

## Reduction of ionic diffusivity through thin-film and nano pore water in geomaterials

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Diffusion is one of elementary processes on the mass transport phenomenon. In nature dissolved solvents move through aqueous pore fluid in rocks and sediments, whose processes are by advection, ionic diffusion or their combine. In deeper part of Earth's surface, ionic diffusion appears as the most dominant because there is generally less hydraulic gradient. It is also known that the rheology of rocks is influenced by diffusion. The diffusional creep at relatively high temperature is rate-determined by the transport of material through mineral lattice or boundary. Intercrystalline fluid significantly affect rheological properties of rocks via pressure solution creep, fluid-assist recrystallization and so on.

Effective diffusion coefficients of iodine ion in non-deformed rocks were measured by through diffusion experiments, and the quantitative relationship between the diffusion coefficient and the pore structures was discussed in this study. Most of effective diffusion coefficient for rocks can be estimated by the De-porosity power law, but the coefficient of the sample involving much nanopores is out of the law and relatively lower. By IR measurements of pore fluid in grain boundary and thin film water sandwiched by glasses, shifted peaks of O-H stretching frequency were observed around  $3400\text{ cm}^{-1}$  to  $3240\text{ cm}^{-1}$ . Because the frequency of O-H stretching bands is reported to be a function of hydrogen bond distance, the molecule of thin film water can have more confined structure with shorter distance of hydrogen bonding. This result could be supported by previous reports by molecule dynamics simulations of confined water in nano space.

Recalculations of the effective diffusion coefficients with the consideration of this effect lead to new knowledge that the ionic diffusion coefficient through thin film water in nanopore is  $1.38 \times 10^{-10}\text{ m}^2/\text{s}$  to  $2.78 \times 10^{-10}\text{ m}^2/\text{s}$  and at least about one order of magnitude lower than the diffusivity in free water. This results can be applied for hydraulics, structural geology and new discipline of nano technology. Highly confined structure of thin film water affects on not only ionic diffusion but also fluid viscosity and so on.

## Geochemical consequences of core-mantle thermal and chemical interactions

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It has been suggested that subducting lithosphere could go down to the core-mantle boundary and partially melt. Such processes could produce distinct geochemical signatures that provide constraints for depths of origin of mantle plumes. We have experimentally determined trace element partitioning data between lower mantle minerals and melts in peridotite and mid-ocean ridge basalt (MORB) compositions at 25-27 GPa that can be used to understand the geochemical consequences of these processes (Hirose et al., 2003). Our results clearly show that CaSiO<sub>3</sub>-perovskite (CaPv) is the predominant host for large ion lithophile trace elements (LILE) in the lower mantle, and partial melting of subducting oceanic crust causes strong enrichment of LILE in the CaPv-bearing solid phase assemblage. If a mantle plume rises up from CMB, picking up CaPv-bearing lighter assemblage from the partially molten crust, the geochemical signatures of CaPv are transported by the plume, and could be detectable in ocean island basalts and/or in mantle xenoliths. Trace element patterns in clinopyroxenes in peridotite xenoliths from Western Samoa and Austral Islands and from Hawaii are remarkably similar to those of experimental and natural CaPv, indicating a CaPv-bearing precursor. The radiogenic Pb isotopic component typically observed in Austral Islands may represent such a CaPv-bearing recycled material. These geochemical signatures could be taken as evidence for the origin of some mantle plumes at CMB.

The composition of the deep mantle may be modified also by the chemical reaction with the iron-rich outer core liquid. We performed reaction experiments between liquid iron and Mg<sub>0.9</sub>Fe<sub>0.1</sub>SiO<sub>3</sub>-perovskite to 78 GPa and 3500-K (Takafuji et al., 2003). The dissolution both of oxygen and silicon into the liquid iron was significantly enhanced with increasing pressure and temperature. These results suggest that composition of the deepest part of the mantle could be variable both in SiO<sub>2</sub> and FeO contents by the consequences of dissolution or exsolution of oxygen and silicon into/from the iron-rich liquid outer core.

### References

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Takafuji, N. et al. (2003) *Nature* submitted.