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Origin and fate of sulfide liquids in hotspot volcanism (La Réunion): Pb isotope constraints from residual Fe–Cu oxides

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Abstract

Immiscible sulfide liquids in basaltic magmas play an important role in trace metal transport and the sulfur budget of volcanic eruptions. However, sulfides are transient phases, whose origin and fate are poorly constrained. We address these issues by analyzing sulfide destabilization products preserved in lavas from La Réunion Island. Iron oxide globules and coatings, typically 20–80 µm in size, were found to occur in vesicles of differentiated lavas from Piton des Neiges, and recent pumice samples from Piton de la Fournaise. Field and mineralogical evidence indicates that the iron oxides are syn-eruptive phases not resulting from hydrothermal processes. Samples were first studied by Scanning Electron Microscopy. The globules were separated, whereas the smaller spherules and coatings were concentrated by magnetic sorting and acid leaching, and samples were processed through wet chemistry. The Fe oxide phases comprise 49–74 wt.% Fe, 26–40 wt.% O, and up to 6 wt.% Cu, 811 ppm Ni, 140 ppm Bi, and 8.5 ppm Pb. Compared to the host lava, Cu, Ni, and Bi are enriched by a factor of 10^1–10^3. Systematic Pb isotope disequilibrium (between 500 ppm and 2.9% for $^{206}Pb/^{204}Pb$) exists between Fe oxides and host rocks, with Fe oxides generally displaying less radiogenic ratios. Unradiogenic Pb is a typical signature of sulfide, which tends to concentrate Pb, but not its parent elements U and Th. Thus, both the chemical and isotopic compositions of the vesicle-hosted Fe oxides suggest that they are more or less direct products of the destabilization of immiscible sulfide liquids. Although Pb dominantly partitions into the gas phase during sulfide breakdown, the original Pb isotope signature of sulfide is preserved in the residual oxide. The composition estimated for the parent sulfides ($^{206}Pb/^{204}Pb = 18.20$–$18.77$, $^{207}Pb/^{204}Pb = 15.575$, and $^{208}Pb/^{204}Pb = 38.2$–38.8) precludes a genetic link with the La Réunion plume, and suggests a lithospheric or crustal origin.

It is estimated that magma ascent velocities at Piton de la Fournaise are high enough to counterbalance the settling velocities of millimeter-size sulfides. Despite their high density, sulfide liquids are thus transferred upward during eruptions and their destabilization contributes to SO_2 emanations. Assimilation of foreign sulfides from the lithosphere can explain why SO_2 emissions sometimes (e.g., during the April 2007 eruption) exceed those predicted from the S content of melt inclusions.

Keywords: Sulfide; Magma degassing; Pb isotopes; Piton de la Fournaise

1. INTRODUCTION

There is natural and experimental evidence that many pre-eruptive basaltic magmas are sulfide saturated (Métrich and Clochiatti, 1996; Jugo et al., 2005). Sulfide exsolution plays an important role in maintaining low

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concentrations of dissolved sulfur (ca. 1400 ppm at Fayalite-Magnetite-Quartz (FMQ) redox buffer, Jugo et al., 2005) and preventing SO_2 accumulation (Wallace and Edmonds, 2011). However, sulfide saturation makes the sulfur budget of pre-eruptive magmas difficult to estimate because both the amount of exsolved sulfide and the fate of sulfides are poorly constrained. Sulfide liquids are generally scarce in sub-aerial lavas, and mostly occur as heterogeneous secondary Fe–Cu–Ni sulfide globules in olivine melt inclusions (Clocchiatti et al., 1979; Di Muro et al., 2014) and in quenched lava samples (Moore and Calk, 1971; Stone and Fleet, 1991). It thus remains unclear whether sulfide saturation is a secondary process, or if it is an active process in high temperature melts producing early S depletion in the plumbing system (Mavrogenes and O'Neill, 1999; Collins et al., 2012). The fate of immiscible sulfides during magma ascent, eruption and degassing is at the heart of this issue: because sulfide liquids are denser than silicate melt, they are expected to settle gravitationally and accumulate in the fractionated solid phase, thus escaping the degassing process. For instance, it is estimated that settling sulfide liquids represent 20–90% and 50% of the sulfur budget at Piton de la Fournaise (La Réunion) and Grimsvötn (Iceland) volcanoes, respectively (Collins et al., 2012; Sigmarsson et al., 2013). Alternatively, sulfides may ascend, possibly attached to gas bubbles (Mungall et al., 2015), and, following magma oxidation, dissolve into the silicate melt, or destabilize into Fe oxides and a fluid phase to which trace metals are transferred (Clarke, 1911; Larocque et al., 1998, 2000; Di Muro et al., 2008; Berlo et al., 2014). The importance of such processes in controlling chalcophile element transport and ore deposit formation in subduction zone settings is well established (Sun et al., 2015; Nadeau et al., 2010, 2013; Lee et al., 2012).

