LETTERS
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Transport of metals and sulphur in magmas by flotation of sulphide melt on vapour bubbles

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Emissions of sulphur[1,2] and metals[3,4] from magmas in Earth's shallow crust can have global impacts on human society. Sulphur-bearing gases emitted into the atmosphere during volcanic eruptions affect climate[5,6], and metals and sulphur can accumulate in the crust above a magma reservoir to form giant copper and gold ore deposits, as well as massive sulphur anomalies[3,4,7,8]. The volumes of sulphur and metals that accumulate in the crust over time exceed the amounts that could have been derived from an isolated magma reservoir[2]. They are instead thought to come from injections of multiple new batches of vapour- and sulphide-saturated magmas into the existing reservoirs[1,4,9,10]. However, the mechanism for the selective upward transfer of sulphur and metals is poorly understood because their main carrier phase, sulphide melt, is dense and is assumed to settle to the bottoms of magma reservoirs. Here we use laboratory experiments as well as gas-speciation and mass-balance models to show that droplets of sulphide melt can attach to vapour bubbles to form compound drops[11] that float. We demonstrate the feasibility of this mechanism for the upward mobility of sulphide liquids to the shallow crust. Our work provides a mechanism for the atmospheric release of large amounts of sulphur, and contradicts the widely held assumption that dense sulphide liquids rich in sulphur, copper and gold will remain sequestered in the deep crust.

Plinian volcanic eruptions typically release as much as 100 times more sulphur than could have been dissolved within the erupted volumes of felsic magma[2,12,13]. Sulphur is emitted during quiescent periods between eruptions at rates far exceeding plausible rates of supply from the felsic magmas within the shallow volcanic feeders[2,10]. Excess sulphur emissions result from eruptive tapping of apical gas-rich cupolas containing excess vapour which comprises up to 30 vol% of the magma in shallow intrusions[1,14].

Intrusion of sulphur-rich mafic magma immediately before eruption, commonly saturated with droplets of an immiscible Fe–(Cu)–(Ni)–S–O liquid (that is, sulphide liquid)[15,16], may trigger eruptions of felsic to intermediate magma, whereas the bulk of the mafic magma remains at depth[17]. However, the co-erupted excess sulphur vapour at Soufriere and Pinatubo volcanoes was probably supplied previously by degassing of underplated mafic magma over protracted periods[1,2,10,18].

Transition metals are also transferred from mafic magmas saturated with sulphide liquid into overlying felsic liquids, leading to enrichment of ore-forming elements. Hydrothermal porphyry deposits of Cu and/or Au at Pinatubo as well as Bingham Canyon, Utah[19] and Bajo de la Alumbrera, Argentina[3,8], form when those felsic magmas solidify and discharge metal- and sulphur-rich aqueous fluids. Although intimate interactions between mafic and felsic magmas undoubtedly occur, the physical mechanism by which sulphur and metals are transferred between them remains a matter of speculation.

Orthomagmatic ore-forming fluids have ratios of transition metals similar to those of the sulphide liquid from which they were derived by hydration or oxidation during quantitative resorption of sulphide liquid by silicate magma; for example, Cu/Au at the Bajo de la Alumbrera porphyry Cu–Au deposit[3] and Cu/Ni and Cu/Co in volcanic gases at Merapi[4]. At the Bajo de la Alumbrera, mafic magma mixed with rhyodacite magma to produce hybrid andesites with mixed phenocryst populations containing sulphide melt inclusions[3]. Groundmass sulphide is not observed in any rock types, presumably owing to subsequent hydration of sulphide and degassing, for example, reactions (1) and (2)

$$\mathrm{H_2O_{(silicate\ melt)}} + \mathrm{FeS_{(sulphide\ melt)}} = \mathrm{FeO_{(silicate\ melt)}} + \mathrm{H_2S_{(vapour)}} \quad (1)$$

$$3\mathrm{H_2O_{(silicate\ melt)}} + \mathrm{FeS_{(sulphide\ melt)}} = \mathrm{FeO_{(silicate\ melt)}} + \mathrm{SO_{2(vapour)}} + 3\mathrm{H_{2(vapour)}} \quad (2)$$

These reactions are favoured at low pressure and high H_2O activity in FeO-poor felsic magmas, especially if vapour is able to leave the system. The mineralized dacite porphyry stocks at Alumbrera were derived from the top of a stratified intrusion, where sulphide melt was not stable, whereas the sulphide melt was present in the more mafic hybrid andesitic melt at the bottom[3]; the authors suggest that fluids must have extracted metals and sulphur from the entire stratified magma body despite the shallow intrusions having tapped only the top, whilst preserving the Cu/Au ratios of the sulphide liquids found only at the base of the system[3].

