

## Calculating the partitioning of the isotopes of Mo between oxidic and sulfidic species in aqueous solution

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Isotopic fractionation is observed between Mo in seawater, where it exists primarily in the form of the Mo(VI) anion molybdate,  $\text{MoO}_4^{2-}$ , and in oxic sediments, where the Mo is isotopically lighter than in sea water and evidence exists for a five- or six-coordinate Mo environment in Fe,Mn oxyhydroxides. In anoxic sediments, where the Mo(VI) is expected to exist as a sulfide, no fractionation is observed compared to seawater. This is presumably because of the stoichiometric conversion of the Mo from  $\text{MoO}_4^{2-}$  to  $\text{MoS}_4^{2-}$  and then to other sulfides. This results from the very high equilibrium constant for the sulfidation reaction. Thus, to understand isotopic fractionation both the equilibrium constants for isotopic fractionation reactions and the equilibrium constants for transformation of one chemical compound to another must be considered.

We here present quantum mechanical calculations of the isotopic fractionation equilibrium constants for the isotopes  $^{92}\text{Mo}$  and  $^{100}\text{Mo}$  between  $\text{MoO}_4^{2-}$ ,  $\text{MoO}_3(\text{OH})^-$ ,  $\text{MoO}_3(\text{OH}_2)_3$ ,  $\text{MoS}_4^{2-}$  and a number of other oxidic and sulfidic complexes of Mo (and scale the results to give Mo 97, 95 fractionations). These fractionation equilibrium constants are calculated directly from the computed vibrational, rotational and translational contributions to the free energy in the gas-phase using quantum methods. Calculated vibrational frequencies and ratios of frequencies for different isotopomers are first obtained using a number of different quantum methods and compared with available experimental data to establish the most reliable methodology. We have also calculated free energy changes in aqueous solution for a range of reactions of  $\text{MoO}_4^{2-}$  and  $\text{MoO}_2(\text{OH})_2$  with  $\text{H}_2\text{O}$  and  $\text{H}_2\text{S}$ . We present evidence for the instability of the monomeric octahedral species  $\text{Mo}(\text{OH})_6$  commonly assumed to exist in acid solution and propose highly distorted six-coordinate  $\text{MoO}_3(\text{OH}_2)_3$  or three-coordinate  $\text{MoO}_3$  as better representations of the species present. We explain the isotopic lightness of oxic sediments as arising from an intermediate step in which a three coordinate  $\text{MoO}_3$  species is formed in aqueous solution, and subsequently attaches to the surface of a Fe,Mn oxyhydroxide mineral.

## Iron and tin isotope equilibrium fractionation factors from Mössbauer and synchrotron radiation data

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We have suggested a new method for determination of the reduced isotopic partition function ratio ( $\beta$ -factor) consisting in (i) computing the vibrational kinetic energy of the nucleus of interest from the phonon partial density of states PDOS obtained by inelastic nuclear resonant X-ray scattering (INRXS) in synchrotron radiation experiments and (ii) calculating the  $\beta$ -factor in terms of the kinetic energy and the difference of isotopic masses. Applications of this method to tin isotopes showed significant dependence of the tin  $\beta$ -factor on oxidation state previously established for iron isotopes (Polyakov and Mineev, 2000). This result enables the dependence on oxidation state to be extended to cover all transition metals. Iron isotope  $\beta$ -factors for hematite, magnetite, pyrite, siderite, etc. have been verified using new traditional Mössbauer spectroscopy data and PDOSs obtained by INRXS. Significant corrections to iron  $\beta$ -factors for magnetite have been made using synchrotron radiation data of Seto et al. (2003). Correlation between the iron  $\beta$ -factor and the iron electrostatic site potential have been found. The analogous correlation was previously observed for oxygen isotopes. (Smyth and Clayton, 1988). The correlation provides an explanation for the dependence of transition metal  $\beta$ -factors on oxidation state.

### References

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