Aqueous iron-sulfur clusters: insights from molecular dynamics

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Aqueous iron-sulfur clusters (FeS(aq)), where water molecules are molecularly coordinated to the ferrous high-spin irons, are of extreme interest in Origin of Life theories. Together with iron-sulfur minerals, it has been postulated that FeS(aq) would be capable of synthesising simple organic molecules on the early Earth, while the underlying mechanism, based on the reduction of CO_2, suggests that they may have a modern role as catalysts for CO_2 conversion [1, 2].

Despite the environmental importance of FeS(aq), we know little about their nucleation in aqueous solution and the subsequent growth of the first condensed mackinawite phase. For instance, the stoichiometry and size of FeS(aq) are still a matter of debate, while the stability constants for the complexes reported in the literature are often controversial [3]. Here, we employ accurate molecular dynamics simulations to study the behaviour of FeS(aq) in water. First, we determine the structures and the hydration shells of a number of FeS(aq). Then, for the smallest units, we investigate the free energy profiles along the reaction coordinate of nucleation. Particular emphasis is given to the aqueous Fe_2S_2 cluster (Fe_2S_2(aq)), which, due to its similarity to the building unit of mackinawite, is thought to have a major role in the nucleation [3]. Finally, we discuss the effects caused by the replacement of Fe with Ni atoms, abundantly present in the Hadean ocean.

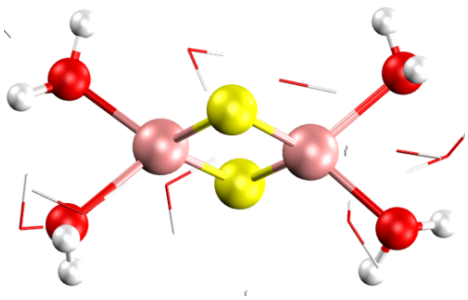

Figure 1: Snapshot from the molecular dynamics trajectory of Fe_2S_2(aq).

[1] Wachtershauser G., (1988) *Microbiol. Rev.*, **52**, 452 [2] Russell & Martin, (2004) *Trends Biochem. Sci.*, **29**, 358 [3] Rickard & Luther, (2007) *Chem. Rev.*, **107**, 514