Solidified remnants of sulphide liquid globules that have undergone breakdown to Cu-sulphide phases and Fe-oxide minerals occur in quenched felsic to intermediate magmas at Pinatubo, Bingham Canyon, Merapi, Popocatepetl, Satsumi-Iōjima, Clear Lake and Mount St Helens[4,16,19,20]. These examples of sulphide melt, which was clearly not at equilibrium with its host magma, have previously been accounted for either as hybrids of sulphide-saturated mafic liquids with initially sulphur-poor felsic magmas, or as the result of vapour transport of sulphur and metals out of mafic magma into felsic magma followed by their reprecipitation in sulphide liquid droplets which subsequently became unstable[15].

A more parsimonious explanation for addition of sulphur, Cu and Au to either shallow pre-eruptive or ore-forming intrusions would have the sulphide melt being physically elevated towards the top of the stratified magma body, where it then underwent

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congruent dissolution via hydration during volatile exsolution (reactions (1) and (2)). However this possibility has not been entertained previously because of the well-documented density contrast between sulphide melt and silicate melt, which promotes settling of sulphide liquid towards to the base of a magmatic system.

We have performed experiments in which sulphide melt, silicate melt and vapour were equilibrated to measure the interface morphologies[21–23]. Sulphide drops preferentially occur at the interface between silicate melt and vapour (Fig. 1a), despite the gravitational body force that tends to pull the sulphide melt to the base of the experimental charge. Topologically identical relationships were observed in evacuated silica tubes with a low-density atmosphere governed by equilibrium with sulphide melt[23], in a gas-mixing furnace under an inert Ar atmosphere[21], and at 200 MPa under water-saturated conditions with 3.2 wt% H_2O dissolved in the silicate melt[22], indicating that the surface energies of the interfaces are not markedly affected by the composition of the vapour phase. Under high acceleration in a centrifuge the sulphide descends to the base of the charge, not in contact with the vapour phase[23]. However, during quench of the centrifuge experiments and consequent degassing of the sulphide droplets, smaller droplets of sulphide melt rise from the main droplet at the base of the charge, pendant from ascending vapour bubbles (Supplementary Fig. 2). Where silicate melt, sulphide melt and vapour have been co-entrapped in minerals[4,24,25]; sulphide melt always occurs attached to the vapour bubble. Sulphide melt droplets attached to vapour bubbles have been noted in komatiitic Ni sulphide ores[26].

We have used high-resolution computed X-ray tomography[27] to measure precisely the shapes of interfaces separating sulphide, silicate and vapour in quenched-run products of two experiments (Fig. 1). Comparison of quenched sulphide drops with their shapes as observed *in situ* at experimental conditions using conventional medical X-radiography[21] allows us to estimate qualitatively the interfacial tensions (γ) of all three types of interface; sulphide–silicate, sulphide–vapour and silicate–vapour (Supplementary Table 1 and Supplementary Information). The shapes of interfaces between sulphide melt and silicate melt are unaffected during quench, permitting quantitative solution of the Bashforth–Adams equation to determine interfacial tensions on quenched experimental run products identical to values determined on X-radiographs of sessile drops imaged *in situ* at run conditions (Supplementary Information). The shapes of pendant sulphide drops both *in situ* and in quenched experimental products are such that for small droplets where surface energy dominates over buoyant body forces the total energy of a system containing all three phases is always at a minimum when the sulphide occurs at the interface between silicate melt and vapour, forming a compound drop[11]. We infer that in any magmatic system undergoing vapour nucleation and bubble growth where sulphide melt is also a stable phase, the sulphide droplets will spontaneously occur attached to vapour bubbles.

We propose that the requirement for sulphur and metals to be transferred from mafic magmas to overlying felsic magmas, whilst preserving metal ratios characteristic of the sulphide melts themselves, is most easily met by upward transport of sulphide as compound drops, lofted by the relatively high buoyancy of the attached vapour bubbles (Figs 2 and 3). We have modelled the evolution of vapour bubbles in an idealized closed system undergoing isothermal decompression[28] (Supplementary Information). We compare the evolution of an andesitic magma initially comprising 0.1 wt% of vapour at 2,600 bar, 1,050 °C, with that of an initially identical magma also containing compound droplets of sulphide and vapour, wherein sulphide comprises 3.3 wt% of the entire system, to simulate the evolution of a single sulphide droplet as a vapour bubble nucleates next to it and then grows during decompression. At all pressures the vapour phase is buoyant with respect to the silicate magma; with the growth of the attached bubble the density of the compound drop falls until it becomes buoyant at pressures less than 2,000 bar. By the time the compound drop has risen to pressures less than 1,000

