

# Liquid–vapour partitioning of trace-elements in boiling hydrothermal systems: laser-ablation ICPMS data from natural fluid inclusions

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Strong segregation of base metals between a hypersaline brine and a lower-salinity vapour has been observed by PIXE analysis of fluid inclusions (Heinrich *et al.*, 1992), but some doubts remained whether the two inclusion types represent coexisting fluids. New micro-analytical data, from liquid and vapour inclusions trapped simultaneously in quartz in a variety of ore-deposits, now provide unambiguous and quantitative evidence for strong fractionation of a range of elements between coexisting fluids in 'boiling' hydrothermal systems. The thermodynamic explanation and the geological consequences of our observations are still speculative, but it is inevitable that the physical separation of brine and vapour has a profound influence on metal transport and ore deposition, especially for the behaviour of Cu, As and Au at the transition between 'porphyry' and 'epithermal' environments.

## LA-ICPMS microanalysis of fluid inclusions

A quadrupole ICPMS has been combined with a 193nm Excimer Laser and an optical system that was specifically designed for controlled sampling of fluid inclusions (Günther *et al.*, 1998). The system provides a flat-profile laser image for smooth UV ablation and allows simultaneous visual observation of the sample. Transient ICPMS signals are recorded during opening and complete ablation of an individual inclusion, integrated, and referenced against element ratios of an external standard. Based on an estimate of the Na-concentration in the inclusion, which is determined by microthermometry prior to ablation, absolute concentrations of major, minor and trace elements are obtained down to typical detection limits of 1ppm for 20 elements in a 20  $\mu\text{m}$  inclusion. By restricting the analysis to a few elements with optimised tuning, the detection limit can be lowered further, which recently permitted the first analyses of gold in individual fluid inclusions.

## Results from coexisting liquid + vapour inclusions

Microanalytical data have been obtained from selected quartz samples containing liquid and vapour inclusions that fit all petrographic criteria for simultaneous trapping as separate homogeneous fluids from a boiling hydrothermal system. Most fluid pairs are from single pseudosecondary trails with well-separated populations of identical inclusions (Audétat *et al.* 1998). Samples from a range of ore deposits were investigated, covering a range of salinities (1–70% in the liquid) and P-T conditions of liquid/vapour equilibrium (350–650°C; 0.2–1.5 kbar). A range of geologic environments were sampled: several magmatic-hydrothermal Sn and W deposits of the Mole Granite (Australia); the potassic ore stage of the porphyry-type Cu-Au deposits of Grasberg (Irian Jaya) and Bajo la Alumbrera (Argentina); magmatic-hydrothermal quartz associated with the Au-mineralised breccia pipe of Kidston (Queensland); and pre-ore stage fluids in a polymetallic vein deposit of low-sulphidation epithermal type (Madan, Bulgaria).

Preliminary interpretation indicates some common trends and some systematic differences in metal behaviour. Two groups of elements can be consistently distinguished.

All elements from the L-fractionating group show similar concentration ratios between liquid and vapour ( $M_V/M_L$ ) in any one sample, but the ratio and the absolute concentrations vary significantly between samples. The elements from the V-fractionating group show variable positive deviations from the constant element ratio of the L-fractionating group. Copper is enriched in the vapour phase of most liquid/vapour pairs. The concentration ratio of Cu to any of the liquid-fractionating elements is 10 to 1000 times higher in the vapour compared to the liquid phase. Gold has been unambiguously detected

in two porphyry-related samples. At least in the Grasberg sample, gold is clearly enriched in the vapour phase (~1–10ppm) but even the high-temperature brine inclusions contain detectable concentrations around 0.3 ppm gold (absolute quantification preliminary). As, Sb, Li and B show variable partitioning behaviour and commonly fractionate in favour of the magmatic vapour phase.

