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Condensation behaviour of volatile trace metals in laboratory benchtop fumarole experiments

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Abstract

Volatile trace metals emitted from volcanoes condense in gas plumes and fumaroles. The transient nature of natural eruptions make it challenging to isolate key variables affecting trace metal condensation in this complex natural system. To emulate these conditions in a controlled setting, we design a laboratory 'benchtop' fumarole to experimentally measure volatilization and condensation behaviour of volatile trace metals from magma. Synthetic silicate melt compositions in the Na_2O-Al_2O_3-SiO_2 and Na_2O-Fe_2O_3-SiO_2 systems doped with dissolved trace metals (V, Cu, Zn, As, Y, Mo, Cd, Sn, Tb, Pb and Bi) are degassed in a furnace at 900°C over periods of days to weeks. The condensates from the gas phase form on a silica glass tube along a thermal gradient from 725 to 125°C, and are examined by electron microscopy and chemical analysis. We observe variable crystallinity of condensates as functions of temperature. The concentrations of Li, Cu, As, Rb, Mo, Ag, Cd, Cs, W, Pt, Tl, Pb and Bi in leachates of the condensates change by orders of magnitude along the glass tube, and show maxima at various temperatures between 250 to 600°C. A comparison of the experiments with natural examples

shows similarities in the condensation pattern for Cu, As, Ag, and Tl. The enrichment of certain metals in the experimental gas condensates (e.g. Mo) is similar to that observed in natural systems, but differs greatly for other elements (e.g Bi and Cd) likely due to lack of Cl, S or other complexing agents for metals in the experiments. Our experimental design is a starting point to investigate the role of these and other variables on trace metal condensation behaviour in natural volcanic emmissions.

1. Introduction

Volcanoes are a natural source for pollution of toxic trace metals in the atmosphere (Nriagu, 1979; Lantzy and Mackenzie, 1979; Bernard and Le Guern, 1986; Calabrese et al., 2011). Anthropogenic activities of fossil fuel combustion, non-ferrous metal production, and waste incineration load the modern atmosphere with volatile trace metals (e.g. Se, Tl, As, Cd, Cu, and Pb - Pacyna and Pacyna, 2001), but over the course of Earth history actively and passively degassing volcanoes contribute to the global cycle of these and other trace metals (Oppenheimer et al., 2014). Quantifying the contributions of toxic trace metals to the atmosphere from volcanism is essential for understanding their overall geochemical cycle and impact on the environment both now and in the past.

Volatile trace metals in volcanic emissions are originally dissolved in a melt, and partition into a gases that exsolve as magmas ascend and erupt (Hinkley et al., 1994). The quantity of metal released during a persistent degassing event can vary with the relative abundance of the metal in the melt and its partition coefficient into the gas phase. An empirical measure of the release of a trace metal to the gas phase is its emanation coefficient, ε defined as:

$$\varepsilon = \frac{C_i - C_f}{C_i} \qquad [1]$$

where C_i is the concentration of the metal in the melt initially and C_f is the concentration of the metal in the melt after degassing occurs (Hinkley et al., 1994; Pennisi, 1988). Emanation coefficients vary over orders of magnitude from 0.35 for highly volatile elements such as Bi to 4.3 x 10^{-7} for non-volatile elements such as Al (Rubin, 1997).

Metals partition from mmelt phase into volcanic gases depending on several factors. Ligands such as S, Cl, and F dissolved in the melt (Aiuppa et al., 2009; Calabrese et al., 2011) may assist with transport of metals to the gas-melt interface, or by complexation to favour their partition into the gas phase for eventual release to the atmosphere (Williams-Jones and Heinrich, 2005; Johnson et al., 2013). Toxic trace metals are then released from volcanoes to the environment as species dissolved in volcanic gases (e.g. H-C-O-S mixture). The metals can condense or adsorb from such gases on to ash particles or other surfaces during an eruption (Hinkley et al., 1994; Mather et al., 2003).

