

***Ab initio* investigations of point defects and ionic diffusion in bulk and grain boundary of silicate and oxide minerals**

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We have performed density functional theory-based simulations to study the formation and migration energetics and geometric structures of various native point defects in the bulk and grain boundaries of several mantle minerals (silicates and oxides). Both individual defects (vacancies and interstitials) and charge-balanced defects (Schottky and Frenkel types) were simulated as a function of pressure. With increasing pressure, the calculated defect formation and migration enthalpies increase monotonically (by up to a factor of two) in each structure and with abrupt jumps across some phase transitions. Energetic favourability of these defects is also sensitive to pressure. The ion migration enthalpies calculated using the nudged elastic band method differ between vacancy-to-vacancy and interstitial-to-interstitial diffusion. The migration enthalpies are not uniform among different species; for example, the Mg migration is easiest in forsterite and ringwoodite whereas the Si migration is easiest in wadsleyite. Our preliminary study of MgO grain boundary implies that the boundary can have higher diffusivity than the bulk region. Our calculated enthalpies and volumes of defect formation and migration are expected to be useful in our understanding of creep processes in mantle minerals and hence to our understanding of the mantle rheology.

Speciation of Fe(III) in natural organic matter (NOM) studied by EXAFS spectroscopy

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Background

The speciation of iron (Fe) in soils, sediments and surface waters is highly dependent on chemical interactions with natural organic matter (NOM). However, the molecular structure and hydrolysis of the Fe species formed in association with NOM is still poorly understood and there are relatively few studies that present results obtained by molecular-level probes [1-5]. Herein we have used extended X-ray absorption fine structure (EXAFS) spectroscopy to determine the coordination chemistry of Fe(III) in organic soils, NOM from river water and a peat humic acid (2000–55 000 $\mu\text{g Fe g}^{-1}$ dry weight; pH 3–7). Data were analyzed by both conventional EXAFS data fitting and by wavelet transforms [6] in order to facilitate the identification of the nature of backscattering atoms.

Results

Our collective results show that Fe forms two predominant species in association with NOM: mononuclear Fe(III)-NOM complexes and polymeric Fe(III) (hydr)oxides. The organic complexes have a structure consisting of five-membered chelate rings and these complexes are sufficiently strong to prevent hydrolytic polymerization of Fe even at pH 7. Furthermore, mononuclear organic Fe complexes seem to dominate the speciation over a wide pH (3–7) and concentration range (2000–55 000 $\mu\text{g Fe g}^{-1}$). Thus, in environments with significant amounts of organic matter organically complexed Fe will be of great importance for the geochemistry of Fe. These findings are also of importance for the speciation of other elements, such as phosphorus, that are strongly associated with Fe, since different Fe species most likely have markedly different reactivities.

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