Evidence for aqueous clusters as intermediates during metal sulphide formation

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The physics of nucleation and crystal growth processes involved in mineral formation are relatively well known. In contrast, the chemical processes involved in the transformation of simple dissolved species to solid products are not well understood. This paper reports the results of an investigation into these processes using the formation of zinc and copper sulphides from aqueous Zn(II) and Cu(II) as the example. Intuitively, the process is complex. Zn(II) and Cu(II) exist in aqueous solution as the hexaaquo $M(H_2O)_6^{2+}$ ion, with the Zn and Cu in octahedral coordination (Burgess, 1988). In the stable ZnS phase, sphalerite, it occurs as continuously repeating series of $[ZnS_4]$ units with both Zn and S in tetrahedral coordination whereas in CuS, covellite, the lattice is more complex because of Cu(II) reduction by sulphide.

In order to get from one state to the other, a series of reactions must occur between divalent metal cations and HS^- which involve substitution of water by sulphide, reaction intermediates that condense and changes in coordination of both metal and S. The process is further complicated by the release of protons, since S(II-) does not have any meaningful activity in aqueous solutions. For Zn, the product is an amorphous zinc monosulphide which develops a preferred structure, usually sphalerite but often with an initial content of its thermodynamically unstable dimorph, wurtzite. The initial copper sulphide precipitate also includes metastable phases such as yarrowite, Cu_9S_8 (Rickard 1972).

One of Ostwald's rules suggests that, in a precipitation process, the first formed product is not the most stable but that which is nearest the form of the species in solution. This rule has been discussed by Morse and Casey (1988). A corollary to this approach is that the final solution moiety should have a form close to the moiety in the first solid product. It is this hypothesis that we address in this paper using zinc sulphide as a primary example. We use the present state of knowledge of metal complexes with sulphur species, including thiols bound to metals and metal sulphide mineral structures, to ascertain the nature of the processes involved in the transition between aqueous M^{2+} ions and precipitated MS. We use a combination of electrochemical, spectroscopic, kinetic and molecular modelling approaches to address the problem which builds on our stability constant work (Luther *et al*, 1996).

Results and discussion

Titrations of aqueous Zn(II) with bisulphide in seawater and chloride solutions indicate that sulphide clusters readily form at concentrations of twenty micromolar (or less) of metal and bisulphide. Precipitation does not occur based on voltammetric measurements at the mercury electrode and UV-VIS spectroscopic data; and the high ionic strength ($I>0.5$) may have acted as a protective agent (see Murphy, 1996). UV-VIS data and filtration experiments indicate that the material passes through 0.1 µm Nuclepore and 1000 dalton filters. The UV-VIS data can be used to estimate the size of the clusters which ranges from < 16 to 24 Å. The complexes form rapidly ($k_f > 10^8\ M^{-1}s^{-1}$), are kinetically inert to dissociation and thermodynamically strong. Although a neutral complex of 1:1 (ZnS) empirical stoichiometry initially forms via electrochemical measurements, an anionic complex with an empirical 2Zn:3S stoichiometry forms on continued addition of sulphide. Molecular mechanic calculations, MM+, indicate that there is significant strain for structures with this 2Zn:3S stoichiometry. Based on known mineral structures and thiol complexes for these systems, a tetrameric cluster unit of $[Zn_4S_6(H_2O)_4]^{4-}$ is likely. MM+ calculations indicate that this cluster is structurally analogous to ZnS minerals (particularly sphalerite) and is a viable precursor to mineral formation and a product of mineral dissolution.

The overall process can be represented by equations 1-3. Eq. 1 shows the formation of a

$[M(H_2O)_5(SH)]^+$ complex (Luther *et al*, 1996) which loses water and protons as ring formation (polymerization, eq. 2) occurs.

(1) $3\ [M(H_2O)_6]^{2+} + 3\ HS^- \rightarrow$
$3\ [M(H_2O)_5(SH)]^+ + 3\ H_2O$ (HS^- substitution)
(2) $3\ [M(H_2O)_5(SH)]^+ \rightarrow$
$M_3S_3(H_2O)_6 + 3\ H^+ + 9\ H_2O$ (ring formation)
(3) $Zn_3S_3(H_2O)_6 + 3\ HS^- \rightarrow$
$3\ [Zn_4S_6(H_2O)_4]^{4-} + 3\ Zn(H_2O)_6^{2+} + 3\ H^+$
(crosslinking of rings by sulphide)

The loss of water to solution from six-coordinate metal in $M(H_2O)_6^{2+}$ to four-coordinate metal in $[M_3S_3(H_2O)_6]$ (eq. 2) and in crosslinking rings (eq. 3) are entropy driven processes which lead to more favourable thermodynamic processes. The formation of $[Zn_4S_6(H_2O)_4]^{4-}$ can occur from condensation of $[Zn_3S_3(H_2O)_6]$ rings which are neutral molecular clusters. The Zn atoms on one $[Zn_3S_3(H_2O)_6]$ ring combine with the S atoms on another $[Zn_3S_3(H_2O)_6]$ to lead to higher order clusters with loss of water. The $[Zn_4S_6]^{4-}$ species can form from the crosslinking of two neutral $[Zn_3S_3]$ rings by added sulphide; thus a Zn-S-Zn bridge forms across the rings with subsequent rearrangement and condensation to $[Zn_4S_6]^{4-}$; this combination results in a sphalerite-like cluster. If the rings condense without additional sulphide, a wurtzite-like structure could form. All condensations result in sulphide displacing water from Zn to form Zn-S bonds and are entropy driven reactions.

The Cu system forms species which have similarities to the Zn system, but Cu(II) reduction occurs after substitution of water by sulphide, possibly accounting for the formation of intermediates such as yarrowite and the X-ray absorption spectroscopic observation that covellite itself is a Cu(I) compound (van der Laan *et al.* 1992). Both $[M_4S_6]^{4-}$ and $[M_4S_5]^{2-}$ stoichiometries have been observed with Cu. The $[M_4S_5]^{2-}$ cluster may form from the crosslinking of two neutral $[M_3S_3]$ rings without added sulphide. Because of redox processes, the S atoms on one $[M_3S_3]$ ring can also combine with the S atoms on another $[M_3S_3]$ ring to form S_2^{2-} species which are found in covellite.

The ZnS clusters would be resistant to oxidation by O_2 and Vazquez *et al.* (1989) indicated that the oxidation of sulphide by O_2 is thirty times faster when Zn(II) is not present. Voltammetric experiments indicate neutral and anionic clusters for Zn and Cu which agree with the ion chromatographic results for these metals in the sulphidic waters of the Black Sea (Landing and Lewis, 1991).

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