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Ligand-Specific Dissolution of Iron Oxides in Frozen Solutions

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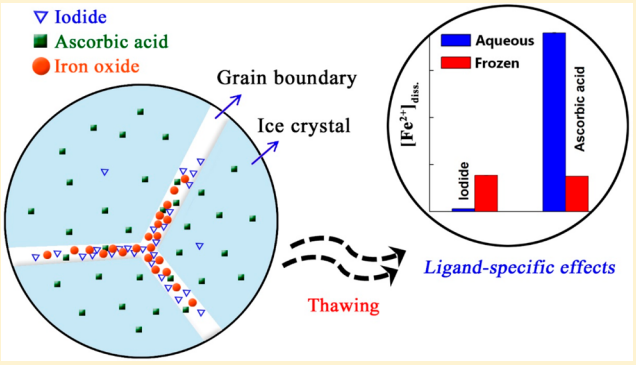
ABSTRACT: The freezing-enhanced dissolution of iron oxides by various ligands has been recently proposed as a new mechanism that may influence the supply of bioavailable iron in frozen environments. The ligand-induced dissolution of iron oxides is sensitively affected by the kind and concentration of ligands, pH, and kind of iron oxides. While most ligands are thought to be freeze-concentrated in the ice grain boundary region along with iron oxides to enhance the iron dissolution, this study found that some ligands, such as ascorbic acid, suppress the iron dissolution in frozen solution relative to that in aqueous solution. Such ligands are proposed to be preferentially incorporated in the ice lattice bulk and not freeze-concentrated in the liquid-like grain boundary. The experimental analysis estimated that the ionized forms of ligands (e.g., iodide ions) are hardly present in the ice bulk region (<3%) and enhance the iron dissolution in frozen solution (relative to that in aqueous solution), whereas some neutral ligands (e.g., undissociated ascorbic acid) are significantly trapped in the ice bulk (>50%) and suppress the iron dissolution compared to the aqueous counterpart. The present results reveal that the ligand-induced dissolution of iron oxide in frozen solution is not always enhanced relative to aqueous solution but depends upon the kind of ligand and experimental conditions.



1. INTRODUCTION

Iron is an essential nutrient for nearly all living organisms.[1] Iron-containing biomolecules are essential cofactors for various cellular level processes [e.g., DNA synthesis, oxygen transport (hemoglobin and myoglobin), electron transport, etc.], which makes this metal an indispensable ingredient of life.[2,3] Because the solubility of most Fe(III) oxides is extremely low,[4] the uptake of iron by living organisms largely requires the reduction to Fe(II) species or the conversion into iron−organic complexes, which are more soluble and more bioavailable.[5,6]

The environmentally relevant chemical transformations taking place in frozen solutions have recently attracted attention among environmental researchers,[7−20] and the studies on them are well-justified considering the fact that the majority of freshwater on Earth exists in the frozen state. The solutes in frozen solutions are highly concentrated in the ice grain boundary region, which contains a small fraction of liquid water between the freezing point and the eutectic point of water, and the liquid-like grain boundary layer may have reaction conditions (e.g., solute concentration, pH, and ionic strength) that are very different from those of aqueous solution.[10,12,21,22] As a result, many kinds of homogeneous and heterogeneous chemical reactions occurring in frozen solutions often exhibit highly accelerated kinetics. Some of the interesting findings of enhanced transformation reactions in/on frozen solutions include the accelerated oxidation of nitrous acid,[12] the enhanced photolysis of nitrates,[23] the formation of dimerized products from the photodegradation of chlorophenols,[11,24] the photolysis and cooperative hydration of pyruvic acid,[15,16] the singlet oxygen-mediated degradation of organic pollutants,[14] the protonation of cresol red,[25] the accelerated reductive dissolution of iron oxides and manganese oxides,[10,26] the accelerated reduction of hexavalent chromium,[8] and the enhanced photooxidation of iodide.[9]

