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Volcanic Outgassing of Volatile Trace Metals

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Abstract

Volcanoes play a key role in the cycling of volatile metals (e.g., chalcophile elements such as Tl, Pb, and Cu and metalloids such as As, Te, and Se) on our planet. Volatile metals and metalloids are outgassed by active volcanoes, forming particulate volcanic plumes that deliver them in reactive form to the environment, where they may be nutrients (e.g., Cu and Zn) or pollutants (e.g., Hg, As, Pb). Volcanic outgassing rates of these elements compare to those associated with building ore deposits in the crust and to anthropogenic emission rates. There are distinct compositional differences between volcanic plumes in different tectonic settings, related to the enrichment of arc magmas in metals transported in slab fluids, metal speciation, and partitioning between silicate melt, vapor, and magmatic sulfide. Volcanic gases have compositions similar to those of quartz-hosted fluid inclusions found in mineralized granites, albeit with a lower density and salinity. Volatile volcanic metals are transported as soluble aerosols in volcanic plumes and may persist for hundreds of kilometers in the troposphere. Volcanic metal chloride aerosols in tropospheric volcanic plumes at high latitudes are recorded in ice cores.

- Volcanoes emit significant fluxes of volatile trace metals such as Cu, Tl, and Pb, as gases and particulates, to the surface environment.
- There is a distinct metal compositional fingerprint in volcanic and hydrothermal plumes at subduction and hotspot volcanoes and mid-ocean ridges, controlled by magma and fluid chemistry.
- Volcanic gases are the less saline equivalent of the fluids forming economic porphyry deposits of chalcophile metals (e.g., Cu) in the crust.
- The metals in tropospheric volcanic plumes may be rained out near the vent, but in dry environments they may persist for thousands of kilometers and be deposited in ice cores.

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1. INTRODUCTION

The cycling of trace metals via tectonic processes on our planet plays a critical role in sustaining life, catalyzing key reactions in biogeochemical cycles, and producing resources that have proved indispensable to society. Some trace metals in our environment are pollutants and have severe consequences for health. Magmatic processes and volcanoes play a key part in the cycling of these elements between the mantle, crust, atmosphere, and ocean. Melts produced in the mantle exsolve dense hydrous fluids during their ascent and differentiation in the crust, into which trace metals partition and are transported (Williams-Jones & Heinrich 2005). Active volcanoes outgas low-density fluids from central vents (**Figure 1a**) that are derived from their denser crustal counterparts by a process of phase separation, involving unmixing of a low-density vapor and a brine (Pokrovski et al. 2005) (**Figure 1b**). Volcanic gases are typically composed of 70–90 mol% H_2O , 5–10 mol% S and CO_2 , and less than 3 mol% HCl, as well as trace species (Symonds et al. 1994). Volcanic gases contain significant concentrations of volatile metals and metalloids (Hedenquist & Lowenstern 1994, Symonds et al. 1992, Taran et al. 1995). They are distinct from fumarolic gases, which are emitted from low-temperature peripheral vents, typically at much lower temperatures than volcanic gases, and that contain lower concentrations of trace metals due to extensive condensation of brine (Hedenquist et al. 1994) and scrubbing processes occurring in the subsurface, where the fluids have interacted with meteoric waters (Hedenquist & Lowenstern 1994, Mandon

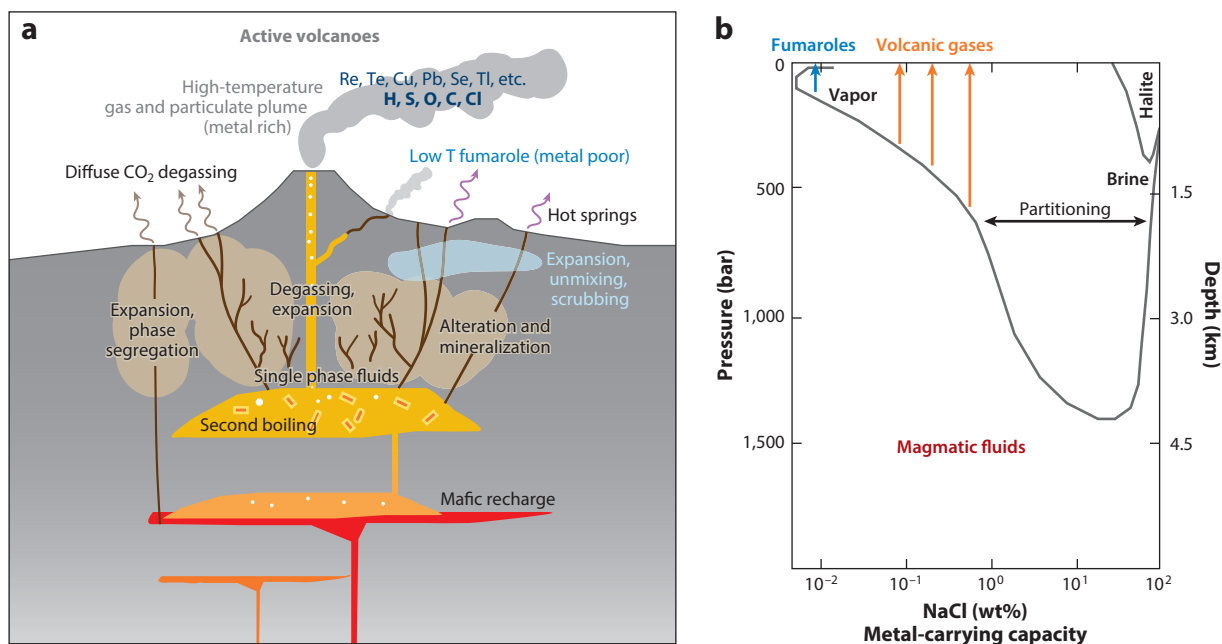


Figure 1

The context of volcanic and fumarolic gases and their link to higher-density exsolved magmatic fluids at depth. (a) Diagram of an active volcano emitting volcanic gases from central vents, derived from both second boiling at depth and decompression degassing at low pressures. Fumaroles may exist on the volcano's flanks, emitting low-temperature gases that have condensed metals in the subsurface as minerals or brines and/or interacted with meteoric waters. (b) Phase diagram to show how single phase magmatic fluids at depth are related to fumaroles (that represent the low-density vapor product of unmixing, with the brine phase sequestered at depth) and volcanic gases, which may be an advected mixture of both vapor and brine phases brought to the surface by high-temperature melts and outgassed at the magma-air interface (Hedenquist & Lowenstern 1994).

et al. 2020). Volcanic gases may include some primary brine aerosols derived from the unmixing process, thereby enhancing their bulk salinity and metal-carrying capacity (Hedenquist & Lowenstern 1994) (**Figure 1b**). High-temperature volcanic gas and aerosol metal systematics are valuable sources of information regarding the processes that control metal fluxes, compositions, and partitioning between different reservoirs in the crust.

Trace metals and metalloids may be volatile when they readily partition from silicate melt into a coexisting exsolved phase (Hinkley 1991, Lambert et al. 1985, Nriagu 1989); this phase is commonly referred to as the magmatic volatile phase (MVP). Metal and metalloid volatility has been quantified in a range of ways (Mather 2015, Zelenski et al. 2021). **Figure 2** shows a compilation of gas-melt partition coefficients, calculated by comparing the concentrations in volcanic gases to those in melt inclusions or whole rocks, using a wide range of published data (Zelenski et al. 2021). The compilation includes high-temperature eruptive plume data from arc volcanoes (e.g., Etna, Stromboli, Ambrym) as well as hotspot volcanoes [e.g., Holuhraun (Iceland), Kīlauea (Hawaii, USA), and Erta Ale (Ethiopia)] (Aiuppa et al. 2000; Allard et al. 2000; Gauthier et al. 2016; Symonds et al. 1987; Zelenski et al. 2013, 2014). Elements we recognize as traditionally volatile, such as S and the halogens Cl, Br, and F, all display high partition coefficients and plot in the field labeled abundant in volcanic gases (designated here as having a gas-melt partition coefficient greater than 0.1). Also in this field are the chalcophile (S-loving) metals, such as Tl, Se, Bi, and Cu, which show volatilities similar to (or greater than, in the case of Se and Te) the halogen species. Some highly siderophile (Fe-loving) elements also display considerable volatility, such as Re, Os, and Au. In contrast, the lithophile (elements with an affinity for silicate minerals) and other siderophile elements, such as the rare earth elements (REE) and the alkaline earth elements, plot toward the right in **Figure 2**. These elements have gas-melt partition coefficients of less than 0.1 and are correspondingly scarce in volcanic gases. The alkali elements Li, K, Rb, and Cs all plot in the intermediate region, with gas-melt partition coefficients ranging from 0.01 to 0.1 (**Figure 2**).

