Equilibrium Mg and O isotope fractionations between silicates at high T and P: the test of a new calculation method

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For the test of a cluster-model-based method which we developed for estimating isotopic fractionations of solids, Mg and O isotope fractionations between spinel, diopside, pyrope, omphacite and forsterite at different temperatures and pressures are investigated. There is a tremendous interest in developing a cluster-model-based method of isotope fractionation calculation for solids because most of the new techniques developed in modern quantum chemistry are for molecules which usually are represented by cluster models. Many local properties of solids (e.g., isotopic effect) can be calculated using much higher theoretical treatments if using cluster models. Another reason we developed this method is to remedy problems raised from a similar method used by Rustad and co-workers (e.g.,[1]), especially to enhance its implementation on isotope fractionation calculations between solids and aqueous species.

Recent studies (e.g., [2],[3],[4]) suggested the possibility of using equilibrium inter-mineral Mg isotope fractionations as a thermometer at mantle conditions. Here, we calculate equilibrium Mg and O isotope fractionation factors of geologically important silicate minerals by using our new method. Although our results of silicate minerals are generally close to those of Schauble (2011), our result of magnesite vs. Mg^{2+}(aq) ion is significantly different from his result. Our results are very close to existing Mg and O isotope experimental data, suggesting broad applications of this method in future.

Because an good isotope thermometer is required to exclude pressure effects, we checked the pressure effects of Mg and O isotopes of those silicate minerals mentioned up to 13GPa (i.e., roughly the upper mantle condition). Very small pressure effects are found within the lower pressure range (e.g. less than 4 GPa). However, slowly increasing pressure effects are found with the increase of pressure to 13GPa. We suggest to correct the pressure effects if the samples are from the lower part of the upper mantle.

[1] Rustad et al. (2010) *GCA*, **74**, 6301-6323. [2]Young et al. (2009) *EPSL*, **288**, 524-533. [3] Li et al. (2011), *EPSL*, **304**, 224-230. [4] Huang et al. (2010) *GCA*, **75**, 3318-3334. [5]Schauble (2011) *GCA*,**75**, 844-869.

Nanoscale Measurement of Manganese Valence in Mn-oxides

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Manganese (Mn) oxides are among the strongest mineral oxidants in the environment and impose significant influence on mobility and bioavailability of redox-active substances, such as arsenic, chromium, and pharmaceutical products, through oxidation processes. Oxidizing potentials of Mn oxides are determined by Mn valence states (II, III, IV). In this study, the effects of beam damage during Electron Energy-Loss Spectroscopy (EELS) measurement in the Transmission Electron Microscope have been investigated to determine the "safe dose" of electrons [1]. Time series analyses demonstrate that some Mn-oxide minerals experience a reduction of Mn valence during intense or prolonged electron beam exposure. We have determined the safe dose fluence (electrons/nm^2) for todorokite (10^6 e/nm^2), acid birnessite (10^5), triclinic birnessite (10^4), randomly-stacked birnessite (10^3) and δ-MnO_2 (<10^3) at 200 kV. The results show that precise measurements of the mean Mn valence can be acquired by EELS if proper care is taken. EELS anayses are shown to be as precise as chemical titration analyses, but with twelve orders of magnitude less volume (~5 attoliters, 10^{-18}).

The value of EELS analysis is demonstrated by two applications: 1) Analysis of run products from experiments reacting 1 mM dissolved Mn^{2+} with δ-MnO_2 in the presence of other cations (Na^+, Ca^{2+} Zn^{2+} and Ni^{2+},). These experiments, designed to determine reaction rates of the reduction of Mn(IV) in poorly-crystalline Mn-oxides by Mn^{2+}, produce mixtures of phases with variable mean valence. Unlike bulk chemical tiration or X-ray absorption spectroscopy, EELS, in concert with energy-dispersive X-ray analysis (EDS), can determine the individual phase valences and their mineral formulae (including other divalent cations). 2) Analysis of todorikite in a Mn-oxide crust from the Pacific ocean floor. This natural todorokite includes Fe(II,III) and other minor elements. EELS is capable of measuring the mean valence for both Mn and Fe, while simulaneously acquiring quantitative EDS analyses.

[1] Livi et al. (2012) *Environmental Science & Technology* **46,** 970-976.