In particular, the accelerated dissolution of iron oxides in frozen solutions (in both dark and irradiated conditions) may provide an alternative pathway of supplying bioavailable iron.[7,26,27] Kim et al. reported a markedly enhanced photoreductive dissolution of iron oxides in the presence of various organic electron donors (formic, acetic, butyric, and humic acids) in frozen solutions compared to its corresponding aqueous counterpart.[26] Another report by Jeong et al. demonstrated an enhanced non-reductive dissolution of iron [mostly Fe(III) species] from goethite [α-FeO(OH)] and

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maghemite (γ-Fe_2O_3) in frozen solutions under a dark condition in the presence of organic ligands,[7] which was largely ascribed to the proton-assisted and ligand-promoted dissolution processes in the ice grain boundary region. All of the previous studies on the dissolution of iron oxides by organic ligands reported significant enhancements in frozen solutions. This study, however, reveals that the iron oxide dissolution in frozen solutions is not always accelerated and can be decelerated from its aqueous phase dissolution depending upon the kind of organic ligands and experimental conditions. The effects of various organic ligands on the iron oxide dissolution were systematically investigated in aqueous and frozen solutions for mostly goethite (regarded as one of the most thermodynamically stable forms of iron oxide in nature[28]) and magnetite (Fe_3O_4) and hematite (α-Fe_2O_3) as well. The highly ligand-specific dissolution of iron oxides in water and frozen solutions was investigated by both experimental and computational methods to provide a reasonable explanation for the observed behavior.

2. MATERIALS AND METHODS

2.1. Materials. The iron oxides used in this study (goethite, magnetite, and hematite) were purchased from Aldrich Chemicals. The specific surface area of these samples was measured as 178, 50, and 8 $m^2\ g^{-1}$, respectively.[7] All other chemicals used in this study, including organic acids (formic, acetic, oxalic, citric, and ascorbic acids), hydroxylamine, and alkali halides, were of analytical-reagent grade. The sample solutions for the experiments were prepared with doubly distilled water. Dilute solutions of perchloric acid (1 M) and sodium hydroxide (1 M) were used to adjust the initial pH of the samples.

2.2. Experimental Procedure. The sample solutions were prepared by adding 0.01 g of iron oxide sample into 50 mL of doubly distilled water to obtain an initial suspension of 0.2 g/L. Then, the calculated amounts of various ligands (e.g., hydroxylamine, ascorbic acid, and iodide) were added to the iron oxide suspension. To enhance the dispersion of iron oxide particles, the suspension was initially sonicated prior to the addition of organic/inorganic ligands. An initial ligand concentration of 1 mM was typically added for most experiments, and the effects of different ligand concentrations (0.1−1.0 mM) were also investigated when needed. The suspensions (5 mL) were placed in 15 mL polypropylene tubes with or without organic/inorganic ligands and kept in a dark condition at room temperature (~25 °C) (for aqueous-phase reactions) or in an ethanol bath maintained at −20 °C (for ice-phase reactions). The time at which the aqueous samples was introduced into the pre-cooled ethanol bath was taken as the reaction starting point (t = 0). At each fixed time interval, the aqueous and ice phase samples (after thawing at 40 °C) were filtered through a 0.45 μm syringe filter to remove any undissolved iron oxide particles. The freezing and thawing process was completed within 10 and 5 min, respectively, which was much shorter than the reaction time in the frozen solution (24 h). Because the dark dissolution of iron oxides in frozen solution slowly proceeds over 50 h,[7] any possible reaction during the freezing or thawing time should be insignificant in this case. The filtered samples were used for further analysis. Further details about this experimental setup were already described earlier.[7,27] To confirm the reproducibility, all of the experiments were conducted at least in duplicate and the average values were used (standard errors indicated by the error bars in figures).

