Vapor Transport and Deposition of Cu-Sn-Co-Ag Alloys in Vesicles in Mafic Volcanic Rocks

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Abstract

Metallic sublimates coated by sulfides and chlorides line the vesicle walls of mafic volcanic lava and bombs from Kilauea, Vesuvius, Etna, and Stromboli. The metallic sublimates were morphologically and compositionally similar among the volcanoes. The highest concentrations of S and Cl occurred on the surface of the sublimates, while internally they had less than 1 wt % S and Cl in most cases, leading us to classify them as alloys. The major components of the alloys were Cu, Sn, Co, and Ag based on electron microprobe analyses and environmental scanning electron microscope element maps. Alloy element maps showed a covariance of Cu-Sn, while Co and Ag concentrations varied independently. Laser ablation-inductively coupled plasma-mass spectrometry analysis of matrix glass and melt inclusions in bombs from Stromboli showed appreciable amounts of Cu, Co, and Sn. We propose a model for the origin of the metallic grains, which involves syneruptive and posteruptive magma degassing and subsequent cooling of the basalt vesicles. During syneruptive vapor phase exsolution, volatile metals (Cu, Co, and Sn) partition into the vapor along with their ligands, S and Cl. The apparent oxygen fugacity (fO₂) in these vapor bubbles is low because of the relative enrichment of the exolved gas phase in H₂ relative to H₂O in silicate melts, due to the much higher diffusivity of the former in silicate melts. The high fH₂ and low fO₂ induces the precipitation of metal alloys from the vapor phase. Subsequently, the reducing environment in the vesicle dissipates as the cooling vapor oxidizes and as H₂ diffuses away. Then, metal-rich sulfides (and chlorides) condense onto the outer surfaces of the metal alloy grains either due to a decrease in temperature or an increase in fO₂. These alloys provide important insights into the partitioning of metals into a magmatic volatile phase at low pressure and high temperature.

Introduction

From their studies of the 1991 eruptive products of Mount (Mt.) Pinatubo (Philippines) and the giant Bingham Canyon porphyry Cu deposit in Utah, Hattori and Keith (2001) concluded that mafic magma was fundamental in delivering sulfur and chalcophile elements to overlying magma chambers and could contribute to the formation of economic deposits. K. Hattori (pers. commun., 2004) found preliminary evidence of vapor transport of Cu in bombs that had erupted from the Miyake-jima volcano only a few days earlier. To test these conclusions, fresh, recently erupted mafic magma needs to be examined from volcanoes worldwide. Consequently, we sampled active flows from the Pu‘u ‘Ō‘o vent on Kilauea volcano, Hawaii. In a preliminary report, Strand et al. (2002, p. 88) found that they had no magmatic sulfides but discovered “heterogeneous particles of Cu-Sn-Co alloys” in the vesicles. We have now examined bombs and flows from other active volcanoes, including Etna, Vesuvius, and Stromboli. Remarkably, as we report here, we found the same metallic alloys, with distinct compositional variations for each volcano, in vesicles from these diverse magmatic systems.

The following observations and experiments demonstrate that volcanic vapors (low-density aqueous fluids) can carry significant quantities of a variety of metallic elements and deposit them as alloys, sulfides, and chlorides. Volcanic eruptions and open-system degassing contribute large quantities of metals into the atmosphere (Meeker et al., 1991; Symonds and Reed, 1993; Hinkley et al., 1999; Allard et al., 2000). Fluid inclusion work provides evidence that the vapor phase is a major mobilizing agent for metals within volcanic systems (Williams-Jones and Heinrich, 2005; Simon et al., 2006; Zajacz and Halter, 2009; Landtwing et al., 2010; Zhai et al., 2018). Additionally, high-temperature, reduced volcanic gases from fumaroles and their sublimates have been explored using silica tube condensation techniques at various volcanoes, including Merapi, Momotombo, Mt. St. Helens (Bernard et al., 1990; Nadeau et al., 2016), Colima (Tiaran et al., 2000), Kudryavyy (Yudovskaya et al., 2006), and Satsuma-Iwojima (Hedenquist et al., 1994; Africani et al., 2002). At these volcanoes, Au-Cu alloys, Cu-Ag alloys, Cu, Zn, Sn, and Fe sulfides, Cu-Fe sulfides, PbCl, BiCl, etc. formed sublimates on the walls of the gas collecting tubes. In addition, sublimates of many varieties, including native Cu and Au, AuCl, and Pb-BiS, have been collected in collecting tubes. In addition, sublimates of many varieties, including native Cu and Au, AuCl, and Pb-BiS, have been collected in collecting tubes.
found deposited inside and around fumaroles at Mt. Erebus (Meeker et al., 1991), Vulcano (Fulignati and Sbrana, 1998), and Kudryavy (Yudovskaya et al., 2006). These occurrences show that many ore metals are transported by magmatic vapor.

If these volatile metallic species are common constituents of volcanic gasses, what is their fate if they are trapped and condensed in the vesicles of cooling lava? Only a few researchers have found metallic sublimates lining vesicle walls by looking inside vesicles with a scanning electron microscope (SEM)—from submarine basalts by Moore and Chalk (1971) and Mathez (1976), and from Popocatepetl volcano by Larocque et al. (1998, 2008). Larocque et al. (2008) noted that the fine-grained vesicle coatings in lavas were similar to mineral assemblages that occur in high-sulfidation epithermal Au deposits and represent crystallization directly from a magmatic volatile phase during or soon after eruption. They speculated whether it would be possible to look at these delicate grains in thin sections and concluded that one would need special preparation techniques to preserve them.

We propose that our innovative technique for vacuum impregnating samples with epoxy before thin sectioning preserves these delicate grains. Using this sample preparation technique, we have found metallic alloys along with sulfide and chloride sublimates not previously characterized in active volcanic systems. The vesicle-hosted Cu-Sn-Co alloys provide significant new data on metal transport and precipitation from high-temperature magmatic vapors. We anticipate that they will be widely recognized in mafic lavas and scoria elsewhere.

### Samples

In reconnaissance studies, we found metallic alloys in vesicles of mafic scoria and lava erupted from several volcanoes in Hawaii and Italy, including Vulcano, Mt. Etna, Stromboli, Vesuvius, Mauna Loa, Mauna Kea, and Kiläuea. In this study, we examined in detail 13 groups of samples from Kiläuea, Etna, Stromboli, and Vesuvius (Table 1). Flows, scoria, and bombs from thousands of years to minutes old were sampled in order to observe the effect of environmental interactions, such as rain and weathering, on sublimate presence. At Kiläuea, we collected fresh lava from 2005 surface breakouts above lava tubes fed from the Pu‘u ‘Ō‘ō vent. In 2005, we sampled from the 2002 and 2005 lava flows on Etna. Stromboli samples, also collected in 2005, consisted of golden pumice and scoria bombs from the 2002 to 2005 eruptive products. On Vesuvius, we collected from seven different eruptive units, with the most recent samples coming from the 1944 flow. The geology of each volcano is briefly described in the next section, and more detailed descriptions of sample types and locations are given in the Appendix text and Figures A1 through A6.

### Geologic Settings

We examined mafic scoria and lava from hot spot (Hawaii) and subduction zone (Italy) settings. Below, we outline the characteristics of the volcanoes that relate to metal transport and deposition, the volcanoes’ eruptive behaviors, their volatile fluxes and degassing styles, and mafic injections in subvolcanic magma reservoirs, as well as the compositions and mode of emplacement of the materials studied.

#### Kiläuea

Kiläuea is a basaltic shield volcano on the southeastern flank of Hawaii that formed as a result of hot spot volcanism (Lipman et al., 2000). Basaltic magma rises beneath the central summit caldera, where, for the most recent eruptions, it intruded laterally into a rift zone, transferring magma to one or more vents on the surface (Poland et al., 2012). Eruptions are typically nonexplosive effusions into tube systems, but sometimes high fountains form when unusually volatile-rich magma erupts (Poland et al., 2012). Our samples were collected during a period of quiet effusions in 2005 from surface breakouts 10.5 km from the Pu‘u ‘Ō‘ō vent. Pu‘u ‘Ō‘ō erupted continuously from 1983 to 2018 (Poland et al., 2012, Neal et al., 2019). The lava we studied is an olivine tholeiite—the most common type of lava to erupt from Kiläuea (Table 1). However, mixed lava compositions have erupted periodically from Pu‘u ‘Ō‘ō and indicate that magma storage and differentiation occur within the rift (Conrad et al., 1997; Neal et al., 2019). Emission rates for SO₂ and CO₂ spiked from approximately 1,000 to 2,000 tons per day (tpd) to approximately 3,000 to 5,000 tpd in early 2005 when we were sampling the lava flow. This, along with other geophysical and geochemical observations, has led scientists to hypothesize a mantle-driven surge in magma supply to Kiläuea from 2003 to 2007 (Elias and Sutton, 2007; Poland et al., 2012).