It is estimated that mantle sulfide remains a solidus phase until ca. 20% partial melting (Rehkämper et al., 1999), although this value depends on the sulfur content of the mantle, the oxidation state and the melt composition (O'Neill and Mavrogenes, 2002). It is likely that low degree melts produced in intraplate settings are initially in equilibrium with residual sulfide. However, because the solubility of sulfide in silicate melts increases with decreasing pressure, melts will evolve away from sulfide saturation during ascent (Mavrogenes and O'Neill, 1999; Hart and Gaetani, 2006). A major implication is that these sulfide undersaturated melts will tend to assimilate genetically unrelated sulfides as they rise through the lithosphere and crust (Di Muro et al., 2008; Hart and Gaetani, 2006). Sulfides trapped in abyssal peridotites display large Pb and Os isotopic variations (Harvey et al., 2006; Burton et al., 2012; Warren and Shirey, 2012; Blusztajn et al., 2013) that record a long history of storage and/or recycling. Assimilation of such sulfides by ascending plume melts is expected to strongly influence the S budget of primary magmas as well as their Pb and Os isotope signatures (Hart and Gaetani, 2006).

Réunion Island volcanism (Indian Ocean) samples a sulfide saturated magmatic reservoir (Métrich and Clochiatti, 1996; Upton et al., 2000), and, as elsewhere, sulfides are rarely transferred to and/or preserved in the erupted lavas. Common occurrences of sulfide globules have been reported in the interstitial glass of wherlitic and gabbroic cumulates entrained during a major explosive event of Piton de la Fournaise 4700 years ago, which produced the Bellecombe Ash deposit (Upton et al., 2000), raising the possibility that sulfides accumulate in the plutonic roots of the volcano (Collins et al., 2012). However, these globules are too Ni-rich to be in equilibrium with the evolved glasses, and contain less S (S <38 wt.%) than sulfides formed in melt inclusions by post entrapment processes (S >45 wt.%). Furthermore, Di Muro et al. (2014) noted that sulfur and chalcophile element co-variations in melt inclusions from the April 2007 eruption are consistent with melt degassing, without major contributions from sulfides. To decipher whether sulfides sink or contribute to SO_2 emanation, this study tracks sulfide fingerprints in erupted lavas, in particular in quenched samples where sulfide remnants are best preserved (Larocque et al., 2000). Our approach relies on Pb isotopes, which are expected to remain unfractionated during sulfide destabilization, although a large fraction of the lead present in sulfide is transferred to the fluid and gas phases (Berlo et al., 2014). The Pb isotopic composition of sulfide destabilization products might also provide information on the origin and history of the parent sulfides.

2. SAMPLES AND METHODS

A first sample (PDN17) was selected for this study based on the abundance of iron-rich globules in vesicles. This sample belongs to the 350–230 ka old differentiated series of Piton des Neiges, where extensive magnetite fractionation might have triggered massive sulfide exsolution (Collins et al., 2012). This is a plagioclase-phyric basalt with 4.0 wt.% MgO, 18.85 wt.% Al_2O_3 and 45.8 wt.% SiO_2 (Smietana, 2011). Loss on ignition (0.68) is within the range reported for fresh Réunion samples. Other samples are from the very recent (2010–2015) eruptions of Piton de la Fournaise. Their compositions are transitional between the tholeitic and alkali fields, as are most samples erupted since 0.5 Ma, and show little variability (MgO between 6.2 and 6.7 wt.%). This study focuses on air-quenched spatters; artificially quenched samples were not considered because they are potentially contaminated with the iron-made sampling tools. All samples were collected during eruptions, with the exception of samples 141118-x, which were collected five months after emplacement. All spatters have negative loss on ignition (from −0.9 to −0.3) indicating that samples are not oxidized. A subset of 2014 samples was studied for texture and crystal content (Gurioli et al., 2015). They include, in the order of decreasing density and crystal content, spiny scoria, fluidal scoria, low-density fluidal scoria and golden pumice. The low-density fluidal and golden textures reflect less degassed magmas that ascended and cooled rapidly.

Samples were surveyed by Scanning Electron Microscopy (SEM) operating in Backscattered Electron (BSE) and Secondary Electron (SE) imaging modes. Semi-quantitative compositions of iron-rich phases lying on vesicles walls were determined using Energy Dispersive