2.3. Analysis. Ferrous and total iron in various samples were analyzed spectrophotometrically using a modified 1,10-phenanthroline method.[29] About 1.5 mL of each sample was mixed with 2.0 mL of 1,10-phenanthroline (2%) and 1.5 mL of acetate buffer. About 100 μL of hydroxylamine hydrochloride (10%) solution was added to reduce any dissolved ferric irons to ferrous ions when the total iron concentration was analyzed. This reaction mixture was shaken well and kept in a dark condition for at least 1 h before the spectrophotometric analysis. The absorbance at 510 nm was recorded on an ultraviolet−visible (UV−vis) spectrophotometer (Agilent Technologies 8453 UV−vis diode array system) and compared to a set of standard values. The residual concentration of various ligands (mainly iodide) after dissolution experiments was measured using ion chromatography (IC, Dionex, Sunnyvale, CA, U.S.A.).

2.4. Computational Method. The binding energies of hydroxylamine and iodide ion on the ice surface and in ice lattice bulk were calculated and compared. A systematic ice modeling on the basis of the quantum mechanical/effective fragment potential (QM/EFP)[30,31] hybrid scheme was suggested,[32,33] which takes into account the long-range electrostatic interactions and hydrogen disorders of crystal ice. The validity and accuracy of our QM/EFP model was thoroughly tested in our earlier studies.[32] The particular combination of a QM and EFP scheme is a three-layer model (QM relaxed region/QM water relax region/EFP water fixed region) for hydroxylamine/6/762, which indicates that the model is composed of a hydroxylamine relaxed, 6 relaxed water molecules, and 762 fixed water molecules. Hydroxylamine and 6 relaxed water molecules were calculated by QM, and 762 fixed water molecules were calculated by EFP. For the calculations of QM regions, a density functional theory of B3LYP functional was used in combination with 6-31G(d,p) basis sets. We adopted the effective fragment potential 1-Hartree−Fock (EFP1-HF) water model for the EFP part of our hybrid models.[30] The general atomic and molecular electronic structure system (GAMESS)[34] program was used for all of the computations. Basis set superposition error (BSSE) corrections to binding energies were performed with the counterpoise (CP) method.[35] CP correction, including monomer deformations, was applied using the following equation:

$$\Delta E_{\mathrm{bind}}^{\mathrm{CP}}(\mathrm{AB}) = [E_{\mathrm{AB}}^{\mathrm{AB}}(\mathrm{AB}) - E_{\mathrm{AB}}^{\mathrm{AB}}(\mathrm{A}) - E_{\mathrm{AB}}^{\mathrm{AB}}(\mathrm{B})] + [E_{\mathrm{AB}}^{\mathrm{A}}(\mathrm{A}) - E_{\mathrm{A}}^{\mathrm{A}}(\mathrm{A})] + [E_{\mathrm{AB}}^{\mathrm{B}}(\mathrm{B}) - E_{\mathrm{B}}^{\mathrm{B}}(\mathrm{B})] \quad (1)$$

where the subscripts and superscripts denote the geometry and the basis, respectively. The chemical system considered is denoted by the symbols in the parentheses. Here, A and B stand for molecule and ice, respectively. Because the geometries of ice (B) in the complex (AB) are different from their isolated forms, the above equation was used to accurately perform the BSSE correction.

3. RESULTS AND DISCUSSION

3.1. Iron Dissolution by Organic Ligands and Halides in Frozen Solution. We carried out the dark dissolution of goethite in aqueous and frozen solutions containing various organic and inorganic ligands. The amount of total dissolved

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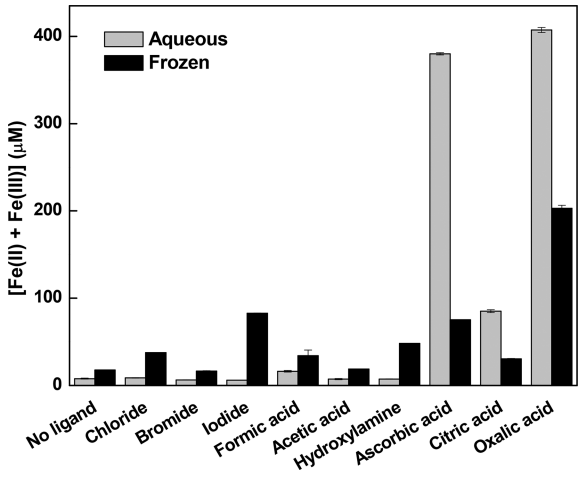

