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Boiling, condensation and vapour contraction in magmatic-hydrothermal Cu-Au ore systems

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A re-assessment of phase stability relations in the salt-water fluid system [1] combined with thermodynamic modelling of minor solutes based on fluid inclusion microanalyses [2] and a comprehensive new experimental data set for gold solubility across a large pressure and temperature range [3,4] indicate that very high concentrations of gold can be efficiently transported from magmas through porphyry-style ore deposits to sites of high-grade gold enrichment in epithermal deposits. The key physical process is the *contraction* of a magmatic vapour phase to an aqueous liquid. This process can be achieved, without crossing of any phase boundary, by fluid cooling in a confined pressure environment, possibly near the lithostatic – hydrostatic interface. An essential chemical requirement for concentrated gold transport is an excess of sulphide over copper and iron in the low-salinity magmatic fluid. This chemical requirement can best be met by initial *condensation* and physical separation of some Fe-K-Na-chloride rich brine from the vapour, before this Fe-depleted but sulphur (H₂S, SO₂) enriched low-salinity fluid cools and ascends to the epithermal deposit. Fluid inclusions show that the process of brine condensation is ubiquitous in porphyry deposits. Acid neutralisation by feldspar destructive alteration further helps maintaining high gold concentrations in the fluid, up to several ppm, indicating that the common quartz – sericite – pyrite veins in many porphyry deposits are the likely gold-transporting fluid pathways towards epithermal gold deposits.

Fluid modelling and published field observations lead to a simple geological model that links porphyry-style and epithermal ore deposits to the cooling of a hydrous magmatic pluton as their common fluid source. As the magmatic systems cools, the melt interface and surrounding isotherms retract downward, while fluid exsolution continues. This shifts the region of brine – vapour coexistence to increasing depth and leads to the typical, ‘telescoped’ overprinting of porphyry-style ores by epithermal veins.

References

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Dual lithophile/chalcophile behavior of Mo in porphyry Cu-Mo systems

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Under the high S activity conditions of porphyry Cu-Mo hydrothermal systems, Mo precipitates mainly as molybdenite (MoS₂) owing to its chalcophile character. However, in these high sulfidation environments, we have also found Mo to behave as a lithophile element, partitioning into co-crystallizing hydrothermal titanium oxides.

PIXE analyses of hydrothermal rutiles from the El Teniente porphyry Cu-(Mo) deposit (Chile) reveal contents of Mo up to ~600 ppm. Similar to other HFSE, Mo incorporates into the rutile structure via coupled substitutions of the type $^{VI}Mo^{+6} + 2^{VI}M^{+3} \rightleftharpoons 3^{VI}Ti^{+4}$, where M⁺³ is mainly Fe.

The Mo content in these rutiles reveals a distribution pattern, where Mo-poor rutiles (mean 6 ppm) are only present in the Mo-rich mafic wallrocks and Mo-rich rutiles (mean 190 ppm) in the Mo-poor felsic porphyries. This metal distribution is a unique feature of rutile chemistry from this deposit, providing important clues concerning Mo behavior, including physicochemical and mineralizing conditions in the El Teniente deposit.

Hydrothermal rutile in porphyry systems is generally coeval with alteration and mineralization events. Therefore, the H₂S activity of incoming mineralizing fluids, which depends in turn, on their redox state, will control the dual behavior of Mo and consequently its content in rutile. Accordingly, changes in the geochemical behavior of Mo may account for the observed distribution pattern of this metal.

The low H₂S activity of fluids exsolved from the highly oxidized ($fO_2 \geq NNO+1$) felsic porphyries, enhances Mo lithophile behavior. Under these conditions, MoS₂ deposition may be delayed or even suppressed allowing hydrothermal rutile to become Mo enriched. Conversely, the Mo-rich mafic wallrocks represents the major area of sulfide deposition. Here, co-crystallizing rutile becomes Mo-poor due to severe Mo depletion in the fluids driven by molybdenite precipitation.

Variation in Mo content of rutile from this porphyry deposit fits the model in which the low ore grade cores (porphyries) are areas of relatively poor deposition of sulfides, yet fluxed by metal-bearing oxidized fluids, migrating away toward the mafic wallrock where most of the metal was deposited.

The dual lithophile/chalcophile behavior observed for Mo in the El Teniente system suggests that the use of rutile chemistry may help to better constrain metal provenance and mineralizing processes in porphyry Cu-Mo systems.

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