The equilibrium Mo isotope fractionations between (Fe,Mn)oxyhydroxides and Mo species in aqueous solutions

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Urey model or Bigeleisen-Mayer equation based theoretical method and the super-molecule clusters are used to precisely evaluate the fractionations between the absorption complexes at the surface of (Fe,Mn)-oxyhydroxides and many possible Mo species in aqueous solution. The B3LYP/(6-311+G(2df,p), LANL2DZ) level method is used for harmonic frequency calculations. 24 water molecules are used to form the super-molecules surrounding the aqueous Mo species. At least 4 different conformers for each super-molecule are used to prevent the errors from the diversity of configurations in solution.

Our results show that the solvation effects can dramatically change the fractionation numbers from the ones in gas-phase. For example, the $MoQ_4^{2-}Mo(OH)_6$ fractionation at 25°C is 0.8‰ (in terms of $^{97/95}Mo$ and same as below) for gas-phase but it is about 2.0‰ in solution. Our results show that no matter the dominant aqueous species MoQ_4^{2-} is adsorbed on the (Fe,Mn)-oxyhydroxides by the mono-dentate or bi-dentate way, it only can bring less than 1‰ isotopic fractionation differences. The polymerized MoQ_4^{2-} forms (e.g. Mo_3O_9) also have less than 1‰ isotopic fractionation relative to aqueous MOQ_4^{2-} . In another word, the 1.7 - 2‰ Mo isotope offset found between the seawater and the Fe,Mn-oxides, is unlikely caused by the absorption of MoQ_4^{2-} into such oxic sediments. This study provides a base for discussing the mechanism of Mo removal from the seawater.

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Experimental and theoretical determination of the kinetics of thermochemical sulfate reduction

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Prediction of the H₂S generation potential of a petroleum reservoir prior to drilling is a major challenge for the oil industry, primarily due to the fact that published estimates of the kinetic parameters that describe the rate of thermochemical sulfate reduction (TSR) vary widely and are inconsistent with geologic observations. The apparent unreactivity of free aqueous sulfate ions (SO₄²⁻) has led previous researchers to conclude that the presence of reduced sulfur is required to catalyze the TSR reaction. Recent experimental and theoretical evidence indicate that TSR in natural environments probably involves a two-stage reaction mechanism. The initial stage involves the reduction of a reactive sulfate species to H₂S in the absence of reduced sulfur; however, once a threshold partial pressure of H₂S has been attained a much more rapid catalyzed reaction becomes dominant. Aqueous geochemical modeling of typical reservoir brines and experimental solutions shows that the reactive sulfate species at common reservoir temperatures (100-200°C) is aqueous MgSO₄ contact ion-pairs (CIP's) while at the higher temperatures (>200°C) used in laboratory simulations it is bisulfate ions (HSO₄). Based on *ab initio* quantum chemical calculations, the kinetic parameters for the reduction of HSO₄ and MgSO₄ CIP are equivalent (Ea~56 kcal mol⁻¹ and A_f~1.5e+13 sec⁻¹), and experiments involving HSO₄ and several different crude oils provide a range of activation energies from 55.3 to 58.9 kcal mol⁻¹ and frequency factors from 5e+16 to 1e+17 sec⁻¹. The variation in the kinetic parameters observed for different oil types appears to be related to the concentration of labile sulfur compounds in the whole crude oil. Once the threshold concentration of H₂S has been exceeded, the rate of TSR increases significantly, and detailed experimental work shows that the activation energy for the catalyzed reaction is directly proportional to the concentration of H₂S. These findings lay the foundation for a predictive model of TSR in geologic environments; however, accurate determination of the H₂S generation potential will likely require some knowledge of the chemistry of petroleum present, the local water chemistry, and the thermal history of the reservoir.