Adsorption of gold(I)-hydrosulphide complexes by iron sulphides

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The aim of this study has been to investigate the possible role of surface adsorption by iron sulphides in the scavenging and precipitation of gold from aqueous solutions. The adsorption of complex ions by sulphide surfaces has been little investigated even though such processes may be important for a wide range of conditions ranging from hydrothermal systems, both within the earth's crust as well as on the ocean floor and other earth surface environments. The dominant complexes responsible for gold transport by hydrothermal fluids in the crust are $AuHS^\circ$ and $Au(HS)^{2-}$. From experimtents on iron sulphide synthesis (Schoonen *et al.*, 1991*a*, 1991*b*, 1991*c*; Rickard *et al.*, 1997) it is known that pyrite does not precipitate directly form solution, but is formed depending on pH and oxygen fugacity through precursor phases like amorphous FeS, mackinawite and greigeite. We have therefore chosen to study the adsorption of hydrosulphidogold(I) complexes by pyrite, pyrrhotite and the precursor phase mackinawite over a range of pH in order to gain insight into the importance of sulphide surface adsorption processes in natural systems.

Results for pyrite are presented below.

Synthetic versus natural sample material

Only the reaction of pristine pyrite surfaces with the gold solution will reflect the natural surface adsorption with regard to capacity and behaviour. Natural material has the advantage of being well crystallised, but the disadvantage of oxidised surfaces, inhomogeneous trace metal distribution and possible inclusions of other minerals. Synthetic material has problems with its grain size and crystallinity but important advantages with respect to unoxidised surfaces and to a controlled metal content.

Synthesis of the pyrite

Pyrite was synthesised by mixing of an Fe(III)chloride solution with an Na_2S solution such that the final concentrations were 0.034 m and 0.067 m respectively. The pH was adjusted to starting values of between 3.5 and 3.9 using hydrochloric acid. All solutions were prepared from deoxygenated water and all the reactions and sample preparations were carried out in closed glass systems with nitrogen over pressure. During the mixing of the reactants, precipitation of amorphous iron monosulphide occurs. The reaction vessel was immersed for 36 h in a waterbath at 80°C, and then the product was separated from the solution by filtering and washing with 1 M HCl for 5 minutes in order to remove poorly crystalline sulphide phases other than pyrite. The product was subsequently studied by XRD and SEM, which showed that the solids consisted of a mixture of framboidal aggregates and individual (0.2 to 0.3 µm) crystals.

Surface properties of pyrite

In order to gain more insight into the surface properties of the pyrite (both natural and synthetic), the point of zero charge (pzc) was determined by potentiometic titration. The surface area was measured with the BET nitrogen adsorption method. Values for synthetic material of ~3.5m^2/g and natural material of ~4.5m^2/g were measured.

Potentiometric titration

The point of zero charge of the synthetic pyrite was found to be at pH = 1.9, whereas for natural pyrite, cleaned with HCl, the pzc was 2.15 to 2.3. Ionic strength (NaCl) and hydrogen sulphide concentration in the solution have a strong influence on the response of the mineral surface. Only in the experiments with no H_2S and 0.01 m and 0.05 m NaCl concentration can the response of the surface be observed.

Gold solution

A solution containing 10–14 mg/kg gold was produced by the reaction of an H2S-HS- solution at pH = 7 with fine grained, elemental gold, in an

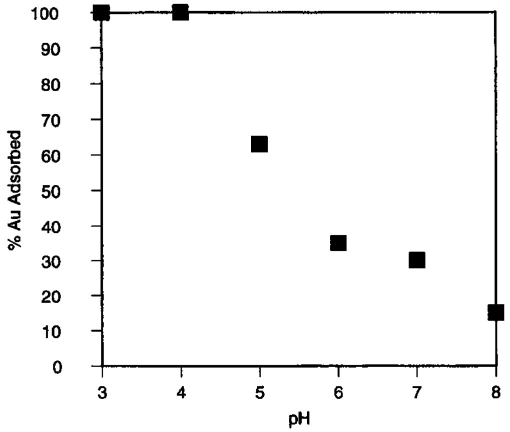

FIG. 1. Percent gold adsorption for natural pyrite as a function of pH at 25°C and 0.1 m NaCl, 30 min after adding the gold solution.

oxygen free environment. 0.15m sulphur solutions were prepared in two ways; a) with $Na_2S{\cdot}9H_2O$, and the pH adjusted to near neutral values by further reaction with H_2S or b), by making a 0.075 m solution of NaOH and further reacting with H_2S such that the pH was finally around 7, where the Au-solubility has a maximum at room temperature (Renders *et al.*, 1989).

An aliquot of elemental gold was added and the sealed flask was then covered with an aluminium foil and stored in the dark to prevent the photoreduction of the gold. After one week, a saturated solution of gold was obtained.

Adsorption experiments

Adsorption experiments were carried out in a multiport, black painted reaction vessel immersed in a constant temperature water bath. The experiments were performed as follows: The pyrite suspension was added to an H_2S-HS^- containing solution and the pH was roughly adjusted with HCl and NaOH to the desired region. To start the experiment, a known amount of the gold-containing solution was added and the pH was then adjusted. Samples of both solid and solution were collected and analysed after treatment by AAS or ICP-MS.

Conclusions

Preliminary adsorption experiments of both natural (Fig. 1) and synthetic pyrite show the highest and fastest adsorption at pH of 3 and 4 where gold is complexed both as AuHS° and $Au(HS)^{2-}$. In this region, the pyrite surface is negatively charged and the uncharged AuHS° species is adsorbed. With increasing pH, the $Au(HS)^{2-}$ species becomes more important and the adsorption process becomes less efficient and slower. Gold adsorption onto pyrite surfaces is clearly an effective and probably important mechanism of gold concentration in aqueous systems over a wide range of temperatures and pressures on and in the earth's crust, especially if we consider submarine black smoker systems where low pH solutions up to 400°C mix with cold seawater and rapid precipitation of iron sulphides occurs.

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