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Sorption Mechanisms of Co and Ni with Precipitated FeS

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Introduction

Trace metal chemistry in anoxic systems is controlled by sulphide chemistry. Sulphides control the bio-availability and mobility of metals by formation of sulphide minerals, aqueous complexes (Rickard, 1995) and sorption of metals with sulphide minerals. Sedimentary iron sulphides are ubiquitous in nature and are recognised as important adsorbents that incorporate trace metals in high concentration. Other metal sulphides (e.g. CoS, NiS, CuS, ZnS, and PbS) also act as significant trace metal sinks. Both co-precipitation and adsorption have been proposed as the means of trace metal incorporation by sulphide minerals (Arakaki and Morse, 1993; Morse and Arakaki, 1993; Morse and Luther, 1999). However, the mechanism of trace metal incorporation with iron sulphide remains unclear.

Methods

Surface sorption of Co and Ni (concentrations added at intervals predetermined from rate data) onto iron sulphide was studied by measurement of their uptake onto the pre-precipitated iron(II) monosulphide at low (μM) concentration at ambient temperature. Solution analyses were performed using a Varian SpectraAA.300 AAS and Perkin Elmer Elan 5000 ICP-MS. Solid products were characterised by XRD.

Results and discussion

Solubility data for precipitated FeS and crystalline metal sulphides suggest that the mechanism of metal sorption onto FeS should principally be a function of the relative solubilities of the Fe and metal sulphide phase.

Plots of Co and Ni sorption are presented in Figure 1. a-f.

The experimental data demonstrate that decrease in Co and Ni concentrations in solution are concurrent with an increase of Fe in solution (Figure 1. a,d). This suggests exchange of Fe and Co, Ni by equilibrium such as:

$\mathrm{FeS} + \mathrm{Co}^{2+} = \mathrm{CoS} + \mathrm{Fe}^{2+}\ \Delta G_r = -16.159$ (1)

$\mathrm{FeS} + \mathrm{Ni}^{2+} = \mathrm{NiS} + \mathrm{Fe}^{2+}\ \Delta G_r = -34.677$ (2)

This process may be simply modelled using standard free energy data (obtained from Davison W, 1991; HSC database V4.0).

$K_1 = a_{(FeS2+)}/a_{(Co2+)}$
$= 7.758 \times 10^4\ K_2$
$= a_{(FeS2+)}/a_{(Ni2+)} = 1.590 \times 10^6$

Thus for K_1 and K_2 activity ratios in solution of $>K_1$ and $>K_2$ (determined above as the ratio at the start of the experiment) we would expect Fe and Co, Ni to exchange. Difficulties in the interpretation of this data arise since there is a lack of established solubility data for the first precipitate of CoS and NiS. With developing crystallinity (identified by XRD as transformation of $\mathrm{FeS}_{(am)}$ to $\mathrm{FeS}_{(mk)}$) an increase in the concentrations of Co and Ni in solution is detected and suggests their slight dissolution from the FeS surface (Figure 1. c,f). Subsequently, Co and Ni concentrations in solution are increased and activity ratios adjust (so that $<K_1$ and $<K_2$) and new equilibria are established. Co and Ni uptake then conform to Langmuir-type adsorption isotherms and the process is best described as adsorption of Co, Ni onto a neo-crystalline metal sulphide coated product (Figure 1. b,e,c,f). Thereafter, CoS and NiS mantling of the FeS prevents continued Fe release and concentrations in solution stabilise (Figure 1. b,e). In experiments where FeS is precipitated in the absence of Co or Ni, Fe concentrations in solution were found to be constant.

Conclusions

Co and Ni are co-precipitated with freshly precipitated FeS. As $\mathrm{FeS}_{(am)}$ is transformed to $\mathrm{FeS}_{(mk)}$ Co and Ni are slightly dissolved from the surface. Subsequently, Co and Ni are adsorbed onto a neo-crystalline Fe(Co,Ni)S surface. This interpretation is consistent with theoretical prediction. To summarise, extensive sorption experiments with the metals Co and Ni have revealed a more complex interaction with the FeS surface than has been reported in other published data-sets (e.g. Morse and Arakaki 1993).

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