

CO₂-fluxing collapses metal mobility in magmatic vapour

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Abstract

Magmatic systems host many types of ore deposits, including world-class deposits of copper and gold. Magmas are commonly an important source of metals and ore-forming fluids in these systems. In many magmatic-hydrothermal systems, low-density aqueous fluids, or vapours, are significant metal carriers. Such vapours are water-dominated shallowly, but fluxing of CO₂-rich vapour exsolved from deeper magma is now recognised as ubiquitous during open-system magma degassing. Here, we show that such CO₂-fluxing leads to a sharp drop in element solubility, up to a factor of 10,000 for Cu, and thereby provides a highly efficient, but as yet unrecognised mechanism for metal deposition.

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Introduction

Aqueous vapour is increasingly recognised as an important agent of element mobility in the crust (Hedenquist and Lowenstern, 1994; Pokrovski *et al.*, 2005; Williams-Jones and Heinrich, 2005; Migdisov *et al.*, 2013). Vapour is particularly common in magmatic environments, and can be sampled directly at fumaroles and volcanic plumes. Compared to the source magma, vapours can be strongly enriched in metals (*e.g.*, Allard *et al.*, 2000; Williams-Jones and Heinrich, 2005; van Hinsberg *et al.*, 2016), and metal mobility in shallow magmatic conduits is well-established (*e.g.*, Berlo *et al.*, 2013; Plail *et al.*, 2014). Although evidence for high metal solubility in vapour inclusions in rocks is debated (Lerchbaumer and Audétat, 2012), experiments reproduce these high solubilities (Migdisov and Williams-Jones, 2013; Migdisov *et al.*, 2013), thereby conclusively confirming that vapours are capable of transporting metals in high concentrations.

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The ligands available to elements in aqueous vapour and liquid are similar, although charged species are unimportant in vapour and, instead, uncharged molecules dominate element transport. However, the concentrations of metals in vapour inferred from fumarole emissions and fluid inclusions are commonly orders of magnitude higher than is predicted from metal volatility. The reason for this is the ability of water molecules to form hydrogen-bonded clusters that incorporate metal-bearing molecules, thereby significantly increasing stability, and hence solubility of the latter in the vapour phase. Recent experiments (Migdisov and Williams-Jones, 2013; Migdisov *et al.*, 2013; Hurtig and Williams-Jones, 2014) have demonstrated this effect for Cu, Ag and Au, and show that the complexity of these hydration clusters, and with them the stability of metal-bearing clusters, increases exponentially with increasing water vapour pressure. At the highest densities, the vapour can no longer be considered a low-density fluid as the previously isolated water clusters merge into the 3D hydrogen-bonded network typical of dense aqueous solutions.

The density-, or pressure-dependence of metal solubility has been used to explain metal deposition during earthquake-induced depressurisation (Weatherly and Henley, 2013) and fluid ascent in volcanic-hydrothermal systems (Henley and Berger, 2013). Depressurisation, however, is not the only mechanism that destabilises these clusters. Reducing the *partial* pressure of water, *i.e.* changing the vapour's composition, produces the same effect. For example, dilution of water-rich vapour with a non-polar gas such as CO₂, results in a drop in the partial pressure of water (*p*H₂O), and hence destabilisation of hydrated metal-bearing clusters, comparable to that occurring during depressurisation. This effect is entirely independent of the total pressure or density of the system, and can be large even when the density (or *P*_{total}) of the mixed fluid rises during this dilution.

In the following, we will show that fluxing of CO₂-dominated vapour, released during degassing of deep-seated magma and known to transit magmatic-hydrothermal conduits, reduces *p*H₂O significantly, leading to near-total collapse of the metal transporting capacity of the vapour. CO₂-fluxing is thereby an efficient metal-deposition mechanism in these systems, although the required conditions are unlikely to be encountered in porphyry-Cu systems.

CO₂-Fluxing in Magmatic Conduits

The solubility of volatiles in magma is controlled dominantly by pressure (Dixon *et al.*, 1995; Spilliaert *et al.*, 2006a) as are, therefore, the resulting exsolved fluid compositions. CO₂ is the first major volatile to exsolve, and deep-released magmatic fluids are CO₂-dominated, with H₂O becoming more important as pressure decreases, followed by S, Cl, and F (Spilliaert *et al.*, 2006a).

