

· 非传统同位素的理论、分析方法和应用 ·

The equilibrium Mo isotope fractionation parameters and their geological implications

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There is a 1.7‰~2.0‰ (in terms of $^{97}\text{Mo}/^{95}\text{Mo}$) Mo isotopic composition offset between the seawater and the oxic sediments. To fully understand this offset, one should have the knowledge of the equilibrium Mo isotope fractionation among the possible aqueous Mo species and the adsorbed Mo surface complexes on the (Fe,Mn)-oxyhydroxides surfaces. This study provides these important equilibrium Mo isotope fractionation factors especially including in careful solvation effect estimation which has been neglected by previous studies.

Urey model or Bigeleisen-Mayer equation based theoretical method and the super-molecule clusters are used to precisely evaluate these fractionations. The B3LYP/(6-311+G(2df,p), LANL2DZ) level method is used for frequencies calculation. LANL2DZ basis set is used for Mo and 6-311+G(2df,p) basis set is used for all other atoms. Twenty four water molecules are used to form the super-molecules surrounding the aqueous Mo species. At least 4 different conformers for each supermolecule are used to prevent the errors from the diversity of configurations in solution. Besides, the possible salt effect in seawater is also checked. Two different ion-pairing situations ($\text{MoO}_4^{2-}\text{-Na}^+$ or $\text{MoO}_4^{2-}\text{-2Na}^+$) have been carefully examined. Our results show that the fractionation numbers can be dramatically changed from gas-phase to liquid-phase. The previous gas-phase results are therefore questionable. Our results show that no matter the dominant aqueous species MoO_4^{2-} is adsorbed on the (Fe,Mn)-oxyhydroxides by mono-dentate or bi-dentate way, it only can produce less than 1‰ isotopic fractionation. The polymerized MoO_4^{2-} forms (e.g. Mo_3O_9) also have quite similar fractionation relative to aqueous MoO_4^{2-} . In another word, the 1.7‰~2‰ Mo isotope offset found between the seawater and oxic sediments, is unlikely caused by the direct absorption of the dominant MoO_4^{2-} species to (Fe,Mn)-oxyhydroxides. However, the minor Mo aqueous species, $\text{MoO}_3(\text{H}_2\text{O})_3$ or $\text{MoO}_2(\text{OH})_2$, can produce the 1.7‰~2‰ fractionation if they are adsorbed onto the (Fe,Mn)-oxyhydroxides surfaces. This two-step Mo removal mechanism can explain the extraordinarily long residence time of Mo in seawater.