

Chemical Species of Boron in Environmental Samples

Yohey Hashimoto¹, and Hirona Yamagishi²

1) Graduate School of Agriculture, Tokyo University of Agriculture and Technology, 2-24-16 Naka-cho, Koganei 184-8588, Japan

2) The SR Center, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu 525-8577, Japan

Precipitated calcium carbonate (PCC; CaCO_3) minerals occur naturally in the environment and can also be found in wastewater and spring water. The major polymorphs of PCCs include calcite, aragonite and vaterite; the latter two are the precursors of calcite because calcite is the most thermodynamically stable phase. The PCCs are known to sequester trace elements from water via adsorption and coprecipitation processes. The interaction and retention of B with calcite and aragonite have been studied using microscopic and spectroscopic techniques, adsorption and kinetic models and isotope analyses. Both calcite and aragonite have a high affinity for B through the adsorption-precipitation process. However, the current information about the chemical mechanisms of the B removal of PCCs is still limited.

Aqueous species of B are dependent on pH and total B concentration. In a dilute solution ($\text{B} < 25 \text{ mM}$), the chemical species of B can be explained solely by pH values and exist as monomers, including uncharged boric acid $[\text{B}(\text{OH})_3]$ and borate anion $[\text{B}(\text{OH})_4^-]$ with a pK_a value of 9.24 at 25 °C [1]. The objectives of this study were to investigate the amount of B adsorption on calcite and the specific mode of B coordination (trigonal and tetrahedral) on calcite, as functions of solution pH.

Calcite was reacted in solution containing boron at pH values of 7 and 10, and the amount of boron adsorption was determined. After reacting with boron, calcite samples were washed to remove excess boron, and freeze-dried for the XAFS measurement. Boron K-edge XANES spectra were collected by TEY and PFY modes at BL-11, Ritsumeikan University SR center.

Figure 1 shows the XANES spectra of standard and calcite samples. The peak observed at 194 eV is derived from trigonal boron ($^{\text{III}}\text{B}$). The peak observed at 197-200 eV indicates tetrahedral boron ($^{\text{IV}}\text{B}$). The broad peak observed at around 200 eV reflects the effects of both $^{\text{III}}\text{B}$ and $^{\text{IV}}\text{B}$. Borax and datolite are standard samples containing 50% and 0% of $^{\text{III}}\text{B}$, respectively. The XANES spectra of calcite samples had a peak indicative of $^{\text{III}}\text{B}$, but lacked in a peak indicative of $^{\text{IV}}\text{B}$, regardless of solution pH. The result suggests that boron in solution adsorbs on the surface of calcite in the form of trigonal coordination.

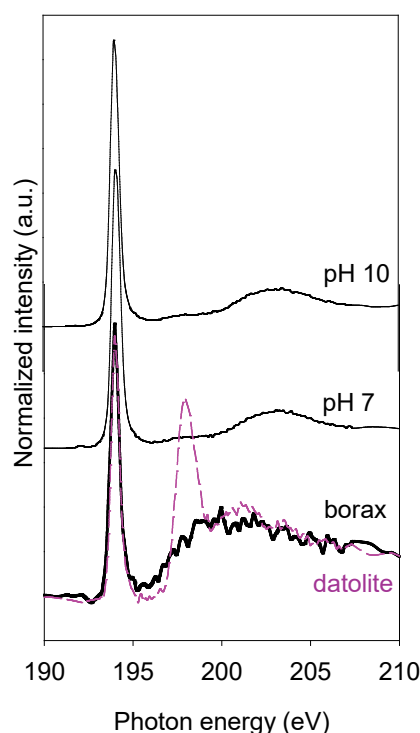


Fig. 1 Boron K-edge XANES spectra of standard minerals and calcite reacted at pH 7 and 10.

References

- [1] Zhou, Y., Fang, C., Fang, Y., Zhu, F. *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* **2011**. 83, 82–87.