

The solubility of sparingly-soluble minerals at 25°C using a flow-through column

B.W. Mountain
T.M. Seward

*Inst. für Mineralogie und Petrographie, Eidgenössische
Technische Hochschule Zürich, Sonneggstr. 5, 8092 Zürich,
Switzerland.*

Introduction

The usual approach used to study the solubility of sparingly-soluble compounds under ambient conditions typically involves the sealing of a small mass of material with a considerably larger mass of solution (i.e. an extremely large fluid/solid ratio). Although these experiments are spared the problems of high temperature and pressure apparatus, they are, however, complicated by slow reaction kinetics. Alternatively, we have used an approach in which the solution is passed through a large mass of solid at a constant flow rate (i.e. a small instantaneous fluid/solid ratio). The assumption is that the small amount of fluid in the pore space will be exposed to a large surface area of solid thus accelerating the approach to equilibrium. This method has been used in the past to study the solubility of sparingly-soluble salts (Money and Davies, 1934).

Methods

At the present time, this study has been restricted to the solubility of two copper compounds: bellingerite ($\text{Cu}_3(\text{IO}_3)_6 \cdot 2\text{H}_2\text{O}$) and chalcocite (Cu_2S). Bellingerite was chosen because it is a naturally-occurring simple cupric salt with a low solubility and because of the possible importance of cupric iodate complexes in the formation of supergene copper deposits. It was synthesized by mixing aqueous solutions of CuCl_2 and NaIO_3 to produce an undersaturated solution with respect to bellingerite. This solution was acidified with HIO_3 to pH 4 to prevent the precipitation of the basic copper iodates. It was then slowly evaporated over several days until it had reached about one tenth of the original volume. Small equigranular blue crystals were produced which were identified by XRD as bellingerite. Chalcocite was produced by combining native copper (99.9%) and native sulphur (99.99%), in the correct atomic proportions, with 0.5 M NH_4Cl solution in silica glass ampoules. The ampoules were evacuated, filled with nitrogen, sealed, and placed in an oven at 300°C for one week. The run products were verified to be chalcocite by XRD.

The bellingerite experiments were undertaken using a flow-through column (Fig. 1). Fluid flow was maintained using a syringe pump which allowed flow rates from 0.1 to 700 ml/hr. The effluent was collected in a glass sample syringe and samples taken from the syringe were acidified and analyzed by AAS. Chalcocite solubility experiments are being undertaken using a similar flow-through column, modified to prevent the incursion of oxygen. Effluents from the experiments were evaporated to dryness, treated with aqua regia and then diluted with HCl. Analyses were done by ICP-MS.

Results

Figure 2 shows the results from the bellingerite flow-through experiments. The relatively flat portion of the data, at low total IO_3^- , is the limiting solubility of bellingerite represented by the reaction:

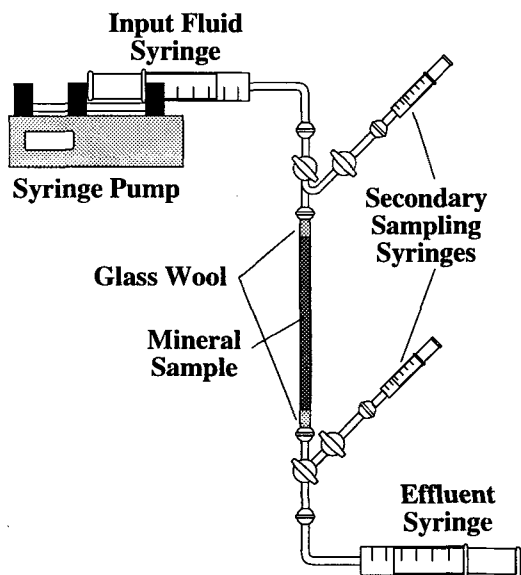


FIG. 1. Schematic diagram of the flow-through system.

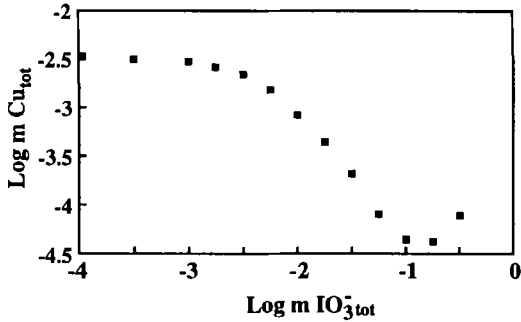
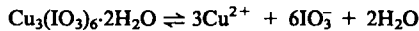
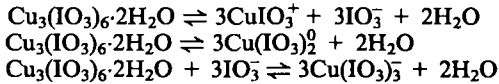


Fig. 2. Copper concentration as a function of total iodate in equilibrium with bellingerite.



In this region, the solubility is high enough that it is not affected by the initial IO_3 concentration. As total IO_3 increases, the solubility decreases along a line with a slope of -1 , flattens-out, and then increases. These trends are explained by the dissolution of bellingerite through the reactions:



which have slopes of -1 , 0 and $+1$, respectively, in $\log \text{Cu}-\log \text{IO}_3$ space. Note that the region where Cu^{2+} predominates is obscured by the high solubility of bellingerite at low total IO_3 .

The data indicate that in solutions with total $\text{IO}_3 > 0.01 \text{ m}$, the dominant copper species will be the iodate complexes. Mathematical treatment of the results will allow the determination of the stepwise formation constants of the di-iodate and

TABLE 1. Preliminary results from the chalcocite solubility experiments

Sample	Time (hours)	Total Cu ($\mu\text{g}/\text{kg}$)
4.28	Flush(10 ml/hr)	1000
CS1-1	0	90
CS1-2	24.75	55
CS1-3a	54.25	50
CS1-3b	54.25	75

tri-iodate copper complexes.

Preliminary data from the chalcocite experiments are listed in Table 1. The input solution had $\text{pH} = 9$ and $\Sigma = 0.04 \text{ m}$. Flow rate was 0.5 ml/hr .

The results show an initially high solubility which may be attributed to dissolution of fine material or to physical transport of fines into the effluent syringe. The concentration decreases, however, to the very low values expected for chalcocite solubility under these conditions. Further experiments are in progress to investigate the complexing of copper as sulphide complexes.

The results described above show the effectiveness of this experimental approach in studying the solubility of sparingly-soluble minerals and the complexing of their component metals. This technique could be applied to many other systems of geochemical importance in which static experiments display problems with the attainment of equilibrium.

References

- Money, R.W. and Davies, C.W. (1934) *J. Chem. Soc.*, 400-3.