Other studies have normalized the volcanic plume abundance of trace volatile metals to the abundance of ^{210}Pb , a short-lived radioactive isotope (Lambert et al. 1985), in order to estimate volatility. These studies have yielded results similar to those shown in **Figure 2**. Extensive research has also been done on fumarole condensates and sublimates, demonstrating that fumarolic emissions transport a range of trace element-bearing minerals that precipitate on cooling, including many that are ubiquitous in economic magmatic-hydrothermal ore deposits [chalcopyrite,

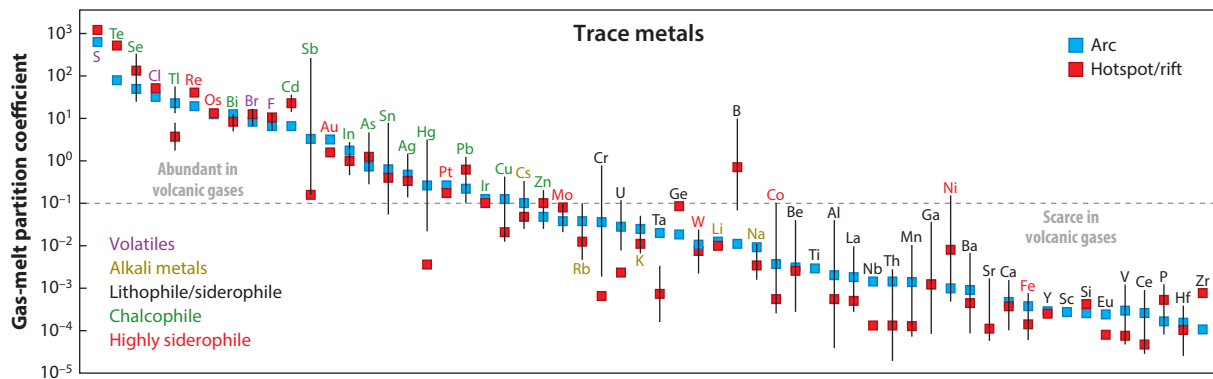


Figure 2

Volatility of trace metals in volcanic systems. Shown are gas-melt partition coefficients for a range of trace metals, calculated using a wide range of published data (Zelenski et al. 2021, and references therein). Element names are color-coded to denote type in the Goldschmidt classification.

wolframite, hydrated metal oxides (e.g., $\text{Mo}_3\text{O}_8 \cdot n\text{H}_2\text{O}$), sulfosalts (e.g., ReS_2), native metals (e.g., Pb, Bi), and chlorides and oxychlorides (e.g., PbCl_2 , CuCl) (Pokrovski et al. 2005). Zonation in precipitation along long silica tubes allows the order of volatility to be determined, which is inversely proportional to sublimation temperature (Symonds et al. 1992; Taran et al. 1995, 2001). Volcanic gases give us similar sorts of information on metal volatility as studies of fluid inclusions. Fluid inclusions in quartz in both barren and mineralized granites, for example, have been analyzed for their trace volatile metal and metalloid concentrations (typically using laser ablation inductively coupled mass spectrometry) and compared to their concentrations in whole rocks to define volatility (Guo & Audétat 2017). This and other studies have found a similar suite of elements enriched in fluid inclusions as are enriched in volcanic gases over silicate melts, suggesting that volcanic gases are the low-pressure equivalents of these denser, more saline magmatic crustal fluids, as shown in **Figure 1b**.

Despite our growing understanding of the significance of volcanoes in processing volatile metals, we have not yet fully realized the potential of such studies for informing our understanding of resources, biogeochemical cycling, and deciphering the geological records of our planet's past. In this review, we discuss the fluxes of metals outgassing from volcanoes and the nature and cause of the systematic differences in metal systematics in volcanic gases in different tectonic settings, such as subduction zones, hotspots, and mid-ocean ridges (MORs). We review how the wealth of information harnessed from volcanoes can be used to infer mechanisms of hydrothermal ore formation. We evaluate the evidence for the behavior of outgassed metals in the atmosphere as particulates, their speciation, and their residence times in tropospheric volcanic plumes. We discuss the implications of such studies for the interpretation of the record of volcanic degassing in ice cores. Finally, we project some thoughts regarding the outlook of such studies in the future, including where the critical gaps exist in understanding and what fundamental questions remain unanswered.

2. VOLCANIC FLUXES OF VOLATILE METALS AND METALLOIDS TO THE ATMOSPHERE

Volcanoes outgas significant mass fluxes of volatile chalcophile metals to the atmosphere and surface environment of Earth (Gauthier & Le Cloarec 1998, Ilyinskaya et al. 2021, Nriagu 1989), similar to mass fluxes of these elements into ore deposits, transported into the ocean by weathering, emitted due to anthropogenic activity from entire countries (**Figure 3**). In particular, mass fluxes of greater than 1,000 kg/s per day of Cu, Zn, Cd, and Se have been recorded from Kīlauea and Mt. Etna volcanoes (calculated using the X/SO_2 ratio in the plume combined with the mass flux of SO_2 from the volcano measured by spectroscopy) (Aiuppa et al. 2000, Mason et al. 2021). Emissions can be sustained over long time periods from months (e.g., Holuhraun, 2014–2015) (Gauthier et al. 2016) to decades (e.g., Kīlauea, 1983–2018) to potentially up to thousands of years during flood basalt eruptions in Earth's past (Self et al. 2006).

Metals are emitted in the form of gases in the high-temperature plume, which are converted to particulates upon sublimation, or through scavenging by aerosols and ash within the short time (seconds) of emission (Hinkley 1991). These rapid chemical transformations mean that most metals are sampled from volcanic plumes as nonsilicate particulate matter of a size ranging from less than 0.01 to approximately 2 μm , comparable in size to desert dust (Delmelle 2003). At Stromboli volcano, for example, 66% of total volcanic plume particulates (both soluble and silicate) are less than 2 μm in size (Allard et al. 2000). Particles in the fine mode result from gas-particle conversion, and then aggregation and growth of these fine modes give rise to the accumulation of mode particles (0.1–2 μm). This particulate matter may be transported many

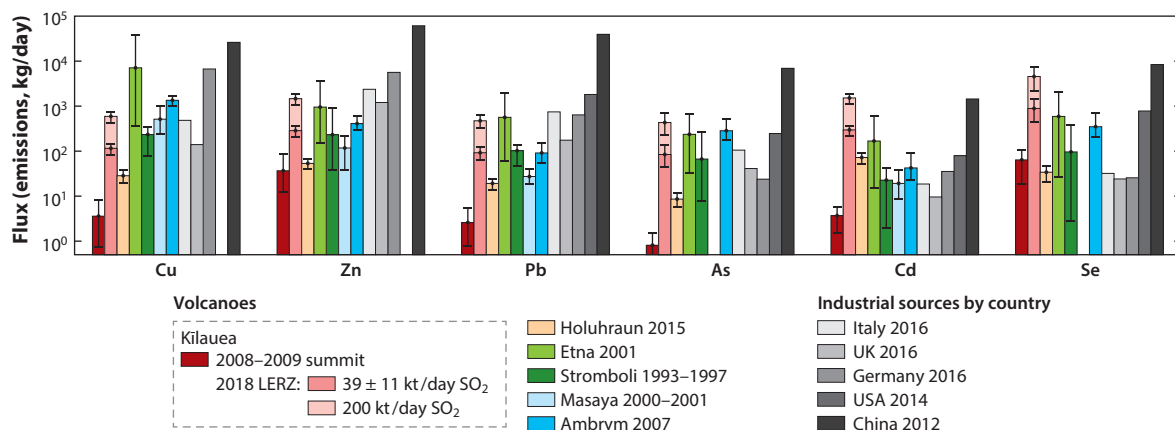


Figure 3

Comparison of the fluxes (daily emissions, in kg/day) of a number of volatile metals and metalloids from volcanoes (*colored columns*) with those from industrial sources in entire countries (*gray columns*), with uncertainties indicated. Kilauea volcano fluxes are broken down into those measured in 2008–2009 and those measured in 2018 at the Lower East Rift Zone (LERZ) eruption. Where bars are not visible, a measurement for this element is not available. Figure adapted from Ilyinskaya et al. (2021) and references therein.

hundreds or thousands of kilometers downwind (**Figure 4**). The volatile metals are eventually deposited to the environment, perhaps mediated by rain or by dry deposition (Delmelle et al. 2001), where they may accumulate in biological (e.g., plant) or hydrological (groundwater) systems. The residence time of metals in the atmosphere is complex and poorly understood, mainly due to a lack of observational data. Residence time is projected to vary with atmospheric conditions, speciation (that affects how soluble in water they will be), and whether the aerosols adsorb to ash, ice, and other environmental aerosols. However, much of the volcanic outgassing flux of metals and metalloids enters the troposphere and has a limited residence time (**Figure 4**). Thermochemical modeling predicts that volatile trace metals and metalloids in volcanic gases are transported as chloride (e.g., CuCl), sulfide (e.g., AsS), and elemental (e.g., Cd) species (Pokrovski et al. 2005, Symonds et al. 1992), while the more refractory lithophile elements (major elements, REE) have longer residence times. Thermochemical modeling using the bulk composition of the Kilauea plume predicts that these species will be complexed with sulfide, chloride, or (hydr)oxide and are therefore removed rapidly via wet deposition within a few hundred kilometers downwind (Ilyinskaya et al. 2021). This study suggests that tropospheric volcanic aerosols, particularly perhaps in tropical environments, may have a rather limited lifetime before they are delivered to the surface environment. These findings have obvious implications for health hazards in proximal areas around active basaltic volcanoes. The lifetime of metal-bearing volcanic aerosols in the stratosphere arising from large explosive eruptions remains unknown.

