

Accelerated redox chemical processes of inorganic compounds in frozen state and its impact on polar environment

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In general, most chemical reactions are slowed down when temperature decreases. However, several chemical processes can be enhanced in frozen state. The bioavailability, mobility, toxicity, and environmental fate of metals or inorganic elements are controlled by their redox speciation. Although the chemical processes in ice play an critical role on various environmental system, they have rarely studied. Firstly, we investigated the dissolution of bioavailable trace elements (Fe(II)aq and Mn(II)aq) from their oxide particles in water and ice. The dissolution of metal (iron and manganese) oxides particles in ice phase was significantly enhanced compared to those in aqueous solution both in the presence and absence of light although the dissolution rate was enhanced under UV irradiation. The dissolution rate depends on crystallinity, BET surface areas, kinds of present organics or inorganics, pH, light sources, presence of oxygen, and etc. We also investigated the reduction of Cr(VI) in the presence of organic/inorganic compounds and the simultaneous transformation of Cr(VI) and As(III) in ice in comparison with those in aqueous solution. The reduction of Cr(VI) by various organic acids (electron donors) or H₂O₂ was negligible in ambient aqueous solution but was significantly accelerated in ice. The reduction of Cr(VI) in the presence of H₂O₂ in ice shows different reaction pathway compared to those in aqueous solution. The simultaneous reduction of Cr(VI) and oxidation of As(III) in ice phase proceeded stoichiometrically, whereas their mutual conversion was insignificant in aqueous solution. The enhanced redox transformation in ice phase is ascribed to the freeze concentration effect (when solution is solidified the existed organic and inorganic compounds are highly concentrated in unfrozen liquid-like regions) in ice crystal grain boundaries. These results imply that understanding the redox conversion of various inorganic/organic compounds in ice phase may provide newer views and insights on the environmental chemical processes in the icy environments (e.g., upper troposphere, permafrost, polar/high latitude environment and mid-latitudes during winter season) where the freeze-thaw cycles repeat. We also found that the oxidation of iodide to form I₃⁻ and I₂ is greatly accelerated in frozen solution, which is even more enhanced under natural solar irradiation. The release of gaseous I₂ upon thawing the irradiated ice was detected by using cavity ring down spectroscopy. The ice-enhanced generation of I₃⁻ and I₂ is ascribed to the freeze concentration of iodide and dissolved O₂ trapped in polycrystalline ice grain boundaries. This finding proposes a previously unrecognized source of gaseous I₂ through a biotic process in polar region. Here, we introduce our previous studies on intrinsic chemical processes of inorganic species in ice phase and its environmental implications.