Magma ponds and exsolves volatiles at different levels in the crust, and can experience stages of closed- and open-system degassing. These volatiles are



buoyant and flux through the overlying magmatic conduit, intermediate ponding levels, and the system's host rocks. Fluxing of CO₂-rich gas through shallower magma results in CO₂ enrichment and melt dehydration (Spilliaert *et al.*, 2006b). High CO₂, low H₂O melt inclusions are now widely recognised, and generally attributed to CO₂-fluxing (Spilliaert *et al.*, 2006b; Blundy *et al.*, 2010). Gas fluxing has also been linked to enrichments in Cl, alkalis, Ti, Fe, and P (*e.g.*, Ferlito *et al.*, 2007), Cu (Collins *et al.*, 2009), and Li (*e.g.*, Berlo *et al.*, 2004). These element enrichments are generally interpreted in terms of repressurisation, fluid boiling or crystallisation, but we argue here that changes in metal-complex stability resulting from CO₂-fluxing are an attractive alternative.

The pressure dependence of volatile-element solubility in magma leads to sharply different compositions of the exsolved fluid at different depths. A fluid in equilibrium with a typical MOR basalt at 1300 °C will contain 83 mole % CO₂ and 4 % H₂O at 1000 bar, but 17 mole % CO₂ and 61 % H₂O at the surface (Gaillard *et al.*, 2012). To evaluate the impact of such drastic changes in composition, in particular in *p*H₂O, on the ability of magmatic vapour to carry metals, and the potential of CO₂-fluxing as a metal deposition mechanism, we modelled a vapour-filled fracture network in a magmatic-hydrothermal system subjected to a pulse of CO₂-rich vapour (Fig. 1). Given that our purpose is to highlight the effects of CO₂, we will explore endmember scenarios, rather than a specific geological case.

Impact of CO₂-Fluxing on Metal Solubility

In the simplest scenario, a CO₂-rich vapour pulse, released from mafic magma at 1000 bar, passes through shallower, water-dominated vapour at 800 °C. To model this, we used gas compositions in equilibrium with mafic magma at various depths (Gaillard *et al.*, 2012) at constant *p*HCl = 0.005 (Migdisov *et al.*, 2013), a Cu content buffered by chalcopyrite-pyrite coexistence (thermodynamic data sources as in Migdisov *et al.*, 2013) and *f*O₂ at Ni-NiO. Speciation for the gas compositions taken from Gaillard *et al.* (2012) was recalculated for our model conditions.

Fluxing the CO₂-rich gas through H₂O-dominated vapour at 100 and 10 bar reduced Cu solubility by a factor of 50 and 100, respectively (Table 1). Decreasing the temperature to 650 °C, where Cu solubility is highest (Migdisov *et al.*, 2013), and reducing the *p*HCl for the deeply-exsolved vapour tenfold to include the low volatility of Cl at high pressure (Spilliaert *et al.*, 2006a), had an even greater effect. Copper solubility at 100 bar dropped by four orders of magnitude (725 to 0.08 ppb). In essence, CO₂ reduces the transporting capacity of the vapour to almost nothing, and Cu is deposited or reabsorbed by the melt. Per bar of pressure change, the drop in Cu solubility is 2.6 bar⁻¹ for the 100 to 10 bar change in *P*_{total} at 650 °C, whereas it is 2.9 bar⁻¹ and 82 bar⁻¹ for Δ*p*H₂O at 100 and 10 bar *P*_{total}, respectively (Table 1). When the accompanying reduction in *p*HCl is taken into account, CO₂-fluxing is 100 to 600 times more effective in lowering Cu solubility per bar than decompression.