Figure 1. Iron dissolution from goethite in aqueous (gray) and frozen (black) solutions at pH 3 in the presence of various ligands. Experimental conditions: [goethite], 0.2 g/L; [ligand], 1 mM; and reaction time, 24 h.

iron [Fe(II) + Fe(III)] generated from goethite was measured after 24 h and compared in Figure 1, which exhibits highly ligand-specific dissolution behaviors. The trend of goethite dissolution induced by formic and acetic acids (Figure 1) is similar to that reported by Jeong et al.[7] Monodentate organic ligands, such as formic and acetic acids, form weak surface complexation with the iron oxide surface, and their efficiency to induce iron dissolution in water is, thus, very limited, which is little different from that without ligands.[7] On the other hand, the freeze concentration effect, which excludes substrates (ligands) and iron oxide particles from the bulk ice (ice crystal lattice) region upon freezing and, subsequently, concentrates substrate molecules within a small liquid-like grain boundary region, can enhance the dissolution of iron oxides in frozen solutions.[7,13,26,27] Earlier works also reported similar effects, which observed higher reactivity in frozen solutions than its aqueous counterpart.[7,8,10,26,27] This work, however, reveals that the freeze concentration effect on the iron oxide dissolution highly varies depending upon the kind of ligands, some of which exhibit even a negative effect. For example, freezing of sample solutions containing hydroxylamine and iodide cause a significant enhancement in the total dissolved iron [Fe(II) + Fe(III)] relative to aqueous phase dissolution (by ~6 and 13 times, respectively), whereas freezing of ascorbic acid solution markedly suppressed the iron dissolution compared to the aqueous counterpart. The reductive dissolution of iron oxides induced by strong reducing agents, such as ascorbic acid,[3,5,36,37] can play an important role in maintaining the iron balance in the human body and natural environment. Oxalic and citric acids also cause freezing-induced suppression in the total dissolved iron. This implies that the presence of these ligands in the frozen environment can cause an unusual reduction in the bioavailable iron compared to that of the aqueous medium. By considering the possible complexity and difference between the dissolution behaviors, the ligand-specific effects on iron oxide dissolution need to be studied.

The concentrations of ferrous and total dissolved iron produced in the presence of various ligands are compared in Table 1. This shows that the dissolution of iron oxides is reductive with ascorbic acid (100%), hydroxylamine (100%), and iodide (91%), whereas the non-reductive dissolution is

Table 1. Speciation of Dissolved Iron from Goethite in Frozen Solution Containing Various Ligands[a]

ligand	[Fe(II)] (μM)	[Fe(II) + Fe(III)] (μM))	reductive dissolution (%)
ascorbic acid	75.2 ± 0.3	75.2 ± 0.3	100
hydroxylamine	48.2 ± 0.1	48.2 ± 0.1	100
iodide	78.2 ± 0.7	85.7 ± 3.1	91.2
formic acid	7.6 ± 0.1	32.4 ± 0.4	23.6
oxalic acid	45.87 ± 0.43	203.0 ± 3.3	22.6
chloride	5.6 ± 0.1	37.6 ± 0.4	14.9
citric acid	3.9 ± 0.4	30.4 ± 0.5	12.8
acetic acid	2.2 ± 0.0	18.8 ± 0.0	11.9
bromide	nd[b]	16.6 ± 0.5	
no ligand	2.6 ± 0.1	17.6 ± 0.1	14.8

[a]Experimental conditions: [goethite], 0.2 g/L; [ligand], 1 mM; pH, 3; and reaction time, 24 h. [b]nd = not detected.

