

Computer simulations of iron-nickel sulphides in water

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The structural analogy between FeS/(Fe,Ni)S minerals and the (Fe,Ni)S clusters present in biological enzymes has led to suggestions that these minerals could have acted as catalysts for the origin of life. It has been suggested that life arose from a redox and pH front on the Hadean ocean floor [1], whereby the meeting between the hydrothermal front generated in the oceanic crust with the acidic oceanic fluid led to a spontaneous precipitation of FeS and NiS 'membranes/bubbles' which acted as reaction centres for carbon-carbon bond forming reactions. Here we present a computational study aimed at investigating the structure, dynamics and stability of Fe_xS_y (x, y ≤ 4) clusters in water. We shall also discuss violarite (FeNi₂S₄) surface structures and stabilities, and their affinity towards water

First, we will present first principles molecular dynamics simulations of the nucleation of iron sulphide clusters from aqueous solution, where our calculations of the Fe and S ions and the primary building unit FeS in water reveal that the effect of sulphur on the hydration structure of iron is to significantly reduce its first coordination shell compared with isolated Fe²⁺ and Fe³⁺ ions in water. However, simulations of Fe_xS_y particles (x, y ≥ 2) show that these clusters are unstable in water under the ambient conditions in our simulations, where we discuss any competing reactions such as the formation of iron hydroxides.

Because Ni is an important impurity in iron sulphides and potentially plays a vital role in the catalytic reactions, we will also present our calculations of the uptake and distribution of Ni ions in greigite-structured materials, employing a joint thermodynamical and statistical mechanical approach.

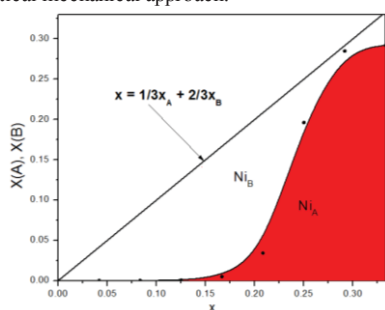


Figure 1: Distribution of Ni over tetrahedral (A) and octahedral (B) greigite sites, as a function of the total Ni concentration (x) at 600 K.

Finally, we have calculated the surface structures and stabilities of violarite - the fully-ordered FeNi₂S₄ mineral - and investigated their interaction with the aqueous environment and propensity towards dissolution.

[1] Russell, Martin, (2004) *Trends Biochem. Sci.*, **29**, 358-363.

Molecular dynamics simulations of Y in silicate melts and implications for element partitioning

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Element partitioning depends strongly on the composition and structure of the involved phases. Whereas the influence of mineral phases is well described by the lattice strain model [1], the dependence of partition coefficients on melt chemistry is still poorly understood. However, there is ample evidence that the distribution of, e.g., rare earth elements between mineral and melt or between two immiscible melts varies considerably with melt polymerization [2]. Hence, if one uses trace element contents of igneous rock samples to constrain *P-T-t* paths of the material, the dependence of geochemical affinities on melt composition has to be understood.

We performed molecular dynamics simulations to investigate the coordination environment of Y (as an exemplary trace element) in silicate melts of different compositions in the model system CaO-Al₂O₃-SiO₂ [3]. This structural information was then linked to the partitioning behavior of Y. A wide range of melt polymerization was sampled by varying the relative abundance of network-modifying CaO. The results show that the local atomic structure around Y depends systematically on melt composition: when melt polymerization decreases (i.e. CaO content increases), the coordination of Y by oxygen decreases, as well as the average Y-O bond length. These changes are reflected by an increased oxygen order around Y and were confirmed by extended x-ray absorption fine structure (EXAFS) spectroscopy on glasses of the same composition as in the simulations. Moreover, we found a tendency of Y to form clusters with Ca and conclude that the presence of network modifiers facilitates the incorporation of Y into melts. This observation is in agreement with the observed trend of rare earth elements to partition preferentially into more depolymerized melts.

In a more quantitative approach, we modelled exchange reactions of trace elements and major elements between different phases. The computational method of thermodynamic integration allows the calculation of equilibrium constants and free energies of these reactions, which are directly related to fractionation processes. The thermodynamic results confirm the more qualitative explanation of partitioning behavior in terms of melt structure.

We emphasize that the method, applied here to Y in silicate melts, is very general and can be used, in principle, to predict element partitioning between arbitrary phases quantitatively. It thus complements the lattice strain model (which focuses on the role of mineral phases) by taking into account the influence of melt or fluid structure on element partitioning.

[1] Blundy and Wood (1994) *Nature* **372**, 452-454.

[2] Schmidt et al. (2006) *Science* **312**, 1646-1650.

[3] Haigis et al. (2012) (submitted)