Systematic studies of the downwind fate of volatile trace metals incorporated into particulate volcanic plumes are rare. A recent study of the speciation and transport of volcanic metals and metalloids at the 2018 eruption of Kilauea volcano, Hawaii, has shed light on the volatility, speciation, and subsequent transport and removal of metals from the volcanic plume. Samples of the gas and particulate volcanic plume were acquired with a network of sampling sites up to 250 km downwind from the active vent. The most volatile metals (as shown in **Figure 2**), such as Cu, Cd, Bi, Pb, and Re, are removed rapidly from the plume, usually within ~19 h of emission (Ilyinskaya et al. 2021), whereas the more refractory lithophile elements (major elements, REE) have longer residence times. Thermochemical modeling using the bulk composition of the Kilauea plume predicts that these species will be complexed with sulfide, chloride, or (hydr)oxide and are therefore removed rapidly via wet deposition within a few hundred kilometers downwind (Ilyinskaya et al. 2021). This study suggests that tropospheric volcanic aerosols, particularly perhaps in tropical environments, may have a rather limited lifetime before they are delivered to the surface environment. These findings have obvious implications for health hazards in proximal areas around active basaltic volcanoes. The lifetime of metal-bearing volcanic aerosols in the stratosphere arising from large explosive eruptions remains unknown.

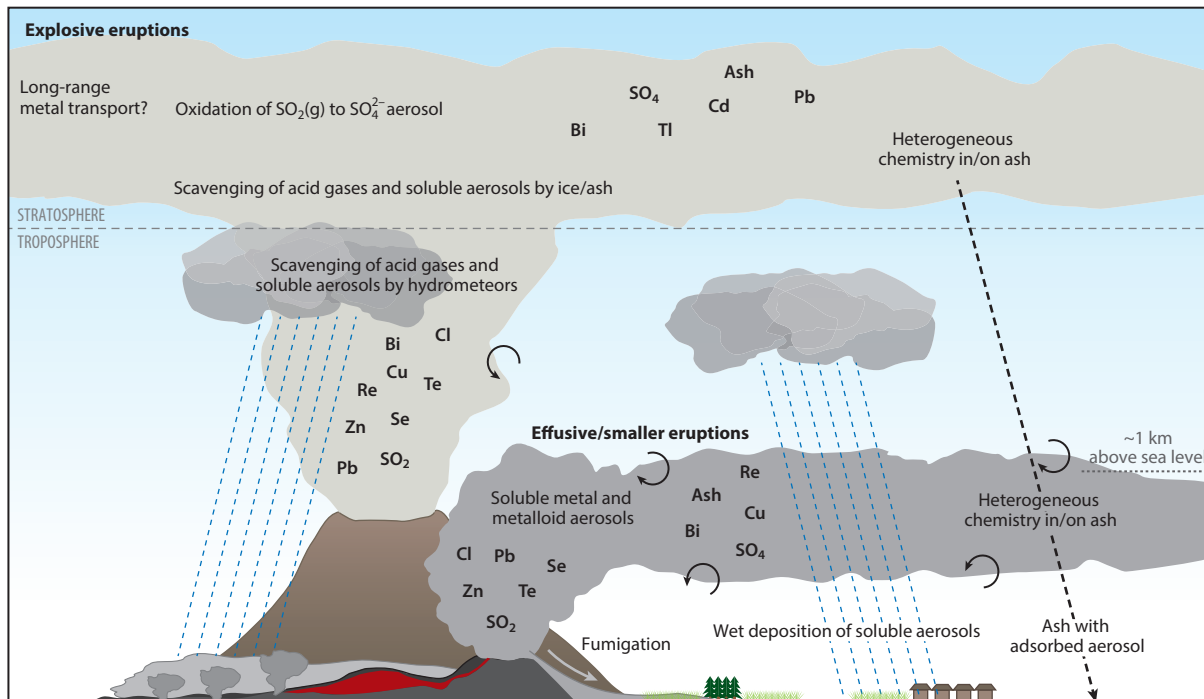


Figure 4

Processes influencing the atmospheric processing and transport of trace volatile metals and metalloids emitted from volcanoes for large explosive eruptions that produce stratospheric plumes and clouds and for smaller and/or effusive eruptions that produce tropospheric plumes (Mason 2021). In the troposphere, soluble chalcophile metal and metalloids are rapidly scavenged by wet deposition, delivering them to the surface environment where they are taken up by vegetation, soils, and the hydrological system. Explosive eruptions result in stratospheric transport of chalcophile metal and metalloid-bearing aerosols. The aerosols have a longer residence time than tropospheric aerosols and are scavenged by ash and ice, eventually settling out to the surface environment.

3. DISTINCT ASSEMBLAGES OF VOLATILE METALS AND METALLOIDS IN VOLCANIC GASES IN ARCS AND HOTSPOTS

It has been shown that the volcanic gases from arc volcanoes differ from those at hotspot and rift settings in terms of their assemblages of volatile metals (Edmonds et al. 2018) (**Figure 2**). Volcanic gases in arc settings tend to show enrichments in elements such as W, As, Tl, U, Sn, Ag, and Sb over gases emitted from ocean island volcanoes such as Kilauea and Iceland. Many of these elements complex with chloride in the gas phase, so one hypothesis to explain the differences in gas compositions between tectonic settings relates to the role of Cl in complexing with and transporting metals in the MVP and, subsequently, the volcanic gas (Zelenski et al. 2021). A gas phase speciation model for a typical arc volcanic gas between 800 and 1,200°C using a bulk gas composition from Villarrica volcano (Chile) (Mason 2021) is shown in **Figure 5**, compared to a typical ocean island volcano (Kilauea) (Mason et al. 2021). The Villarrica volcanic plume is more oxidized than the Kilauea plume (an fO_2 of ΔFMQ of -0.7 and -2.5 , respectively) and is richer in Cl and H_2O (0.8 mol% HCl, 93 mol% H_2O and 0.2 mol% HCl, 80 mol% H_2O , respectively) (Mason 2021).

There are some notable differences in the speciation of metals and metalloids between these two types of volcanoes. At Kilauea, Te, Se, Pb, As, and Sn are predominantly (>75%) complexed as sulfide species, while at Villarrica, sulfide complexes make up only a relatively minor contribution

