# Sulfide breakdown controls metal signature in volcanic gas at Kawah Ijen volcano, Indonesia

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## ARTICLE INFO

## ABSTRACT

Immiscible sulfide liquid is thought to be an important intermediary in volcanic degassing of sulfur and chalcophile elements by concentrating and transferring metals from magma to hydrous fluid. Here, we track the interaction of sulfide liquid with a fluid exsolving from basalt at Kawah Ijen volcano in Indonesia. As in many other volcanic systems, neither sulfide nor fluid is preserved. Instead, the reaction is recorded in changes in metal and sulfur concentrations in the melt during magma ascent, and shows a two-stage evolution; deep-seated progressive breakdown of sulfide during which metal concentrations in the melt are largely controlled by the sulfide, followed by fluid–melt partitioning controlling metal concentrations at shallow depth once this sulfide has been exhausted. Present-day fumarole gases have similar Zn/Cu, Pb/Cu and Mo/Cu ratios to the reconstructed sulfide, but are enriched in Tl, As and Sb. These enrichments are also observed in melt inclusions in the most recent dacitic deposits at Kawah Ijen. This suggests that the fumarole gases are sourced from a deep, degassing sulfide-saturated basalt, preserved in Zn/Cu, Pb/Cu and Mo/Cu ratios, which subsequently interact with a shallow dacitic melt that enhances Tl, As and Sb emissions.
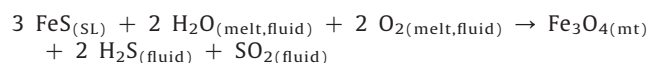
## 1. Introduction: Metals in magma

Volcanic emissions account for a sizable fraction of the global metal flux to the Earth's surface and atmosphere (e.g. Lepel et al., 1978; Pennisi et al., 1988; Hinkley et al., 1999). Porphyry and epithermal ore deposits are spatially and temporally closely related to (ancient) magma reservoirs, indicating an important sub-surface flux of metals from magmatic systems, although the precise nature of this link remains a matter of debate (e.g. Hedenquist and Lowenstern, 1994; Arribas et al., 1995; Hattori and Keith, 2001; Williams-Jones and Heinrich, 2005). Both in volcanic emissions and ore deposits, the medium transporting the metals is likely a fluid, whether one- or two phase (in the following, we will use *fluid* for the volatile phase released by the magma and present at depth, whereas *gas* will refer to surface emissions). The ultimate source of the metals, however, is the magma, be it during leaching of solidified magma or by direct release in magmatic processes such as degassing. Thus, it is crucial to study the mechanisms by which metals become concentrated in a magmatic phase; an enrichment that can lead to a punctuated release and a potential for ore formation.

Many metals, including the high mass post-transition metals (e.g. Sb, Tl, and Pb), are relatively incompatible in the main crystallizing phases, e.g. olivine, pyroxene and plagioclase, and, therefore, tend to concentrate in the melt. However, some (e.g. Cu, Ni, Mo) are commonly compatible in accessory phases such as oxides and sulfides, and fluid, and it is the timing of crystallization and segregation of these phases, or their subsequent breakdown, that determines the ore-forming potential of a magmatic system (Mustard et al., 2006; Simon et al., 2008; Jenner et al., 2010).

Of particular interest is the exsolution of an immiscible sulfide liquid (SL) from the silicate melt. These immiscible sulfide liquids have high partition coefficients for metals and are a major repository of these elements, diminishing their availability to degassing (e.g. Keith et al., 1997; Halter et al., 2002). However, the stability of sulfide liquid is sensitive to changes in the composition and redox state of the melt, and to magma degassing drawing away volatile sulfur species, as can be described by a reaction of the general form (after Larocque et al., 2000; Nadeau et al., 2010):

$$3\ FeS_{(SL)}\ +\ 2\ H_2O_{(melt,fluid)}\ +\ 2\ O_{2(melt,fluid)}\ \rightarrow\ Fe_3O_{4(mt)}\ +\ 2\ H_2S_{(fluid)}\ +\ SO_{2(fluid)}$$

$O_2$ is used here to represent the oxidizer, but given that this is likely to be Fe, the reaction can also be represented as:

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$$3 \, FeS_{(SL)} + 2H_2O_{(melt,fluid)} + 24 \, FeO_{1\frac{1}{2}(melt)} \rightarrow 9 \, Fe_3O_{4(mt,melt)} + 2 \, H_2S_{(fluid)} + SO_{2(fluid)}$$

Note that the consumption of ferric Fe will be (in part) compensated by preferential uptake of ferrous Fe by olivine and pyroxene.

The above reaction results in the formation of Fe-oxide, commonly magnetite, which is a more limited repository of metals such as Pb, Tl, As and Cu. These metals must, therefore, either re-enter the melt, or partition into the fluid phase. This process has been observed directly at Merapi volcano, where sulfide globules were quenched in the process of reacting with a fluid to produce magnetite (Nadeau et al., 2010). At Merapi, as in the Bajo de la Alumbrera porphyry ore deposit (Halter et al., 2002), the metal ratios in the original sulfide are similar to those of fluid samples, indicating that the fluid becomes the host for the metals released in sulfide breakdown, and, moreover, that the metal signature of the sulfide is transferred to the fluid.