Le Guern and Bernard (1982) established a method to measure gas condensates from an active volcanic fumarole along a thermal gradient in a silica tube inserted into a fumarole. Particulate and volatile metals in volcanic plumes can also be collected by pumping gas through filters during an eruption (e.g Hinkley, 1991). These methods are widely used to study the precipitation and budget of metals from volcanic emissions at volcanoes worldwide (e.g. Bernard et al., 1990; Symonds, 1993; Cheynet et al., 2000; Zelenski and Bortnikova, 2005).

Both the silica glass tube and filter methods provide information on the chemistry of phases with changing temperature, gas composition, or oxidation state of volcanic gases. Many of these variables, however, can change erratically depending on the phase or nature of the volcanic eruption. To investigate the role of these variables in condensation of trace metals in volcanic gases in a more controlled environment, we constructed a ‘benchtop fumarole’ apparatus, wherein volatile trace metals are degassed from a silicate liquid and precipitated on a silica glass tube along a stable temperature gradient. Our method is a simple analogue for natural systems and allows for investigation of the volatilization of trace metals from melts and their condensation behaviour, with independent control of the variables of temperature, melt, and eventually gas composition. The mineralogy and chemistry of the condensates that are collected inform what metallic species may be present in volcanic gases as well as their condensation behaviour. Such data can be compared with natural observations (e.g. Toutain and Meyer, 1989; Taran et al., 2001), or thermodynamic calculations used to model natural systems (e.g. Symonds et al., 1992). In this paper, we describe the method and some initial experiments and observations. The ultimate aim is to increase our understanding of the condensation behaviour of trace metals to inform interpretations of the trace metal loading from volcanoes, and their impact on the atmosphere and environment.

2. A 'Benchtop' Fumarole Design

For these experiments, we suspended a 1 cm diameter, 30 cm long silica glass tube from a ring stand above a crucible of degassing silicate melt inside a high-temperature box furnace (Fig. 1). The silica glass tube exited through the top of the furnace near room temperature, creating a strong thermal gradient. Before each experiment, the temperature gradient inside the silica glass tube was measured at 0.5 cm intervals using an S-type ($Pt_{90}Rh_{10}$-Pt) thermocouple. A peak of ~925°C is observed inside the furnace, just above the crucible, decreasing to near room temperature after exiting the furnace (Fig. 2). During the experiment, volatile trace metals dissolved in the synthetic silicate melt degas across the air-melt interface, rise and condense along the silica glass tube along a temperature gradient. An exhaust funnel with minor suction was placed at the top of the tube to obviate traces of toxic metals in the gas from entering the lab atmosphere.

Our design was limited by the annealing point of silica glass (viscosity of 10^{13} Pa.s) to peak temperatures of 1190°C (Bansal and Doremus, 2013), well within the temperature range of most natural volcanic gas emission measurements (Symonds et al., 1992), but above the temperature limit of the box furnace. Given these upper temperature limits, we used synthetic melts with low melting points in the systems Na_2O-Al_2O_3-SiO_2 (NAS) and Na_2O-Fe_2O_3-SiO_2 (NFS), having eutectic points of 740±5°C and ~800°C respectively (Schairer and Bowen, 1956; Bailey and Schairer, 1966). These two melts represent broadly phonolitic compositions with and without Fe, to compare the effect of Fe on metal degassing behaviour in silicate liquids. Starting materials were made by weighing out dried reagent grade SiO_2, Al_2O_3, Fe_2O_3 and Na_2CO_3, which were then mixed by shaking in a canister for 15 minutes. The oxide mixture was then decarbonated and fused in a Pt crucible at 1400°C for 24 hours. The starting material was quenched to a glass, removed from the crucible, crushed, and powdered. Trace elements of varying volatility observed in natural systems (V, Cu, Zn, As, Mo, Cd, Sn, Y, Yb, Pb and Bi) were doped into the glass powder at a concentration of 100 ppm in a solution of in 2% HNO_3. The final slurry was dried under a heat lamp and mixed. The trace element concentrations in the starting material powder determined by solution ICP MS are slightly higher than in the added doping solution of 100 ppm and some elements are present that were not directly added (Table 1). These trace elements were likely contributed by the reagent grade oxides.

