Elements included in the Gibbs736free energy minimization calculations are indicated with an X.

	Included in calculations	MO-S-Cl		МО		MO-S		MO-Cl	
		mol%	g	mol%	g	mol%	g	mol%	g
S	х	39.1	0.0053	-	-	83.0	0.0170	-	-
NaCl	х	37.8	0.0093	-	-	-	-	55.9	0.0063
Sc_2O_3		0.6	3.2E-04	2.4	6.4E-04	0.4	3.6E-04	1.1	2.8E-04
V_6O_{13}		0.2	4.0E-04	0.8	7.9E-04	0.1	4.5E-04	0.4	3.5E-04
Cr_2O_3		0.6	3.6E-04	2.4	7.0E-04	0.4	4.0E-04	1.1	3.1E-04
CoO		1.1	3.5E-04	4.8	6.9E-04	0.8	3.9E-04	2.1	3.1E-04
NiO		1.1	3.5E-04	4.8	6.9E-04	0.8	3.9E-04	2.1	3.1E-04
CuO	х	1.1	3.7E-04	4.8	7.4E-04	0.8	4.1E-04	2.1	3.3E-04
ZnO	х	1.1	3.8E-04	4.8	7.5E-04	0.8	4.2E-04	2.1	3.3E-04
Ga ₂ O ₃	х	0.6	4.4E-04	2.4	8.7E-04	0.4	4.9E-04	1.1	3.8E-04
GeO ₂	х	1.1	4.9E-04	4.8	9.7E-04	0.8	5.4E-04	2.1	4.3E-04
Y ₂ O ₃		0.6	5.3E-04	2.4	1.0E-03	0.4	5.9E-04	1.1	4.6E-04
ZrO ₂		1.1	5.8E-04	4.8	1.1E-03	0.8	6.4E-04	2.1	5.0E-04
Nb ₂ O ₅		0.6	6.2E-04	2.4	1.2E-03	0.4	6.9E-04	1.1	5.4E-04
MoO ₂	х	1.1	6.0E-04	4.8	1.2E-03	0.8	6.7E-04	2.1	5.2E-04
Ag ₂ O	х	0.6	5.4E-04	2.4	1.1E-03	0.4	6.0E-04	1.1	4.7E-04
CdO	х	1.1	6.0E-04	4.8	1.2E-03	0.8	6.7E-04	2.1	5.3E-04
ln_2O_3	х	0.6	6.5E-04	2.4	1.3E-03	0.4	7.2E-04	1.1	5.7E-04
TeO ₂	х	1.1	7.5E-04	4.8	1.5E-03	0.8	8.3E-04	2.1	6.5E-04
BaO		1.1	7.2E-04	4.8	1.4E-03	0.8	8.0E-04	2.1	6.3E-04
La ₂ O ₃		0.6	7.6E-04	2.4	1.5E-03	0.4	8.5E-04	1.1	6.7E-04
Pr_6O_{11}		0.2	8.0E-04	0.8	1.6E-03	0.1	8.9E-04	0.4	7.0E-04
Nd_2O_3		0.6	7.9E-04	2.4	1.6E-03	0.4	8.8E-04	1.1	6.9E-04
Sm_2O_3		0.6	8.1E-04	2.4	1.6E-03	0.4	9.1E-04	1.1	7.1E-04
Eu ₂ O ₃		0.6	8.2E-04	2.4	1.6E-03	0.4	9.2E-04	1.1	7.2E-04
Gd_2O_3		0.6	8.5E-04	2.4	1.7E-03	0.4	9.4E-04	1.1	7.4E-04
Lu ₂ O ₃		0.6	9.3E-04	2.4	1.8E-03	0.4	1.0E-03	1.1	8.1E-04
HfO ₂		1.1	9.8E-04	4.8	1.9E-03	0.8	1.1E-03	2.1	8.6E-04
Ta ₂ O ₅		0.6	1.0E-03	2.4	2.0E-03	0.4	1.1E-03	1.1	9.0E-04
ReO ₂	х	1.1	1.0E-03	4.8	2.0E-03	0.8	1.1E-03	2.1	8.9E-04
Tl ₂ O ₃	Х	0.6	1.1E-03	2.4	2.1E-03	0.4	1.2E-03	1.1	9.3E-04
PbO	Х	1.1	1.0E-03	4.8	2.1E-03	0.8	1.2E-03	2.1	9.1E-04
Total w	eight of		0 0100		0 0305		0 0222		0.0174
metal o	xides		0.0199		0.0393		0.0222		0.0174
Total weight of			0.0346		0.0395		0.0392		0.0238
pellet			0.0040		0.0000		0.0002		0.0230