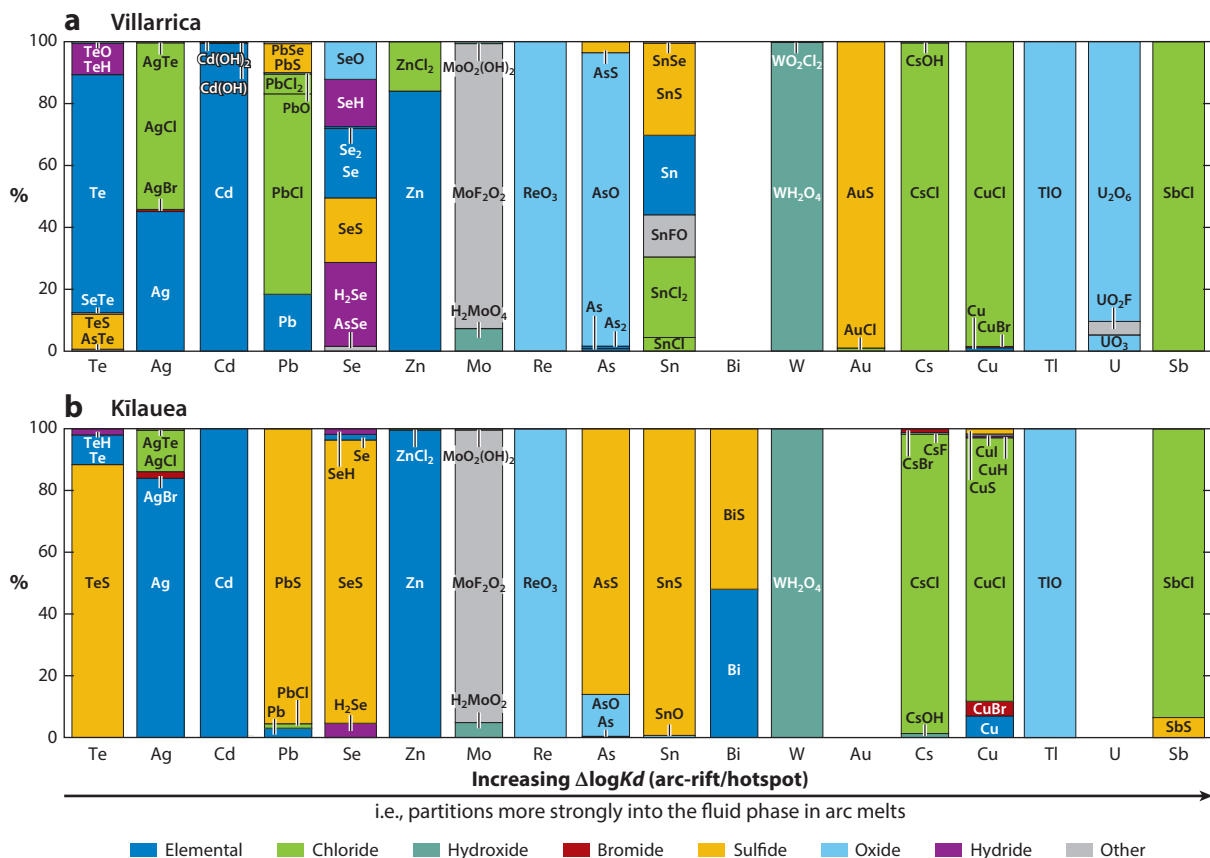


Figure 5

Gas phase equilibrium speciation models at 1,150°C for Villarrica and Kilauea volcanoes (constructed using HSC Chemistry) to represent typical arc and ocean island volcanic gases. Elements are ordered by increasing difference between the fluid-silicate melt partition coefficients for arc volcanoes and rift/hotspot volcanoes as calculated by Zelenski et al. (2021). (a) Villarrica speciation outputs. (b) Kilauea speciation outputs, using plume composition data from Mason et al. (2021) and Mason (2021).

to the equilibrium speciation of these elements (**Figure 5**). These differences are likely due to the greater availability of S in the gas plume from Kilauea (13.6 versus 1.8 mol% for Villarrica) and the higher fO_2 of the Villarrica gas mixture. Greater proportions of some elements (e.g., Zn, Pb, Cu, Ag, and Sn) are predicted to be present as chloride species in the gas plume of Villarrica, compared to Kilauea. Villarrica's plume is relatively Cl rich compared to Kilauea and therefore has a higher proportion of chloride ligands. The speciation of some elements, however, appears to be relatively insensitive to the compositional differences between the two plumes. For example, Cs, Cu, and Sb are speciated dominantly as $CsCl(g)$, $CuCl(g)$, and $SbCl(g)$ in both plumes; this may suggest that when the Cl availability in the vapor phase is lower, degassing of these elements from the silicate melt into the vapor phase may be less extensive (i.e., the volatility may be lower). For the elements Re, Tl, Cd, W, and Mo, neither Cl nor S act as major ligand-forming elements in volcanic gases, and so one might expect degassing of these elements to be relatively insensitive to changes in S/Cl ratios of the gas phase. The predictions of these models agree well with observations: Good correlations between the abundances of Zn, Cu, Ag, Sb, and Cs are observed with the S/Cl ratio of volcanic gases globally (Mason 2021, Zelenski et al. 2021).

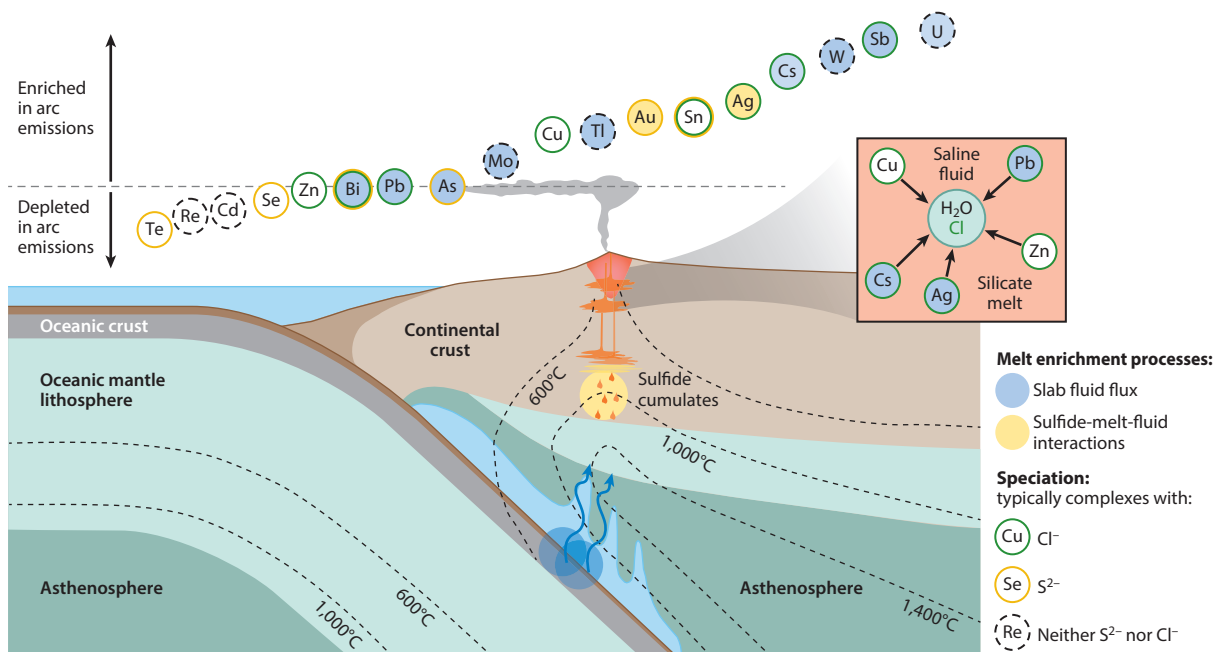


Figure 6

Controls on the enrichments of particular suites of metals and metalloids in arc volcanic gases. Some fluid-mobile chalcophile elements are transferred from the slab to the mantle wedge, resulting in primary melts displaying enrichments in these elements (Pb, As, Tl, Ag, and Cs). Upon ascent and exsolution of a magmatic volatile phase (MVP), sulfide saturation may occur, which may sequester metals in the crust. Metals partition into the MVP, with those metals that complex with chloride ligands partitioning strongly. Arc volcanic gases are therefore enriched in those elements that are fluid mobile at high pressures and that partition strongly into saline MVP. Figure adapted from Mason (2021).

The availability of chloride ligands in the gas phase fails to explain the entire series of compositional differences that exist between volcanic plumes in different tectonic settings. Several studies have described enrichments in a particular set of elements, those known as fluid mobile in the melt or whole rocks from arc settings. These elements include the large ion lithophile elements as well as the chalcophile elements W, Tl, As, Pb, Mo, Sb, and Bi (Cox et al. 2019, Jenner 2017, Mason 2021). These elements are thought to be transferred to the mantle wedge via slab-derived fluids during devolatilization and incorporated into the primary melts in arcs. Cd, Zn, Sn, and Cu are not observed to be enriched in primary arc melts relative to ocean island or rift melts, perhaps indicating that these elements are not particularly fluid mobile under slab conditions and that they are derived mainly from the mantle wedge instead (Lee et al. 2012, Mason 2021).

The distinct compositional enrichments in arc volcanic gases over ocean island/rift volcanic gases are therefore a result of (a) enrichment of primary melts by addition of fluid-mobile elements from the devolatilizing slab; (b) partitioning of metals into other phases (including sulfides) during magma transport and ascent (Barber et al. 2021, Chen et al. 2020, Edmonds et al. 2018, Wieser et al. 2020); and (c) the salinity of the exsolved MVP, which determines the partitioning behavior of a subset of metals and metalloids that become enriched in the MVP and, subsequently, the volcanic gases in arc settings (Mason 2021, Zelenski et al. 2021) (**Figure 6**).