For each experiment, 10 g of starting material was loaded into a Pt crucible and positioned on a ceramic stand inside the box furnace below the silica glass tube, at a temperature of 500°C (Fig. 1). The temperature was raised in increments of 100°C every 10 minutes. At

900°C, the crucible was removed and an alumina rod was used to puncture the surface of the melt, which would often inflate due to rise and coagulation of air bubbles during initial degassing. The crucible was then replaced in seconds into the furnace and the degassing experiment carried out for 2 or 7 days. At the end of the experiment the silica glass tube was removed from the furnace and allowed to cool. The glass tube was then cut into 1 cm segments along the length of its thermal gradient using a diamond saw. Temperatures were assigned to the mid-point of each 1 cm segment from a polynomial function fit to the measured thermal gradient (Fig. 2). Segments of the silica glass tube were reserved for further analysis and examination of the condensates.

3. Analytical Methods

The crystal sizes, textures and X-ray chemical maps of the condensates on the glass segments at different temperatures along the tube were imaged by SEM (Scanning Electron Microscope) using a Hitachi S-4800 FESEM instrument with an Energy Dispersive detector (EDS) at the University of Victoria. Solution ICP-MS (Inductively coupled plasma mass spectrometry) analyses were used to determine the trace metal content of leachates of the condensates on the silica glass tube segments. Condensates from a piece of each tube segment were leached in 5 ml of 16M HNO_3 on a hotplate for 2 days. The glass was then removed and the solution was diluted with 30 ml of deionized water. Four aliquots of each solution were analysed using a Thermo X-Series II (X7) quadrupole ICP-MS. The counts-per-second (CPS) data were corrected for drift using In from an internal standard SLRS-5 (Ottawa River Water - Jochum et al., 2005) measured after every eight unknown samples. The reproduction of SLRS-5 standard values was better than 20% for Al, Ca, Cr, Mn, Fe, Cu, As, Sr, Mo, Ba, between 20-30% for V, Co, Ni, Zn, and above 40% for Cd (Table 2 – supplementary material). All other elements did not have certified values for SLRS-5. Metals concentrations in leachates were lower than in the standard for many elements. Values below the detection limit of the ICP-MS were removed from further consideration. Platinum and Cs had no reliable calibration standards and their concentrations are reported as CPS values (Fig. 6).

The major element composition of quenched glass after an experiment was determined using the Cameca SX50 electron microprobe at the University of British Columbia (Table 1).Trace elements in glasses after two experiments were measured at the University of Victoria by laser ablation-inductively coupled plasma-mass spectrometry (LAICP-MS) using a New Wave Research, solid-state, 213 nm Nd:YAG UV laser coupled with a Thermo-Instruments X-Series II ICP-MS (Table 3). A peak counting time of 10 ms was used for all elements. Each analysis consisted of measuring an initial background signal for 25–30 seconds, after which the laser was fired at 10 Hz and a fluence of 0.4-1 mJ for 40 seconds, using a spot size of 80-100 μm rastered over a line length of 100 μm at a scan rate of 10 μm/s. The data was recorded as time-resolved spectra of counts per second and counts were reduced to concentrations in a custom spreadsheet. NIST glasses (611, 613, and 615 - Jochum et al., 2005) were used with ^{29}Si as the internal standard. Accuracy on USGS BCR2g reference glass is better than: 5% for Li, Ti, V, Rb, Sr, Cs, Cd, Y, Mo, Pb and W; 10% for Cr; 20% Cu and Sn; and 30% Zn. Reference values for As, Ag, or Pt in BCR2g are either unknown or highly uncertain. Detection limits for each element are calculated as three times the standard deviation of the gas background signal.

4. Results

4.1 Petrography of Condensates

In all experiments, condensates on the silica glass tube are visible as frosting over an approximately 10 cm long interval corresponding to a temperature range from 125 to 725°C (Fig. 2). An SEM image of the highest temperature segment (553°C) from a 7-day experiment with the NFS composition (Fig. 3a), shows anhedral crystals and > 1μm cubic crystals. At 427°C (Fig. 3b) the cubic crystals are absent, but elongated crystals appear, with a maximum length of 5μm. At 350°C (Fig. 3c) there are anomalously large, anhedral crystals of ~15μm. At 295°C (Fig. 3d) the elongated crystals from higher temperature samples persist and hexagonal crystals of >10μm appear. At 218°C (Fig. 3e) the hexagonal crystals are absent and elongated crystals are longer, >20μm, and more densely packed. At 138°C (Fig. 3f) all crystals are <5μm and anhedral.