In this study of Kawah Ijen volcano in Indonesia, we use the compositions of melt inclusions trapped at a range of depths in the magmatic system to reconstruct the role of sulfide liquid in controlling metal concentration and release, and compare these results to the compositions of active fumarole emissions.

## 2. Kawah Ijen volcano

Kawah Ijen volcano is the only currently active volcano in a group of volcanoes clustered in, and on the flanks of, the Pleistocene Ijen caldera, located on the eastern tip of the island of Java in Indonesia. It last erupted juvenile material in 1817, although the summit crater lake has had more recent phreatic activity, and is currently (August 2012) in a state of unrest (Delmelle et al., 2000; Smithsonian Institution http://www.volcano.si.edu). Continuous passive degassing takes place from fumarole vents located on a sulfur-coated hill on the shore of the lake (see Fig. 1a).

Kawah Ijen has mostly erupted basaltic to andesitic material, including scoria and lava flows. The most recent basaltic deposit is a well exposed, up to a meter thick unconsolidated scoria layer that is intersected at several locations on the outer flanks of the volcano (Vigouroux, 2011; Vigouroux et al., 2012). More recently, dacitic tephra was erupted, which contains both dense and vesicular bombs up to 1 m in diameter. Evolved material has further been recovered from the surface of the active fumarole, which potentially hides a lava dome (van Hinsberg et al., 2010b). More detailed information on the Ijen caldera and Kawah Ijen systems is available in Kemmerling (1921), Delmelle and Bernard (1994, 2000), Delmelle et al. (2000), Takano et al. (2004), Handley et al. (2007), van Hinsberg et al. (2010a,b), and Vigouroux et al. (2012).

## 3. Methodology

### 3.1. Melt inclusions

Melt inclusions hosted by olivine and clinopyroxene phenocrysts from the most recent basaltic scoria layer, as well as melt inclusions hosted by clino- and orthopyroxene from dacitic pumices, form the
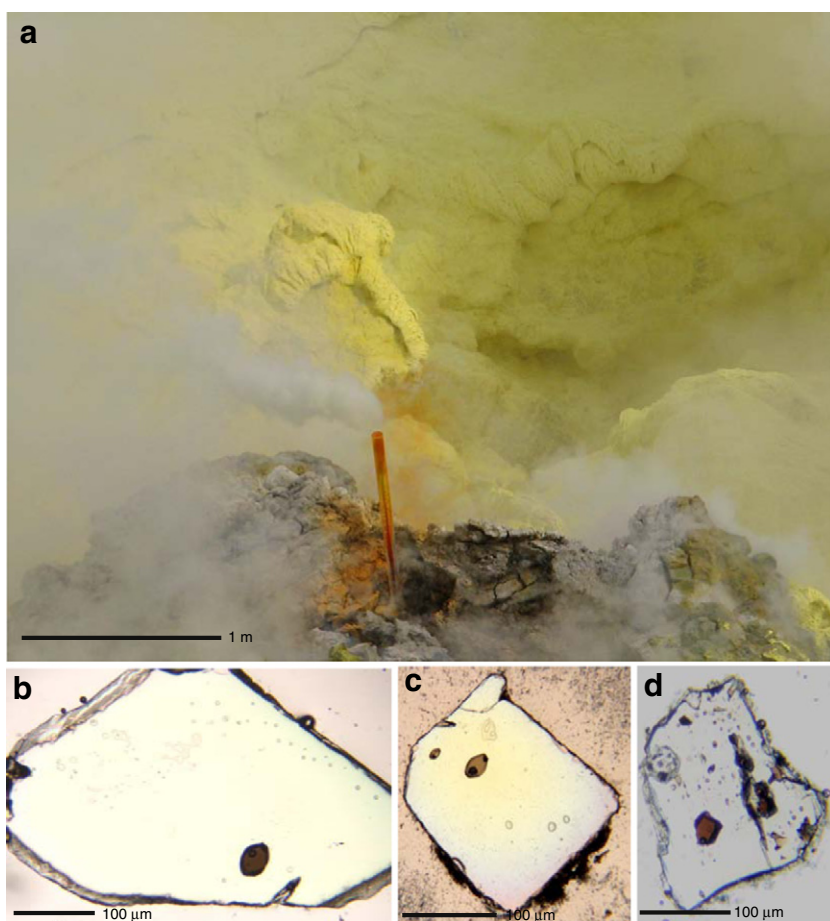


**Fig. 1.** One of the sample locations of high temperature fumaroles at Kawah Ijen (a) and typical melt inclusions in olivine (b & c) and orthopyroxene (d). Gas samples were taken at high flow fumaroles devoid of any precipitates around the vent. The vent shown emits gas at >450 °C (1 meter quartz tube gives scale).