Ocean island volcanic gases have been well studied for their compositions at Kilauea volcano (Mason et al. 2021, Mather et al. 2012) (**Figure 5**) and at the Holuhraun eruption, Iceland (Gauthier et al. 2016). The distinctive metal fingerprint of ocean island volcanic gas plumes may

be caused by a number of important factors (Edmonds et al. 2018, Gauthier et al. 2016). Kīlauea basalts are relatively water poor (compared to arc basalts), so the MVP that coexists with basalts during differentiation and ascent through the lithosphere is CO₂ rich until the magmas ascend to very low pressures (<50 MPa) (Gerlach 1986). Icelandic basalts are typically even drier (Hartley et al. 2015). The volatile metal outgassing signature in these gas plumes is therefore fixed at a relatively late stage (at shallow depths) in the degassing process, and kinetic factors associated with their diffusion into bubbles (Johnson & Canil 2011, MacKenzie & Canil 2008), or sulfide breakdown (that may redistribute chalcophile elements within the sulfide-silicate melt-MVP system) (Edmonds & Mather 2017, Mungall et al. 2015), may play a more important role than in arc settings. It has been shown, through a study of melt inclusions, that Kīlauea magmas undergo saturation in a sulfide phase during differentiation at MgO contents of ~12 wt% (Stone & Fleet 1991, Wieser et al. 2020). Syn-eruptive degassing of S then drives the resorption of sulfides in contact with the carrier liquid, thereby liberating chalcophile elements, including Cu, Te, Sn, Mo, and other elements, back into the silicate melt-MVP system. Silicate melt-MVP partitioning controls the chalcophile composition of the plume, which will then be strongly influenced by sulfide resorption for those elements (e.g., Se, Cu) that are (a) strongly enriched in sulfide and (b) moderately to highly volatile. The breakdown of sulfides may contribute a significant fraction of the S, and some other metals, to the volcanic plume at Kīlauea and other volcanoes (Wieser et al. 2020).

The volcanic gas compositions are also influenced strongly by the availability of ligands, as discussed earlier for arc volcanic gases. Typically, volcanic gases in ocean island settings are S rich and relatively poor in Cl. The magmatic plume emitted from fissure 8 during the 2018 eruption of Kīlauea, for example, had an SO₂/HCl molar ratio of 32–35 (Mason et al. 2021). Before mixing with air, volatile trace elements at Kīlauea complex with either S²⁻ (e.g., TeS, SeS, BiS, AsS, PbS, SnS) or Cl⁻ (InCl, AgCl, and CuCl), or they exist as elemental species (Cd, Bi, Ag, Zn, Cu) (**Figure 5**). After mixing with air, sulfide-complexing elements (e.g., Se, Te, As) are now present as oxides, and those that were present as elemental forms are now present as chlorides, hydroxides, or oxides [e.g., Cd(OH)₂, AgCl₂, ZnCl] (Mason 2021). This increase in abundance of chloride species in the plume after mixing with air is consistent with previous studies showing that oxidation is accompanied by the formation of reactive halide species (Gerlach 2004).

4. FLUXES OF VOLATILE CHALCOPHILE METALS DERIVED FROM MAGMA DEGASSING INTO THE OCEANS

Hydrothermal vents emit a mixture of gases and particulates into the ocean from low- and high-temperature vents, mainly situated at MORs but also in backarc settings in the western and north-western Pacific (Lau, Manus, Marianas basins). Hydrothermal vents play a key role in the cycling of energy and mass from the interior of Earth (Elderfield & Schultz 1996): Hydrothermal circulation, where cold seawater circulates through the upper oceanic crust, transfers the heat brought up from the mantle as basalt to the overlying ocean. As well as heat, hydrothermal fluids transfer significant fluxes of gaseous and particulate matter to the ocean, including nutrients and chalcophile species. Once ejected from seafloor vents, many of the elements dissolved in hydrothermal fluids precipitate (as oxides and sulfides) upon mixing with cold seawater, creating a dark plume—the origin of the term black smoker. The flux of seawater through hydrothermal circulation systems at MORs is so large that the entire ocean is thought to cycle through hydrothermal vents in less than 10 Ma (Elderfield & Schultz 1996). The starting fluid for a submarine hydrothermal vent is seawater (**Figure 7**), which becomes modified by water-rock interaction at increasingly elevated temperatures as the water is circulated through the young basalt of the oceanic crust. Vent fluids are, in general, modified seawater characterized by a loss of Mg, sulfate, and alkalinity, and they are

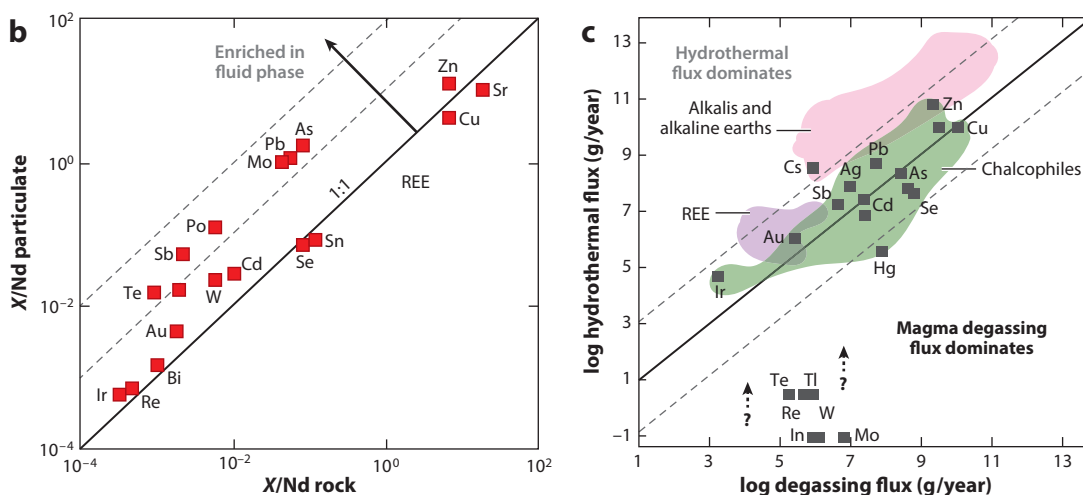
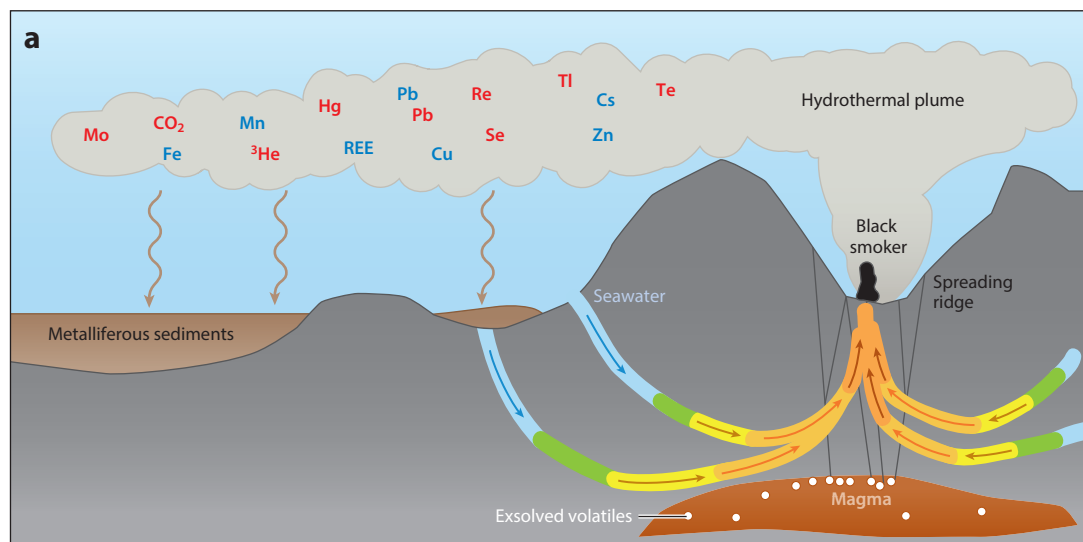


Figure 7

The contribution of magma degassing to submarine hydrothermal plumes. (a) Schematic diagram to show the mechanisms involved in the formation of hydrothermal plumes, e.g., released from high-temperature black smokers at mid-ocean ridges. Seawater circulates in hot basalt, becoming enriched in those metal species leached from basalt during water-rock interactions (colored *blue* in the plume), and mixes with exsolved volatiles (CO_2 , ^3He , Ti, Te, Re, etc.) derived from the degassing of magma (colored *red* in the plume). (b) Plot of the normalized concentrations of elements in a particulate hydrothermal plume emitted from the submarine volcano Loihi (X/Nd) against the same ratio in whole rocks. The data show that chalcophile metals Sb, Te, Mo, and Pb and metalloid As are significantly enriched in the particulate plume over whole rocks. (c) Comparison of flux of elements from hydrothermal vents derived from magma degassing (x axis) to that derived from water-rock interactions (y axis). The degassing fluxes are estimated by assuming a volatility of Pb constrained by short-lived radioactive isotopes (Lambert et al. 1985). Note that the hydrothermal fluxes of Te, Ti, Re, W, and Mo are poorly constrained. Chalcophile elements, rare earth elements (REE), and alkali and alkaline earth element fields are marked with colored areas. The fields dominated by magma degassing and by hydrothermal degassing are marked. Panels *b* and *c* adapted from Rubin (1997).

enriched in different metals, including REE, alkaline earths, alkali metals, chalcophile elements, and other transition metals (German & Von Damm 2003). The fluids are modified by additional processes (German & Von Damm 2003), including phase separation (that occurs at low pressures and results in a vapor-brine mixture), biological processes, and magmatic degassing. The contribution of magmatic degassing to hydrothermal fluids is at present not well constrained, but it seems likely to be significant because (a) volatile trace metals are present in subaerial volcanic plumes in significant quantities and (b) hydrothermal fluids can contain high concentrations of ^3He and CO_2 , which we know are degassed from magmas.