Chemical maps reveal some semi-quantitative chemical information of the condensates from a 7-day NAS experiment (Fig. 4). At 427°C a small cubic (>1μm) phase appearing as bright white squares in the SEM image (Fig. 4a), is mostly Pt metal. A hexagonal Na-Mo-oxide phase appears with maximum length of crystals of 10-20μm appears at 350°C (Fig. 4b, c, d). At 253°C individual elongated crystals longer than 200μm occur together in a dendritic pattern and also contain Mo, Na, and K (Fig. 4e, f, g) . Similar Na-K-Mo compounds were observed as condensates in the NFS experiments and are likely molybdates. Molybdates are common in incrustations from fumaroles (Stoiber and Rose, 1974), and in condensates from volcanic gases (Symonds et al*.,* 1992; Africano et al., 2002). A more detailed mineralogical investigation of the condensates is in progress.

4.2 Bulk Chemistry of the Condensates

The trace metals added to the starting melt have varying volatility in natural volcanic systems. Several trace elements (Cu, Rb, Mo, Cd, Pb and Bi) are present in lower concentrations in the post-experiment glass than in the initial starting material (Table 1, Table 3) confirming they were volatile. For example, emanation coefficients (ε) for the NAS experiments calculated using equation [1] (Rubin, 1997) with initial and post-experiment glass (Table 1, Table 3) are high for Pb, Cd and Cu, 1.5 x 10^{-2}, 2.6 x 10^{-1} and 1.0 x 10^{-2} respectively, and lower for Mo and Li (1.4 x 10^{-3} and 1.7 x 10^{-4}).

The minute abundance (by weight) of the condensates along the tube precluded physical removal for direct bulk analysis, and necessitated an estimate of their trace metal composition by acid leaching. We assume the composition of the acid leachate for a given segment along the silica glass tube reflects that of the condensate. Although not originally added to the starting melt composition, trace amounts of Li, Cr, Mn, Rb, Cs, Ag, W, Pt and Tl were also detectable in the condensate leachates. The Cr or Mn may be sourced from the Kanthal FeCrAl alloy heating elements used in the furnace. Platinum is derived from the Pt crucible used to contain the starting material. Trace levels of the remaining elements may be present due to: (1) their occurrence as impurities in the silica glass tube, or in the reagent grade oxides used to produce the starting melt material, or (2) residual 'memory' of trace element contamination in the box furnace from previous use in our laboratory.

As observed in natural fumaroles and volcanic gases (Toutain and Meyer, 1989; Taran et al., 2001; Vlastelic et al., 2013; Zelenski et al., 2014; Mather, 2015) all of Li, Cu, As, Rb, Mo, Ag, Cd, Cs, W, Pt, Tl, Pb and Bi are found to be volatile and present in enhanced concentrations in the condensates from the experiments. Several elements (Mg, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Ga, Ge, Se, Sr, Zr, Nb, Yb, Rh, Pd, In, Sb, Ba, Re Zn, Y, Sn and Au) are not enriched in the condensates, and will not be discussed further.

To examine element trends as functions of temperature of condensation, the concentration of volatile elements in the condensate leachates along the silica glass tube are normalized to a non-volatile but leachable element. Cobalt is chosen as a normalizing element due to the fact that it is leachable but non-volatile. Other elements used in the study of trace metals in natural gases (e.g. Al, Y) are non-volatile but also not leachable in our analytical protocol.

The Co-normalized concentration of volatile elements in leachates of condensate along the silica glass tube in the experiments can be compared with background levels from blank experiments. For a blank experiment, a silica tube was inserted in the furnace without a crucible of melt for several days. The trace metals detected along the tube during the blank experiments, presumably provided from degassing the furnace components, are in significantly lower concentrations than in experiments with a melt present (Fig. 5a,b; Table 2), confirming that the melt is the dominant contributor of most volatile trace metals to the condensates.

