

由铁、镁水合氢氧化物表面吸附 导致的 Mo 同位素分馏

唐茂, 刘耘

(中国科学院 地球化学研究所 矿床地球化学国家重点实验室, 贵州 贵阳 550002)

Although Mo isotopes have been increasingly used as a paleoredox proxy in the study of paleo-oceanographic condition changes (Barling et al., 2001; Siebert et al., 2003, 2005, 2006; Arnold et al., 2004; Poulson et al., 2006), some very basic knowledge about Mo isotopes geochemistry have not been fully established yet. First, although there are several previous studies on the equilibrium Mo isotope fractionation factors, the accurate fractionation factors considering solvation effects have not been determined. Our recent results show that the solvation effects can dramatically change the fractionation numbers from the ones in gas phase. For example, the MoO_4^{2-} - $\text{Mo}(\text{OH})_6$ fractionation at 25 °C is 0.8‰ for gas phase but it is changed to 2.0‰ in solution. In another words, the fractionation factors provided on vacuum condition are not accurate enough. Second, except the dominant dissolved Mo species in seawater known as molybdate ion (MoO_4^{2-}), the possible other minor species are elusive. Third, the Mo removal mechanisms from seawater are only known for at the anoxia and euxinic conditions (e.g. Helz et al., 1996; Zheng et al., 2000), the details of Mo removal mechanism at oxic condition are still arguing. Such as how to explain the 1.7‰ ~ 2.0‰ (in terms of $^{97}\text{Mo}/^{95}\text{Mo}$) Mo isotopic composition offset between the seawater and the oxic sediments. Fourth, the adsorption effects on Mo isotope fractionation are almost completely unknown. Without the above knowledge, it is difficult to understand many distinct Mo isotope fractionations

found in a number of geologic systems and it is difficult to explain the exceptionally long residence time of Mo in seawater.

This study provides accurate equilibrium Mo isotope fractionation factors between possible dissolved Mo species and the adsorbed Mo species on the surface of (Fe, Mn)-oxyhydroxides. We checked the salt effect, temperature effect, various adsorption surface structures on the Mo isotope fractionations. Urey model or Bgejisen-Mayer equation based theoretical method and the supermolecule clusters are used to precisely evaluate the solvation effects. The B3LYP/(6-311 + G(2df,P), LANI2DZ) level method is used for frequencies calculation. Twenty-four water molecules are used to form the supermolecules surrounding the Mo species. At least 4 different conformers for each supermolecule are used to prevent the errors from the diversity of configurations in solution. Our results show that the fractionation between the dominant aqueous Mo species and the adsorbed ones can only 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‰ ~ 2.0‰ Mo isotope offset found between the seawater and the Fe, Mn-oxides is unlikely caused by the absorption of MoO_4^{2-} in oxic sediments. It must be caused by other mechanisms. This study provides a base for discussing the mechanism of Mo removal from the seawater.