#### Italian volcanoes

Etna, Stromboli, and Vesuvius are proposed to result from the subduction of the African plate margin beneath the European block (Scandone, 1979; De Natale et al., 2001). Such convergent plate magma sources are tied to many different types of hydrothermal metal deposits along with explosive eruptions.

#### Etna

Etna is a mafic stratovolcano on the island of Sicily. It is the most active volcano in Europe, and its quiescent, continuous gas release from summit craters and peripheral

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**Table 1. Summary of Samples and Alloys Located in Thin Section**

| Volcano   | Rock type          | Eruption                          | Alloys present |
|-----------|--------------------|-----------------------------------|----------------|
| Kiläuea   | Olivine tholeiite  | Lava from the Pali (2005)        | 20             |
|           |                    | Two-day-old flow (2005)          | 20             |
| Etna      | Trachybasalt       | Scoria (2002)                     | 20             |
|           |                    | Scoria (2005)                     | 19             |
| Stromboli | Potassic trachybasalt | Pumiceous bomb (2005)      | 33             |
|           | Golden pumice      | Pumiceous bomb (2005)            | 70             |
|           |                    | Pumiceous bomb (2005)            | 28             |
|           |                    | Pumiceous bomb (2005)            | 62             |
|           | Trachybasalt andesite | Scoriaeous bombs (2002)    | 26             |
|           |                    | Scoriaeous bombs (2002)          | 2              |
|           |                    | Scoriaeous bombs (2002)          | 11             |
|           |                    | Scoriaeous bombs (2002)          | 14             |
| Vesuvius  | Phonolitic tephrites | Basalt (1944)                   | 10             |
|           |                    | Scoria (1944)                     | 5              |
|           |                    | Vesuvius (1913–1944)             | 0              |
|           |                    | Vesuvius (1913–1944)             | 0              |
|           |                    | Vesuvius (1906–1913)             | 0              |
|           |                    | Vesuvius (1906)                  | 0              |
|           | Tephritic leucitites | Vesuvius (1700 B.P.)            | 0              |
|           |                    | Vesuvius (1700 B.P.)             | 0              |
|           |                    | Vesuvius (1700 B.P.)             | 0              |
|           |                    | Vesuvius (1700 B.P.)             | 0              |
fumaroles make it one of the world’s largest continuous contributors of volcanic volatiles to the atmosphere (Allard et al., 1991, 1994; Ferlito et al., 2013). It erupts unusually alkaline lavas (including trachybasalts and basalts) for a volcano in a subduction setting. Some have linked the unusual characteristics to back-arc spreading (Cocchi et al., 2009). During Etna’s frequent periods of high activity, emissions as high as 25,000 tpd of SO$_2$ and 40,000 tpd of CO$_2$ occur (Allard et al., 1991). A study of olivine melt inclusions trapped in historical and recent alkali basalts discovered higher amounts of H$_2$O, S, and Cl than in melt inclusions from older alkali basalts (Métrich et al., 1993). We sampled trachybasalt lava flows from a powerful flank eruption in 2002 and from effusive eruptions in 2005. The samples were collected about 3 km from the vent in 2005. The 2002 flank eruption was unique in that it brought volatile-rich alkali basalt up from the deep feeding system, as evidenced by the multidisciplinary data collected (Andronico et al., 2005). The 2005 effusive eruptions are also thought to have originated from the input of deeper, volatile-rich magma sources (Aiuppa et al., 2006).

**Stromboli:** Stromboli is an active stratovolcano located off the coast of Sicily that has erupted both calc-alkaline and alkaline magmas. Explosions are spaced from 20 min to a few hours apart and are caused by the accumulation of slugs of volatiles in the near-surface plumbing system. Its eruptive style is generally strombolian with effusive activity every 10 to 20 years interspersed with rare explosive paroxysms (Laiolo and Gigolini, 2006). This eruption style has been consistent for the last 14,000 to 18,000 years (Rosi et al., 2000). Métrich et al. (2001, 2010) proposed a model wherein the crystal-rich, degassed basaltic scoria is ejected in strombolian and effusive eruptions from an actively degassing magma in the cone of the volcano (100 MPa, about 3.5 km depth). In contrast, the explosive paroxysms eject high-K basalt characterized as “golden pumice” (crystal poor and volatile rich) from volatile-rich magma originating deeper in the volcano, at ~270 MPa and about 10 km deep, that rises quickly to the surface before it can substantially degas (Di Carlo et al., 2006). Francalanci et al. (2004) found evidence for mixing between the volatile-rich (golden pumice) and volatile-poor (scoria) magmas. Reversely zoned olivine and clinopyroxene and variable volatile concentrations in melt inclusions and matrix glass of the 2005 golden pumice also point to influences of magma mixing. We sampled golden pumice (potassic trachybasalt) erupted from a 2005 paroxysm as well as scoria bombs (trachybasaltic andesite) from more typical eruptions (Baxter, 2008). In addition to the volatile-driven explosions, degassing is continuous and releases 6,000 to 12,000 metric tons of H$_2$O, CO$_2$, SO$_2$, HCl, and HF per day (Allard et al., 1994).

**Vesuvius:** Vesuvius, east of Naples, represents the southernmost active area of K-rich volcanism (leucite-bearing tephrites) in central Italy (Cioni et al., 2008). Although related to the presence of a continuously subhudding slab (De Natale et al., 2001), erupted lavas are highly unusual for this setting and include a wide variety of silica-undersaturated magmas. It has a long history of Plinian and non-Plinian effusive eruptions (Belkin and De Vivo, 1993). Magma resides in shallow 1- to 5-km-deep reservoirs within the Mesozoic carbonate basement (De Natale et al., 2001). We collected scoriaceous lava from the surface of flows ranging from 1,700 years old to those erupted in 1944. The last eruption in 1944 was significant in that it transitioned from effusive eruptions of phonotephritic lavas to fountaining of porphyritic K-tephrites. The commonly believed cause for this eruptive transition is that a volatile–rich magma batch rose from a depth of 11 to 22 km and mixed with a higher-level magma, thus triggering the 1944 eruption (Marianelli et al., 1999).

**Analytical Methods**

**Epoxy vacuum impregnation**

Samples were vacuum impregnated with epoxy before being made into polished thin sections following the technique developed by Wagner Petrographic (Lehi, Utah). The samples were dried to prevent moisture from interfering and then submerged in a specially formulated, low-viscosity proprietary epoxy. The thin-section billets were placed in a vacuum chamber, and the pressure was reduced to 100 to 200 torr to remove air in the exposed vesicles and pore spaces. A vacuum was pulled until all the bubbles were removed. Pressure was then increased to 500 to 600 torr to overcome the surface tension of the epoxy and force it into the vesicles. Samples were then allowed to cure. This procedure has been found to preserve sublimes that are loosely attached to the vesicle wall, which would otherwise be lost in a standard thin-sectioning process.

**Environmental SEM (ESEM) analysis of vesicles in rock fragments**

To image and analyze the uncut sublimes attached to the vesicle walls, 25 whole-rock samples (2- to 5-cm pieces) were mounted on aluminum stubs, carbon coated, and explored using a Philips XL30 ESEM at Brigham Young University (BYU). The backscattered electron (BSE) detector was used to locate metallic sublimes and sulfides. Elements were identified using an energy dispersive X-ray analyzer (EDXA) Genesis system with a SiLi detector for semiquantitative analysis.

X-ray element maps of the thin sections of metallic sublimes were also obtained with the Philips XL30 ESEM. During analyses, an acceleration of 20 kV was used. Additionally, the ESEM was used to create detailed BSE photos of the alloys found in the thin section.

**Electron microprobe analysis**

Metallic sublimes in polished thin sections were analyzed on a Cameca SX50 electron microprobe. Light and dark portions of the metallic sublimate surface were analyzed using the conditions outlined in Appendix Table A1. Many of the alloys are so thin that the analytical volume extended beyond the boundaries of these small grains (5–80 μm across). Consequently, many of the totals are low. We have reported the concentrations to two decimal places in Table 2, but the analyses should be considered to be semiquantitative.