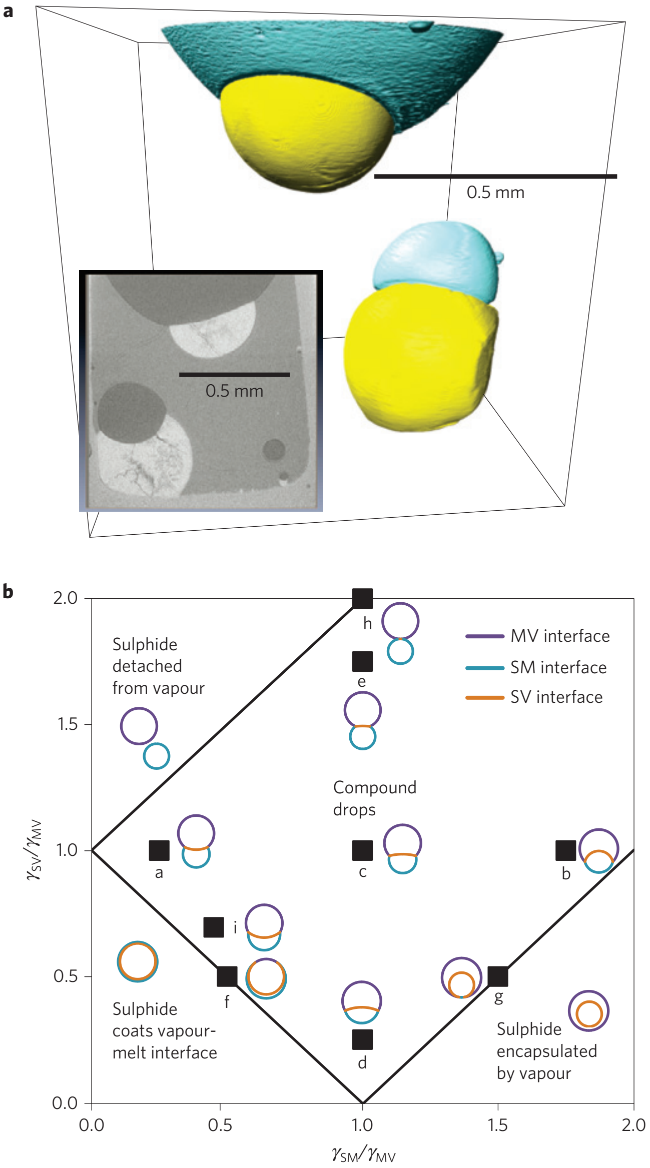

Figure 1 | Morphologies of compound drops. a, 3D tomographic image of a heavy compound drop comprising a small vapour bubble and a large sulphide drop and a second sulphide drop pendant from the meniscus, which would float if the vapour was detached from the enclosing chromite crucible, quenched after being held at 1,200 °C for 48 h. Yellow represents the Fe–Ni–Cu–S–O liquid; the vapour is coloured blue, and the basaltic silicate melt is colourless. The diameter of the contact line joining the pendant drop to the meniscus is 0.4 mm. Inset: 2D slice through the X-ray tomographic image of the same experiment, showing the lower compound drop attached to the base of the chromite crucible (light grey) and a smaller compound drop at the lower right. **b**, Morphologies of compound drops for ratios of surface tensions between sulphide melt (S), silicate melt (M) and vapour (V) at squares labeled a–i[11]. In all of the cases shown the volume of the vapour bubble is the same, being three times that of the sulphide drop. For combinations of surface tensions falling outside the bold black lines, there is no three-phase contact line because two of the three phases are repelled by one another and do not make contact. Observed experimental and natural sulphide–vapour compound drops fall to the far left-hand side of the diagram.