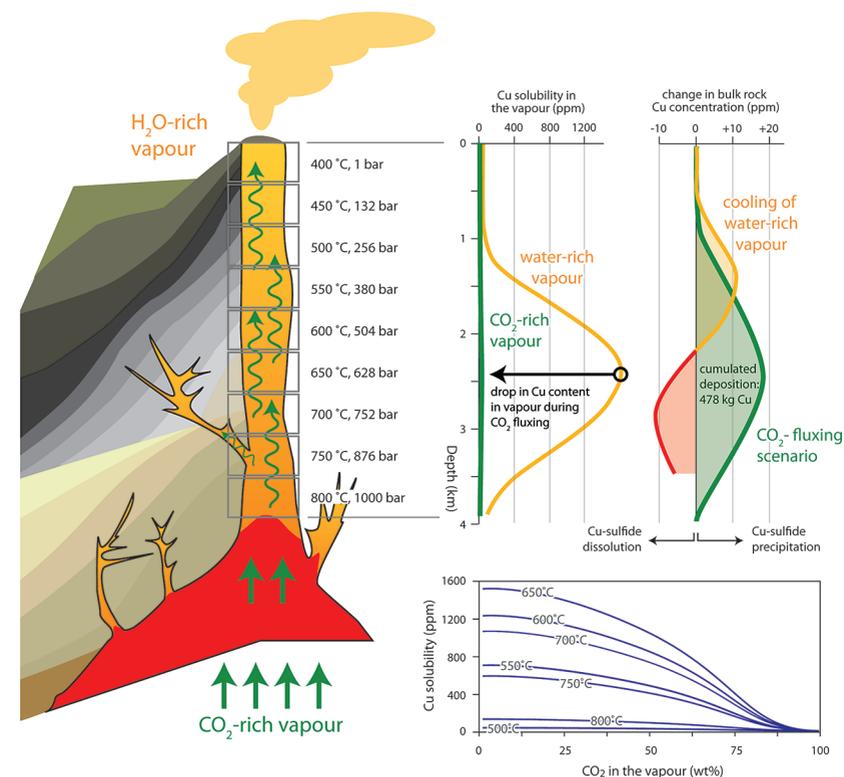


Figure 1 Impact of CO₂-fluxing on Cu solubility in a volcanic conduit filled with vapour. Fluxing deep-sourced CO₂-rich vapour through shallower, water-dominated vapour reduces Cu solubility as the water partial pressure is reduced. Cu contents are significant for the water-dominated vapour. Assuming upward flow, Cu is dissolved from wall rocks to 2.2 km, and subsequently deposited. In contrast, contents in the CO₂-rich vapour are negligible. Therefore, a single pulse of CO₂-rich vapour will deposit essentially all Cu in the water-vapour, with deposition at all depths and all temperatures.

Collins *et al.* (2009) report that melt inclusions from Etna volcano record an approximately twofold enrichment in Cu content, which was attributed to CO₂-fluxing, with gas CO₂ content increasing from 70 to 98 mole %. Unfortunately, the stability constants for the hydrated Cu-chloride species of Migdisov *et al.* (2013) cannot be extrapolated to the 1140 °C reported for these inclusions, which precludes quantitative modelling of this system. To a first approximation, a 270 times decrease in Cu solubility is predicted from the change in *p*H₂O, for a *P*_{total} of 1000 bar and fayalite-magnetite-quartz buffered *f*O₂. The Etna melt is unlikely to be saturated in chalcopyrite, and this drop therefore represents a maximum concentration change. Nonetheless, it shows that CO₂-fluxing



introduces a sharp reduction in the Cu transporting capability of the gas that can indeed explain the observed correlation between fluxing and Cu contents in Etna melt inclusions.

Table 1 Predicted Cu solubility in vapours of varying $p\text{H}_2\text{O}$ and $p\text{HCl}$ with $f\text{O}_2$ and Cu buffered by NiO-Ni and $\text{CuFeS}_2\text{-FeS}_2$, respectively.