dominant with formic and acetic acids. The extensive dissolution of iron oxide by ascorbic acid, iodide, and hydroxylamine should be ascribed to their strong reduction power. The mechanism of reductive iron dissolution in water has been extensively studied,[4,7,38,39] which is initiated by the complex formation of organic/inorganic ligands (represented as $>Fe^{III}$-L^n in reaction 2) on the surface of iron oxide.

$$>Fe^{III} + L \rightarrow >Fe^{III}-L^n \quad (2)$$

The reductive dissolution of iron oxides requires an electron transfer from the ligand to the surface metal ion (reaction 3). The resulting Fe(II) species is then detached from the surface of the iron oxide and released as dissolved ferrous ions (reaction 4).[38]

$$>Fe^{III}-L^n \rightarrow >Fe^{II}-L^{(n-1)} \quad (3)$$

$$>Fe^{II}-L^{(n-1)} \rightarrow Fe^{2+}_{aq} \quad (4)$$

The dissolution of ferrous ions from different commercial iron oxide samples (goethite, magnetite, and hematite) in aqueous and frozen solutions, which was induced by ascorbic acid and iodide, are compared in Figure 2, of which the *x* axis represents the Brunauer–Emmett–Teller (BET) surface area of each iron oxide sample. Note that ferrous ions dissolved from hematite and magnetite in the aqueous solution of iodide are below the detection limit (indicated as "zero" in Figure 2B). Figure 2 exhibits a general trend that iron oxide samples with a higher surface area dissolute more ferrous ions,[7] although it is not quantitatively proportional. Goethite with the highest surface area (BET surface area of 178 $m^2\ g^{-1}$) induced more dissolution of Fe(II) than magnetite (50 $m^2\ g^{-1}$) and hematite (8 $m^2\ g^{-1}$) in both aqueous and frozen solutions. It should be noted that the freezing in the presence of ascorbic acid (or iodide) consistently suppressed (or enhanced) the iron dissolution compared to the aqueous-phase dissolution, regardless of the kind of iron oxide. The significantly enhanced dissolution of iron oxides in the presence of iodide in frozen solutions (pH 3) can also be explained in terms of the freeze concentration effect as we did in previous studies,[7,27] whereas the opposite results obtained with ascorbic, citric, and oxalic acids cannot. This seems to imply that the freeze concentration of solutes in frozen solution is not always observed and should depend upon the kind of solutes. That is, some solutes, such as ascorbic acid, could be preferentially incorporated within the ice lattice upon freezing. In such a case, ascorbic acid

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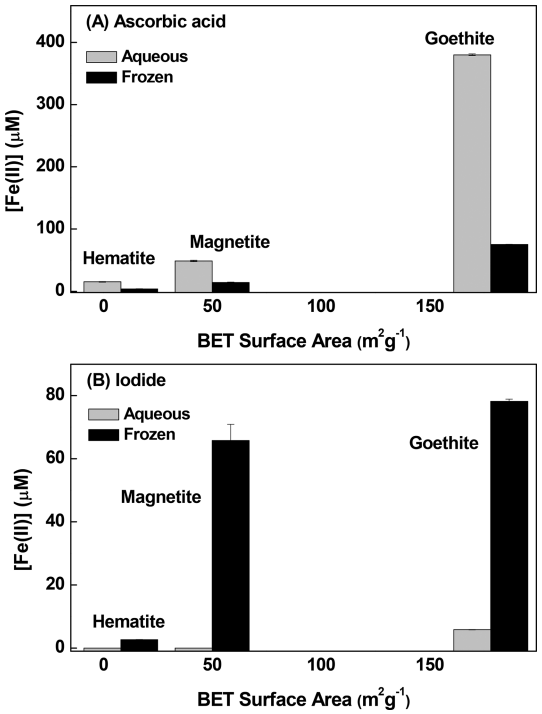

Figure 2. Dissolution of ferrous ions from three kinds of iron oxides having different surface areas in aqueous (gray) and frozen (black) solutions at pH 3 in the presence of (A) ascorbic acid and (B) iodide. Experimental conditions: [iron oxide], 0.2 g/L; [ligand], 1 mM; and reaction time, 24 h.

