

Flotation of magmatic minerals

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Iron-rich, dense magmatic phases such as magnetite and sulfide liquids might be expected to undergo efficient gravitational settling in magma reservoirs in the crust, which sequesters the iron and volatiles in cumulates, impacting the redox state of the system and the availability of these elements for volcanic outgassing and formation of ore deposits. The locus of fractionation through settling has important implications: if sulfides are not sequestered by fractionation in the lower crust, sulfur- and metal-rich deposits such as Ni–Cu–PGE (platinum group element) ore bodies may be generated in the upper crust (Naldrett, 1999), in which sulfides and magnetite phases are arranged in concentrated layers by crystal settling, or disseminated through in-situ crystallization.

Magnetite and sulfide liquids, are, however, among the few phases wetted by low-density magmatic fluids, with important consequences for their dynamical behavior. These phases may become buoyant by the attachment of a low-density vapor bubble during magma degassing, increasing the potential for shallow crustal segregation and atmospheric outgassing of volatiles and associated metals.

Magnetite is a liquidus phase of water-rich, relatively oxidized arc magmas. Bubbles nucleate on magnetite crystals with a high wetting angle (Gardner and Denis, 2004; Hurwitz and Navon, 1994), making the crystal-bubble-melt configuration energetically favorable over bubble-melt and crystal-melt configurations: this is heterogeneous nucleation. The bulk density of the magnetite-bubble aggregates, which may harvest more bubbles as they move through the melt, varies with pressure, the relative sizes of magnetite and bubbles, and the volatile content of the magma. A range of complex behaviors may result. Magnetite-bubble aggregates could be negatively buoyant, so that magnetites sink into crystal piles and bubbles are resorbed. Rising into the crust, the aggregates may become buoyant as the mass of the fluid bubbles increase and thus rise relative to the melt. The aggregates might segregate and accumulate in a tectonically mediated accommodation zone or at a density interface.

Mineral flotation mechanisms similar to those used in industrial ore processing (Matveev and Ballhaus, 2002), were theoretical in natural systems until recently. In this issue of *Geology*, Knipping et al. (2015, p. 591) present a model to account for “Kiruna-type” iron oxide–apatite (IOA) deposits. These magnetite-rich (~90% modal) deposits have been interpreted to be formed from immiscible Fe-rich liquids (Nystrom and Henriquez, 1994) or in a hydrothermal system (Barton, 2014). Fe and O isotopic evidence suggests that the magnetite cores crystallized from a silicate liquid, with only the rims reflecting interaction with hydrothermal fluids (Knipping et al., 2015). The key question is how magnetites become segregated and concentrated. The geochemical trends in the magnetites support the hypothesis that they formed in vapor-saturated magma. The aggregates grow by coalescence and sweeping up more magnetites, forming a buoyant suspension in which the magnetite chemistry becomes controlled by the aqueous fluid phase wetting the crystals. This phase contains sufficient Fe (complexed with chloride) to precipitate hydrothermal magnetite on the crystal rims. Local tectonics influence the dynamic behavior of the suspension, with extension promoting rapid rise through a crystal-rich mush, to be frozen in as dike-like structures (Fig. 1).

The “flotation” of magnetite has been suggested for other magmatic systems. A single bubble observed in the Bishop Tuff was coated in small magnetite crystals (Gualda and Anderson, 2007), interpreted as reflecting heterogeneous nucleation of bubbles on magnetite, as commonly observed

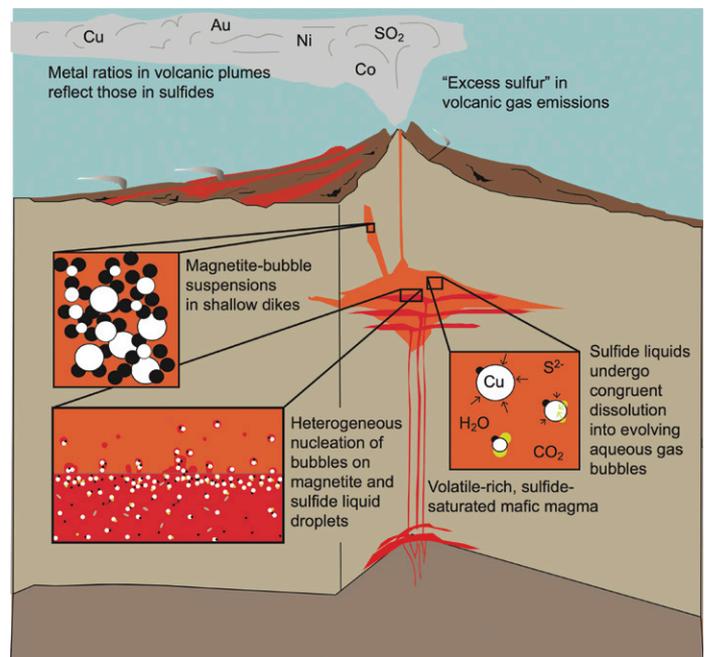


Figure 1. Schematic diagram of a volcanic system to illustrate processes involving bubble-crystal or bubble-liquid aggregates. The magmas are volatile-rich and bubbles are largely attached to magnetite and sulfide liquid phases. Discussed are: intrusion of a magnetite-rich foam into shallow faults (Knipping et al., 2015); accumulation of magnetite-bubble aggregates at interfaces between underplating mafic magmas and overlying intermediate magmas (Edmonds et al., 2014) and the congruent dissolution of sulfide liquid into aqueous vapor, which then outgasses from the volcano (Mungall et al., 2015).