	Vapour	T (°C)	Pressure (bar)			Cu (ppb)	pair	Cu reduction factor	
			P_{total}	$p\text{H}_2\text{O}$	$p\text{HCl}$			absolute	per bar
1	H ₂ O-rich	800	100	24.42	0.005	1.2			
2	CO ₂ -rich	800	100	5.76	0.005	0.02	1 - 2	53	2.9
3	CO ₂ -rich	800	100	5.76	0.00005	0.0002	1 - 3	5232	280
4	H ₂ O-rich	800	10	1.41	0.005	0.004			
5	CO ₂ -rich	800	10	0.21	0.005	0.0001	4 - 5	99	82
6	CO ₂ -rich	800	10	0.21	0.00005	0.0000	4 - 6	9706	8104
7	H ₂ O-rich	650	100	23.54	0.005	724			
8	CO ₂ -rich	650	100	5.72	0.005	8	7 - 8	91	5.1
9	CO ₂ -rich	650	100	5.72	0.00005	0.08	7 - 9	8957	503
10	H ₂ O-rich	650	10	0.81	0.005	3.1			
11	CO ₂ -rich	650	10	0.1	0.005	0.02	10 - 11	148	208
12	CO ₂ -rich	650	10	0.1	0.00005	0.0002	10 - 12	14566	20515
	H ₂ O-rich	800	100 - 10		0.005		1 - 4	263	2.9
	H ₂ O-rich	650	100 - 10		0.005		7 - 10	237	2.6

In our simple model, re-establishing a water-rich vapour composition following CO₂-fluxing re-solvates the Cu, and the mechanism is fully reversible. However, kinetic barriers, collapse of a bubble foam as a result of CO₂-fluxing, or choking of vapour pathways by fluxing-induced mineral deposition may preserve these deposits. Moreover, deposition of these elements on conduit walls will lead to their diffusion into the host rock or melt, as a local concentration gradient develops. Transient CO₂-fluxing should thus be best preserved by the fastest diffusing elements, *e.g.*, Li. Melt inclusions with elevated Li content and derived from a magma ponding horizon affected by CO₂-fluxing have indeed been observed (*e.g.*, Berlo *et al.*, 2004; Blundy *et al.*, 2010). However, the lack of stability constants for hydrated Li species in vapour prevents us from evaluating whether CO₂-fluxing is capable of inducing a sufficient drop in Li solubility to generate the observed enrichments.

Metal Enrichment by CO₂-Fluxing

Magmatic-hydrothermal systems can be vertically extensive (*e.g.*, Hedenquist and Lowenstern, 1994). To better represent these, we added a pressure-temperature

gradient (Fig. 1). We assumed that the host rock had reacted to an equilibrium alteration assemblage prior to CO₂-fluxing and therefore did not participate in the reactions. The initial, H₂O-dominated vapour ($X\text{CO}_2 = 0.04$) was Cu-saturated by equilibrating with chalcopyrite, and Cu solubility was tracked along the conduit length. Subsequently, the conduit was fluxed with CO₂-rich vapour ($X\text{CO}_2 = 0.91$) as in the simplified model above. In natural systems, Cu concentrations are unlikely to be at Cu-phase saturation throughout the system and throughout their lifespan (Landtwing *et al.*, 2005), and these calculations thus provide maximum estimates. However, this is also true for other depositional mechanisms, and saturation therefore provides an appropriate benchmark for comparison.

Copper solubility in the water-rich vapour reaches a maximum of 1575 ppm at 650 °C, resulting from the hydrated Cu-chloride species being most stable at this temperature (Migdisov *et al.*, 2013; Fig. 1). In contrast, only 0.2 ppm Cu dissolves in the CO₂-rich vapour at these conditions. Copper solubility decreases with increasing $X\text{CO}_2$ for all temperatures (Fig. 1). Any vapour passing through the conduit will dissolve Cu at temperatures up to 650 °C, and only precipitate it after cooling below this temperature (Fig. 1). In contrast, CO₂-fluxing will result in Cu deposition at *any* temperature, because of the drastic reduction in solubility. In addition, the total amount of Cu deposited in a fluxing scenario is higher than by simple cooling, because of the greater overall reduction in solubility.

Given that water is a more abundant volatile than CO₂, permeable gas networks such as bubble foams in magma and interconnected fracture networks will develop dominantly during release of water-rich fluid. However, once established, such networks allow volumetrically minor CO₂-rich gases to flux through. CO₂ is not consumed by fluxing-induced metal deposition, and a single pulse of CO₂-rich gas can therefore lead to deposition of a significant mass of metal. Using the values calculated in the model above, a single pulse of CO₂-rich vapour would deposit 478 kg of Cu along this 4 km long conduit for a 1 m² conduit cross-section. Assuming a host-rock percolation threshold of 15 vol %, this single pulse would enrich the bulk host rock in Cu by 8 ppm; at 650 °C the maximum pervasive enrichment would be 20 ppm. Depositing the Cu in veins, rather than pervasively, leads to locally higher concentrations, *e.g.*, if these account for 5 % of rock volume, their Cu content peaks at 400 ppm. Although still small, this is for a single batch of fluid, and a single CO₂-pulse, whereas many ore-forming systems are characterised by large fluid volumes in extensive hydrothermal circulation systems (*e.g.*, Sillitoe, 2010).