The Co-normalized concentration of volatile elements in the condensate leachates as functions of temperature for an NAS composition experiment show peaks at various temperatures between 200 to 600°C (Fig. 5a, Fig. 6a,c,e). Molybdenum has the highest overall concentration of all volatile elements in the leachates (Fig. 5a). Lead, Li, Cd, Cu, Bi, As, W, and Tl (Fig. 5 , 6a-d)) appear in relatively high concentrations and condense over a large range of temperatures. Cadmium, Bi, As, and Ag (Fig. 6a and 6b) have concentration maxima between ~300-550°C. Copper and Rb have peaks in concentration close to 300°C (Fig. 6c and 6d). Tungsten shows no particular trend for the NAS composition experiment, but shows peaks at ~300°C for the NFS composition (Fig. 6c,d). Cesium has a peak concentration at 350°C and the concentration of Pt peaks around 160°C (Fig. 6e).

Similarly, in the NFS experiments, Mo (Fig. 5b) has the highest overall concentration with peaks in abundance between 215-300°C. Lead and Li have the next highest peak normalized leachate concentrations at 425°C (Fig. 5b). Bismuth, As and Ag have distinct peak concentrations at 425°C and Cd has a peak concentration between 250-300°C (Fig. 6b). Copper, W and Rb have less defined peak concentrations between 250-685°C (Fig. 6d). Thallium (Fig. 6d) has a peak concentration at 295°C for the NFS composition, significantly higher than the peak at 160°C observed in the NAS experiment. Due to the sharp decrease in concentration above the peak temperature, some condensate samples have Tl concentrations below the detection limit. Cesium has a peak (Cps data only) at ~220°C and Pt peaks between 250°C and 425°C (Fig. 6f). Comparison of 2- and 7-day experiments in the NFS composition indicate that concentrations are lower in the 2-day experiments for a given temperature, but that experimental duration does not affect the condensation pattern or sequence of volatile elements.

5. Discussion

5.1 Volatile Trace Metal Transport in the Gas Phase

The concentration of trace elements in the starting material, and in the glass after an experiment, were determined by solution ICP-MS and LA-ICP-MS (Tables 1, 3). For the volatile elements Cu, As, Rb, Mo, Cd, Pb, and Bi, the loss from the starting melt in a 7-day experiment is ~ 15 to 40%, and 5-20% relative, for the NAS and NFS compositions, respectively. These losses suggest a significant amount of the volatile elements were mobilized from the melts, degassed from the crucible across the melt-gas interface, and transported in a gas phase to form condensates at lower temperatures along the glass tube. On the other hand, using experimentally determined diffusion coefficients in melts of basalt, dacite and rhyolite (Mackenzie and Canil, 2008; 2011; Johnson and Canil, 2011), the calculated diffusion distances over 7 days vary from ~ 10^{-5}m for Tl to ~ 10^{-13}m for As. These diffusion distances are orders of magnitude less than the crucible depth ($3.1x10^{-2}$m) suggesting it would be difficult to degas much of the volatile trace metals. To explain this dichotomy, we note that samples of melt taken by dipping an alumina rod during initial start of the experiments contain numerous bubbles (~ 50% vesicularity). We surmise that during the frothing of the starting material at the inception of the experiments, volatile trace metals degassed into free air/gas bubbles that were trapped between particles of the starting glass. These bubbles subsequently rise over time to the surface of the melt, and degas deeper parts of the crucible more thoroughly than simple volume diffusion through the melt –gas interface, and explain the element depletion in the glass of the crucible post-experiment.

5.2 Comparison with Natural Condensates

To compare results from our simple experimental design to nature, we contrast the normalized concentrations of volatile elements in condensates from the experiments with those measured in natural fumaroles at Colima (Taran et al., 2001) and Piton de la Fournaise from two studies 23 years apart (Toutain and Meyer, 1989, Vlastélic et al., 2011). In this comparison, Pb is used as the normalizing element as, despite being volatile, it is an element that is included in several studies of natural system. Thallium, Ag, As, and Cu show volatile behaviour in both the experimental and natural systems (Fig. 7). Scatter of the natural data is to be expected given that the conditions of sampling a natural volcanic system are variable and can change over time scales of minutes to hours. The experimental condensates are typically within one order of magnitude of the natural fumarole data, however the experimental condensate concentrations are lower than natural data for Tl and Ag especially, possibly because fluxes in natural volcanic gases are higher. Natural volcanic gases also contain fluid species that are important complexing agents for metals (e.g. HCl, HF, H_2S), which are absent in our initial simple system experiments.

