

## Cluster formation of dissolved Si and its effect on the mobility of Si

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Information of the mobility and chemical behavior of dissolved Si is essential for understanding water-rock interaction. The charge and polymerization degree of dissolved Si vary depending on pH and Si concentration, which leads to a large difference in diffusivity<sup>[1]</sup>. For neutral pH at ambient temperature, thermodynamic calculation predicts that dissolved Si exists almost exclusively as monomeric  $\text{Si}(\text{OH})_4$ . A molecular dynamics (MD) simulation to evaluate the self-diffusion coefficient  $D_{\text{aq}}$  of  $\text{Si}(\text{OH})_4$ ,  $\text{K}^+$  and  $\text{Cl}^-$  in water (Fig. 1a) showed that if plural  $\text{Si}(\text{OH})_4$  molecules were inserted in a cell then  $\text{Si}(\text{OH})_4$  molecules assembled and moved as a cluster without forming Si-O-Si bond. The value of  $D_{\text{aq,Si}}$  obtained under the presence of four  $\text{Si}(\text{OH})_4$  molecules in a cell was  $\sim 20\%$  smaller than that obtained for single  $\text{Si}(\text{OH})_4$  molecule. The variations of  $D_{\text{aq,K}}$  and  $D_{\text{aq,Cl}}$  with increasing the numbers in a cell were within the margin of error. Experiments to evaluate the effective diffusion coefficient  $D_e$  of Si,  $\text{K}^+$  and  $\text{Cl}^-$  in rock pore water at pH 5–7 and 25°C showed that  $D_{e,\text{Si}}$  was smaller than  $D_{e,\text{K}}$  and  $D_{e,\text{Cl}}$  by a factor of 2.3–3.0 and this extent was greater than predicted from differences of  $D_{\text{aq,Si}}$ ,  $D_{\text{aq,K}}$  and  $D_{\text{aq,Cl}}$  (a factor of 1.7)<sup>[2]</sup>. Considering the result of MD simulation, a reason of the slow diffusion of Si compared with  $\text{K}^+$  and  $\text{Cl}^-$  in the experiments may be the presence of Si cluster (Fig. 1b).

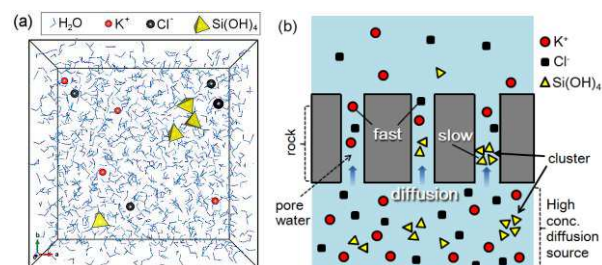


Fig. 1. (a) Snapshot of MD simulation. Four  $\text{Si}(\text{OH})_4$ ,  $\text{K}^+$ ,  $\text{Cl}^-$  were inserted in a cell containing 1000  $\text{H}_2\text{O}$ . Three  $\text{Si}(\text{OH})_4$  are forming a cluster, while K and Cl are moving individually. (b) A schematic of diffusion of Si, K and Cl in pore water.

[1] Yokoyama T. and Sakuma H. (2018) *Geochim. Cosmochim. Acta* 224, 301-312.

[2] Yokoyama T. (2013) *Water Resour. Res.* 49, 8299-8309.