It is well known that some MOR vent fluids contain significant quantities of ^3He and CO_2 , both of which must derive from underlying magmas, particularly those associated with areas of the mid-ocean spreading ridge system with abundant magma supply and that are frequently volcanically active (Marty & Tolstikhin 1998, Resing et al. 2004). The correlation observed between CO_2 and ^3He has allowed estimates to be made of the flux of CO_2 from the MOR system of $2.2 \pm 0.9 \times 10^{12}$ mol/year (Marty & Tolstikhin 1998) and $3.3_{-0.85}^{0.77} \times 10^{12}$ mol/year (Le Voyer et al. 2019) similar to the flux of CO_2 from subaerial volcanoes (1.2×10^{12} mol/year) (Fischer et al. 2019). As well as CO_2 and ^3He , there is also evidence that Po and Bi degas from submarine basalts on eruption, e.g., on the East Pacific Rise, where lavas have degassed ~ 75 – 100% of their Po on eruption, as deduced from disequilibrium between ^{201}Pb and ^{210}Po (Rubin et al. 1994). Given the volatile nature of a large suite of chalcophile and siderophile metals, it is extremely likely that hydrothermal vents of the MOR system are emitting trace metals and metalloids that degassed from magma, as well as a fraction that have been produced by water-rock interaction (**Figure 7a**).

Measurements of the particulate plume from a submarine eruption of Loihi volcano, Hawaii, showed that the plume was highly enriched in volatile chalcophile metals over the lava compositions (Rubin 1997) (**Figure 7b**). In particular, the plume showed enrichments of 10–33 times in Te, Sb, Po, Pb, Mo, and As over the whole rock compositions (**Figure 7b**), suggesting that these elements partitioned into the exsolved volatile phase and were then rapidly precipitated (probably as oxides and sulfides) on mixing with cold seawater. By comparing estimates of MOR trace metal degassing flux (using the lava production rate and estimates of metal and metalloid volatility, which are assumed to be similar to the subaerial case) to the hydrothermal flux of metals and metalloids to the ocean (using heat loss-based estimates of seawater flux combined with compositional data for hydrothermal fluids assumed to be purely the result of water-rock interaction), Rubin (1997) evaluated the likely balance between these two sources for a range of chalcophile and siderophile metals and metalloids. The REE and alkaline earths are in general not enriched in magmatic exsolved fluids, whereas some transition metals—e.g., Mo, W, Re, Se, and Hg—are highly enriched (**Figure 7c**). For hydrothermal fluids the order of element enrichment is almost exactly reversed: REE, alkaline, and alkaline earth metals and some transition metals (Zn, Pb, Ag, Ir) are enriched (**Figure 7c**).

At submarine arc volcanoes the contribution to the metal flux by magmatic degassing may be more significant (Hedenquist et al. 1994, Williams-Jones & Heinrich 2005). Brothers Volcano in the Kermadec Islands arc is now one of the best-studied examples of an arc-related submarine hydrothermal-magmatic system (de Ronde et al. 2005, 2011). Fluids, enriched in CO_2 and ^3He , suggest a significant magmatic component (de Ronde et al. 2005, 2011; Keith et al. 2018), and petrological studies of melt inclusions have suggested that Cu in the fluids may be sourced from magmatic degassing (de Ronde et al. 2011, Keith et al. 2018). Some of the Cu-rich sulfide chimneys present in the northwestern caldera vent field of Brothers volcano are also enriched in Mo, Bi, Se, Co, and Au (de Ronde et al. 2011). Melt inclusion studies show that the magmas are relatively volatile rich [1 wt% H_2O , $\sim 5,000$ ppm Cl, and up to 60 ppm Cu (de Ronde et al. 2011)]. This arc volcano may be an excellent end member example of an active submarine volcanic system

that is accumulating massive sulfide mineralization dominated by metals derived from magmatic degassing.

5. THE VOLCANIC-PORPHYRY CONNECTION

Metalliferous deposits in ancient volcanoes formed at depths of around 1,500 m in fractures beneath paleo-fumaroles and deeper, up to a few kilometers in depth, associated with subvolcanic intrusions (Henley & Berger 2013). These metal-rich deposits were precipitated from hydrous, saline magmatic fluids as they expanded upon decompression. Through building on the parallels between the metal assemblages recorded by or in volcanic gas plumes, fluid inclusions, sublimates, and condensates at active subaerial volcanic systems and in porphyry copper-type deposits, it seems likely that metals are precipitated as metal-metalloid sulfide and sulfosalt minerals at temperatures well above 500°C in brittle fractures concurrent with ongoing volcanism (Blundy et al. 2015, Henley & Berger 2013, Sillitoe 2010, Zelenski et al. 2021).

Fluid inclusions trapped in hydrothermal minerals in porphyry granites record a range of fluids that correspond to different parts of the magmatic-hydrothermal system. Plutons that crystallize at high pressures ($> \sim 120$ MPa for rhyolite) contain quartz that entrapped single phase supercritical fluids with a salinity of typically 5–15 wt% (Audétat 2019). Plutons that crystallize at lower pressures may record two sorts of fluids as inclusions: low-density vapor and a denser brine (Heinrich et al. 1992). The brine droplets condense out of the vapor if the two phase field is intersected on the vapor limb (**Figure 1b**). Vapor inclusions commonly have low densities and salinities (< 10 wt% NaCl), whereas brine inclusions have higher densities and salinities (> 30 wt% NaCl). Given that many ore-forming minerals form complexes with Cl, salinity is a very important control on metal-carrying capacity of the fluid (Williams-Jones & Heinrich 2005). It has been shown, through analysis of coexisting fluid and melt inclusions, that chalcophile metals partition strongly into the fluid, with fluid-melt partition coefficients of between 1 and 80, which are in good agreement with experimental data (Audétat 2019, Zajacz et al. 2008). Chloride-complexed elements, such as Pb, Cu, and Zn, generally partition more strongly into the brine phase over the low-density vapor, whereas elements such as As (and S in reduced form) tend to remain in the vapor phase (Audétat 2019; Candela & Holland 1984; Frank et al. 2011; Zajacz et al. 2008, 2011).

How do these fluids compare to volcanic gases in terms of their metal contents? Volcanic gases form by boiling or unmixing of hydrothermal-magmatic fluids during ascent and decompression in the crust (Hedenquist & Lowenstern 1994) (**Figure 1b**). Volcanic gases generally contain Cl speciated as HCl instead of NaCl (Shinohara 2009) and contain between 0.1 and 2.0 wt% Cl, or 0.2 to 2.5 wt% NaCl (equivalent). For comparison, vapor inclusions in quartz in both barren and mineralized granites contain 4.2 to 16 wt% NaCl, consistent with their equilibration at higher pressures (**Figure 1b**), and brine inclusions contain 31 to 58 wt% NaCl (Audétat 2019).