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Figures



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Fig. 1: Schematic drawing of the experimental setup. a) A sealed and evacuated silica tube is suspended in the upper part of a vertical tube furnace (see text for details). Note that the starting material pellets were placed in the bottom of the silica glass tube, which is within the hot zone of the furnace. Depicted are examples of deposited mineral phases, green minerals at high T, blue minerals at lower T, and the red minerals deposited at even lower T. The silica glass tubes were 300 mm long, and had inner diameters of 4 mm and wall thicknesses of 1 mm. The tube furnace was sealed at the top and at the bottom to avoid convection. b) Sketch of the temperature gradient (ca. 1000°C) within the tube furnace.



Fig. 2: Temperature gradient within the tube furnace at a set temperature of 1250 °C. The temperature decreases to ~300 °C at the top of the furnace. The hot zone of the furnace is reached at 35 cm depths. The photo shows a silica glass tube (experiment MO-S-Cl) with deposits (dark and yellowish areas within the tube) superimposed on the temperature gradient.





Fig. 3: Experiment MO-S-Cl, backscattered electron images of phases deposited on the inner silica
tube wall. a) Ba- and Ga-oxide in quenched melt, 1203-1222 °C; b) Ag₂S-Cu₂S droplets, 1005-1041 °C; c) ReS₂
(rheniite), 885-934 °C; d) ReS₂ and quenched NaCl melt, 826-885 °C; e) (Cd,Zn)S (greenockite), NaCl, GeO₂,
707-763 °C; f) ZnS (wurtzite), NaCl, CdIn₂S₄ (cadmoindite), 581-646 °C; g) ZnS, NaCl, In-Pb-S, 535-581 °C; h)
ZnS, In-Pb-S, PbS (galena), 535-581 °C; i) PbS, PbCl₂ (cotunnite), 496-535 °C; j) TlPb₂Cl₅ (hephaistosite),
417-435 °C; k) TlCl (lafossaite), 396-417 °C; l) TlCl, S, Te, 320-337 °C.



764Fig. 4: Experiment MO, backscattered electron images of phases deposited on the inner silica tube765wall. a) Ga, Zn, Co in quenched melt, 1222-1238 °C; b) In_2O_3 , 1108-1131 °C; c) In_2O_3 , native Ag, 1005-1041766°C; d) Pb, Ag, Cd, Zr, Tl in quenched melt, 973-1005 °C; e) CdO, 934-973 °C; f) 3CdO-2TeO_2-MoO_3, 763-707767°C; g) quenched Tl-Te-Re-oxide melt, 535-581 °C; h) Re-Tl-oxide, 435463 °C; i) Tl-oxide, 337-352 °C



769Fig. 5: Experiment MO-S, backscattered electron images of phases deposited on the inner silica tube770wall. a) Ba & Ga in quenched melt, 1222-1238 °C; b) $(Ag,Cu)_2(S,Te)$, 1131-1157 °C; c) $(Ag,Cu)_2(S,Te)$, 1041-7711075 °C; d) $(Ag,Cu)_2(S,Te)$, In-Ge-oxide, 1005-1041 °C; e) $(Ag,Cu)_2(S,Te)$, In-Ge-oxide, GeO2, 885-934 °C; f)772PbTe, 707-763 °C; g) PbS (galena), CdS (greenockite), 581-646 °C; h) Pb(Te,S), CdS, 535-581 °C; i) PbS,773Pb(Te,S), CdS, 535-581 °C; j) Tl_2S (carlinite), ReS2 (rheniite), 496-535 °C; k) Tl_2S, Re-Tl-S, 435-463 °C; l)774Tl_2S, Te, S, 379-396 °C



