

## Triggers for the formation of porphyry ore deposits in magmatic arcs: predisposition or perfect storm?

### Supplementary Information

#### Mineralization model for porphyry ore deposits

The model for exsolution of fluids from porphyry intrusions and mineralization is well-established in the literature, e.g.<sup>1-4</sup>. Once a magma body stalls in the crust it will start to lose significant heat to its wallrocks and will crystallize around its margins to form a solid carapace. The formation of anhydrous minerals increases the water content in the residual melt and this can lead to magmatic volatile phase (MVP) saturation in a previously undersaturated melt or to accelerated exsolution in an already fluid saturated melt. This is the classic “second boiling” process that has long been regarded as a key stage in the formation of porphyry deposits<sup>1</sup>. Exsolution of water and other volatiles from the melt results in a volume increase that cannot be accommodated by plastic deformation of the magma and its wallrocks so that the internal pressure within the carapace increases<sup>5</sup>. Ultimately, this leads to brittle failure of the enclosing rocks, sometimes with spectacular consequences, including the generation of explosive breccia pipes that may vent to the Earth’s surface<sup>6</sup>. The overpressured MVP drains into the fracture permeability produced during failure, cooling and precipitating minerals to form veins – the characteristic vein stockwork of porphyry deposits – and breccia cements, typically in about a cubic kilometre of rock. Pressure quenching of the magma by fluid release produces the characteristic porphyritic texture.

Mass balance constraints indicate that the calculated tens to hundreds of cubic kilometres of magma required to source mineralizing fluids to a large porphyry deposit is vastly in excess of the volume of the porphyry intrusions themselves (~1 km<sup>3</sup> for a pipe with a radius of 250 m and height of 5 km) so that a deeper source of much of the fluid involved is inescapable, e.g.<sup>1-4,7,8</sup>. The porphyry fingers are regarded as conduits or “exhaust valves”<sup>6,9</sup> that focus the flow of mineralizing fluids from a crustal staging chamber, and their apices act as a fractured trap where ore minerals can precipitate. Consequently, the pressures and temperatures at which metalliferous volatiles separate from the magma are significantly higher (e.g. 200 MPa, 900°C) to those extant in the shallower deposit setting (50-100 MPa, 500-700°C). However, in both cases, conditions are likely to be close to the two-phase surface for H<sub>2</sub>O-NaCl so that the exsolving MVP could exist as a homogeneous supercritical fluid, or as separate hypersaline brine and coexisting low density vapour, with an attendant impact on ligand and metal partitioning behaviour and the physics of fluid movement<sup>10</sup>.

Metal partitioning into the exsolving MVP is a complex function of a range of variables, including pressure, temperature, oxidation state, the water, chlorine and sulfur content of the melt, and how chlorine, sulfur and other volatiles partition into the MVP when it exsolves. The efficiency of metal transfer into the MVP is also limited by the competition for metals by crystallizing magmatic phases, especially sulfides. The timing of volatile exsolution relative to crystallization progress is therefore regarded as critical, because early exsolution (e.g. in volatile-rich magmas) favours the removal of metals by the MVP before they can be sequestered by crystals<sup>7,11</sup>.

Exsolved, buoyant fluids are channelled upward into fractures and breccia pipes where depressurization, phase separation and cooling lead to precipitation of Au and Cu and Mo sulphides, mostly between about 425°C and 300°C and at <100 MPa<sup>12</sup>. Often sulfides are deposited in secondary

permeability within earlier quartz veins that is produced by fluids passing through a window of retrograde quartz solubility<sup>13</sup>. Two key processes in this temperature-pressure interval are the expansion of liquids or vapors which can reduce metal sulfide solubility<sup>14</sup>, and the disproportionation of magmatic SO<sub>2</sub> to SO<sub>4</sub><sup>2-</sup> and H<sub>2</sub>S which also drives the precipitation of sulfides (and anhydrite). This reaction, and the dissociation of other acid species such as HCl, generate increasingly acidic fluids, leading to the progressive replacement of early feldspar-stable potassic alteration by muscovite/illite-stable (phyllic), then clay-stable (argillic) and ultimately alunite-stable assemblages (advanced argillic)<sup>15</sup>.

1. Burnham, C. W. in *Geochemistry of Hydrothermal Ore Deposits* (ed H. L. Barnes) 71-136 (3<sup>rd</sup> Edition, Wiley, New York, 1979).
2. Hedenquist, J. W. & Lowenstern, J. B. The role of magmas in the formation of hydrothermal ore deposits. *Nature* **370**, 519-527 (1994).
3. Cloos, M. Bubbling magma chambers, cupolas, and porphyry copper deposits. *Int. Geol. Rev.* **43**, 285-311 (2001).
4. Richards, J. P. Magmatic to hydrothermal metal fluxes in convergent and collided margins. *Ore Geol. Rev.* **40**, 1-26 (2011).
5. Fournier, R. O. Hydrothermal processes related to movement of fluid from plastic to brittle rock in the magmatic-epithermal environment. *Econ. Geol.* **94**, 1193-1211 (1999).
6. Sillitoe, R. H. Porphyry copper systems. *Econ. Geol.* **105**, 3-41 (2010).
7. Candela, P. A. & Holland, H. D. A mass transfer model for copper and molybdenum in magmatic hydrothermal systems: the origin of porphyry-type ore deposits. *Econ. Geol.* **81**, 1-19 (1986).
8. Shinohara, H., Kazahaya, K. & Lowenstern, J. B. Volatile transport in a convecting magma column: Implications for porphyry Mo mineralization. *Geology* **23**, 1091-1094 (1995).
9. Cooke, D. R., Hollings, P., Wilkinson, J. J. & Tosdal, R. M. in *Geochemistry of Mineral Deposits* (Treatise on Geochemistry, 2nd Edition, Elsevier, Amsterdam, in press).
10. Candela, P. A. Physics of aqueous phase evolution in plutonic environments. *Am. Mineral.* **76**, 1081-1091 (1991).
11. Candela, P. A. A review of shallow, ore-related granites: textures, volatiles and ore metals. *J. Petrol.* **38**, 1619-1633 (1997).
12. Landtwing, M.R., Furrer, C., Redmond, P.B., Pettke, T., Guillong, M. and Heinrich, C.A., 2010, The Bingham Canyon porphyry Cu-Mo-Au deposit. III. Zoned copper-gold ore deposition by magmatic vapor expansion. *Econ. Geol.* **105**, 91-118.
13. Rusk, B. & Reed, M. Scanning electron microscope-cathodoluminescence analysis of quartz reveals complex growth histories in veins from the Butte porphyry copper deposit, Montana. *Geology* **30**, 727-730 (2002).
14. Pokrovski, G. S., Roux, J. & Harrichoury, J. C. Fluid density control on vapor-liquid partitioning of metals in hydrothermal systems. *Geology* **33**, 657-660 (2005).
15. Hemley, J. J. & Hunt, J. P. Hydrothermal ore-forming processes in the light of studies in rock-buffered systems: II. Some general geological applications. *Econ. Geol.* **87**, 23-43 (1992).