X-ray element maps were also generated with the electron microprobe. A beam scan was used with a magnification tailored to the size of the alloy and a beam current of 200 nA with a beam size of 10 μm. Dwell time was 50 ns with a definition of 256 × 256 pixels.

**Whole-rock chemistry**

For samples containing metallic sublimes, trace element analyses of whole rocks by commercial inductively coupled...
| Table 2A. Electron Microprobe Analyses of Alloys, Kīlauea (2005) |
|---------------------------------------------------------------|
| **Sample** | **KC-K8** | **KC-K8** | **Kh-K9** | **Kh-K9** | **Kh-K9** | **Kh-K9** | **Kh-K9** | **Kh-K9** | **Average** |
| Si (wt %) | 0.02 | 0.07 | 0.05 | 0.05 | 0.23 | 5.23 | 0.05 | 0.17 | 0.74 |
| S | 0.06 | 0.18 | 0.02 | 0.06 | 0.02 | 0.25 | 0.05 | 0.05 | 0.09 |
| Cl | 0.00 | 0.00 | 0.04 | 0.07 | 0.02 | 0.05 | 0.20 | 0.03 | 0.05 |
| Fe | 1.28 | 2.00 | 1.65 | 3.88 | 0.75 | 1.51 | 1.00 | 0.65 | 1.59 |
| Co | 0.62 | 1.27 | 1.38 | 4.10 | 0.41 | 0.26 | 0.52 | 0.76 | 1.20 |
| Ni | 0.02 | 0.07 | 0.02 | 0.13 | 0.01 | 0.01 | 0.11 | 0.11 | 0.01 |
| Cu | 84.58 | 78.17 | 52.91 | 75.70 | 82.03 | 70.74 | 69.58 | 64.66 | 76.04 |
| Zn | 0.04 | 0.02 | 0.01 | 0.04 | 0.03 | 0.06 | 0.04 | 0.03 | 0.03 |
| As | 0.00 | 0.00 | 0.08 | 0.08 | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 |
| Pd | 0.04 | 0.00 | 0.04 | 0.07 | 0.02 | 0.05 | 0.20 | 0.03 | 0.05 |
| Ag | 0.00 | 0.00 | 0.07 | 0.08 | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 |
| Sn | 13.19 | 17.89 | 13.51 | 13.18 | 15.33 | 13.27 | 15.95 | 16.95 | 16.96 |
| Pt | 0.05 | 0.07 | 0.00 | 0.00 | 0.05 | 0.00 | 0.00 | 0.01 | 0.02 |
| Total | 100.01 | 99.69 | 99.91 | 97.31 | 98.96 | 91.49 | 88.80 | 98.83 | 96.88 |

| Table 2B. Electron Microprobe Analyses of Alloys, Etna (2002) |
|---------------------------------------------------------------|
| **Sample** | **E9** | **E9** | **E9** | **E9** | **E9** | **E9** | **E9** | **E9** | **Average** |
| Si (wt %) | 0.06 | 0.05 | 0.05 | 0.05 | 0.02 | 0.09 | 0.07 | 0.06 | 0.07 |
| S | 0.15 | 0.14 | 0.13 | 0.17 | 0.05 | 0.13 | 0.19 | 0.10 | 0.11 |
| Ag | 0.44 | 0.36 | 0.36 | 5.04 | 3.06 | 2.40 | 2.07 | 7.60 | 2.63 |
| Sn | 2.12 | 2.27 | 0.27 | 12.00 | 9.06 | 3.53 | 3.27 | 5.47 | 4.93 |
| Fe | 0.14 | 0.16 | 0.11 | 0.15 | 0.15 | 0.11 | 0.10 | 0.11 | 0.13 |
| Co | 80.16 | 80.76 | 80.76 | 80.76 | 80.76 | 80.76 | 80.76 | 80.76 | 80.76 |
| Ni | 0.00 | 0.02 | 0.00 | 0.05 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 |
| Cu | 13.07 | 12.92 | 15.00 | 55.84 | 45.83 | 26.00 | 19.77 | 29.33 | 26.08 |
| Total | 96.48 | 96.68 | 97.32 | 90.45 | 90.87 | 107.35 | 100.68 | 98.85 | 94.65 |

| Table 2C. Electron Microprobe Analyses of Alloys, Vesuvius (1944) |
|---------------------------------------------------------------|
| **Sample** | **V10-J8** | **V10-J8** | **V10-J8** | **V10-J8** | **V10-J8** | **V10-J8** | **V10-J8** | **V10-J8** | **Average** |
| Si (wt %) | 0.16 | 0.97 | 0.58 | 0.57 | 0.09 | 0.20 | 0.36 | 0.47 | 0.30 |
| S | 0.08 | 0.09 | 0.09 | 0.09 | 0.32 | 0.11 | 0.12 | 0.12 | 0.11 |
| Ag | 0.96 | 0.57 | 5.79 | 2.44 | 1.00 | 4.65 | 5.44 | 4.64 | 3.75 |
| Sn | 4.30 | 1.91 | 2.33 | 2.55 | 5.51 | 1.37 | 2.10 | 2.90 | 2.08 |
| Fe | 0.37 | 0.45 | 0.09 | 0.30 | 0.03 | 0.07 | 0.06 | 0.16 | 0.05 |
| Co | 47.51 | 54.45 | 66.95 | 56.30 | 58.34 | 82.55 | 75.83 | 62.20 | 60.97 |
| Ni | 0.03 | 0.02 | 0.00 | 0.00 | 0.05 | 0.00 | 0.04 | 0.01 | 0.01 |
| Cu | 36.33 | 14.47 | 9.78 | 20.19 | 12.58 | 5.90 | 8.86 | 12.39 | 7.84 |
| Total | 90.06 | 73.00 | 85.80 | 82.95 | 78.36 | 95.13 | 92.40 | 84.94 | 91.96 |

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### Table 2D. Electron Microprobe Analyses of Alloys, Stromboli (2005)

| S1-K12 | S1-K12 | S1-K12 | S5-K6 | S5-K6 | S5-K6 | S5-K6 | S5-K6 | S5-K6 | Average |
|--------|--------|--------|-------|-------|-------|-------|-------|-------|---------|
| Si (wt %) | 0.12 | 0.07 | 0.35 | 0.08 | 0.12 | 0.07 | 0.07 | 0.07 | 0.11 |
| S | 0.11 | 0.15 | 0.23 | 0.13 | 0.04 | 0.17 | 0.10 | 0.07 | 0.16 |
| Cl | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| Fe | 0.36 | 0.04 | 0.08 | 0.09 | 0.41 | 0.17 | 0.10 | 0.07 | 0.16 |
| Co | 89.17 | 95.99 | 76.14 | 95.99 | 16.22 | 86.11 | 96.41 | 41.59 | 77.22 |
| Ni | 0.00 | 0.00 | 0.03 | 0.00 | 0.06 | 0.00 | 0.00 | 0.02 | 0.01 |
| Cu | 4.14 | 2.24 | 2.52 | 1.90 | 68.11 | 6.03 | 3.09 | 1.66 | 7.61 |
| Zn | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| As | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| Pd | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| Ag | 0.70 | 0.52 | 1.58 | 0.02 | 2.64 | 0.08 | 0.15 | 0.00 | 42.25 |
| Sn | 0.55 | 0.36 | 0.82 | 0.14 | 12.16 | 1.58 | 0.65 | 0.16 | 6.10 |
| Pb | 0.29 | 1.52 | 1.00 | 0.91 | 1.25 | 1.24 | 1.20 | 2.14 | 1.25 |
| Pt | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| Au | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| Hg | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| Total | 95.45 | 99.37 | 81.73 | 98.35 | 99.71 | 94.36 | 100.62 | 99.52 | 97.75 |

### Table 2C. (Cont.)

| V10-k11b | V10-k11b | Average |
|-----------|-----------|---------|
| Si (wt %) | 0.15 | 0.86 | 0.50 |
| S | 0.13 | 0.15 | 0.14 |
| Cl | NA | 0.11 | 0.11 |
| Ag | 0.05 | 0.00 | 0.02 |
| Sn | 0.44 | 13.35 | 6.90 |
| Fe | 0.13 | 0.87 | 0.50 |
| Co | 85.41 | 0.72 | 43.06 |
| Ni | 0.00 | 0.00 | 0.00 |
| Cu | 3.39 | 62.79 | 33.09 |
| Zn | NA | 0.04 | 0.04 |
| As | NA | 0.00 | 0.00 |
| Pb | NA | 0.07 | 0.07 |
| Total | 89.68 | 79.01 | 84.48 |

