Metal sulfide complexing – What we know and what we should know

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Reduced sulfur occurs ubiquitously in aqueous fluids within and on the Earth's crust over a wide range of conditions extending from ambient to high temperatures and pressures. In all these environments, metal ions may be complexed to varying degrees by simple inorganic ligands such as HS-, S2-, and SxS2- (polysulfide) as well as by thio-organic electron donors. Metal sulfide complexes and clusters play an important role in element sequestration and transport and biogeochemistry in aquatic (e.g. wetland) systems as well as in the ocean water column and in particular, in anoxic marine environments (e.g. the Black Sea dead zone). In seafloor and subaerial hydrothermal systems, metal-sulfide complexing (i.e. transport) and precipitation are in important not only in ore formation but also in defining many aspects of biodiversity in seafloor and surface discharge environments. At more extreme conditions within the Earth's crust, metal sulfide complexes are considered to partition into volatile rich fractions during phase separation of saline, magmatic (hydrothermal) fluids. In volcanic gas environments, volatile metal sulfide complexes account significantly for the transition metal transport budget to the atmosphere.

Despite the overall importance of metal sulfide complexing in understanding many geo(bio)chemical phenomena, the stability and stoichiometry of many aqueous metal sulfide complexes are not well known, particularly at ambient temperature where the experimental determination of reliable equilibrium constants is fraught with problems. A few metal-sulfide complex are quite well defined over a range to temperatures extending to supercritical conditions such as with the formation of silver and gold hydrosulfide/sulfide complexes. Both Ag and Au are soft Lewis acis and thus form very stable molecular moieties with reduced sulfur. Reliable equilibrium thermodynamic data also exist for sulfide complexes of Cu, Zn, Cd and Hg and some other elements (e.g. As, Mo) but there is a dearth of information available for many other metals with respect to the stability of the complexes as well as their related clusters and their structures. Our current state of knowledge will be discussed together with an assessment of the crucial gaps in our knowledge in metal-sulfide interactions under a variety of conditions.

A geochemical scenario for evolution of the Nain-Baft back arc basin

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The Nain-Baft ophiolitic complex is categorized as an oceanic back arc basin, opened during the middle Cretaceous in the active continental margin of the Central Iranian continental block (the Sanandaj-Sirjan zone), due to the oblique subduction of the Tethys Ocean beneath the Iranian block. This extensional basin is behind the Mesozoic magmatic arc of the Sanandaj-Sirjan zone but crosscutting by the Eocene magmatic rocks of the Urumieh-Dokhtar magmatic belt. The Upper Cretaceous is believed to be the time of crystallization or metamorphism of the rock units in this oceanic basin based upon the K-Ar age determination. Clinopyroxene grains in the basaltic rocks of the Nain-Baft ophiolitic complex are characterized by low content of TiO_2 content, similar to those of basalts, erupted in arc related environments. The basaltic-gabbroic rocks and the more acidic terms of this belt are of both tholeiitic (IAT) and calc-alkaline affinity. Depletion in HFSE and enrichment in LILE are the more distinctive features. Fractional crystallization and various degrees of depletion/enrichment in the mantle source associated with different degrees of partial melting are the main mechanisms, responsible for the geochemical evolution of the rock series in these ophiolitic complexes.