

Mechanisms of isotopic fractionation of Mo on ferromanganese oxides based on the systematics of its surface complex structures

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Molybdenum (Mo) shows a large mass-dependent isotopic fractionation during adsorption on ferromanganese oxides, which is responsible for isotopic composition of Mo in modern oxic seawater [1]. This fractionation process is the basis of the utility of Mo isotope system 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 the isotopic fractionation, and discussed the relationship among the degree of isotopic fractionation, surface complex structures, and characteristics of various oxides.

Our XAFS analyses revealed that Mo forms a *Td* outer-sphere complex on ferrihydrite and distorted *Oh* inner-sphere complexes on δ -MnO₂ [2]. In addition, Mo forms inner-sphere complexes as *Td* edge-sharing (46%) and *Oh* double corner-sharing (54%) for goethite, and as *Td* double corner-sharing (14%) and *Oh* edge-sharing (86%) for hematite [3]. This structural information showed the excellent correlation with the degree of isotopic fractionation of Mo reported in previous studies: the proportion of *Oh* species in surface Mo species becomes larger in the order of ferrihydrite < goethite < hematite < δ -MnO₂, a trend identical to the degree of isotopic fractionation [4]. Based on the comparison with previous reports for surface Mo species on various oxides such as MgO, Al₂O₃, and TiO₂, the symmetry change from *Td* to *Oh* is suggested to be driven by the formation of inner-sphere complexes on specific sites of the oxide surfaces. In addition, the mode of attachment (inner- or outer-sphere) of surface Mo species is well correlated with the hydrolysis constant of the cation (e.g. Mg²⁺, Al³⁺, Fe³⁺, Ti⁴⁺, and Mn⁴⁺) in oxides. These facts imply that large isotopic fractionation as the case of Mo between seawater and marine ferromanganese oxides could occur as a general phenomena for other unknown elements and/or adsorbents[5], which would considerably influence their isotope systems in the environment.

[1] Barling et al., (2001) *Earth Planet. Sci. Lett.*, **193**, 447-453.

[2] Kashiwabara et al., (2009) *Geochem. J.* **43**, e31-e36.

[3] Kashiwabara et al., (2011) *Geochim. Cosmochim. Acta.* **75**, 5762-5784.

[4] Goldberg et al., (2009) *Geochim. Cosmochim. Acta.* **73**, 6502-6516.

[5] Kashiwabara et al., (2010) *Chem. Lett.* **39**, 870-871.

Sr and Nd isotopes from Diorites and Granites (Damara Orogen, Namibia): Partial melting of juvenile mafic crust?

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The high-grade central zone of the Pan-African Damara Orogen in Namibia hosts abundant granitoids with ages from c. 540 to c. 480 Ma. New LA-ICP-MS zircon ages of 541±3 Ma obtained on Qtz diorites show that these rocks intruded close to the first peak of regional metamorphism, whereas granodiorites and granites intruded close to the main peak of metamorphism (506±6 Ma). Qtz diorites are meta-aluminous with A.S.I. (A.S.I.: Al/(Ca+Na+K)(molar)) up to 0.8. The granites are slightly peraluminous high-K calc-alkaline I-type granites. All rocks are enriched in light rare earth elements relative to heavy rare earth elements with La_N/Yb_N ranging from 13 to 18 in the Qtz diorites and from 9 to 26 in the granodiorites and granites. The Qtz diorites have Eu/Eu* (Eu/Eu*: Eu/√(Sm*Gd)) from 0.8 to 0.9 whereas the granites have Eu/Eu* = 0.1-0.4. The Qtz diorites have the most radiogenic Nd isotope composition among the Qtz diorites of the Damara orogen (εNd_i: -1.50 to -1.78) together with unradiogenic Sr isotope compositions (⁸⁷Sr/⁸⁶Sr_i: 0.7049-0.7058). The granodiorites and granites have less radiogenic Nd isotopic compositions (εNd_i: -2.74 to -5.31) and more radiogenic initial Sr isotope ratios (⁸⁷Sr/⁸⁶Sr_i: 0.7071-0.7082). Although fractional crystallization processes were operative, the lack of correlation between isotope ratios and elemental concentrations indicate that both rock types represent partial melts of juvenile crustal sources. Compared to experimental studies, a medium-K/high-Al-metabasaltic rock is the most plausible source for the Qtz-diorites. For the granites, high-K andesitic to tonalitic rocks are plausible sources. Although both rock types were formed during the main phases of regional metamorphism, internal crustal heat production rates are probably not sufficient to generate Qtz diorites and I-type granites from pre-existing crustal sources. One plausible model involves underplating of mantle derived magmas followed by sill-like intrusions in the lower crust close to the peak of high-grade metamorphism producing excess temperatures that promote partial melting of fertile crustal sources.