### Table 2A. (Cont.)

| V10-k11b | V10-k11b | Average |
|-----------|-----------|---------|
| Si (wt %) | 0.12 | 0.07 | 0.03 |
| S | 0.11 | 0.15 | 0.23 |
| Cl | NA | NA | NA |
| Fe | 0.36 | 0.04 | 0.08 |
| Co | 85.41 | 0.72 | 43.06 |
| Ni | 0.00 | 0.00 | 0.00 |
| Cu | 3.39 | 62.79 | 33.09 |
| Zn | NA | 0.04 | 0.04 |
| As | NA | 0.00 | 0.00 |
| Pb | NA | 0.07 | 0.07 |
| Total | 89.68 | 79.01 | 84.48 |

### Table 2B. (Cont.)

| Si (wt %) | 0.04 | 0.10 | 0.07 |
|----------|-------|------|------|
| S | 2.43 | 0.01 | 0.02 |
| Cl | NA | 0.05 | 0.00 |
| Fe | 0.29 | 1.52 | 1.00 |
| Co | 1.53 | 1.20 | 0.72 |
| Ni | 0.00 | 0.03 | 0.02 |
| Cu | 68.56 | 79.68 | 80.71 |
| Zn | NA | 0.02 | 0.02 |
| As | NA | 0.05 | 0.00 |
| Pb | NA | 0.00 | 0.00 |
| Ag | 10.60 | 0.00 | 0.04 |
| Sn | 11.69 | 14.78 | 14.58 |
| Pt | NA | 0.00 | 0.00 |
| Au | NA | 0.00 | 0.00 |
| Hg | NA | 0.05 | 0.00 |
| Pb | NA | 0.03 | 0.00 |
| Total | 95.14 | 97.52 | 97.35 |
plasma-mass spectrometry (ICP-MS) were completed. Samples from each volcano were analyzed for base and precious metals at the Vancouver (Canada) ALS laboratory using a four-acid near-complete digestion. Uncertainties based on comparisons with the standards analyzed with the unknowns range from 5 to as much as 20% for the lowest concentrations. Au, Pt, and Pd were analyzed using fire assay fusion and inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Sulfur was analyzed using a Leco furnace technique with an uncertainty of about 5% relative.

Laser ablation-ICP-MS (LA-ICP-MS) analyses were conducted at the Magmatic and Ore-Forming Processes Research Laboratory at the University of Toronto, Canada. An Agilent 7900 quadrupole mass spectrometer attached to an NWR 193 UC laser ablation system was used to determine the trace element composition of the matrix glass and silicate melt inclusions in minerals. Sixteen unknown analyses were bracketed by two U.S. Geological Survey GSD-1g basalt glass standard analyses at the beginning and end of each analysis block. The instrument was tuned to oxide and doubly charged ion production rates of approximately 0.3% as monitored on ThO/Th and mass 21/42Ca count rates while ablating the NIST 610 standard glass. Data quantification was conducted using the software SILLS (Guillong et al., 2008). The total of the major element oxides was used as an internal standard. Ag and Au count rates were corrected for the contribution of polyatomic interferences (91Zr16O on 107Ag and 181Ta16O on 197Au). The production rate of these oxides was determined using natural zircon and rutile, which were ablated before and after each analysis block.

Results
Uncut vesicle-hosted metallic sublimates

Vesicles within the volcanic products of Kīlauea, Etna, Stromboli, and Vesuvius were imaged and analyzed for

Table 2E. Electron Microprobe Analyses of Alloys, Stromboli (2005)

|       | Si (wt %) | S  | Cl | Fe | Co | Ni | Cu | Zn | As | Pd | Ag | Sn | Pt | Au | Hg | Pb |
|-------|----------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| S5-K6 | 0.08     | 0.02| 0.03| 0.06| 0.06| 0.02| 0.08| 0.07| 0.12| 0.06|
| S5-K6 | 0.03     | 0.02| 0.04| 0.03| 0.01| 0.01| 0.06| 0.16| 0.10| 0.04| 0.05|
| S5-K6 | 0.01     | 0.01| 0.00| 0.00| 0.03| 0.00| 0.00| 0.04| 0.00| 0.01| 0.01|
| S5-K6 | 3.45     | 1.59| 1.59| 4.14| 0.50| 0.51| 2.48| 0.96| 3.83| 2.12|
| S5-K6 | 3.47     | 1.47| 1.37| 3.66| 0.44| 0.15| 2.69| 0.57| 3.25| 1.93|
| S5-K6 | 0.00     | 0.01| 0.04| 0.03| 0.01| 0.01| 0.01| 0.03| 0.02| 0.02|
| Cu    | 73.23    | 50.33| 84.02| 76.88| 76.47| 89.73| 70.61| 78.28| 71.39| 77.58|
| Zn    | 0.06     | 0.02| 0.05| 0.03| 0.05| 0.04| 0.03| 0.07| 0.04| 0.04|
| As    | 0.00     | 0.12| 0.00| 0.13| 0.29| 0.05| 0.27| 0.00| 0.10| 0.01|
| Pd    | 0.01     | 0.00| 0.00| 0.05| 0.00| 0.03| 0.00| 0.00| 0.03| 0.01|
| Ag    | 0.00     | 0.00| 0.00| 0.04| 0.00| 0.00| 0.00| 0.00| 0.05| 0.01|
| Sn    | 17.95    | 14.26| 12.00| 14.48| 22.02| 22.00| 22.63| 17.36| 19.28| 16.44|
| Pt    | 0.00     | 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.04| 0.00|
| Au    | 0.00     | 0.05| 0.00| 0.00| 0.00| 0.01| 0.00| 0.03| 0.00| 0.01|
| Hg    | 0.00     | 0.00| 0.03| 0.00| 0.05| 0.00| 0.10| 0.05| 0.07| 0.03|
| Pb    | 0.00     | 0.00| 0.09| 0.01| 0.13| 0.04| 0.00| 0.00| 0.00| 0.03|
| Total | 98.29    | 97.91| 99.26| 99.39| 99.89| 98.88| 98.87| 98.13| 98.13| 98.75|

Notes: Low totals are due to the small sizes (5–80 μm) and variable thicknesses of the grains, which allows the electron beam to excite surrounding epoxy or vesicle wall; some analyses did not include all of the major elements.
three-dimensional grains in situ using rock fragments in an ESEM. Numerous bright metallic phases containing Au, Ag, Cu, Sn, Co, Fe, S, Cl, Bi, Ba, Zn, Ni, Pb, and Ti decorated the vesicles. Minerals lining the vesicles were identified based on major element peaks in the EDXA spectra and are listed in Table 3. Examples of some of the sublimates imaged by BSE imaging are shown in Figure 1. Various textures, fine compositional zonation, and compositions similar to those described in other studies—from Popocatépetl by Larocque et al. (1998, 2008), Volcano by Fulignati and Sbrana (1998), and Kudryavy by Yudovskaya et al. (2006)—of vesicle-lining minerals and fumarole sublimates indicated formation from a vapor phase trapped within the vesicle.

Etna’s 2002 eruptive products contained an abundance of Fe-Ti oxides and Cu-Fe sulfides within the vesicles. A 20-mm grain of Cu-Au alloy (Fig. 1A), which had a similar composition and anhedral rounded texture to fumarole sublimates from the Kudryavy volcano (Yudovskaya et al., 2006, 2008), was found. A CoZnFe sulfide grain (Fig. 1E) had a very similar size and euhedral texture, composed of randomly oriented blades similar to those pictured in vesicle sublimates from Popocatépetl (Larocque et al., 2008) and fumarole condensates from the Kudryavy volcano (Yudovskaya et al., 2006).

The CuFe sulfide sublimates found at Etna (Fig. 1B, C) had compositions similar to those of the Cu-Fe sulfides reported by Larocque et al. (2008). A porous ball of Cu sulfide was found (Fig. 1D, E) from Etna that appeared to have beehive-shaped outgrowths containing Cu and possibly S, similar to those described by Mavrogenes et al. (2010).

The 1944 eruptive products from Vesuvius contained a mix of sulfide, sulfate, chloride, and oxide sublimates lining the vesicle walls. A Cu sulfide compound in the vesicles showed concentric layers indicative of nucleation and sequential deposition (Fig. 1J). The AgSnFeCuClS (Fig. 1H) and BaS concentric layers indicative of nucleation and sequential deposition and anhedral rounded texture to fumarole sublimates (e.g., Fig. 2). No previous studies have reported on the internal composition and nature of these vesicle-lining alloys. Using epoxy vacuum-impregnated thin sections of the scoria or pumice samples, the small metallic sublimates lining the vesicle walls could be preserved, examined, and analyzed using microanalytical techniques.

