Boron K-edge XANES Analysis of Amorphous Silica Synthesized at Different pH and Salinity Conditions

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Diatom frustules, preserved in lake and sea sediments, are a potential geological archive. Dissolved boron species mainly have two chemical forms, boric acid and borate ion, whose proportion changes with the ambient pH. These two species show strong isotopic fractionation, and hence the isotopic values of each species change with the proportion. Thus, boron isotopic signature has been recognized as a paleo-pH proxy [1]. In this study, we examined boron coordinates in amorphous silica precipitated in a solvent with known pH and salinity, to understand the reaction pathway during boron coprecipitation with amorphous silica.

We synthesized amorphous silica following the traditional sol-gel method. We tested two types of salinities, 0% and 3.5% using sodium chloride. For non-saline conditions, ammonium carbonate and ammonium acetate were dissolved with the mixture of ethanol and water to achieve pH 8.3-9.4. For saline conditions, ammonium carbonate and ammonium chloride were used to achieve pH 7.9-9.4. In both cases, total ammonium concentrations were fixed at 3.6 mol/L. Boric acid was added to the solvent to obtain approximately 1 wt% of the final boron concentration. After the titration of tetraethyl orthosilicate under 25°C, the precipitate was separated from the solvent using filtration.

Boron K-edge XANES spectra were analyzed at BL-11 of SR center, Ritsumeikan University. Five standard materials were used: boric phosphate and henmilite as representatives of the 4-coordinate form, boric acid and ludwigite as representatives of the 3coordinate form, and borax as the intermediate. Because of the charge-up effect on TEY spectra and the surface hydration effect on PEY spectra [2], we only used the results of PFY mode for the following discussion.

The amorphous silica synthesized in saline solvent showed a clear peak at 199 eV, which is characteristic in the standard materials having 4coordinate boron (Fig. 1). The peak at 199 eV is weakened in the sample precipitated in non-saline solvent, and the spectra well resemble those of the standard materials having 3-coordinate boron. In addition, the peak at 199 eV becomes clearer for the samples precipitated at relatively lower pH.

There are three considerable reactions during boron coprecipitation with amorphous silica as: (1) $Si(OH)_4 + B(OH)_3^0 = Si(OH)_3 - OB(OH)_2^0 + H_2O$ (2) $Si(OH)_4 + B(OH)_3^0 = Si(OH)_3 - OB(OH)_3^- + H^+$ (3) $Si(OH)_4 + B(OH)_4 = Si(OH)_3 - OB(OH)_3 + H_2O$ Taking the results of isotopic analysis into account, the reactions (1) and (2) may play a dominant role in non-saline solvents, while (2) and (3) may be important in saline solvents. The 4-coordinate boron is compatible with the tetrahedral structure of silica, although the excessive oxygen generates a negative ion. Sodium ions in saline solvent may compensate for the charge balance to stabilize 4-coordinate boron in amorphous silica. The reactions of boron species depending on the ambient salinity suggest the different isotopic exchanging processes in freshwater and seawater systems.



Fig. 1. The B K-edge XANES spectra of synthesized amorphous silica and standard materials.

References

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