Structure of the non-crystalline diatom exoskeleton and its evolution by heat treatment

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Introduction

Exoskeletons of diatoms are constructed of amorphous silica and organic matters which is called the frustules(Simpson and Volcani, 1981; Pickett-Heaps et al., 1990). The morphology of the frustules were investigated by electron microscopy to be porous and show many variations. The biogenic silica were also characterized by techniques such as 29Si NMR and small and wide angle X-ray analysis (Vrieling et al., 1999). However, the non-scale structure of diatoms has not been investigated. In this study, the averaged structure of pennate diatom was investigated based by IR spectroscopy and X-ray diffraction technique. The structural evolution of diatom by heat treatments up to 1150C was also investigated.

Specimen and experimental

Pennate diatoms collected from acidic hot spring at Kamuiwakka Falls, Shiretoko Peninsula, Hokkaido, Japan, were used for X-ray diffraction and IR spectroscopic studies. Pennate diatoms heat treated at 50, 100, 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1150C were also used for IR spectroscopic study. This pannate diatom show elongated ellipsoid with 40x10 micron size. EDX analysis showed that this diatoms are composed of large amount of Si. IR spectra of these specimen were carried out by Microscopic FT-IR spectrometer (Jasco FT/IR-610 + Micro-20) with x32 objective by transmission mode in the range of 650 - 4000cm-1. X-ray powder diffraction measurement of diatom was carried out on a X-ray powder diffractometer (Rigaku, RINT2200) with Cu-K radiation.

Results and discussions

X-ray powder diffraction profile of diatom shows no sharp diffraction peak of crystalline component. It shows a broad amorphous profile. The position and profile of first diffraction peak is similar to that of fused SiO2 glass. These facts show that this diatom is composed by non-crystalline SiO2 material, basically. IR spectrum of non treated diatom showed strong Si-O stretching band at 1000 - 1300cm-1 . This may indicate that the structure of diatom have composed by SiO4 tetrahedra, basically. The spectrum also showed Si-OH stretching band at about 950cm-1, C=O, C-N-H and H2O band at about 1600cm-1, and broad O-H band at 3100 - 3700cm-1. These results may show that diatom has Si-OH bond as well as Si-O bond and also organic matters such as peptides. In other words, diatom made up of SiO2 non-crystalline materials which includes H2O, Oh, and other organic matters. The Si-O-Si bending band at about 800cm-1 of this spectrum is smaller than those of fused SiO2 glass and quartz. The profile of strong Si-O stretching band at 1000 - 1300cm-1 is similar to that of SiO2 gel. Therefore, the degree of polymerization of SiO4 tetrahedra of diatom is low and similar to that of SiO2 gel.

By heat treatment, the C=O, C-N-H, Si-OH, O-H, and H2O bands of diatom IR spectra disappear at 400C. The Si-O band at at 1000 - 1300cm-1 shift to higher wavenumber and has become more sharp from 600C. These facts suggest that diatom has lost organic matters, H2O and OH and SiO4 tetrahedra were highly polymerized and ordered by heat treatment.

References

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