The cut sublimates were easily located in thin sections under a microscope with 20× magnification in reflected light and are best classified as alloys because the anions present amounted to less than 1% in most cases (Table 2). We found alloys in thin sections from volcanic products collected at Kilauea, Etna, Stromboli, and Vesuvius, as shown in Table 1. The alloys were found within vesicles usually detached from the wall and were a highly reflective yellow-gold color (Fig. 3). They range in size from a few to 150 μm. The alloys all had a similar appearance, with slight color differences showing variable compositions. Microprobe analysis (Table 2) constrained the compositional bands in the alloys (Fig. 4).

The alloys have never been found on lava surfaces or in the matrix glass but almost always in vesicles found in both glassy and crystallized matrices. Rarely, the alloy grains are found in fractures surrounding the vesicles (Fig. 3D). The alloy grains are commonly found directly adjacent or attached to the vesicle wall, and the curvature of the alloy usually matches that of the nearby vesicle wall (Fig. 3E, F). This suggests that the alloys were originally attached to the vesicle wall and grew into the interior of the vesicle. Many of them became detached from their original growth surface either due to shrinkage of the vesicle (or expansion of the wall) during cooling or during sample collection and preparation (Fig. 3E, F).

Morphology of metallic sublimates

Metallic sublimates come in many shapes (Fig. 4) depending on how the three-dimensional grain was cross sectioned (Fig. 5). Generally, the euhedral sulfides, chlorides, and oxides that decorate the outer surfaces of the sublimates have very distinctive compositions and shapes and are not easily confused with metal alloys.

Compositions of metal alloys

The internal structure and compositions of metal alloys from each of the investigated volcanoes were analyzed using both an electron microprobe and ESEM. Internally, the alloys showed compositional banding. Microprobe spot analyses

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Table 3. Examples of some of the sublimates imaged by BSE imaging are shown in Figure 1. Various textures, fine compositional zonation, and compositions similar to those described in other studies—from Popocatépetl by Larocque et al. (1998, 2008), Volcano by Fulignati and Sbrana (1998), and Kudryavy by Yudovskaya et al. (2006)—of vesicle-lining minerals and fumarole sublimates indicated formation from a vapor phase trapped within the vesicle.

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Table 3. Outer Surface Composition of Metallic Sublimates in Vesicles

| Etna (2002) | Mt. Vesuvius (1949) | Stromboli (2005) | Kilauea (2005) |
|-------------|---------------------|------------------|----------------|
| Cu-Au       | Ba sulfide          | Fe-Cu sulfide    | Bi-Cu          |
| Cu-Fe sulfide | Fe-Ti oxides       | Fe-Cr-Ni        | Ni             |
| Fe-Ti oxides | Cu sulfide         | Au              | Au-Fe          |
| Ba sulfide   | AuCuAg sulfide     | Sn chloride     | Bi             |
| Cu-Fe       | Cu-Fe Oxide        | Pb sulfide      | Fe-Ti oxides   |
| Cu-Fe-Ni    | Cu sulfide         | Cu-Pb-Zn        | Cu sulfide     |
| Ag-Sn-Fe    | Cu-Ni sulfide      | Cu-Zn chloride  | Fe sulfide     |
| Co-Zn-Fe    | Fe sulfide         | Sn-Fe chloride  |                |
| sulfide     | Fe-Ni sulfide      | Na chloride     |                |
|             | Sn chloride        | (halite)        |                |
|             | Ag-Sn-Cu           | chlorosulfide   |                |
|             | Cu-Fe sulfide      |                 |                |
Fig. 1. (A-X) Metal sublimates attached to the vesicle walls of pumice and scoria samples from Etna (A-F), Vesuvius (G-L), Stromboli (M-R), and Kilauea (S-X) volcanoes. BSE images of vesicle-lining materials on broken rock surfaces. In BSE images, darker shades of gray represent glass and silicate minerals while metals are white and were identified based on EDXA spectra. Important surface coatings are labeled.
METALLIC ALLOYS IN VESICLES IN MAFIC VOLCANIC ROCKS

Fig. 1. (Cont.)

Stromboli 2005 Bomb

- CuZn chloride
- CuFeZn sulfide
- SnFe chloride

Kilauea 2005 Flow

- Cu sulfide
- Au
- BiCu

- Fe sulfide

CuFe sulfides
Sn chlorides

Fig. 1. (Cont.)

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within a single grain yield substantially different compositions, which we interpret to be the result of exsolution on the submicrometer scale. Nevertheless, multiple spot analyses of alloys on the microprobe (Table 2), element maps from the microprobe (Fig. 6), and from the ESEM (Figs. 2, 7, 8) revealed three major exsolved components—Co, Cu-Sn, and Ag. Maximum abundances (in wt %) of other trace or minor elements analyzed on the electron microprobe were Fe (3.0), Zn (0.11), As (0.50), Pd (0.05), Pt (0.05), Au (0.05), Hg (0.10), and Pb (0.13), as shown in Table 2.

An element map of an alloy grain from a 2005 Kilauea lava flow displays at least two exsolved bronze components: one Sn rich (5–13 wt %) and the other Sn poor (<5 wt %) (Fig. 7). Microprobe spot analyses suggest considerable variability in the ratio of Cu to Sn (or our inability to resolve each exsolved region during analysis).

A BSE image of an alloy grain from a 2005 pumiceous bomb from Stromboli shows an uncut surface down in the epoxy that represents the alloy’s outer growth surface (Fig. 2). This outer surface had higher concentrations of S and Cl than the interior of the grain.

A BSE image of an alloy grain from the 1944 flows on Vesuvius with ESEM element maps for Cu, Sn, Co, Fe, Ag, and S is shown in Figure 8. This grain was predominantly...
composed of Co, but it is remarkably rich in Ag as well. In low-Co areas, Cu and Sn are strongly correlated. Fe was concentrated in the material coating the alloy grains. The highest concentrations of S and Cl occurred on the brighter portions of the grain that appeared to have a rough texture, which may be representative of an uncut surface thinly coated with epoxy.

The relative abundances of these three components (Co, Cu-Sn, Ag) varied substantially in alloys from the four volcanoes studied. Remarkably, the alloys located in the Kiālauea lava samples were morphologically similar but compositionally distinct from the alloys found in the volcanic products of Vesuvius, Etna, and Stromboli (Fig. 9). Kiālauean alloys were predominantly Cu-Sn (bronze) with little Co and Ag. There is a systematic decrease in the bronze component and an increase in Co in grains from Stromboli to Etna to Vesuvius (Fig. 9). Average Ag abundances peaked at about 3% in Etna and Stromboli samples.

**Metal concentrations in melt inclusions and matrix glasses from Stromboli bombs**

LA-ICP-MS analyses were acquired for the melt inclusions and matrix glasses in pumiceous and scoriaceous bombs from Stromboli, providing information on the abundance of the metals. The analyses showed high concentrations of Cu in the scoriaceous bombs (groundmass glass: 187 ppm [±25, 1 standard deviation], melt inclusions: 189 ppm [±56]) and pumiceous bombs (groundmass: 121 ppm [±12], melt inclusions: 124 ppm [±68]). Cobalt was also abundant in the scoriaceous bombs (groundmass: 25 ppm [±1], melt inclusions: 25 ppm [±2]) and pumiceous bombs (groundmass: 31.0 ppm [±0.2], melt inclusions: 22 ppm [±3]), and the analyses showed a few parts per million of Sn (App. Tables A2, A3).

**Distribution of metal alloys**

The vesicles in the 2005 bombs from Stromboli hosted the largest and most abundant alloys found in our study. In order to better understand the distribution of these alloys in individual samples, the size and number of alloy grains were measured in thin sections under reflected light from both the crystallized interiors and the glassy rims of two types of bombs (pumiceous and scoriaceous) from Stromboli (Fig. 10). The alloy grains range in size from ~2 to 150 μm across. The size distributions were skewed to the right (non-normal distribution), so the Wilcoxon rank-sum test (Keller, 2001) was used to determine if the alloy grain sizes and abundances in the volatile-rich pumiceous bombs were statistically distinct from the degassed scoriaceous bombs. Although the sample size is small, most sample pairs indicated strong evidence that the pumiceous bombs contained more metal alloys of
a larger size than the scoriaceous bombs (Fig. 10). The Wil- 
coxon rank-sum test was also used to compare the alloys in the 
slowly cooled, crystallized interior of the bombs to those in 
the quenched, glassy rinds. The crystallized interiors of both 
types of bombs contained more alloy grains than the glassy 
rinds. However, the test indicated that the size distributions 
of the alloy grains in the bomb interiors were not statistically 
different from those in the crystallized rinds. This could mean 
that the processes forming the metal alloys in the crystallized 
interior of the bomb were the same as the processes forming 
metal alloys in the glassy rind, the only difference being the 
abundance of grains (Fig. 11).

