

## Mechanism and kinetics of smectite dissolution under alkaline conditions

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Smectite-cement fluid interaction has been a key research issue in performance assessment of radioactive waste disposal because the smectite presumably lose some of their desirable properties by the interaction. In this context, stirred-flow-through dissolution experiments were carried out to determine reliable dissolution rates of smectite from neutral to highly alkaline condition and to formulate the effect of pH on smectite dissolution rate. *In situ* observations also performed to understand mechanism of the dissolution.

The experiments were performed for mixed NaOH-NaCl or KOH-KCl aqueous solutions with ionic strength of 0.3 M. Purified smectite (Kunipia-P® provided from Kunimine Industry Co Ltd) was reacted at the pHs from 8-13 and the constant temperature of 30, 50 and 70°C. The dissolution rates were calculated from the steady-state Si and Al concentrations. The preparation and stock of input solutions, and sampling of output solutions were carried out in a globe box under N<sub>2</sub> gas atmosphere. The processes of smectite dissolution were *in situ* observed by atomic force microscopy (AFM) and attenuated total reflection infrared spectroscopy (ATR-IR)

The smectite dissolution rates increased as function of pH from 8 to 13. Obvious pH effect on the dissolution rate was observed in the present study. On the other hand, no effect of interlayer species on the rate was observed by comparison of the dissolution rates from NaOH-NaCl system with that from KOH-KCl system. The rate laws were calculated by fitting the dissolution rates to the pHs of output solution. For example, at 50°C in NaOH-NaCl solution, the following equations was obtained from Si concentrations;

$$\text{Rate (mol m}^{-2} \text{ s}^{-1}) = 10^{-14.11} a_{\text{H}^+}^{-0.25} \text{ (in NaOH solution).}$$

The dependence of pH on the dissolution rate is different in the dissolution at different temperatures. The activation energy of the dissolution is also different. The activation energy, ranged from 27-62 kJmol<sup>-1</sup>, obtained from the experiment at higher pH is greater than that from the experiment at lower pH. *In situ* observations by AFM and ATR-IR show that the dissolution of smectite is congruent and the edge of smectite dominantly contributed to the dissolution as reactive surfaces.

## Coseismic changes in SO<sub>4</sub><sup>2-</sup>/Cl<sup>-</sup> of hot-spring water in Ito, Japan

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### Introduction

Coseismic changes in SO<sub>4</sub><sup>2-</sup>/Cl<sup>-</sup> of hot-spring water were detected at the HRN well in Ito, Japan (Sato et al., 1992). The ratio rose after the two earthquakes in 1990, which magnitude is greater than 5 and the hypocentral distances are about 30 km. The cause of the changes is thought to be changes in mixing ratio between two types of waters with different values of SO<sub>4</sub><sup>2-</sup>/Cl<sup>-</sup>.

The one type with high SO<sub>4</sub><sup>2-</sup>/Cl<sup>-</sup> is characterized as relatively high temperature and low salinity. This type is thought to be closely related to the origin of the hot spring in this area. The other type with low SO<sub>4</sub><sup>2-</sup>/Cl<sup>-</sup> which is likely to be produced by mixing of seawater and usual groundwater, has high salinity and is located near the coast. The HRN well is located near the boundary of the two types of hot springs. Therefore, coseismic changes in the mixing ratio might easily occur and cause the changes in SO<sub>4</sub><sup>2-</sup>/Cl<sup>-</sup> of the hot spring water at HRN.

### Observation and discussion

The hot-spring water of HRN is used in the downtown of Ito about 2 km apart from the well. Sampling of the hot-spring water has been conducted at the downtown once a week since 1995. The concentrations of SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> of the hot-spring water are analyzed by ion chromatography, and determined to be about 350 and 80 mg/L, respectively.

Both of coseismic permeability enhancement and crustal strain are possible to change the mixing ratio between two types of waters. Increases of groundwater flux, which were likely to be caused by coseismic permeability enhancement, were observed (e.g. Sato et al., 2000). On the other hand, groundwater level changes due to crustal strain changes were observed in Ito (e.g. Koizumi et al, 1999).

### References

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