Elucidation of effective diffusion coefficient along grain boundaries by hydrothermal experiment using low porosity rocks

*Naoki Sugisawa[1], Masaoki Uno[1], Noriyoshi Tsuchiya[1]

1. Graduate school of environmental studies Tohoku university

Elucidation of the time scale of the fluid activity recorded in the rock is important for understanding the actual condition of fluid activity in the crust. In recent years, it has become possible to estimate time-scale of fluid activity in the crust from isotopes and element concentration profile of natural metamorphic rocks. (e.g.John et al.,2012) To estimate the time-scale, the effective diffusion coefficient (Deff) is important as an indicator of diffusion via grain boundary fluid. It is known that the effective diffusion coefficient depends on the porosity (Φ) of rock and time due to grain boundary diffusion. (e.g.Boving and Grathwohl, 2001) The effective diffusion coefficient is conventionally substituted by the product of self-diffusion coefficient (D_{self}) and porosity ($D_{self}\Phi^{x}$). However, the effective diffusion coefficient varies depending on the power factor (x) of the porosity, and the estimated timescales depend significantly on the power factor (x). Therefore, we clarified the relationship between porosity vs effective diffusion coefficient and confining pressure vs effective diffusion coefficient using hydrothermal experiment under crustal condition with various low porosity granite. In this paper, we mention the following two experiments as the first step : (1) Fluorapatite (F-Ap) substitution reaction (2) Determination of effective diffusion coefficient using low porosity hydroxyapatite sintered body (OH-Ap).

In this study, natural F-Ap from Mexico and OH-Ap (Wako Pure Chemical corporation) were used as starting materials. In experiment (1), first, natural F-Ap was cut in the c-axis direction. And it was put in the gold tube with 0.0006-6 M HCl or 0.01-1 M NaOH two types solution. After that gold tube was putted in the batch type hydrothermal equipment and conducted hydrothermal experiment under 400 ℃, 50 MPa for168 hour. In experiment (2), OH-Ap powder was pressed under 200 MPa for 30 minutes and then the porosity was varied by sintering at deference temperature from 1500 ℃ to 1200 ℃. After cooling, the porosity was measured by the wet method. NaF solution saturated at room temperature and OH-Ap sintered body was added to the same apparatus as above and a hydrothermal experiment was conducted at 300 ℃ and 20 MPa for 168 hours. After the experiment (1) and (2), the samples were evaluated by quantitative analysis and mapping analysis with EPMA in both cases. Before the experiment, phase diagram of apatite under experimental temperature and pressure was prepared using SUPCRT92, GEMS to expect these reactions.

As a result of the hydrothermal experiment, in the experiment (1), it is suggested that the OH in F-Ap is substituted with Cl under HCl solution and the NaOH substitutes OH for F. In experiment (2), F diffusion zoning was generated along the clacks in the sintered OH-Ap, and an effective diffusion coefficient was calculated using diffusion equation. There was no apparent porosity dependency of the effective diffusion coefficient at porosities 1.68-5.83%. The effective diffusion coefficient obtained in this experiment was equivalent to the self-diffusion coefficient of fluorine multiplied by the porosity 2.26 power. ($D_{eff} = D_{self}\Phi^{x}$) (e.g. Oelkers and Helgeson, 1988) However, the porosity measured by the wet method needs to be investigated because it contains the cracks generated in making the sintered body. (e.g. mercury porosimeter)

Based on the above experimental results, it is discussed that the influence of temperature, pressure, solution condition, on substitution of monovalent halogen and hydroxyl group between apatite and fluid and relationship between porosity and effective diffusion coefficients.

References
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