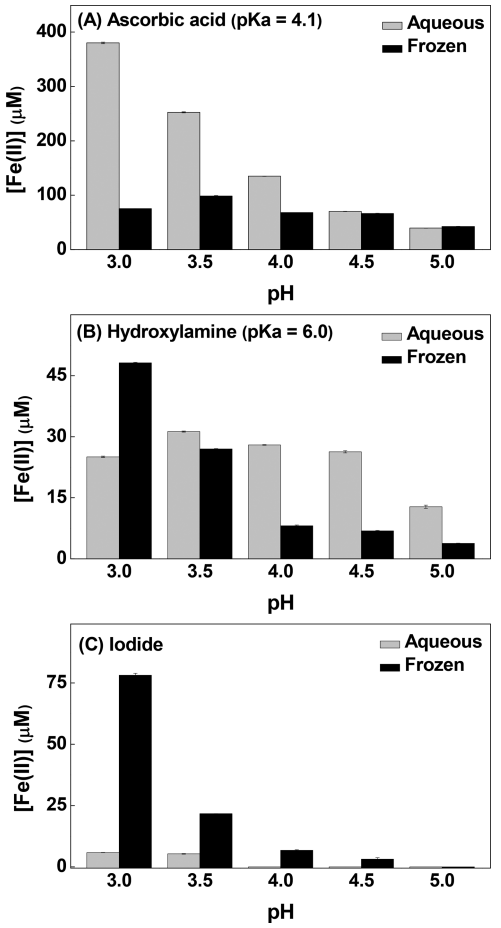

Figure 3. pH-dependent dissolution of ferrous iron from goethite in aqueous (gray) and frozen (black) solutions in the presence of (A) ascorbic acid, (B) hydroxylamine, and (C) iodide. The pH values indicate the pH of the aqueous solution before freezing. Experimental conditions: [goethite], 0.2 g/L; [ligand], 1 mM; and reaction time, 24 h.

molecules become less accessible to the iron oxide particles, which are concentrated in the ice grain boundary region;[26] hence, a suppressed dissolution of iron oxide in frozen solutions (relative to the aqueous counterpart) could occur. The preferential incorporation of some anions or cations into the ice crystal bulk upon freezing was experimentally supported through freezing potential measurements.[40,41] On the basis of the present observations, it is proposed as a hypothesis that some ligands that suppress the iron dissolution in frozen solution compared to that in aqueous solution are not freeze-concentrated in the ice grain boundary region but more preferentially incorporated within the ice crystal lattice. To test the validity of such a hypothesis, more systematic experimental and theoretical investigations were carried out and discussed below.

3.2. pH-Dependent Ligand Effects on Iron Oxide Dissolution. It is well-known that protons can accelerate the dissolution of iron oxides.[4] Moreover, pH can change the acid−base speciation of ligands[42−45] and, subsequently, their relative distribution between the ice bulk and liquid-like grain boundary region because of the change of the charge on ligand molecules, which should influence the iron oxide dissolution process. Therefore, the effects of pH on the dissolution of iron in aqueous and frozen solutions were additionally investigated for ascorbic acid, hydroxylamine, and iodide (see Figure 3), which revealed distinguished and contrasting pH-dependent behaviors. Each ligand exhibits a unique pH-dependent behavior. The general trend of higher dissolution at lower pH, which was consistently observed for all ligands, should be ascribed to the proton-assisted dissolution of iron oxides. Incidentally, it should be mentioned that the pH values shown in Figure 3 indicate the pH of aqueous solutions before freezing and not the real pH in the liquid-like grain boundary region in the frozen solution. Goethite dissolution in the presence of ascorbic acid was most suppressed in the frozen solution relative to the aqueous solution at pH 3. The relative suppression of the dissolution gradually decreased with increasing pH to show a negligible difference at pH > 4.5 (Figure 3A). On the other hand, the frozen solution containing hydroxylamine enhanced the iron dissolution at pH 3 but suppressed it at pH ≥ 3.5 in comparison to the corresponding aqueous-phase dissolution (Figure 3B). Iodide whose speciation is not dependent upon pH induced the freezing-enhanced dissolution of iron oxide consistently in the tested pH range,[46] which was the highest at pH 3 and gradually decreased with pH (Figure 3C). The iron dissolution in aqueous and frozen solutions containing iodide at pH 5 was below the detection limit. For all cases tested in Figure 3, the reductive dissolution of goethite was negligible in the absence of ligands.