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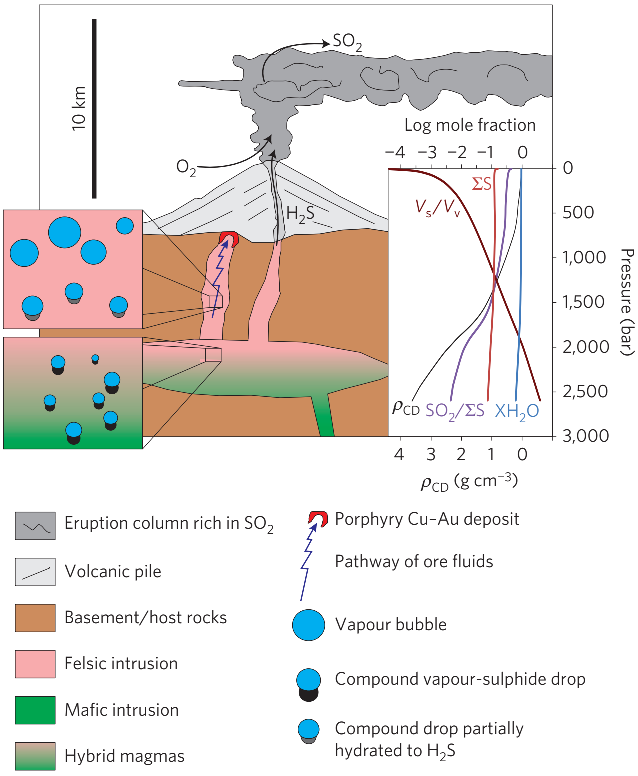

Figure 2 | Cross-sectional cartoon illustrating sulphide flotation in subvolcanic environments. Buoyant compound drops formed in the zone of hybridization of sulphide-saturated mafic magma and felsic magma rise into felsic magma, where they are destroyed by hydration at low pressure, releasing H_2S and metals to a vapour phase which may be erupted or may form hydrothermal mineral deposits. Inset panel: ΣS and XH_2O are total mole fractions of sulphur species and water vapour respectively, $SO_2/\Sigma S$ shows speciation of oxidized over total S, V_s/V_v is volume of sulphide/volume of vapour in the compound drop, ρ_{CD} is bulk density of the compound drop during decompression of a compound drop. The evolution of vapour with the same initial composition but not subsequently re-equilibrated with sulphide melt is shown in Supplementary Fig. 9.

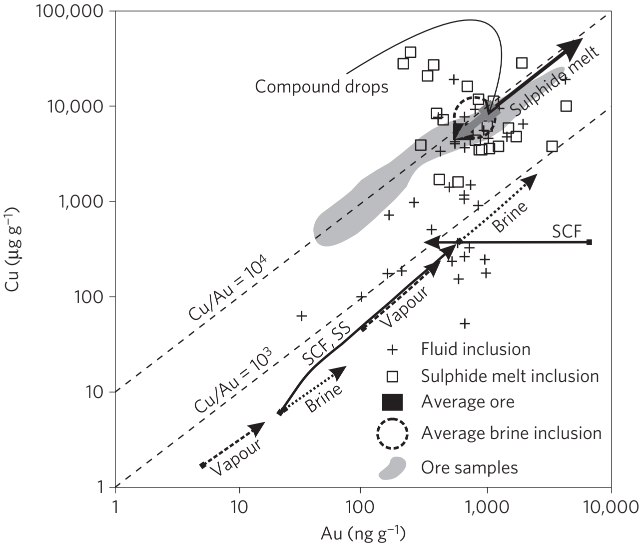

Figure 3 | Cu versus Au for modelled and measured compositions of sulphides, fluids and ores at Alumbrera[3,29]. Model trends run from square terminations at 2,600 bar to arrow terminations at 2.7 bar. SCF, supercritical fluid; SCF–SS, supercritical fluid–sulphide saturated; trends of pairs of vapour (dashed) and brine (dotted) at 2,600 bar and at 2.7 bar run from 90:10 vapour:brine at square terminations to 10:90 vapour:brine at arrow terminations. The model methods are described in the Supplementary Information. Compound drops (grey arrow) have nearly constant bulk compositions coincident with both ore-forming brines and with average ore at Alumbrera, whereas fluids alone never have compositions similar to ore, even if they separate into metal-rich brines and metal-poor vapours.

bar, the sulphide drop comprises only 1/25th of the volume of the compound drop, a value that falls to infinitesimal proportions at the lowest pressures. Such small quantities of sulphide liquid adhering to bubbles would be difficult to observe. The gas evolves from CO_2-rich with sulphur species dominated by H_2S to being nearly pure H_2O at low pressure (Fig. 2, inset). At the very lowest pressures SO_2 rises to comprise nearly half of the sulphur budget of the vapour in the case of the compound drop, whereas under sulphide-absent conditions the sulphur speciation becomes strongly SO_2-dominated at very low pressure (Supplementary Fig. 9). The total mass of sulphur residing in the vapour phase at pressures below 5 bar is 1.3% of the mass of the magma, more than 20 times higher in the case of the compound drop than in the case of the isolated bubble. Sulphur loads of this magnitude are sufficient to explain the excess sulphur paradox alluded to in the earlier paragraph.