**Discussion**

To explain the genesis of the metal precipitates, the following 
key questions need to be answered: (1) How were the metals 
transported into the inflating vesicles? (2) Why was this spe-
cific set of metals enriched in the fluid phase filling the vesi-
cles? (3) Why did the metals precipitate in elemental form as 
alloys rather than as metal sulfides or oxides? In the following

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**Fig. 4.** BSE images of vesicle walls and Cu-Sn-Co alloys in epoxy vacuum-impregnated thin sections of basalt. (A) Metal alloy 
grains are commonly contoured the same as the vesicles that contain them (Stromboli). (B) A BSE image of an alloy showing 
compositional variation (Stromboli). (C) Alloy with convex surfaces, which follow the contours of the vesicle wall, and a cocks-
comb texture, which is common and visible depending on the orientation in which the grain was cut (Vesuvius). (D) Alloys 
commonly float in the epoxy—a consequence of separation from the vesicle after growth and perhaps during thin-section 
preparation (Stromboli). (E) Alloy showing light and dark compositional bands (Etna). (F) Alloy detached from vesicle wall 
(Stromboli). (G) Alloy floating in epoxy within vesicle (Stromboli). (H) Alloy floating in epoxy within vesicle (Stromboli). (I) 
Alloy showing light and dark compositional bands surrounded by epoxy in vesicle (Vesuvius).
sections we address these points, first by considering metal transport into the vesicles and then by providing a hypothesis that explains the occurrence of the metallic precipitates.

The role of Cl and S in the solubility and transportation of metals

Separation of magmatic volatiles and the portioning of metals into an aqueous phase may occur over a broad range of depths (van Hinsberg et al., 2016). The magmatic volatile phase (MVP) and associated metals can rise through low-viscosity magma or may be transported via magma convection followed by escape to the atmosphere during open-system degassing. We suggest that early formed volatile phases are not the ones trapped in vesicles, the condensation products of which are examined here, because these would likely have sufficient concentrations of H₂S to stabilize metal sulfide rather than metal alloys, due to the strong partitioning of reduced S species into the fluid phase at subvolcanic depths, even from
Rather, the vesicles formed during rapid decompression during or after eruption. As syneruptive formation of vesicles is a rather fast process, both equilibrium thermodynamics and the kinetics of the mass transfer processes must be considered when trying to understand the transfer of elements into the vesicles. First, we focus on the equilibrium partitioning aspect.

Copper, Sn, Ag, and Au are known to be extracted from magmas by exsolving volatiles, which are major contributors to the metal budgets of magmatic hydrothermal deposits.
Unfortunately, very little is known about the partitioning behavior of Co between silicate melts and the MVP, and it is not commonly analyzed in magmatic fluid inclusions. Therefore, we focus our discussion on Cu, Sn, Ag, and Au.

Cu, a major component of most metal alloys described in this study, is known to form stable complexes with both chloride- and sulfur-bearing ligands in magmatic volatiles (Candela and Holland, 1984; Williams et al., 1995; Etschmann et al., 2010; Zajacz et al., 2011; Mei et al., 2013). At a temperature similar to that of the erupted magmas studied here but a higher pressure, Zajacz et al. (2011) concluded that Cu forms stable bisulfide and chloride complexes, with the latter being more significant at the weight percent level of dissolved chloride concentrations. Similarly, studies conducted at lower-temperature hydrothermal and ambient conditions concluded that Cu hydrosulfide complexes predominate only at low temperature and relatively high S/Cl ratios in the fluid phase (Mountain and Seward, 1999, 2003; Louvel et al., 2017). At lower temperatures but more closely matching fluid (vapor) density, Migdisov et al. (2014) found CuCl complexes to be stable and Cu solubility to be an exponential function of $f_{H_2O}$ partial pressure due to increasing hydration numbers with increasing $f_{H_2O}$. Direct fluid/melt partitioning experiments also concluded that both S and Cl may play a role in

| V10-a | V10-b | V10-c | V10-d |
|-------|-------|-------|-------|
| EDX Wt% | Wt% | Wt% | Wt% |
| S     |  3   |  0   |  0   |  0   |
| Cl    |  0   |  0   |  0   |  0   |
| Ag    | 13   |  0   | 16   | 17   |
| Sn    | 12   |  6   |  0   |  6   |
| Fe    |  0   | 46   |  0   |  3   |
| Co    |  4   | 25   | 84   | 46   |
| Cu    | 69   | 23   |  0   | 28   |
| W     |  0   |  0   |  0   |  0   |
| Zn    |  0   |  0   |  0   |  0   |
| Au    |  0   |  0   |  0   |  0   |

Fig. 8. BSE image of cross-sectioned alloy grain from Vesuvius with element maps for Cu, Sn, Co, Fe, Ag, and S. This grain is predominantly Co. In low-Co areas, note the strong correlation of Cu and Sn. Fe is detected in the rind surrounding the alloy. The highest concentrations of S and Cl occur in a sulfide- and chloride-rich crust that can be seen in the brighter portions of the grain.
Cu extraction from magmas (Candela and Holland, 1984; Williams et al., 1995; Simon et al., 2006). The most relevant fluid/melt partition coefficients for mafic magmas were estimated by Zajacz et al. (2012b), who proposed modest Cu partitioning into the MVP (\(D_{\text{Cu fluid/melt}} \approx 1-2\)); however, these numbers were estimated for pressure in subvolcanic magma reservoirs.

The relative enrichment of Au in the alloys compared to the host magma was even higher than that of Cu. Gold in the alloys from Stromboli had a concentration of about 0.01 wt % on average (Table 2) versus 0.001 ppm in the whole rock (App. Table A4), with an enrichment factor of about 100,000. Copper in the alloys from Stromboli had a concentration of about 60 wt % versus 84 ppm in the whole rock, with an enrichment factor of about 7,000. Just like Cu, Au is known to form complexes with both S and Cl in high-temperature, aqueous fluids. However, the stability of complexes formed with sulfur-bearing ligands is much higher than those with chloride in most hydrothermal fluids (Williams-Jones et al., 2009) and even in high-temperature, relatively low density magmatic vapors (Zajacz et al., 2010). Indeed, Zajacz et al. (2012b) proposed \(D_{\text{Au fluid/melt}} \approx 200\) for mafic magmas at \(f_{O_2}\) less than the Ni-NiO buffer (NNO). This may have contributed to the observed relative enrichment of Au being higher than that of Cu.

Silver shows transitional behavior between Cu and Au, because both bisulfide and chloride complexes may play an important role in its solubility in magmatic fluids (Yin and Zajacz, 2018). Simon et al. (2008) determined that Ag partitions \(\approx 100\) times more strongly into the fluid phase than Na in an S-free rhyolite melt-aqueous vapor/brine system, and Ag shows increasing preference for the fluid phase with decreasing pressure. Unfortunately, to our knowledge, no fluid/melt partitioning experiments have been done on Ag using S-bearing fluids.

Very few experimental data exist to assess whether Sn may have efficiently degassed from mafic magmas, as the available studies are restricted to S-free and predominantly chloride- or fluorine-bearing felsic systems (Keppler and Wyllie, 1991; Duc-Tin et al., 2007; Hu et al., 2008, 2009). These studies reported \(D_{\text{Sn}}\), fluid/melt in the range of 0 to 10, with generally increasing values with increasing Cl concentration, which was consistent with the data obtained from coexisting natural fluid and melt inclusions (Zajacz et al., 2008). Additionally, Sn oxides are known to be rather volatile at high temperatures (Lamoreaux et al., 1987; Migdisov and Williams-Jones, 2005). Therefore, though no quantification is possible, our observations suggest that Sn may degas not only from felsic magmas but also from mafic magmas, at least at relatively low pressures.

All things considered, it is apparent that Cu, Au, Ag, and Sn tend to partition into the MVP, however, no experiments resemble the pressure-temperature-composition (P-T-X) conditions of the vesicle formation in the studied mafic magmas closely enough to allow a quantitative estimation of the equilibrium metal concentrations in the gas phase. It is also evident that the presence of either chlorine or sulfur is required to facilitate the transfer of the metals into the volatile phase for most of the metals considered.

