

Paleoceanographic reconstruction in the Okhotsk Sea: Evidence from calcareous microfossil record in MD01-2412

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The Okhotsk Sea is characterized as the region with the seasonal sea-ice coverage in the world's lowest latitude. This significant seasonal feature in this region has been considered as the influential factor for the origin of the North Pacific Intermediate Water (NPIW). There are two main purposes of this study: 1) to reconstruct the climate history such as sea-ice coverage, and 2) to decipher the sinking process of the calcareous plankton using the microfossil records. Here we present the high-resolution records of planktonic foraminifers and chemical components such as total organic carbon (TOC) and CaCO₃ in a core obtained in the Okhotsk Sea.

Core MD01-2412 (44° 31.65' N, 145° 00.25' E; water depth: 1225 m; core length: 58.11 m), off Hokkaido in the southwestern Okhotsk Sea, was recovered during the IMAGES cruise in 2001. The faunal assemblages of planktonic foraminifers represented typical subarctic fauna, which were mainly comprised of *Neogloboquadrina pachyderma* and *Globigerina umbilicata*. The relative abundances of *N. pachyderma* were approximately 90% of total planktonic foraminifers throughout the core except for several sections (e.g. 1,200 to 1,000 cm; 200 cm bsf). During these notable periods, the level of their abundances decreased down to 70%. Furthermore, the ratios in the coling direction of *N. pachyderma* (dextral), known as the temperature proxy, showed their highest values around the core top, whereas that values stayed low around 1,000 cm. That fact points out that two notable changes in %*N. pachyderma* represents the different environmental conditions.

In addition to the faunal composition of planktonic foraminifers, the extent in preservation of the biogenic particles is also debatable. The percentage of the fragmented shells (%FRAG) showed an increasing trend with small cyclic rise and fall toward the core top. This trend in the degree of preservation coincides with that of the export production. The CaCO₃ contents showed a significant decrease around the core top, whereas that of TOC reached their highest value in that period. These suggest that the oxidation due to high organic carbon export production influenced the preservation of the foraminifer shells.

Local structure analysis of alkali silicate glasses containing sulfur

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Sulfur compounds are widely used as colorant and refining agents in glass industry. However, the behavior of sulfur in glasses has not been made clear in the previous studies. In this study, glass network anions are partly substituted from oxide to sulfide ions in the system of alkali silicate glasses. Chemical bonding states of sulfur and coordinating state around silicon atoms were discussed by spectroscopy.

Binary R₂S-SiO₂ glasses were prepared from mixture of reagent grade silica sand and anhydrous alkali sulfide. The local structure analysis of the obtained glass was investigated by using high resolution XPS and ²⁹Si MAS-NMR measurement.

Figure 1 shows S2p photoelectron spectra for each samples. The S2p mean values are located near the value in Na₂S. Therefore, neither sulfate nor sulfite anions can be seen in the glasses. Sulfurs in the glasses exist as sulfide having electron density equal to negative valence, and which show strong ionic bonding character. Figure 2 shows ²⁹Si MAS-NMR spectra for each samples. Three peaks appeared clearly in the range of 0 to -120ppm. In full oxide glass systems, only Peak3 can be observed. However, both peak1 and peak2 appeared in the glass containing sulfur. Therefore, it is considered that Peak1 and Peak2 are attributed to silicon atoms coordinated sulfur atoms substituting for oxygen atoms.

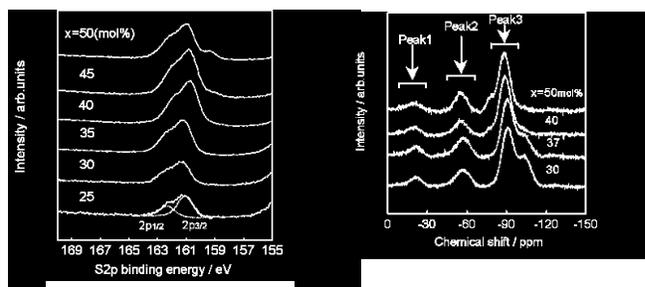


Figure 1. S2p Photoelectron spectra for Na₂S-SiO₂ glasses

Figure 2. ²⁹Si MAS-NMR spectra of Na₂S-SiO₂ glasses

The values of S2p binding energy for glasses were close to that of Na₂S. Therefore, it was assumed that sulfurs in the glasses had an electron density close to ionic S²⁻. By the ²⁹Si MAS-NMR measurement, three sharp peaks were detected between 0 and -120ppm. Two peaks between -25 and -55 ppm were attributed to a silicon tetrahedron coordinated both sulfur and oxygen atom simultaneously because these peaks could not be seen for full oxide glasses.