Enrichment of a fracture network to wt. %-level Cu concentrations, *i.e.* economic levels, necessitates involvement of a water-rich vapour that transports Cu. Metal solubilities in CO₂-rich vapour are negligible, preventing it from acting as a metal carrier, and its role is restricted to providing a highly efficient depositional mechanism. To explore a system where water- and CO₂-rich vapours interact, we limited fluxing to 5 vol. % of the conduit network (Fig. 2a). After each CO₂-pulse, H₂O-rich vapour re-establishes itself in the fluxed part of the fracture network and mixes with the H₂O-rich vapour in the 95 vol. % of the



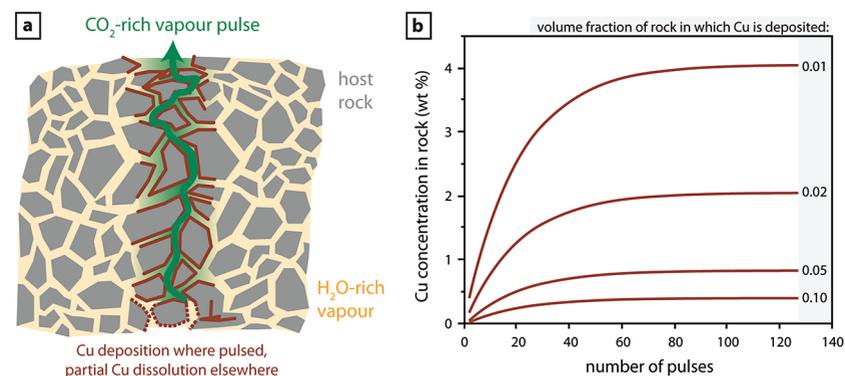


Figure 2 Progressive Cu enrichment in a fracture network intermittently pulsed with CO₂-rich vapour in its centre. **(a)** Schematic section showing Cu deposition on fracture walls followed by partial re-dissolution after each pulse, except for fractures sealed by precipitation. **(b)** Progressive enrichment of Cu assuming partial Cu re-dissolution, and fluxing of 5 vol. % of the fracture network. Cu is sourced from the 95 vol. % of the network filled with water-rich vapour.

fracture network. Repeatedly fluxing this 5 vol. % section leads to a rapid increase in Cu content (Fig. 2b). Effectively, this redistributes Cu from the full system and concentrates it in the CO₂-fluxed part. We included a re-dissolution fraction of 5 wt. % of total Cu in each calculation step, which can be interpreted as slow kinetics of re-dissolution, or short lifespans for individual fractures. Choosing a higher fraction necessitates more CO₂-pulses to reach these Cu concentrations, but otherwise does not affect the model. Cu contents in the fluxed part of the fracture network readily reach wt. % concentrations (Fig. 2b).

Conclusions

We propose that CO₂-fluxing is a highly efficient metal deposition mechanism that rivals established ore-depositing mechanisms. It can concentrate Cu to levels that are economic to mine in porphyry-Cu ore deposits. However, porphyry-Cu systems provide a benchmark only, and we do not advocate their formation by CO₂-fluxing, because the combination of invoked geological conditions is unlikely to be present in these systems. Rather, CO₂-fluxing has the potential to control metal contents in gas-fluxed magmas and on a local scale in associated hydrothermal systems. In the models presented here, metal deposition results from lowering water partial pressure and this can be brought about not only by fluxing with CO₂, but also by fluxing with other gases (e.g., N₂). It is moreover not restricted to vapours, but will also impact solubility for hydrated species in aqueous solutions (e.g., Akinfiev and Diamond, 2009), albeit less drastically.

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Additional Information

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