

U020-04

会場:304

時間:5月23日 09:45-10:00

表面錯体構造の比較による鉄マンガン酸化物への吸着に伴うモリブデンの同位体分別機構の解明

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

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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.

Keywords: molybdenum, isotopic fractionation, surface complex structure, ferromanganese oxides