Such pH-dependent behaviors can be related with the pH-dependent relative distribution of each ligand between the ice bulk and the liquid-like grain boundary region. Ascorbic acid exists mainly as the neutral form at pH 3 (pK_{a1} = 4.1),[45,47] and the pH increase causes the deprotonation of this ligand to the anionic form. On the other hand, the protonated cationic form

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of hydroxylamine ($HONH_3^+$) exists in the acidic pH (pK_a = 6.0),[48,49] and increasing pH should gradually convert the cation to the neutral form. Although the concentrations of each ligand and pH in the bulk ice and the grain boundary region could not be measured in this work, it is reasonable to assume that the dissolution of iron oxide in frozen solutions should be enhanced when the ligands are preferentially concentrated in the grain boundary region along with the iron oxide particles. Similarly, the iron oxide dissolution should be suppressed (relative to the aqueous phase) when the ligands are preferentially incorporated within the ice crystal bulk. On the basis of the pH-dependent dissolution trends observed for ascorbic acid (Figure 3A), hydroxylamine (Figure 3B), and iodide (Figure 3C), it is suggested that some ligands (i.e., protonated hydroxylamine and iodide anion) are preferentially concentrated in the liquid-like grain boundary region and facilitate the dissolution of iron oxide in frozen solutions.[26,27] On the other hand, other ligands (i.e., undissociated ascorbic acid and neutral hydroxylamine) seem to be preferentially trapped in the bulk ice (not in the grain boundary region) and are consequently less accessible to the iron oxide particles in the grain boundary region, which should result in the freezing-induced suppression of iron oxide dissolution. This seems to be the similar case for citric and oxalic acids, as shown in Figure 1. The observation that the relative effect of hydroxylamine on the iron oxide dissolution in frozen solution was reversed when the pH increased from 3 to higher values implies that the pH-dependent speciation[48,49] of ligands critically influences the ligand distribution between the ice bulk and the grain boundary.

3.3. Ligand Distribution between the Ice Lattice (Bulk) and Grain Boundary (Surface) Regions. From the above considerations, we propose that (1) the ligand molecules that induce the freezing-enhanced dissolution of iron oxides (e.g., iodide and protonated hydroxylamine at pH 3) are likely to be excluded from the ice lattice and concentrated in the grain boundary region[26,27] and (2) ligand molecules that induce the freezing-suppressed dissolution of iron oxide (e.g., ascorbic acid at acidic pH and hydroxylamine at pH $\geq$ 4) are likely to be trapped in the ice lattice to hinder the direct contacts between the ligand molecules and the iron oxide particles in the grain boundary region. To confirm such hypothesis, we carried out the following experiment to estimate the relative distributions of ligand molecules between the ice lattice (bulk) and the grain boundary (surface) region (see Figure 4).