Figure 8 shows a comparison of the compositions of the three fluid types in terms of the ratios between different elements, X , in the fluid, with the concentration of Cl (**Figure 8a,b**) and S (**Figure 8c,d**). Before we consider how volcanic gases compare to these fluid inclusion compositions, we must first review how low-density vapor fluid inclusion compositions compare to brine compositions. It has been shown that some elements partition more strongly into a low-density vapor over a brine, such as As, S, and perhaps also Sb and Mo (Audétat 2019). The large compositional range of both vapor and brine inclusions reflects differences in metal partitioning with pressure, temperature, and salinity, discussed further by Audétat (2019). In general, the X/Cl ratios in vapor and brine fluids are similar, which reflects the fact that many of these metals speciate with chloride and their partitioning is dependent on fluid salinity (Williams-Jones & Heinrich 2005). Exceptions to this are Cs, As, Se, and Sb, which are clearly enriched in the vapor over the

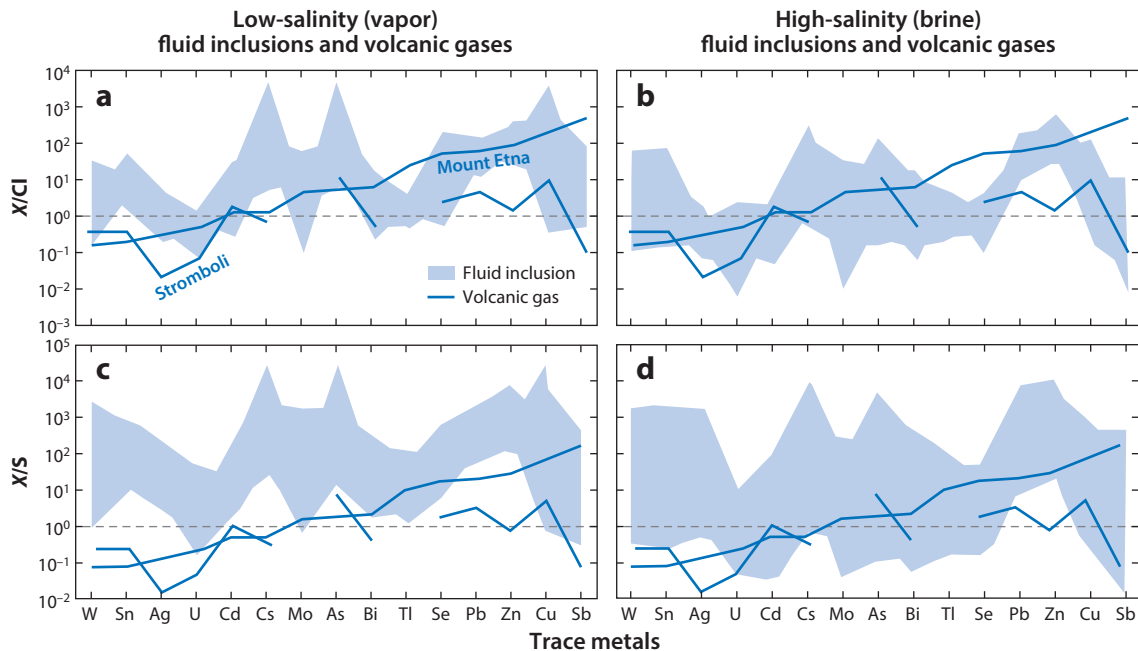


Figure 8

Comparison between the composition of volcanic gases versus the fluids analyzed in inclusions hosted by quartz in both barren and mineralized granites. Panels *a* and *b* show X/Cl mass ratios in the fluid inclusions and volcanic gases; panels *c* and *d* show the X/S mass ratios. Vapor fluid inclusions are shown in panels *a* and *c*, and brine fluid inclusion compositions are shown in panels *b* and *d*. Fluid inclusion data are from Audetat et al. (2019), and volcanic gas/particulate compositions are from Allard et al. (2000) (Stromboli) and Aiuppa et al. (2000) (Etna). Fluid inclusion compositions are shown as a range, shaded in light blue. Volcanic gas compositions are shown as thick dark blue lines labeled with the volcano name.

brine phase, regardless of salinity (**Figure 8a,b**). These are elements, with the exception of Cs, noted previously for their preference for the lower-density vapor (Audétat 2019) and for their speciation in forms other than as a chloride (Pokrovski et al. 2005). Volcanic gases display similar X/Cl ratios to the lower-density vapor fluid inclusions (**Figure 8a**), consistent with many of the elements' abundances being controlled by salinity. Volcanic gases are notably depleted relative to Cl, in Sn, Ag, Cs, and As, which might be explained by either pressure-dependent partitioning or differences in element speciation between the two fluid types. Volcanic gases are enriched in Tl and Sb relative to Cl over both vapor and brine fluid inclusions and in Se and Cu over the brine phase (**Figure 8a,b**). When element concentrations are plotted relative to S (**Figure 8c,d**), volcanic gases are depleted in most elements shown relative to the higher density vapor inclusions; this is due to volcanic gases being enriched in S (that degasses extensively at low pressure) relative to the fluid inclusions. The exceptions are Tl, Cu, and Sb, which show similar X/S ratios in volcanic gases and in vapor fluid inclusions. Volcanic gas X/S ratios are similar to brines (**Figure 8d**) but are relatively depleted in W/S, Sn/S, Ag/S, and Cs/S relative to brines, which may be explained by the very strong affinity of these elements for Cl.

Overall then, volcanic gases show similar X/Cl and X/S ratios to ore-forming fluids over a wide range of elements. Owing to the lower salinity of volcanic gases, metal concentrations in volcanic gases are lower than in vapor fluid inclusions. Although the fluxes of metals to the atmosphere from active volcanoes are likely to be similar to those that build ore deposits in the crust, with 8,000 kg/day Cu outgassed from Etna and 9,000 kg/day Se from Kilauea recorded (**Figure 3**),

emissions may well exceed these at other times and will be directly proportional to magma supply rates (Edmonds et al. 2018, Mason et al. 2021). In contrast to low-temperature fumarolic gas emissions, there is no clear evidence that high-temperature volcanic gases have condensed a brine prior to emission into the atmosphere, and it may well be the case that at active volcanic vents, where magma is advecting a high-temperature fluid to the surface via large gas slugs or permeable degassing, the unmixed vapor and brine phases are outgassed together to form the gas and particulate volcanic plume (rather than the brine phase being left behind in the subsurface, although this may indeed occur for more evolved intermediate and felsic volcanic systems).

6. ICE CORE ARCHIVES OF VOLCANIC VOLATILE METALS

Our improved understanding of the fluxes and degassing systematics of volatile metals and metalloids from volcanoes may be used to assess the potential for interrogation of geological archives (e.g., ice cores) as records of volcanic activity. It has long been recognized that trace metals (Pb, Cd, and In) are more abundant in ice core records than can be accounted for by terrestrial dust and ocean salt (Matsumoto & Hinkley 2001). We know that volcanoes are significant sources of trace volatile metals and metalloids to the atmosphere (Edmonds et al. 2018, Ilyinskaya et al. 2021), comparable to the emissions from entire countries, and we know from estimates of volatility and emanation coefficients that some volatile metals are released overwhelmingly as gas rather than in silicate material (70–90% for Tl and Cd; 1% for Pb) (Lambert et al. 1985, Mason et al. 2021, Mather et al. 2012). After emission, volatile metal-bearing gases condense rapidly to particulates of $\sim 0.2 \mu\text{m}$ diameter (Hinkley 1991, Mandon et al. 2019, Moune et al. 2010).

The long-term transport rates and ranges of these soluble aerosol particles in the atmosphere, however, are largely unknown. Eventually they are removed and deposited, incorporated into biological systems such as plants (Barghigiani et al. 1988) and hydrological systems (Aiuppa et al. 2000). There have been very few studies of long-range transport of volcanic metals. A downwind study of the gas and particulate boundary layer plume produced by the 2018 eruption of Kīlauea volcano showed that volatile metal and metalloid-bearing soluble aerosols (sulfates, oxides, and chlorides) are removed rapidly, within a few hundred kilometers of the source vent (Ilyinskaya et al. 2021). An eruption of Etna in 2018 created a particulate tropospheric plume that produced enrichments in Tl and Te in samples acquired by wet and dry deposition from the plume, up to 80 km downwind of the vent (Brugnone et al. 2020). The fate of metals transported as volcanic aerosols in the stratosphere, arising from explosive volcanic eruptions, is unknown.

Previous studies have proposed that Tl, Bi, and Cd may be tracers of preindustrial volcanic activity in ice cores (Kellerhals et al. 2010, Matsumoto & Hinkley 2001, McConnell et al. 2014). It has been proposed that perhaps as much as 50–95% of the Bi in Greenland ice cores was supplied by volcanism, whether local or further afield (Ferrari et al. 2000). It has also been suggested that persistent tropospheric volcanic degassing may be a significant contributor to the metal budgets of ice cores, particularly with respect to Zn, Cu, Cd, In, Pb, Sb, and Se (Matsumoto & Hinkley 2001, Weiss et al. 1978).

