

Speciation of magnesium in calcium carbonate using X-ray absorption fine structure (XAFS) spectroscopy related to the variation of magnesium isotopes in nature

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Recent improvements in MC-ICP-MS have enabled us to measure magnesium isotopic variations in the environmental samples, and magnesium isotope geochemistry plays an important role in the field of paleoenvironmental research. Carbonate precipitation experiments indicate the degree of magnesium isotopic fractionation during the precipitation can be expected as a new paleoenvironmental proxy.¹ In order to verify the new proxy, the possible mechanism of magnesium isotopic fractionation was studied.

X-ray absorption near edge structure (XANES) is one of the most useful techniques for the determination of the coordination environment of magnesium. The coordination environments of magnesium in calcium carbonates can be estimated by comparing the shape of the XANES spectra of samples to those of the reference materials.²

In this study, calcite and aragonite samples were synthesized in the laboratory. The calcite sample was prepared by mixing 8 mM CaCl₂, 5 mM MgCl₂, 1.5 mM SrCl₂, and 10 mM NaHCO₃. The Mg content in the calcite sample was about 6000 mg/kg. The aragonite sample was prepared by mixing 8 mM CaCl₂, 80 mM MgCl₂, 0.2 mM SrCl₂, and 10 mM NaHCO₃. The Mg content in the aragonite sample was about 1000 mg/kg.

The Mg K-edges XANES measurements using synchrotron radiation were conducted at BL-10 of the SR center at Ritsumeikan University. A Golovchenko-type double-crystal monochromator with a beryl(10-10) crystal for MgK-edge was used to monochromatize the incident X-ray energy. Powdered samples (synthesized calcite, synthesized aragonite, Mg-doped ferrihydrite, Mg-doped δ -MnO₂, Mg-doped cation exchange resin, and natural

aragonite) were fixed with conductive double-sided carbon tape onto an aluminum sample holder. XANES spectra were obtained by fluorescence X-ray yield mode with silicon drift detector.

Fig. 1 shows the Mg K-edge XANES spectra of the synthesized calcite, the synthesized aragonite, ferrihydrite, δ -MnO₂, cation exchange resin, and natural aragonite. The XANES spectra of calcite, δ -MnO₂, cation exchange resin, and natural aragonite exhibit different shapes to that of the synthesized aragonite. On the other hand, the shape of XANES spectra of the synthesized aragonite was similar to that of the Mg-doped ferrihydrite, indicating that the coordination environment of magnesium in the synthesized aragonite is similar to that in the Mg-doped ferrihydrite.

The shape of the XANES spectra of aragonite differed to that of calcite. In addition, the XANES spectra of natural aragonite exhibit different shapes to that of the synthesized aragonite. These features indicate that the Mg speciation in the synthesized aragonite is not identical to those in calcite and natural aragonite. On the other hand, the shape of XANES spectra of the synthesized aragonite was quite similar to that of biogenic aragonite², indicating that the coordination environment of magnesium in the synthesized aragonite is almost identical to that in biogenic aragonite. It should be noted that the degree of magnesium isotopic fractionation between biogenic aragonite and seawater is equal to the degree between the synthesized aragonite and mother solutions within analytical errors.

The results of the Mg K-edge XANES spectra suggest that the difference of the carbonate crystal structure should affect the coordination environment of magnesium in carbonates, and that the coordination environments of magnesium in calcite and aragonite can influence the degree of magnesium isotopic fractionation during the precipitation.

References

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- (2) A. A. Finch, and N. Allison, *Mineralogical Magazine*, **71** (2007) 539 - 552.

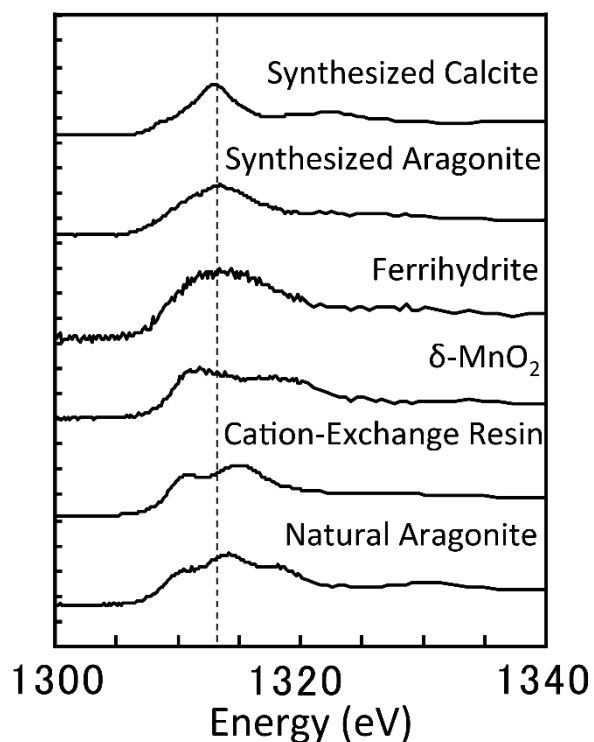


Fig. 1. Observed Mg K-edge XANES spectra