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Vapours, Volcanoes and Ore Deposits

Williams-Jones, A.E.¹

¹ Earth and Planetary Sciences, McGill University, Montreal, QC, Canada, H3A 0E8; willyj@eps.mcgill.ca

The idea that aqueous vapours can transport metals in concentrations sufficient to form ore deposits is not new. Indeed, Georgius Agricola in his “De Re Metallica” (1556) proposed that “metal exhalations are drawn up from the depths, and the rising fumes pass in veins and stringers”. Experimentalists in the late 19th and early 20th century subsequently showed that significant quantities of metal oxides, including UO_2 , SnO_2 , Fe_2O_3 and SiO_2 , could be dissolved in steam at ppm levels. However, these findings were largely ignored by the ore deposits community after Krauskopf (1957) showed that the vapour pressures of Cu, Ag and Au, the metals of most interest in porphyry and epithermal environments, where transport by vapour might be a possibility, are negligible.

Fluid inclusion studies by Heinrich and co-workers in the 1990’s reporting ppm levels of Au and Ag and percentage levels of Cu in vapour inclusions from porphyry deposits revived the idea of aqueous vapour as an ore fluid. However, this again was placed in doubt when Lerchbaumer and Audétat (2012) showed that Cu diffuses through quartz and that the high values of Cu reported in vapour inclusions from porphyry deposits might be artefacts of post-entrapment modification.

In a series of experimental studies we have shown, contrary to the predictions of Krauskopf (1957), that Cu, Ag and Au, all dissolve in vapours in concentrations high enough for the latter to constitute ore fluids for these metals. For example, we have shown that the solubility of Au in a H_2O -HCl, 0.2 g cm^{-3} vapour exceeds 30 ppm at 400 °C (Fig 1)!

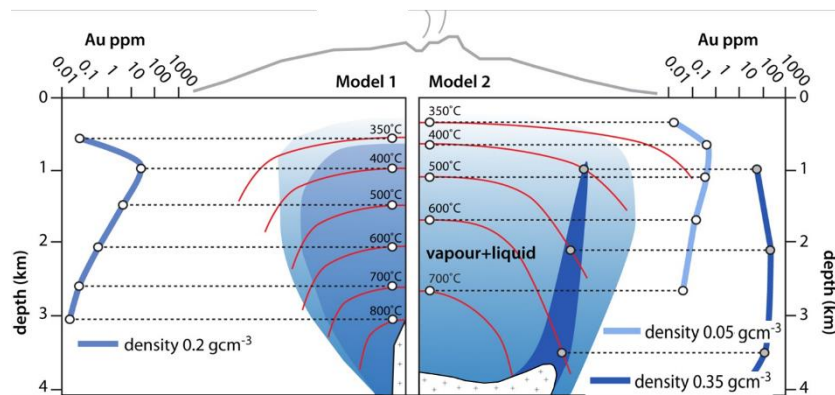


Figure 1: The solubility of Au in H_2O -HCl vapour as a function of depth (pressure) and temperature (Hurtig and Williams-Jones, 2014).

The reason for the high concentrations is that water molecules form clusters that hydrate metal complexes, greatly increasing their solubility. Thus large clusters (high hydration numbers) promote high solubility. At constant density, solubility increases with temperature, reaching a maximum. This is because the partial pressure of water increases with temperature, promoting formation of species with high hydration numbers. However, increasing temperature decreases cluster stability, favouring less hydrated species. The maximum corresponds to the condition above which the positive effect of temperature on partial pressure is outweighed by its negative effect on cluster stability.

We have validated the predictions of our experiments with data on the compositions of volcanic gases confirming the thermal maxima in metal concentration, evidence of Au-Ag-Cu concentration in the

crater of an active volcano and discovery of identical alteration/mineralisation in a high sulphidation epithermal deposit on a presently forming volcanic island. In effect, we have shown that hydrothermal vapours can form porphyry and epithermal ore deposits.

References:

[1] Krauskopf K (1957) *Economic Geology*, 52: 786-807

[2] Lerchbaumer, L and Audétat (2012) *Geochimica et Cosmochimica Acta*, 88: 255-274

[3] Hurlig N and Williams-Jones A (2014) *Geochimica et Cosmochimica Acta*, 127: 305-325.