Thallium shows peaks at lower temperatures when normalized to Pb in both experimental compositions compared and decreases at higher temperatures, similar to the Piton de la Fournaise measurements from 1985 (Fig. 7a). Copper and Ag show similar trends to the natural data, with peaks in concentration at higher temperatures (Fig. 7b and 7d). The temperature for peak condensation for As varies between studies (Fig. 7c).

The offset of the temperature for peak concentrations of volatile elements in condensates in the experiments compared to natural data could be due to several factors. Firstly, our design necessitated a simple bulk chemical composition of the melts. that lack Cl and S , key species that complex with trace metals in melt and the gas phase (Williams-Jones et al., 2002; Williams-Jones and Heinrich, 2005). For example, Cu can complex with Cl^- (Pasteris, 1996; Liu and McPhail 2005) and HS^- (Heinrich et al., 1999). Secondly, water and acidic vapour is another key component that helps transport metals in natural systems (Williams-Jones et al., 2002) and is not possible to include in our experiments performed at atmospheric conditions. The length of the experiment (days) also differs from a natural system collection (on the order of months) and may be contributing to differences in the total quantity of condensed volatile trace metals. These variables all deserve further study.

The concentration of volatile elements measured in volcanic gases relative to that in a degassing parent magma is commonly expressed as the enrichment factor:

$$EF_X = \frac{C_X / C_{R\ (gas\ condensate)}}{C_X / C_{R\ (starting\ melt)}} \qquad [2]$$

where C_X is the concentration of the element and C_R is the concentration of a reference element (Symonds et al., 1987). The EF value indicates how enriched or depleted in a trace metal the condensates are compared to in the starting material. Elements having EF>1 are considered more compatible in the vapour phase. Using Co, , as the reference element (C_R) the EF values of volatile elements from the experimental condensates of NAS experiments at 350°C are compared to those measured at three volcanoes, Piton de la Fournaise, Kudryavy, and Tolbachik, that erupt basalt, basaltic andesite, and basaltic trachyandesite, respectively (Vlastélic et al., 2011; Taran et al., 1995; Chaplygin et al., 2016) (Fig. 8). Enrichment factors are above 1 for all elements in the natural samples, indicating that these elements are more compatible in the vapour phase than the melt. Enrichment factors for the elements can vary nearly orders of magnitude between volcanoes. The EF values for Mo are the only ones that are similar for the experiments and natural systems. This is possibly related to the fact that Mo can be transported as an oxide species in natural volcanic gases (Bernard et al, 1990; Symonds et al, 1992), as would also be expected in our experiments in air. It is notable that Mo-oxides are observed both in natural condensates, and in our experiments. In contrast, there are order of magnitude differences in EF values for Tl, Cd, As and Bi, but these differences depend on what system is being compared (Fig. 8). The enrichment of the natural condensates in Pb, Cd, As and Bi is likely from enhanced transport into the volatile phase from ligands (Cl, S) present in the natural systems. These and other variables can be added in our experiments to test the effects of various parameters on metal degassing and condensation at natural volcanoes.

6. Summary and Implications

Our preliminary experiments show that the benchtop fumarole experimental apparatus can be used to study the volatility and condensation behaviour of trace metals commonly found in natural volcanic fumaroles. We degas melts in simple three component systems with doped trace metals and collect condensates along a silica glass tube over a temperature gradient of 900°C to 25°C. Elevated concentrations of Li, Cu, As, Rb, Mo, Ag, Cd, Cs, W, Pt, Tl, Pb, and Bi are observed in the condensates therefore showing these elements to be volatile in our experiments. Each tarce lement also shows a maxima in concentration at certain temperatures, Condensate crystals imaged by SEM and mapped using EDS are found to vary and contain Pt or occur as Mo-Na-K oxides. When compared to natural fumarole condensates, the enrichment factors of experimental condensates compare particularly well for Mo. Natural samples have much higher enrichment factors for Pb, Cd, As, and Bi, most likely be due to the lack of ligands in our simple experimental system. Given the demonstrated utility of our simple experimental design, however, future work can examine the roles of ligands (F, Cl, and S), melt composition and oxygen fugacity in the transport and condensation of volatile trace metals in volcanic emissions.