**Formation of metal alloys**

Perhaps the most intriguing feature of the precipitates in the vesicles was that the metals were present in their native form and were coated with only a thin layer of sulfides or oxides (Fig. 5), as opposed to the oxides and sulfides that dominate...
magmatic-hydrothermal ore deposits and high-temperature condensates of fumarolic gases in silica tubes (Bernard et al., 1990; Hedenquist et al., 1994; Taran et al., 2000; Africano et al., 2002; Yudovskaya et al., 2006). This observation indicates that the fugacities of oxygen and sulfur in the vesicles of the studied rocks were lower in the gas phase than during subvolcanic, quiescent degassing.

To put constraints on maximum oxygen and sulfur fugacities in the vesicles, we conducted thermodynamic calculations to predict the phase boundaries between native metals, metal oxides, and metal sulfides. The calculations were done for the Cu and Co end-member systems, because these are the two most abundant metals in the alloys. We assumed either 1 or 30 bar as end-member internal pressures, because the low viscosities of these mafic melts would likely not allow the buildup of much higher pressure in the vesicles after eruption.

In Figure 12, we show the phase diagram calculated from basic thermochemical data. It is apparent that the mole fraction of S allowed to be present in the volatile phase without stabilizing metal sulfides is dependent on oxygen fugacity (with a minimum at the H₂S to SO₂ transition), temperature, and pressure. The effect of pressure is mainly due to the fact that higher pressure yields higher $f_{\text{H}_2\text{O}}$, which shifts the $\text{SO}_2 + \text{H}_2\text{O} = \text{H}_2\text{S} + 1.5\text{O}_2$ reaction to the right. It is apparent that...
the presence of metallic Cu is feasible over a very wide range in $f_{O_2}$, as the Cu-Cu$_2$O buffer reaction is only at about $f_{O_2} = NNO + 4$. However, over much of the $f_{O_2}$ range, only 0.01 to 1.00 mol % of S was allowed to be present in the gas phase, except at above NNO + 1, which is a more oxidizing condition than that of most magmas studied here. The absence of CoS$_{0.89}$ allowed for a somewhat higher concentration of S in the volatile phase than the absence of Cu$_2$S, again with the values strongly dependent on $f_{O_2}$, with a minimum at about NNO – 1.5. The maximum concentration of S outside the sulfide stability field decreased about one order of magnitude in response to a temperature drop from 1,100°C to 900°C in both systems. This is consistent with the observed narrow sulfide overgrowth on some of the alloy grains.

The allowed range of S concentrations without the stabilization of metal sulfides was somewhat lower than what is typically found in syneruptive gases discharged by mafic volcanoes (Williams-Jones and Heinrich, 2005). This mismatch may be explained by kinetic limitations. The diffusivity of S in the silicate melt is about four orders of magnitude lower than that of H$_2$O (Baker et al., 2005; Freda et al., 2005; Zhang et al., 2010), and therefore it is likely that during rapid syneruptive vesicle growth, the amount of S effectively transferred to the gas phase is less than expected from equilibrium partitioning.

**Fig. 11.** Model of the processes at Stromboli that may be involved in the formation of the metal alloy grains. The pumiceous bombs rich in metal alloys likely originate from a deeper magma that is more primitive and volatile rich. The scoriaceous bombs (alloy poor) originate from a shallower magma that is relatively degassed. (A) When the bombs are erupted, volatiles and the metals they complex with (metal-rich sulfides and chlorides) move toward inflating vesicles. (B) During cooling, the metals are reduced (perhaps by the addition of H$_2$ gas) to form the metal alloy grains; H$_2$S and HCl (products of the reducing reactions) fill the vesicle. (C) Eventually, the reducing environment in the vesicle disappears as H$_2$ is consumed. Then, the excess metal-rich sulfides (and chlorides) condense onto the outer surface of the metal alloys. Pressure of scoria magma from Métrich et al. (2001). Pressure of golden pumice magma and temperature from Di Carlo et al. (2006).
The higher total concentration of S in volcanic gases is likely due to the onset of volatile exsolution at depth before the eruption, resulting in a population of more S-rich bubbles in the magma, the rise of which has been proposed to explain the excess sulfur phenomenon in volcanic eruptions (Westrich and Gerlach, 1992; Wallace and Gerlach, 1994; Pasteris, 1996). However, because of their small sizes and closed outlines, the vesicles studied here are thought to have nucleated only during eruption and emplacement.

In addition to S, Cl may promote the transfer of most metals found in the precipitates into the exsolving volatile phase. The diffusivity of chlorine in silicate melts is about two to three orders of magnitude higher than that of S and only one to two orders of magnitude lower than that of water (Freda et al., 2005; Alletti et al., 2007; Zhang et al., 2010). This suggests that during rapid syneruptive degassing, it is feasible that the volatile phase filling the vesicles is characterized by much higher Cl/S ratios than equilibrium partitioning would dictate. Although the partition coefficient for Cl between magmatic volatiles and mafic-intermediate melts is generally <5 even at subvolcanic pressures (Stelling et al., 2008; Alletti et al., 2009; Zajacz et al., 2012a), this, combined with the measured Cl concentrations, still predicts thousands of parts per million Cl in the volatile phase. Considering the small volume fraction of alloy grains in the vesicles, it is conceivable that this amount of Cl along with the relatively low S concentrations was sufficient to extract the metals from the silicate melt.

Assuming a typical vesicle diameter of 1 mm and a pure Cu sublimate (or summation of grains) that is 2 × 10 × 20 μm in size, the concentration of Cu in a vapor that completely filled the vesicle would have only been 7 ppm. The vapor/melt partition coefficients found by Simon et al. (2006) for Cu were 316 (±22) for an S-bearing rhyolite and 63 (±31) for an S-free system, which, combined with a whole-rock concentration of 100 ppm of Cu, would yield an equilibrium value of about 6,300 to 31,600 ppm of Cu in a magmatic vapor. Thus, the metal concentrations in vapors implied by typical sizes are not excessive. Closed-system partitioning of Cu into a vapor appears feasible.

When discussing kinetically limited degassing, one must also consider the diffusivities of the metals themselves. Using the compilation by Zhang et al. (2010) on element diffusivities in silicate melts, our best estimates for a nearly anhydrous mafic melt at around 1,100°C expressed in m²/s are as follows: lnDs ≈ –28, lnDpb ≈ –28, lnDco ≈ –26, lnDaz ≈ –26, lnDag ≈ –23, and lnDcu ≈ –21. As no experimental data is available for Cu and Ag, these values were estimated by using analogy to Na and Li, respectively, based on the identical charge and nearly equal ionic radius of Ag⁺/Na⁺ and Cu⁺/Li⁺ pairs. These values were higher overall than the estimated value for S (lnDs ≈ –30 m²/s) but partly overlapped with that of Cl (lnDcl ≈ –25.5 m²/s). Therefore, it is conceivable that the metals and Cl are simultaneously transferred into the gas phase while S lags behind. Absolute concentrations, of course, would depend on the composition of the melt.

However, it appears that diffusion-limited mass transfer does not explain separation between chloride-complexed elements that occur as (Cu, Ag, Co) alloys and those (Pb, Zn, Fe) that form sublimes coating the alloys (Table 1). One must consider not only the transfer of the metals into the gas phase but also their precipitation mechanism. Metal precipitation is likely induced by decreasing temperature, pressure, and potentially fO₂. Unfortunately, there is not sufficient experimental data to put any quantitative constraints on the effect of pressure and temperature on the solubility of the metals of interest at the relevant conditions. Overall, metal solubility decreases with decreasing fO₂, because the metals first need to be dissolved in a fluid phase, independent of the
complex formation of ligands. In the case of chloride complexes, the dissolution reaction can be generalized as follows:

\[ M_{(s)} + n \text{HCl}_{(g)} = M\text{Cl}_{(g)} + n/2 \text{H}_{2}(g), \]  

where \( M \) stands for metal with a valence state of \( n \). The value of \( f_{\text{H}_2} \) is inversely linked to \( f_{\text{O}_2} \) through the water decomposition reaction.

