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Development of *in-situ* XAFS analysis of $MnCO_3$ formation in frozen solutions

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Due to the critical role of manganese (Mn) in the environment as its cycle strongly influences the fate and transport of various chemical substances, there have been extensive studies on its biogeochemical processes under a wide range of aqueous conditions. Recently, reports on the chemical reactions accelerated in frozen solutions are growing and ascribing the acceleration mainly to the freeze concentration effect that solutes are expelled from ice crystals and concentrated in the liquid-like layers of the crystal boundary. It is probable that this effect may also affect some of Mn geochemical processes, especially those controlled by dissolved Mn, in natural aquatic systems. In our preliminary experiments, dissolved Mn(II) rapidly precipitated as rhodochrosite ($MnCO_3$) upon freezing the solutions under- or slightly over-saturated with respect to this solid at -5 and -20 ℃ but not at room temperature. So far, most of chemical reactions in frozen solutions have been analyzed *ex-situ*, i.e., after thawing, which could dramatically change the state of the frozen solution as did the freezing. Currently, we try to develop *in-situ* X-ray absorption fine structure (XAFS) analysis to examine the $MnCO_3$ formation in frozen solutions to directly examine this process without thawing processes.

In-situ XAFS analysis was conducted at beamline 12BM-B of Advanced Photon Source with a custom-built cold stage. The solutions containing 1 mM Mn(II) with 2 mM $NaHCO_3$ were frozen at -20 ℃ in the cold stage up to 6 h. The XANES spectra of aqueous solutions resembled that of $MnCl_2$(aq) and kept unchanged for 6 h at room temperature. When the solutions were frozen, by contrast, the corresponding XANES spectra were gradually changed to that of $MnCO_3$ within 1 h, which was consistent with the preliminary *ex-situ* batch result. Our on-going study would expand our understanding on the chemical processes induced by the freeze concentration effect in more detail.