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Figure Captions

Figure 1: Schematic of the experimental design for the benchtop fumarole. The Pt crucible contains the melt composition doped with added trace metals. The gases released from the melt rise through the silica glass tube, cool and condensate forms along the tube as a function of decreasing temperature. Upper insulation insures a reproducible temperature gradient inside the tube and the exhaust funnel collects and disposes of excess gas.

Figure 2: Temperature gradient over the length of the in silica glass tube measured with a S-type ($Pt_{90}Rh_{10}$-Pt) thermocouple. Lower image shows visible precipitates (white) occurring between 10 to 20 cm on a silica glass tube (~ 125-725°C) after 7-day experiment with NFS composition.

Figure 3: Secondary electron images of condensates forming with decreasing temperature (°C) along the glass tube for a 7-day experiment NFS composition. Scale bars vary. Temperatures given are the mid-point of the range of temperatures from a 1-cm segment of tube. a) Condensates at 553°C have 1-2µm bright white cubic crystals and a larger anhedral phase. b) Condensates at 427°C have elongated crystals, with a maximum length of 5µm. c) An anomalously large, anhedral crystal of ~15µm at 350°C. d) Condensates at 295°C have elongated crystals >10µm and hexagonal crystals of >10µm. e) Condensates at 218°C have longer elongated crystals, >20µm, and are more densely packed than at 295°C. f) All crystals in condensates at 138°C are <5µm and anhedral.

Figure 4: Secondary electron images and chemical maps of crystals from condensates from a 7-

day experiment in the NAS composition. a) At 427°C bright cubic phases contain Pt. b) At 350°C a hexagonal phase contains Mo (c) and Na (d). e) At 253°C elongated crystals occur in a dendritic pattern, and contain Mo (f) , Na (g) , and K (h) .

Figure 5: The concentration of volatile elements in leachates of condensates from silica glass tube normalized to Co. Normalized values increase to a maximum at a particular temperature for each element. Concentrations in blank experiments for a few elements are also shown a) Leachate concentration of Mo, Pb and Li versus temperature (°C), for 7-day NAS experiment b) Leachate concentration of Mo, Pb and Li normalized to Co versus temperature (°C), for 7-day NFS experiment

Figure 6: Normalized concentrations for (a,b) Cd, Bi, As, Ag, (c,d) Cu, W, Pb and Tl and (e, f) Cs and Pt in condensates for 7 day experiments in NAS and NFS compositions. Cesium and Pt reported in counts per second (CPS).

Figure 7: Co-normalized concentrations of leachates of volatile elements in condensates from 7 day experiments for NAS and NFS compositions, compared to those for condensates collected from 1985 and 2008 Piton de la Fournaise (Toutain and Meyer, 1989; Vlastélic et al., 2011) and 1996 Colima (Taran et al., 2001) eruptions. Experimental values are potentially lower due to the lack of important complexing ligands (e.g. HCl, HF, H_2S) that are present in natural volcanic gases but not present in experiments.

Figure 8: Enrichment factors (EF; calculated using equation [2] in text) for volatile experimental condensates from two NAS composition experiments (Vul5 and Vul6), sampled at 350°C compared to those from various natural volcanic condensates from 1976 and 2013 Tolbachik

(Zelenski et al., 2014), 1990 Kudryavy 1990 (Taran et al., 1995), and 2008 Piton de la Fournaise 2008 (Vlastélic et al., 2011) eruptions. Experimental and natural samples use Co as the reference element (C_R). The EF of Mo is most similar between the experimental and natural samples, whereas that of Tl, Cd, Bi and As are much higher in natural condensates, likely due to the lack of ligands (Cl, S) or water vapour in the initial experiments.