

Crystallization of amorphous silica derived from diatom frustules under hydrothermal conditions

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Diatom fixes dissolved silica in terrestrial water and forms frustules as a skeletal structure of a cell. The frustules consist of opal-A (amorphous silica), and supply most of the silica component of biogenic siliceous sediments. In natural diatomaceous sediments, Tertiary or Quaternary diatomite, opal-A in frustules changes to porcellanite, which consists of opal-CT (cristobalite and tridymite) as diagenesis progresses. Final diagenesis product of diatomite should be chert, which consists of thermodynamically stable quartz under normal temperature and pressure. Crystallization kinetics of amorphous silica in diatomites has important role for understanding of diagenesis processes at subsurface conditions. In this study, hydrothermal experiments of natural diatomites were carried out to examine the crystallization behavior and kinetics of amorphous silica derived from diatom frustules.

Opal-CT in crystallized diatomite is a metastable phase. It has ordered layers of crystalline cristobalite and tridymite in a disordered matrix of amorphous silica. By powder X-rays diffraction, opal-CT shows almost identical diffracted peaks to those of alpha-Cristobalite.

The starting material of the experiments is natural diatomite, which have been collected from Nogami formation (middle Pleistocene) in southern Kusu basin of Oita Prefecture. The hydrothermal experiments were carried out at temperature range of 200 C - 525 C and pressure of 50MPa or water vapor pressure. Approximately 35mg of starting material was sealed in a silver capsule with equivalent weight of distilled water. A welded capsule was placed in a cold-seal pressure vessel. Run durations vary from 6 hours to 261 days. Fractions of crystalline silica phases in the run products were quantitatively measured by powder X-ray diffraction with an internal standard of crystalline CaCO₃.

In the run products, cristobalite and/or quartz are identified. The transformation rate constants of k_1 and k_2 , for amorphous silica to cristobalite, and cristobalite to quartz, respectively, are calculated based on equations of the silica polymorphs transformation by Mizutani (1966). The abundance of amorphous silica in run products, however, is not obviously on a simple first-order reaction. The induction period, τ_0 , prior to cristobalite formation should be adopted to correctly fit the abundances of amorphous silica in the run products.

Rate constants, k_1 and k_2 , are calculated by equations modified from those of Mizutani (1966). Activation energy of each reaction obtained by Arrhenius plot of k_1 and k_2 is 65.6 kJ/mol and 124.9 kJ/mol, respectively. The logarithms of τ_0 , moreover, linearly correspond to inverse of absolute temperature very well. It is suggested that the extrapolated τ_0 below 100 C would be correspond to the age of the diatomite used in this study.

SEM observations of the run products suggest that dissolution of amorphous silica diatomite frustules is followed by precipitation of spherical lepispheres of cristobalite. Crystallization of euhedral quartz crystals was also observed in high temperature and long duration run products. The induction periods should represent nucleation kinetics of cristobalite and quartz from hydrothermal solution.