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# Economic geology: Volatile destruction

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## Abstract

Direct evidence for the role of volatiles in magmatic ore formation has been elusive. Magma degassing at Merapi volcano in Indonesia is found to be directly linked to the selective leaching of metals from sulphide melts that ultimately form ore deposits.

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## Introduction

Sulphur carried by magmas plays a pivotal role in many geological processes. A great chemical affinity exists between sulphur and metals that is important for ore formation. Thus many ore deposits of economic interest are intimately associated with magmatic activity. The sulphur and metals merge together at the magmatic stage to yield immiscible sulphide melts. At some stage during magma evolution, the ore-forming elements are removed or concentrated, but the reasons for this, particularly in subduction-zone settings, remain obscure. The volatile content of the magma has long been thought to play an important role in the separation process<sup>1</sup>, but direct evidence has been lacking. Writing in *Nature Geoscience*, Nadeau *et al.*<sup>2</sup> report observations from Merapi volcano, Indonesia, that indicate that present-day arc magmas, produced during the subduction of water-rich oceanic crust, owe their ore potential to the abundance of volatiles associated with this tectonic setting.

After water and carbon dioxide, sulphur is the third most abundant dissolved volatile in magmas. Concentrations of sulphur range from a few hundred to a few thousand parts per million<sup>3,4</sup>. When placed in the upper crust, the majority of magmas soon saturate with an immiscible sulphide melt that hosts numerous economically interesting elements, such as copper, nickel, gold and the platinum-group elements<sup>5</sup>. According to the classic mechanism of magmatic sulphide ore formation<sup>6</sup>, sulphide melts readily settle out of the main molten body of magma because they are much denser than the surrounding silicate melt. They accumulate at the base of the magma chamber or intrusion (Fig. 1a). This mechanism works well for dry iron- or magnesium-rich (mafic) magma, which is typical for magmatic activity at intraplate or extensional rift-related settings. These tectonic settings are associated with many metallic deposits of huge economic interest, such as at Norilsk in Siberia<sup>7</sup>. There, some 250 million years ago profuse intraplate volcanism created the largest nickel–copper–palladium deposits in the world.

The abundance of water in arc magmas, however, adds an intriguing complexity to this scenario. As far as we know, water does not significantly affect the solubility of sulphur in

silicate melts<sup>8,9</sup>, at low pressures at least. Therefore, hydrous magmas, such as those formed in arc settings, should follow the same pattern of sulphide removal as that of dry magmas. In fact, water should lower the density of silicate liquids, amplifying the density difference and accelerating the settling out of sulphides. Yet, hydrous magmas are not observed to produce layers of accumulated sulphides. Instead, field evidence shows that sulphur-bearing rocks related to arc magmas accumulate above the main silicate–magma intrusion, and not in it, forming the so-called hydrothermal ore deposits. One of the reasons for this observation lies in the degassing processes at work in such settings, in particular the loss of water by the magma. During their ascent to the surface, magmas lose their volatiles continuously because water solubility in silicate melts decreases with decreasing pressure<sup>1</sup>. The escaping gas rises towards the upper reaches of the magma plumbing system. As the volatiles percolate through the magma they scavenge elements and essentially destroy the sulphide melt (Fig. 1b). The volatiles thus provide a mechanism for the removal and transport of metal elements, depositing them either above the main magma intrusion or carrying them into the atmosphere as a gaseous emission.

Nadeau *et al.*<sup>2</sup> present detailed petrological analyses of rocks ejected during an explosive event at Merapi volcano in 2006. They provide a comparison between some preserved sulphide melt, the main silicate–magma intrusion that carries the sulphide melt, and the magmatic fluids (emitted as volcanic gas) that produce the hydrothermal ore deposits. Analysis of the silicate magma reveals widespread destruction of the majority of sulphide melt in the main magma intrusion, indicating that elements such as cobalt, copper and nickel have been scavenged and removed by passing fluids. A comparison between the concentrations of metals in the preserved sulphide melts and the volcanic gases emitted immediately after the 2006 eruption are found to be remarkably similar. This indicates that the metals in the ore fluids are derived from the sulphide melts. Unlike those gases sampled immediately after the eruption, volcanic gases sampled during periods of quiet volcanism were not found to have high metal concentrations. This implies that destruction of sulphide melts by volatiles is not a continuous process, but is instead related to the reservoir dynamics at depth and the periodic injection of volatile-rich magmas. Thus, a stagnant magma reservoir may not be as productive in terms of ore deposits as a periodically replenished chamber.

The opportunity to directly correlate chemical variations monitored at the surface to the putative source at depth is a rare one. Needless to say, such a link is hard to establish because it requires access to synchronous gas and rock samples, a combination not often met in the context of ore deposits related to magmatism. Previous petrological studies on ancient magmatic intrusions have suggested that sulphides could supply the magmatic ore fluid with metals, but in such an ancient example the accompanying gas obviously could not be collected<sup>10</sup>.