It is clear that compound drops, rather than isolated fluids, are necessary to explain the Cu and Au concentrations of the ore-forming fluids at Alumbrera[3,29] (Fig. 3). Model compound drop compositions coincide with the bulk ore[29], average ore-forming brines[29] and many of the sulphide melt inclusions from Alumbrera[3], all close to Cu/Au = 10^4. Model supercritical vapours at equilibrium with sulphide liquids follow a trend of increasing metal contents with decreasing pressure just below Cu/Au = 10^3, whereas model supercritical vapours not equilibrated with sulphide liquids have Au contents that fall as pressure decreases but nearly constant Cu contents. Also shown are two trends of coexisting brine and vapour that would form if the modelled supercritical vapours were to fall within the miscibility gap separating hydrosaline melts (that is, brines) from low-density aqueous vapours if the system contained sufficient Cl. Subcritical magmatic fluids are not expected to fractionate Cu from Au.

Within a depressurizing compound drop, the amount of sulphide melt falls as the amount of vapour increases, drawing sulphur into the vapour phase. The metal budget of the compound drop as a whole changes very little because metal is transferred almost quantitatively from the sulphide melt to the vapour. We propose that the ore-forming magmatic volatile phase at Alumbrera shown in Fig. 3 was composed of compound drops that completely consumed their attached load of sulphide. The removal of compound drops from deep in the magma plumbing system to shallow levels will effect the same net transfer of metals and sulphur into the shallow hydrothermal system regardless of whether it occurs as modelled here, at equilibrium with the host silicate magma (as would be expected in slowly rising crystal-rich magma), or if it occurs suddenly by rapid flotation of the compound drop from considerable depth (as might occur in hybrid intermediate magma at depth with low crystal content). Both sulphur and metals, formerly contained in sulphide melt at depth, are quantitatively transferred to the vapour phase by the time they reach low pressures.

The key to the process of sulphur and metal transfer to shallow or erupted fluid phases is the buoyancy of the compound drop. If the dense sulphide liquid did not form compound drops, the excess sulphur and metals would remain sequestered deep in the crust.

Our observations of compound sulphide liquid–vapour bubble drop formation demonstrate that whenever magma saturated with sulphide melt undergoes vesiculation and degassing, some or all

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of the sulphide melt should accompany the vapour phase upwards instead of settling to the base of the mafic magma as is generally supposed, constituting a markedly enhanced vector for upward transfer of sulphur and transition metals to ore-forming systems or to the atmosphere. The implications extend to the transport and deposition of Ni-, Cu- and Pt-rich sulphides in magmatic ore deposits, where it is clearly not safe to assume that sulphide melt will always tend to migrate downwards into structural traps. Flotation of sulphide drops and their ultimate release to H_2S-rich vapours may also provide a mechanism to support the recent proposition that catastrophic end-Permian global climate change resulted from massive transfers of Ni to the atmosphere from mafic magmas[30]. It is intriguing to note that flotation of sulphide minerals on vapour bubbles is also the principal means used in the beneficiation of the ores that form in these magmatic and hydrothermal systems.

Methods

Backscattered electron (BSE) images of axial cross-sections of experimental charges or published images of charges from previous studies[21–23] were used to estimate the radii and contact angles of interfaces between quenched sulphide liquid, silicate glass and vapour. Readers are referred to those previous publications for further details of experimental methods. Because the experiments were all performed in cylindrical capsules, it was assumed that all three types of interface are spherical caps for small drops.

Two experiment run products were scanned at the Australian Resources Research Centre in Perth (Western Australia) using an XRADIA (now Zeiss) XRM 500 high-resolution three-dimensional X-ray microscope system. The scanner was set up a voltage of 160 kV, a power of 10 W, a voxel size of 1.16 μm and used built-in dynamic ring-artefact removal allowing imaging of the the interior of the capsule and to reduce potential artefacts. A total of 2,000 projections were used to reconstruct a three-dimensional volume of the sample. The resulting data set was processed using dedicated image processing procedures using AvizoFire(r) software combined with dedicated CSIRO-developed workflows[27] to separate sulphide droplets from silicate and vapour phases and generate 3D isosurfaces. Cartesian coordinates of numerous points on each interface were determined using Corel Photopaint and used to fit model spherical caps by least squares error minimization for small drops, or compared with the Adams–Bashforth equation for larger sessile drops as described in the Supplementary Information.

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Author contributions

J.M.B. performed experiments; J.E.M. performed modelling of interfaces and metal mass balance and wrote the manuscript; B.G. performed CT scanning and related data reduction; F.G. performed gas-speciation modelling, S.J.B., J.M.B. and J.E.M. contributed to the original concept. All authors discussed the results and edited the manuscript.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to J.E.M.

Competing financial interests

The authors declare no competing financial interests.

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