It is clear from equation (1) that increasing \( f_{\text{H}_2} \) and therefore decreasing \( f_{\text{O}_2} \) will promote metal precipitation. In a magma, \( f_{\text{O}_2} \) is mostly imposed by the ratio of heterovalent elements in various oxidation states, most notably \( \text{Fe}^{2+}/\text{Fe}^{3+} \) ratios, whereas \( f_{\text{H}_2} \) will be controlled by \( f_{\text{H}_{2}O} \) and \( f_{\text{O}_2} \). Hydrogen is known to diffuse faster than \( \text{H}_2 \) in silicate melts (Zhang and Ni, 2010), and therefore it is conceivable that upon fast vesicle growth, hydrogen is preferentially enriched in the vesicle relative to \( \text{H}_2 \)O, while the \( \text{Fe}^{3+}/\text{Fe}^{2+} \) ratio increases in the residual silicate melt. As the gap between the diffusivity of \( \text{H}_2 \) and \( \text{H}_2 \text{O} \) increases with decreasing temperature, it may be possible that \( \text{H}_2/\text{H}_2 \text{O} \) ratios increase with decreasing temperature in the gas phase trapped in the vesicles, which may promote metal precipitation.

The changes in oxidation state do not need to be large (Fig. 12), and thus the vapor would not need to be pure \( \text{H}_2 \) but just have an elevated \( \text{H}_2/\text{H}_2 \text{O} \) ratio. The presence of Co-rich alloys in some of the vesicles shows that the \( f_{\text{O}_2} \) in the vesicles was near or below the Co-CoO buffer (\( \text{NNO} - 1.5 \)), which is near that of the magmas (\( \text{NNO} - 2 \) to \( \text{NNO} + 2 \)) involved here (Chou, 1987). The same holds for Cu that would be stable at magmatic \( f_{\text{O}_2} \) if the fugacity of sulfur was low enough (Fig. 12). Elements expected to be transferred into the vesicles but missing from the alloy grains (e.g., Fe, Pb, and Zn) may have lower redox potentials, meaning that they tend to remain oxidized despite the higher \( f_{\text{H}_2} \), helping them to stay in solution. An indication of this, for example, is that the Fe-FeO buffer is at about 3 log units lower \( f_{\text{O}_2} \) than the Co-CoO buffer (Chou, 1987). The narrow sulfide overgrowth on the alloy grains (Fig. 11) may be due to the fact that the sulfide stability fields extend to lower S concentrations in the fluid phase at constant \( f_{\text{H}_2} \) as discussed above (Fig. 12), or potentially due to decreasing \( f_{\text{H}_2} \) and thus increasing \( f_{\text{O}_2} \) induced by the consumption of \( \text{H}_2 \) during metal alloy precipitation.

Another possible mechanism for formation of metallic alloys in vesicles was suggested by the works of Mungall et al. (2015) and Knipping et al. (2015). They suggested that blebs of immiscible sulfide melt form and then adhere to bubbles; the sulfides could then be dissolved into the bubbles and released through volcanic vents, thus explaining observations made by Nadeau et al. (2010), Keith et al. (1997), and Larroque et al. (2000). If some of that metal-laden vapor was trapped as a vesicle, eventual precipitation on the walls might ensue. This might explain the concentric layering (Fig. 1) where an alloy rim (altered material) covers fresh material (from an entrapped sulfide bleb). It is possible that this mechanism might explain the transport and concentration of some metals with high solubilities in immiscible sulfides (Cu, Ag, Au), but it doesn’t explain why Sn and Co, which have very low solubilities in sulfide melts, would also be concentrated.

A third mechanism to form alloy-filled vesicles also bears consideration. Perhaps the metals were transported in hydrothermal fluids (rather than in low-density vapors) as suspended or colloidal particles, transferred to the vesicles, and eventually aggregated as metallic clusters. This possibility is hard to address in the absence of information on the behavior of suspended particles or colloids at magmatic conditions, but it seems unlikely based on the textures and distributions observed. This physical mechanism of transport should leave deposits along the passageways for the fluids, for which we see no evidence. However, the mechanism begs the question as to how the particles of Cu-Au-Ag-Sn-Co formed in the first place. Why weren’t particles of other metals (e.g., Ti, V, Zn) also formed and transported?

It seems more reasonable to conclude that the metals were complexed with ligands and dissolved into low-density fluids that formed vesicles. The nature of the precipitated metals (which are known to form complexes with Cl, S, etc.) better accords with this process. In general, we conclude that the unexpected but apparently widespread presence of Cu, Co, Sn, and Ag alloy precipitates within the vesicles of volcanic rocks is a result of kinetically controlled mass transfer into the vesicles and such induced element separation upon volcanic eruption (Fig. 11).

Economic implications of metal alloys and ore deposits

The low-pressure, kinetically controlled nature of the processes proposed here as responsible for the precipitation of the metal alloy grains does not allow for making direct links to magmatic-hydrothermal ore-forming processes, as these typically occur at greater pressure and much longer time scales. However, there are a few key observations that may indirectly enhance our understanding of ore metal extraction from magmas and raise questions that could be addressed by future research.

One of these is the surprisingly high mobility of Sn, Co, Cu, Au, and Ag in low-density fluids at temperatures characteristic of mafic magmas. Although Cu, Ag, and Au have been shown to be soluble in low-density vapors (Zajacz et al., 2010, 2011; Migdisov et al., 2014; Hurtig and William-Jones, 2015), no data are available for Sn and Co. Some researchers have suggested that the ratios of metals such as Cu, Au, and Ag present in magmatic sulfides are inherited by ore deposits from the associated magmatic system (Halder et al., 2005; Stavast et al., 2006; Nadeau et al., 2010, 2016; Nadeau, 2015). The model invoked in these papers is that the ultimate source of most of the metals and sulfur in large porphyry systems is from underplated degassing mafic magma. Although such mafic magmas would degas at a much greater depth, the increase of pressure and thus \( f_{\text{H}_2} \) would only further increase the solubility of Cu and Au (Hurtig and William-Jones, 2014; Migdisov et al., 2014) and potentially other metals as well. Thus, the alloy precipitates observed in this study support the hypothesis that mafic magmas are able to donate ore metals to more overlying felsic systems.

The other interesting observation is the preferential degassing of \( \text{H}_2 \) into the vesicles, leading to reducing conditions adequate for precipitating metal alloys rather than oxides. A corollary of this would be the oxidation of the residual magma during nonequilibrium degassing, as demonstrated by Burnham (1975), Stolper (1982), Mathez (1984), and Waters and Lange (2016). It remains unclear if this may be a viable mechanism of magma oxidation under certain conditions, affecting the potential for magmatic-hydrothermal ore genesis.
Conclusions

Newly discovered alloys are present as scattered grains along vesicle walls in several volcanic systems from contrasting tectonic settings. Our finding of Cu–Sn–Co–Ag metal alloys in volcanic rocks from Kililaeua, Etna, Vesuvius, and Stromboli suggests that metal partitioning to the vapor phase exsolving from mafic magmas at low pressure is a common process. It is likely that the unexpected but apparently widespread presence of Cu, Sn, Co, and Ag alloy precipitates within the vesicles of volcanic rocks is a result of kinetically controlled mass transfer into the vesicles at high temperatures (>900°C) and low pressure (a few bars).

The conditions under which the metal alloys form are likely varied, but there are several factors that seem to be especially important in their formation. We hypothesize that ore metals along with sulfur and chlorine are transferred into syneruptively formed vesicles within cooling lava. Kinetically induced preferential enrichment of H₂ over H₂O and S in the vesicles induces the precipitation of metal alloys rather than sulfide minerals, whereas a subsequent drop in temperature and/or potential increase in fO₂ leads to the formation of a narrow sulfide overgrowth on the alloy grains.

Chlorine and sulfur are especially vital and likely reflect the importance of these elements in larger-scale ore deposits. We suspect that although the number of alloy grains in vesicles is sparse, they are widespread and will soon be recognized in many basaltic systems.

Acknowledgments

The authors would like to thank Keiko Hattori, Dana Griffen, David Tingley, Claudio Scarpati, Jani Radebaugh, and Don Swanson for their help, observations, and insights on this project. We also appreciate the invaluable assistance from Mike Standing, Jeff Furrer, and all those in the BYU microscopy lab during ESEM analysis. The authors extend thanks to Elizabeth Ryscamp, Megan Pickard, and Annika Quick for helping collect the many samples needed. Thanks is also given to Wagner Petrographic for their excellent sample preparation. The authors are also grateful for the help of family in attending to young children during the editing process. Finally, the authors would also like to thank Larry Meintert, Nicole Hurstig, Oliver Nadeau, and Anthony E. William Jones for their insightful and pertinent reviews, which have helped make this manuscript more robust. This publication has been supported in part by a research grant from the SEG Foundation.

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