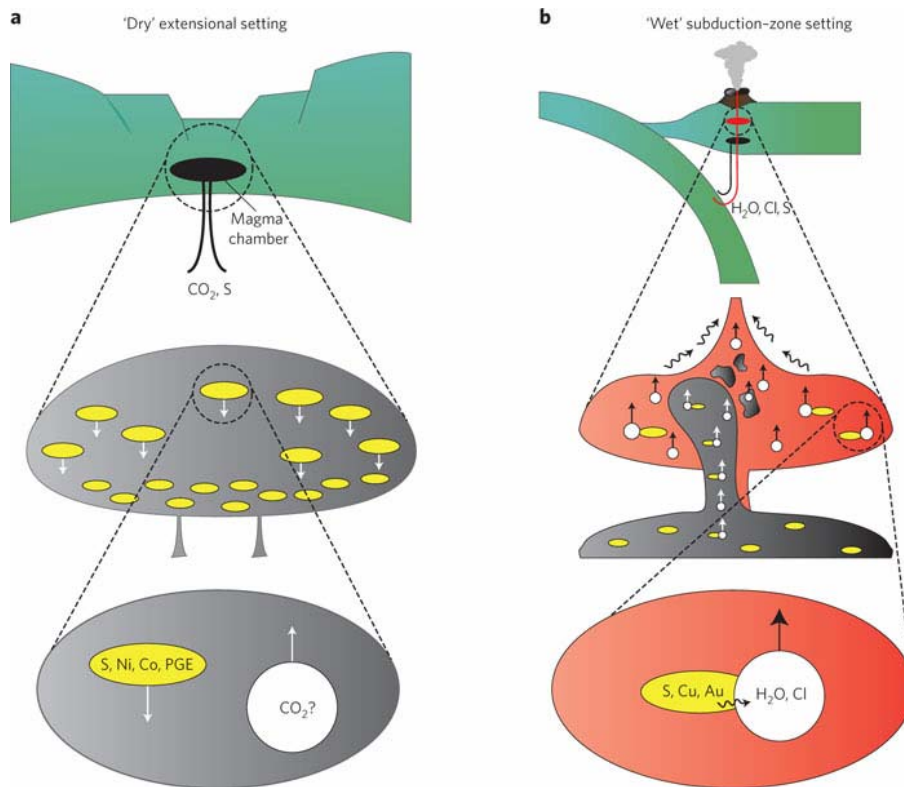
Insights gained at Merapi volcano illuminate one critical step that can lead to the concentration of some elements in the crust. However, the proposed model requires a subtle combination of various processes and some precise timing. Future studies will need to assess whether this represents a common scenario for the production of hydrothermal ore deposits. The study also highlights, once again, the important role of water. It is because sulphur is highly soluble in hydrous fluids<sup>11</sup> that sulphide minerals cannot survive prolonged exposure to fluid percolation. However, the effects of other volatiles remain unknown. Arc magmas are notoriously rich in chlorine, which certainly plays an important role in metal transportation through fluids<sup>12</sup>. The role of chlorine has yet to be quantified, especially when taken in combination with volatiles other than water. Carbon dioxide is generally ignored in ore

processes, yet there is growing evidence of its abundant presence in magmas, including in arc settings<sup>13</sup>. Whether carbon-dioxide-rich fluids inhibit or enhance sulphide breakdown is simply unknown.

The work by Nadeau *et al.*<sup>2</sup> sheds light on a decisive step in the formation of ore deposits and the transfer of economically interesting metals from sulphide melts into the magmatic ore fluid. But there is clearly still considerable work to be done before we fully understand the origin of the metal-rich rocks that are vital to human economic activity.

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**a**, In an extensional or intraplate setting, basaltic magma (black) saturates with an immiscible sulphide liquid (yellow), which scavenges many ore-forming elements such as nickel, cobalt and the platinum-group elements (PGE). Owing to its high density, sulphide settles and accumulates at the floor of the magma chamber, forming igneous sulphide ore. Very little interaction between the sulphide melt and the CO<sub>2</sub>-rich gas (white) that typifies such magmas is anticipated. **b**, In a subduction zone, the magma is also sulphide saturated, but acidic (red). However, arc magmas are rich in volatiles such as water and chlorine. Decompression causes large amounts of water-rich gas (white) to separate out, which dissolves the pre-existing sulphides. Nadeau *et al.*<sup>2</sup> show that economically important elements such as copper and gold are stripped out of the magma body by the volatiles (shown by wiggly arrows), forming metal-rich ore fluids. The ore fluids are deposited above the main magma chamber, where the wiggly arrows end.