in experiments (Gardner and Denis, 2004). Bubbles and magnetites were coupled in mafic enclaves within crystal-rich andesite from the Soufrière Hills volcano (Edmonds et al., 2014). This spatial association may reflect heterogeneous nucleation of bubbles on magnetite, and the subsequent formation of a magnetite-rich foam at the interface between intruding, vapor-saturated, mafic magma and the crystal-rich andesite (Edmonds et al., 2014) (Fig. 1).

The host magma shows no spatial association between magnetites and bubbles, and perhaps this might not be expected. Rapid vesiculation and open-system degassing of magma during eruption likely overprints the bubble structure that existed prior to decompression, which probably explains why erupted magmas generally do not preserve bubble-crystal aggregate textures (Gualda and Ghiorso, 2007). The quenching of the enclaves as closed vessels, with glassy rinds, may have been key to preserving the textures.

Magnetite fractionation, by crystal settling or flotation, is implicated in the development of calc-alkaline trends in arc magmas and in controlling the redox state of magma, as well as triggering other geochemical processes, including sulfide saturation (Jenner et al., 2010). Mafic magmas are often saturated with an immiscible sulfide liquid (Li and Ripley, 2005). The fate of sulfide liquids in magma reservoirs in the crust is thought to be settling into crystal mushes. The limited tendency

of sulfide liquids to wet silicate minerals (Mungall and Su, 2005) means that sulfide liquids do not tend to flow through porous crystal mushes, and instead accumulate in situ, as seen in Ni-PGE sulfide ore deposits (Naldrett, 1999). The transition metal composition of volcanic gases and ore-forming fluids is similar to that of the sulfide liquids thought to exist in the magma; e.g., the Cu/Au ratio of the Bajo de la Alumbrera porphyry Cu-Au deposit (Argentina; Mungall et al., 2015) and the Cu/Ni ratio in volcanic gases from Merapi volcano (Indonesia; Nadeau et al., 2010). These similarities were ascribed to fluids percolating through the upper parts of magma reservoirs, entraining metals and sulfur (Nadeau et al., 2010). This explanation is problematic, however, if the sulfide liquids accumulate near the base of the system, whereas magmas and hydrothermal fluids are sourced from near to the top.

An alternative solution is offered by Mungall et al. (2015), who conducted experiments with silicate liquid, sulfide liquid, and vapor. Sulfides always occur at the interface between silicate liquid and vapor, despite the gravitational force that tends to pull them to the bottom of the experimental capsule, illustrating the affinity of sulfide liquid for vapor. Based on these experiments, and the observations common to many volcanic and hydrothermal systems, Mungall et al. propose that vapor bubbles may nucleate on sulfide liquid droplets with high wetting angles, and the resulting compound drops may be “floated” to the upper reaches of the magmatic system. The sulfide liquid may undergo congruent dissolution, whereby the sulfide liquid, FeS, reacts with liquid water to form dissolved iron (FeO) and H₂S gas (or at lower pressures, SO₂ and H₂) (Fig. 1). Many arc volcanic eruptions give rise to enormous emissions of SO₂ gas, far more than can be explained by the concentration of dissolved sulfur in melt inclusions (Wallace and Edmonds, 2011). Traditionally, this excess has been explained by invoking the existence of pre-eruptive fluids carrying the bulk of the sulfur (Scaillet et al., 1998), or transfer of sulfur from underplating mafic magmas. Transfer of merely sulfur, however, does not explain the outgassing metal assemblage, so that the existence of the sulfide-vapor aggregates (or “compound drops” of vapor and sulfide liquid) is a necessary requirement.

We must clearly consider the effects of heterogeneous nucleation of bubbles on the dynamics of dense phases such as magnetite and sulfide liquid, but it is less clear whether this will substantially change our understanding of metal and volatile budgets of magmatic systems; further observations are required. The timing of the saturation of magnetite or sulfide liquid in the silicate melt, and vapor, is critical. Magnetite fractionation, sulfur systematics, and degassing are inextricably linked in convergent margin magmas (Sun et al., 2004). The onset of magnetite fractionation in oxidized arc magmas involves the removal of Fe³⁺ from the melt, resulting in a reduction of sulfur from sulfate (SO₄²⁻) to sulfide (S²⁻). This triggers sulfide saturation and fractionation of metals from the melt due to the lower solubility of sulfide (Jenner et al., 2010). One might speculate whether these fractionation signatures are dominated by crystal settling, or might be explained by flotation mechanisms, if sulfide saturation were to occur in the upper crust where an aqueous vapor phase is present. As yet unexplored are the potential effects of transporting (by aggregate settling) exsolved vapor into shallow crustal cumulate piles, where it may play some role in the expulsion of residual liquids during compaction or in the disaggregation of crystal mushes.

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