Volcanic trace metals in ice cores may also be linked directly to local eruptions. Ice core records from the West Antarctic ice sheet, Byrd, Taylor Glacier, and Dome C ice cores from Antarctica, for example, all show a chemical signature related to the 17.7-ka eruption sequence of Mount Takahe, a subglacial volcano located on an incipient rift in Marie Byrd Land, Antarctica (McConnell et al. 2017) (**Figure 9**). It has been shown that a range of trace volatile metal concentrations (e.g., Bi) correlated with a strong Cl signal throughout the period of the eruption, ~ 192 years, interpreted to be linked to the deposition of aerosol particulates from a halogen-rich volcanic plume that

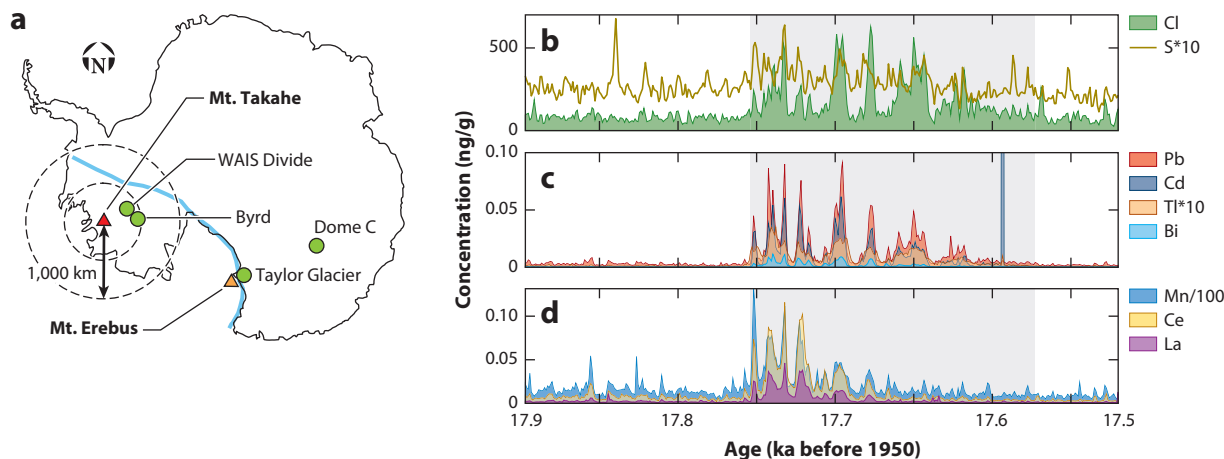


Figure 9

Mt. Takahe and the 17.7-ka eruption sequence. (a) Location of Mt. Takahe and Mt. Erebus on the West Antarctic Rift System (the boundary of the Transantarctic Mountains is shown by a *light blue line*). Ice core drilling locations are shown as green circles. (b–d) Concentrations (in ng/g, uncorrected for sea salt or background) of elements measured in the West Antarctic ice sheet (WAIS) divide ice core, as reported by McConnell et al. (2017). Figure adapted from Mason (2021).

is uncorrelated with refractory lithophile elements such as REE, which are interpreted to have been deposited as silicate ash (McConnell et al. 2017). Chemical speciation modeling using a typical rift-related volcanic gas composition shows that Cd, Bi, and Pb are predicted to be present as chloride gaseous species after mixing with air, whereas Tl is predicted to exist dominantly as an oxide (Mason 2021). Chloride species are known to be removed more rapidly than S species from volcanic plumes in the lower atmosphere through scavenging by hydrometeors (water and ice particles), which may remove up to 99% of HCl over SO₂ (25%) (Halmer et al. 2002). HCl gas is also more effectively scavenged than SO₂, resulting in estimates of only 25% HCl reaching the stratosphere during explosive eruptions versus 80% of SO₂ gas (Textor et al. 2003). Chloride aerosols will attain larger sizes, causing them to fall out more rapidly, thereby reducing the residence time of chloride particulates. The 17.7-ka Takahe ice core record, therefore, may represent the case whereby local early deposition of volcanic chloride particulates is recorded (Mason 2021), with the longer-lived and possibly finer-grained metal-bearing sulfate aerosol being transported further afield. The Summit ice core in Greenland, in contrast, preserves volatile metal concentrations (Pb, Cd, Cu, Zn) related to fallout from the tropospheric 1783–1784 Laki eruption cloud, which correlate with sulfate concentrations (Hong et al. 1996). Hong et al. (1996) estimate that the total mass of metal deposition related to this one eruption is comparable to the annual deposition arising from anthropogenic activities in the 1960s and 1970s.

Identification of metal signatures in the ice cores that are linked to larger, explosive stratospheric eruptions remains poorly constrained. The vast distances volcanic emissions travel from large tropical stratospheric eruptions may lead to the majority of the metal-bearing chloride aerosol being lost between the source and Antarctic or Arctic ice sheets. Speciation and correlation analysis results indicate that Tl has little affinity for Cl, which may extend its atmospheric residence time and makes it a more promising distal tracer of volcanism. Many questions remain, however, over the transport mechanisms of residence times of volcanic metals that may be recorded in ice cores, particularly with regard to stratospheric chemical scavenging and transport processes.

7. FUTURE DIRECTIONS AND PERSPECTIVES

Our understanding of the flux, composition, behavior, and role of volatile metals and metalloids in volcanic systems has increased immensely over the past few decades and rightly so, as this understanding is fundamental to models of economic metal deposits, biogeochemical cycles, and reconstructing volcanic activity in the past using ice core records. However, much remains to be learned. The precise role of volcanic metals in the global tectonic geochemical cycling of these elements has yet to be fully constrained but has immense importance for understanding the links between tectonics and life on our own and other planets.

Experimental and observational data on metal partitioning between minerals, silicate melt, and exsolved fluids are generally lacking for many elements under the range of conditions relevant to the upper crust and in particular for the highest-temperature (basaltic) and oxidized magmatic systems. These data are critical for understanding metal pathways during magma differentiation in the crust (crystallization, degassing, and mixing processes) that impacts outgassing fluxes, formation of porphyry metal and metalloid deposits, and, through speciation, the environmental processing of volcanic metals.

Questions remain as to the nature of the fluids outgassing from high-temperature volcanic systems, directly from the magma-air interface. It is likely that the composition of the bulk fluids (vapor and brine together) is not modified to any great extent over the top kilometer or so of magma ascent and magma-gas separation, and brine separation is not a fundamentally important process to those volcanoes outgassing from the magma-free surface at lava lakes and open vents. Fumarolic emissions from more evolved volcanic systems, where the exsolved vapor is transported through permeable fracture systems before being vented to the atmosphere, are the end product of fluid expansion, cooling, and segregation of brine phases, as well as sublimation of metal-bearing minerals, and scrubbing upon interaction with hydrothermal systems and meteoric water. There will be opportunities to fully characterize and quantify these differences, particularly using new unoccupied aerial system platforms that will allow close approach to magma-air interfaces to capture very young, high-temperature volcanic plumes.

The deconvolution of hydrothermal and degassing sources for the constituents of hydrothermal vents on the seafloor, in both MOR and arc/backarc settings, will be of great value in reconstructing the influences on ocean chemistry and tectonic processes in the past, e.g., MOR spreading rates, if geochemical trace metal proxies for magma degassing may be identified with confidence in deep-sea sediments. A better understanding of the role of magmatic fluids in transporting metals that are precipitated as massive sulfide deposits around seafloor vents, including in backarc settings, will be of great value in developing sustainable and environmentally sound exploration models for such resources. In this regard, laboratory volcanoes that are studied in detail, such as Brothers volcano (Kermadec Islands arc), will prove invaluable. On the topic of sustainable resource use and extraction, the studies and understanding presented here open new avenues of thought regarding the potential for extracting resources from presently active volcanoes (Blundy et al. 2021), which in many cases are regarded to be ongoing sites of volatile metal and metalloid accumulation at depth. Other volcanoes are venting their metal loads predominantly into the atmosphere at rates comparable to those that build ore deposits in the crust.

Finally, there is much to be learned about how metals are transported, processed, and deposited from volcanic plumes, in both the troposphere and stratosphere. Observational and experimental data are sparse in this field, despite the importance of tracking the fate of some of these highly toxic (Tl, As, Se) metals and metalloids, which find their way into biological and hydrological systems. The long-range transport of these elements is poorly understood, yet ice core records hint that some of these volatile metals may be proxies for volcanic activity (e.g., Pb, Cd, and Bi) and some

may persist in the atmosphere for sufficiently long timescales that they may even provide information on global volcanism (e.g., Tl). Opportunities in this area range from in situ observational data, particularly within the plumes of long-lived stratospheric tropical eruptions, to experimental studies of particulate formation, growth and settling, heterogeneous chemistry on ash surfaces, and scavenging processes. These studies will impact not only understanding of geological archives but also mitigating risks associated with delivery of toxic trace metals into biological and hydrological systems.

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The authors are not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

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