### Tentative thermodynamic considerations

Considering the P-V-T-X relations in the system NaCl–H<sub>2</sub>O (Anderko and Pitzer, 1993) and limited experimental data on minor components in magmatic-hydrothermal systems, it seems likely that the partitioning of ore-forming trace metals between two coexisting water-rich fluids is most significant in saline fluid systems within a window of intermediate P-T conditions (~ 300–1500 bar and 400–700°C). At conditions approaching the critical curve, which extends to about 2 kbar and 900°C, the differences in density and salinity between the two fluid phases vanish and so must the trace-element fractionation factors. Such a tendency is indicated by the field data from the Mole Granite, where the smallest degree of selective partitioning between V-fractionating Cu and all L-fractionating elements is associated with the fluid pair trapped at the highest temperature and pressure. At lower pressures and temperatures, the differences in salinity and density of coexisting liquid and vapour phases in the NaCl–H<sub>2</sub>O system increase and so does the tendency for selective behaviour of trace elements. At low temperatures below the critical point of water, vapour-phase transport will again become insignificant for all except the most volatile chemical elements.

In the intermediate P-T-X region of the two-phase field, the behaviour of the ore-forming metals will be governed by differences in metal speciation in the two coexisting fluids. Metal partitioning is expected to be mainly dependent on (1) differences in metal complex stability and (2) the partitioning of ligand components between the two fluids. The geologically most important ligand-forming elements, Cl and S, have a strong tendency to fractionate, respectively, into the saline liquid and a S-rich vapour phase (with the degree of fractionation depending on acidity and redox potential). We have previously speculated that chloride complexing dominates the consistent fractionation behaviour of the L-fractionating group of elements, whereas sulphur complexing is responsible for the selective fractionation of Cu into the vapour phase (Heinrich *et al.*, 1992). The recent Au analyses by LA-ICPMS seem to confirm the earlier prediction

that gold bisulphide complexation (which is known to be very strong over a wide range of temperatures) should cause gold to partition into the vapour phase. As and Sb form stable sulphur as well as hydroxy complexes, which may explain the variable intermediate fractionation behaviour of these elements.

### Selective transfer of ore metals from 'porphyry' to 'epithermal' environments

Although our analytical observations on metal partitioning mainly come from high-temperature 'porphyry' environments (in the widest sense), their most important consequences probably relate to the overlying regime of lower-temperature 'epithermal' deposits.

The brine in the high-temperature magmatic-hydrothermal Sn and Cu-Au deposits show high concentrations of the main ore-forming metals and probably represents the main ore fluid in these environments. The ratio of the two main economic metals in the brine inclusions from the two porphyry-Cu-Au deposits (Cu/Au ~1000) are of the same order of magnitude as the concentration ratios of Cu/Au in the bulk ore of these two major deposits. These observations and the close textural association of gold and chalcopyrite in the ores suggest coprecipitation of Cu and Au from the brine, by similar chemical reactions dominated by chloride-complexed metals. The main role of brine – vapour separation in the porphyry environment probably is in the chemical and thermal mechanisms of ore-mineral precipitation (e.g. vapour condensation and brine refluxing; Eastoe, 1982).

While vapour separation and selective loss of Cu and Au as sulphur complexes may have a relatively minor influence on the metal budget of large porphyry-type deposits, it is likely to be a key factor in the formation of overlying gold-rich epithermal deposits. Cu, Au, As and S – the four most strongly vapour-fractionating elements measured in the fluid inclusions – constitute the characteristic element suite of kaolinite-alunite-enargite (Cu<sub>3</sub>AsS<sub>4</sub>) deposits. Some of these 'high-sulphidation' epithermal deposits (Hedenquist and Löwenstern, 1994) overly coeval porphyry-copper deposits and are believed to form by a mixing process between a S-rich magmatic vapour and surface-derived oxidised groundwater. For 'low-sulphidation' epithermal systems, which are more distal to deeplying igneous intrusions, a magmatic fluid component is indicated by high S- and Cl-fluxes in active geothermal analogues.