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Metal-containing thioanions: their stability and role in gold and other element transport in hydrothermal ore solutions

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Sulfur occurs in hydrothermal fluids throughout the Earth's crust in various oxidation states, depending on the redox environment as well as temperature and pressure. In deep crustal fluids having appreciable hydrogen fugacities, reduced sulfur (i.e. H₂S and HS⁻) predominates and the weak acid ionization of H₂S has been well studied up to near critical conditions and up 500°C and 500 bar [1,2]. The higher oxidation state species (i.e., the univalent and divalent polysulfides, thiosulfate, sulphite, and sulfate) may also occur in less reducing environments but the divalent polysulfides and thiosulfate disproportionate at temperatures above about 300°C. In the boiling/phase separation regime of epithermal ore systems, the intermediate oxidation state species may be important in the residual liquid phase but have been little studied under these conditions [3].

It is well known that the group 1B(11) elements (i.e. Cu, Ag, Au) form stable hydrosulfide complexes at elevated temperatures and pressures, however, the complexing of other metals (and metalloids) by reduced sulfur ligands (and/or higher oxidation state sulfur species) under hydrothermal conditions has been much less studied. The deprotonation of the simple arsenous and antimonous (i.e. As(III) and Sb(III)) acids, H₃AsO₃ and H₃SbO₃, to form arsenite and antimonite has been studied at equilibrium vapour pressures up 300°C [4,5]. The thioarsenite and thioantimonite adducts have been the subject of a number of studies at elevated temperatures and pressures but the results are not in good agreement, partly because of the difficulties in studying these systems experimentally [6,7,8]. In addition, the thio- and oxythio-antimonate (i.e. AsV and SbV) species have been identified in surface hot springs/pools associated with active geothermal systems [9]. These species will also occur in the upper parts of geothermal systems where deep fluids undergo boiling and mixing with oxygenated meteoric waters, giving rise to fluids having elevated redox potential.

Molybdic and tungstic acid deprotonation and the stability of anionic molybdate and tungstate in hydrothermal fluids are known from only a few studies [10,11,12]. The corresponding thiomolybdates and thiotungstates have been extensively studied at ambient temperatures [13] but data at elevated temperatures and pressures are essentially non-existent.

The stability of the oxy- and thio-anions of As, Sb, Bi, Mo, and W under hydrothermal conditions will be discussed. The role of these thiometallate species in complexing and transporting other metals (e.g., Au) in high temperature systems in the Earth's crust will also be considered.

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