Physicochemical properties of confined water and inonic diffusion phenomenon in nanopore

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A significant effect of fluids on the rock deformation has long been recognized, and the diffusion in aqueous fluids is often considered to be the key process. The diffusivity in rocks depends not only on porosity but also on pore size distribution, tortuosity, connectivity and orientation of the pore network. It is therefore important to elucidate how the pore geometry influences on the diffusion process.

Effective diffusion coefficient (De) of iodine ion in various rocks were measured together with the pore size distribution by mercury intrusion porosimetry.   The data can roughly be fitted by the De-p power law:

$De = 0.83 \times Do \times p^{2.8}$

where Do denotes the molecular diffusion coefficient (diffusivity in pure water) and p is the porosity. Previous research and above-mentioned empirical   relationship assumes that diffusion coefficient in pure water for pores of any size is the same as the one in free water (Do). However, the downward deviation of some data from the above regression line suggests the limit of this assumption.

For the samlpes with abundant nanopores, the diffusion coefficient seems to be lower than is expected from the above relation. The D0 value for these nanopore-bearing rocks should be treated as an unknown parameter. If we assume the tortuosity-porosity relationship (tortuosity = $1.00/ p^{0.82}$), derived from the fitting of data among samples without nanopores, to be applicable to the samples with nanopores, the diffusion coefficient within nanopores can be estimated. By putting this relation into $Do = De \times (tortuosity)^2/ p$, the diffusion coefficient within nanopores can be caclulated by the relation $D0 = De / p^{2.64}$ as, 2.33×10^{-10} m^2/s to 8.99×10^{-11} m^2/s.

These diffusion coefficients for nanopores (smaller than 100nm) is at least about one order of magnitude lower than the ionic diffusivity in pure free water (1.32×10^{-9} $m2/s$) and show the decrease for decreasing peak pore sizes (from 80, 50 to 25 nm). The origin of this diffusion delay effect by nanopores can be attributed to the highly constrained structures of hydrogen-bonded $H2O$ molecules in restricted pore spaces, which is suggested by the infrared measurements of thin film water.

Thus the diffusion coefficient of an ion through nanopores has been estimated for the first time from the diffusion experiments. and will be studied further by means of diffusion in synthetic rocks with controled pore structures. The effect of rock deformation on the pore structure and diffusivity will also be studied.