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Arsenic Speciation and Transport in Hydrothermal Vapour and Low-density Crustal Fluids

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Knowledge of the identity and thermodynamic properties of As aqueous and gaseous complexes and solid phases is necessary for prediction of the behaviour of As in hydrothermal and volcanic systems, toxic waste sites, and industrial processes of the extraction of heavy metals associated with arsenic in their ore deposits. Recent studies indicate that $As(OH)_3{}^{(aq)}$ is the dominant As(III) species in most moderate and high temperature hydrothermal aqueous fluids with densities higher than 0.5 $g.cm^{-3}$ (Pokrovski et al., 1996; 2000). However, very little is known about As speciation and behaviour in vapour phases and supercritical fluids of low density, commonly produced during boiling and brine - vapour separation in magmatic and hydrothermal environments.

In this study, liquid-liquid and solid-solid partition coefficients for As(III) and As(V) were determined to 350ºC using a special titanium reactor which allows *in situ* sampling of the vapour phase. The values of partition coefficients for As(III) between water vapour and aqueous solution ($K = mAs_{vapour}/ mAs_{liquid}$) at P_{sat} were found to be independent of As(III) solution concentrations (up to 1 mol As/kg H_2O), and equal to 0.01±0.002 and 0.13±0.02 at 250 and 350ºC, respectively. These values are close to those reported for the steam/water As fractionation measured in natural hydrothermal vents, and can be interpreted by the formation in the vapour phase of the monomer species $As(OH)_3{}^{(g)}$, probably hydrated by several water molecules. In the case of NaCl-rich solutions the values of K are slightly lower (e.g. K=~0.04 at 350ºC in the presence of 20 wt% NaCl in the solution). This can be explained by both salting-in effects for arsenious acid in the liquid phase and the lowering of water vapour pressure in the presence of NaCl, which diminishes the stability of hydrated gaseous species. In the presence of HCl in the vapour phase, As vapour concentrations slightly increase, indicating the formation of weak mixed hydroxy-chloride complexes. However, the calculations using our experimental data and the HCl concentrations found in natural fluids indicate that such complexes are minor in most hydrothermal and magmatic systems. Arsenic (V) acid (H_3AsO_4) liquid-liquid partition coefficients were found to be lower (e.g. by a factor of 5 at 350ºC) than those of As(III). These data, together with those available on the stability of aqueous As(V) hydroxide complexes and minerals, suggest that As(V) gaseous species are likely to be negligible in most reduced hydrothermal environments. As a result, $As(OH)_3{}^{(g)}$ complex is believed to be the predominant As species in the vapour phase of most water-dominated boiling hydrothermal systems. Arsenic partition coefficients between vapour and As-rich solutions (with As concentrations greater than 2 mol As/kg H_2O) are interpreted by the formation in the vapour phase of arsenic polymerised oxy-hydroxide species similar to those found in dense As-concentrated solutions (Gout et al., 1997). The stability of the polynuclear As(III) complexes greatly increases with increasing temperature and decreasing fluid density, which is also confirmed by EXAFS spectroscopy. Arsenic partition coefficients between solid As_2O_3 and dry water vapour (PH_2O ranging from 0 to P_{sat}) were found to be independent of water pressure and, thus, can be interpreted by the formation of the anhydrous As_4O_6(g). As a result, these polymerised species may dominate As speciation and transport in high temperature fluids of reduced water activity such as volcanic gases and mixed H_2O-CO_2/N_2 fluids.

The data obtained in this study allowed generation of the thermodynamic properties of $As(OH)_3{}^{(g)}$ and $As_4O_6{}^{(g)}$. These new results were applied to quantify arsenic transport and fractionation in boiling hydrothermal systems, and to model As behaviour during the formation of arsenopyrite-bearing gold and copper ore deposits. It was found that the arsenic(III) oxy-hydroxide species are likely to be responsible for the preferential partition of arsenic into the vapour phase as observed in fluid inclusions from Au-Cu porphyry type ore deposits (Heinrich et al., 1999).

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