

Evaluation on reactivities of metal ions with hard ligands having oxygen donor

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Complexation of metal cations by ligands such as hydroxide ion, carbonate ion, carboxylate ion, and phosphate ion is one of the most important factors to control behavior of metal ions in natural environment. Previous study showed that these ligands were classified as intermediate hard ligands having oxygen donor, which favors to form the ionic bond [1]. However, it was found that the reactivity of each ligand greatly depends on ionic radius and that there is a great difference of the reactivity between hydroxide ion and other ligand such as carbonate and carboxylate. For example, among the divalent alkaline earth metal ions, Mg^{2+} mainly precipitates as hydroxide (brucite), while Ca^{2+} prefer to form carbonate (calcite) or phosphate (apatite) minerals than hydroxide. However, quantitative discussion on the selectivity of metal cations is not quantitatively performed.

In this study, we evaluated the standard Gibbs free energy (ΔG_R^0), enthalpies (ΔH_R^0) and entropy (ΔS_R^0) for the complex formation of hydrated metal cations with these ligands based on a critical thermodynamic database including ΔG_R^0 , ΔH_R^0 , and ΔS_R^0 . As a result, we found that the entropic contribution to the free energy was large in the case of hydroxide complex of small radius cation. In contrast, the entropic contribution to the free energy was small in the case of hydroxide complex of large radius cation and other complex. In addition, the enthalpy contribution was not significant in the reaction. In the aqueous complexation reaction, ΔS_R^0 was controlled by the number of water molecules replaced by the ligand, suggesting that hydroxide complex for large cation was not stable due to the small effect of dehydration.

[1] D. Turner *et al.* (1981) *Geochim. Cosmochim. Acta* **45** 855-881

Progress of serpentinization reactions triggered by silica addition: Petrological evidence from Iwanai-dake ultramafic body, Hokkaido, Japan

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Transformation of peridotite into serpentinite in the mantle wedge is one of the key processes that influence geodynamic regimes of subduction zones, because serpentinization changes the physical properties of peridotite, such as density, magnetic susceptibility, electric conductivity and rheology. Recent petrologic studies have proposed that serpentinization reactions proceed via a two-stage process involving the early formation of serpentine + brucite and subsequent magnetite formation. Magnetite, which is the key mineral controlling magnetic properties, electrical conductivity and density of peridotite as well as the efficiency of hydrogen generation, is thought to be formed by the second-stage reaction, but there has been little consensus among researchers regarding what factor promotes the formation of magnetite during serpentinization. We investigated successive changes in mineralogical textures associated with the progress of serpentinization observed in serpentinized harzburgite and dunite samples from Iwanai-dake ultramafic body (Hokkaido, Japan), which probably derived from a mantle wedge. Two kinds of mesh rim types were observed in the serpentine mesh texture of serpentinized harzburgite: a rim consisting of both serpentine and brucite (type-A rim) and a rim consisting solely of serpentine (type-B rim), which are always accompanied by brucite-magnetite veins. The formation of type-B rims and brucite-magnetite veins appears to have occurred concurrently with the serpentinization of orthopyroxene, suggesting that serpentinization reactions of harzburgite took place in two stages, with magnetite being formed by the second-stage reactions, which were triggered by a supply of silica component from serpentinization of orthopyroxene. In the case of serpentinized dunite, type-A rim was predominant and the fraction of magnetite does not increase with the progress of serpentinization. These observations suggest that silica supply is the trigger for the second-stage serpentinization reactions, in which magnetite and hydrogen are generated.