

U020-04

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Mechanisms of adsorptive isotopic fractionation of Mo on ferromanganese oxides based on the systematics of its surface c

Teruhiko Kashiwabara^{1*}, Yoshio Takahashi¹

¹Earth and Planetary Systems Science, Hir

Molybdenum (Mo) shows large mass-dependent isotopic fractionation during adsorption on ferromanganese oxides, which affects isotopic composition of Mo in modern oxic seawater. Due to this fractionation process, isotopic ratio of Mo in marine environment is expected to be used as a paleocean redox proxy. The aim of this study is to reveal the fractionation mechanisms of Mo isotopes during adsorption on natural ferromanganese oxides. We investigated surface complex structures of Mo on various Fe/Mn (oxyhydr)oxides, key factors for isotopic fractionation, and compared them with previously-reported isotopic fractionations.

Adsorption experiments were conducted using synthetic amorphous ferrihydrite and *delta*-MnO₂, and crystalline goethite and hematite as adsorbents. Solutions were adjusted to pH 8 and I = 0.70 M (NaNO₃). The structures of adsorbed species were investigated by conventional fluorescence XAFS method. Measurements for Mo K-edge EXAFS were performed at BL01B1 in SPring-8, and those for Mo L₃-edge were at BL-9A in Photon Factory.

Our XAFS analyses revealed that Mo forms a *Td* outer-sphere complex on ferrihydrite and distorted *Oh* inner-sphere complexes on *delta*-MnO₂ (Kashiwabara et al., 2009). In addition, Mo forms inner-sphere complexes on crystalline goethite and hematite: *Td* edge-sharing (46%) and *Oh* double corner-sharing (54%) for goethite; *Td* double corner-sharing (14%) and *Oh* edge-sharing (86%) for hematite. These structural information showed the excellent correlation with the degree of isotopic fractionation during adsorption reaction of Mo reported in previous studies: the proportion of *Oh* species or their magnitude of distortion in Mo surface complexes become larger in the order of ferrihydrite < goethite < hematite < *delta*-MnO₂, a trend identical to the degree of isotopic fractionation (Goldberg et al., 2009). Based on the comparison with previous reports for Mo surface species on various oxides such as MgO, Al₂O₃, and TiO₂, chemical factors that affect Mo surface complex structures were also discussed. The hydrolysis constant of cation in oxides, log K_{OH}, (or the acidity of the oxide surfaces, PZC) is well correlated with the mode of attachment (inner- or outer-sphere) of Mo surface complexes. Furthermore, the symmetric change in Mo species from *Td* to *Oh* is suggested to be driven by the formation of inner-sphere complexes on specific sites of the oxide surfaces.

References

- Barling J., Arnold G.L. and Anbar A.D. (2001) *Earth Planet. Sci. Lett.*, **193**, 447-457.
Kashiwabara et al., (2009) *Geochem. J.*, **43**, e31-e36.
Goldberg et al., (2009) *Geochim. Cosmochim. Acta*, **73**, 6502-6516.

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