776Fig. 6: Experiment MO-Cl, backscattered electron images of phases deposited on the inner silica tube777wall. a) Ba & Ga in quenched melt, 1222-1238 °C; b) In-Ge-Na-oxide, 973-1005 °C; c) In-Ge-Na-oxide, 885-778826 °C; d) Mo-Na-oxide reacted with silica-tube wall, 763-826 °C; e) NaCl, ReCl₂, PbCl₂, 646-707 °C; f)779quenched chloride melt (Na, Cd, Re, Co, Pb, Ag), 581-646 °C; g) NaCl, PbCl₂, CuCl₂, Te-In-Pb-Cl-phase, 535-780581 °C; h) PbCl₂, CuCl₂, CdCl₂, 496-535 °C; i) PbCl₂, CuCl₂, CdCl₂, 463-496 °C; j) Te, (Tl,Zn)Cl, 396-417 °C;781k) TlCl, 396-417 °C; l) Te, 379-396 °C



Fig. 7: Observed deposited mineral phases along the inner silica tube wall. a) experiment MO-S-Cl; b)
experiment MO; c) experiment MO-S; d) experiment MO-Cl (MO: Metal Oxide).



Fig. 8: The stability of different metal compounds and gas species calculated (closed system
equilibrium calculations) in the system MO-S-Cl using the software package HSC9 by Outotec. Stippled lines
denote gas species. We normalized the mole fractions of the gas and solid species of each respective metal to 1.
a) Cu; b) Zn; c) Ge; d) Ag; e) Cd; f) Pb



Fig. 9: The stability of different metal compounds and gas species calculated (closed system equilibrium calculations) in the system MO using the software package HSC9 by Outotec. Stippled lines denote gas species. We normalized the mole fractions of the gas and solid species of each respective metal to 1. a) Cu; b) Zn; c) Ge; d) Ag; e) Cd; f) Pb



Fig. 10: The stability of different metal compounds and gas species calculated (closed system
equilibrium calculations) in the system MO-S using the software package HSC9 by Outotec. Stippled lines
denote gas species. We normalized the mole fractions of the gas and solid species of each respective metal to 1.
a) Cu; b) Zn; c) Ge; d) Ag; e) Cd; f) Pb



Fig. 11: The stability of different metal compounds and gas species calculated (closed system
equilibrium calculations) in the system MO-Cl using the software package HSC9 by Outotec. Stippled lines
denote gas species. We normalized the mole fractions of the gas and solid species of each respective metal to 1.
a) Cu; b) Zn; c) Ge; d) Ag; e) Cd; f) Pb



Fig. 12: Comparison of experimental data with results from thermodynamic calculations for the
elements Cu, Zn, Ge, Ag, Cd, and Pb. The four different starting material compositions are indicated by color;
MO-S-Cl red, MO blue, MO-S green, MO-Cl yellow (MO; metal oxide). The dotted bars depict the calculated
temperature ranges in which metals were deposited, whereas the solid bars show the temperature ranges over

811 which the metals were deposited in the experiments. See text for details.



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Fig. 13: Comparison of experimental results (run MO-S-Cl, black solid bars) with data from natural fumaroles (grey dotted bars) on the volcanoes Kudriavy (Wahrenberger et al., 2002; Africano et al., 2003; Chaplygin et al., 2004; Yudovskaya et al., 2006), Vulcano (Garavelli et al., 1997; Roberts et al., 2006; Campostrini et al., 2008) and Momotombo (Quisefit et al., 1989). Note that the lower temperature limit of the experiment is at 300 °C. See text for details.