The solidified ice samples containing iron oxide particles and ligand molecules (in both the ice lattice and the grain boundary) were taken out from the ethanol bath and were immediately crushed to fine particles in a mortar, followed by rapid washing with 10 mL of cold water to melt away only the surface region of the crushed ice particles. The washed fine ice particles were immediately recollected via filtration and then fully melted to liquid samples that were analyzed for remaining ligands using ion chromatography. Because the ligand molecules present in the ice surface (grain boundary) region can be preferentially washed out before the ice bulk starts to melt down, it is assumed that the measured concentrations of ligands in the thawed samples represent mostly the ligand molecules trapped in the ice lattice (bulk). Although this is a very rough method with large errors expected and it is not possible to wash out the grain boundary layer only in a precise way by this method, this analysis should show the relative

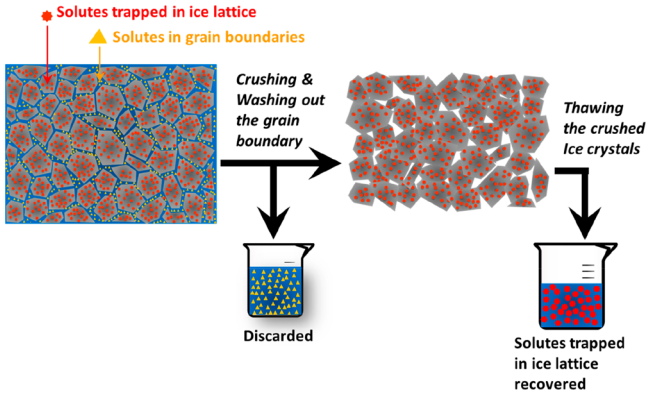

Figure 4. Illustration of the experimental procedure for estimating the concentrations of solutes (ligands) trapped in ice lattice.

Table 2. Proportion of Ligands Trapped in the Ice Lattice (Bulk) among the Total Ligands and the Ratio of Dissolved Fe(II) between the Frozen and Aqueous Solutions[a]

ligand	$[ligand]_{ice\ bulk}/[ligand]_{total}$ (%)	$[Fe(II)]_{frozen}/[Fe(II)]_{aqueous}$
iodide	2.6	13.4
ascorbic acid	58.0	0.2

[a]Experimental condition: [goethite], 0.2 g/L; [ligand], 0.5 mM; and pH, 3.

distribution of the ligand between the ice bulk and surface regions at least qualitatively. Much precaution was made to ensure the reliability of the measurements. The experimental results are summarized in Table 2, which clearly shows the contrasting distribution trends of iodide and ascorbic acid, which exhibited the opposite effects on the iron oxide dissolution in frozen solution. The proportion of the iodide ions trapped in the ice lattice (bulk) is very small (<3%), whereas that of ascorbic acid is markedly higher (>50%). This suggests the preferential concentration of iodide ions in the ice surface region[9,26] and the preferential incorporation of ascorbic acid in the ice bulk region, which is consistent with the proposed hypothesis. As a result, frozen solutions containing iodide ions exhibited the freezing-enhanced dissolution of iron oxide ($[Fe(II)]_{frozen}/[Fe(II)]_{aqueous} \gg 1$), whereas those with ascorbic acids showed the freezing-suppressed dissolution ($[Fe(II)]_{frozen}/[Fe(II)]_{aqueous} \ll 1$). A similar attempt for the determination of the hydroxylamine content in bulk ice, however, was not successful as a result of the technical difficulties associated with the accurate concentration measurement. Although ascorbic acid seems to be too big to be incorporated into the ice crystal without causing a significant distortion of the ice lattice, several hydroxyl groups present in its molecular structure should form multiple hydrogen bonding with water molecules in the ice lattice, which seems to stabilize ascorbic acid in the ice lattice with compensation for the lattice distortion energy. The fact that citric and oxalic acids, which exhibit the freezing-suppressed dissolution of iron oxide, such as ascorbic acid, also have multiple hydroxyl groups supports such explanation.

Additional evidence to support the ligand-specific distribution between the ice bulk and ice surface was obtained from theoretical calculations.[32,33] The binding energies of a hydroxylamine (both protonated and neutral forms) and an iodide ion on the ice surface and in the bulk ice lattice were theoretically estimated. The optimized structures and binding

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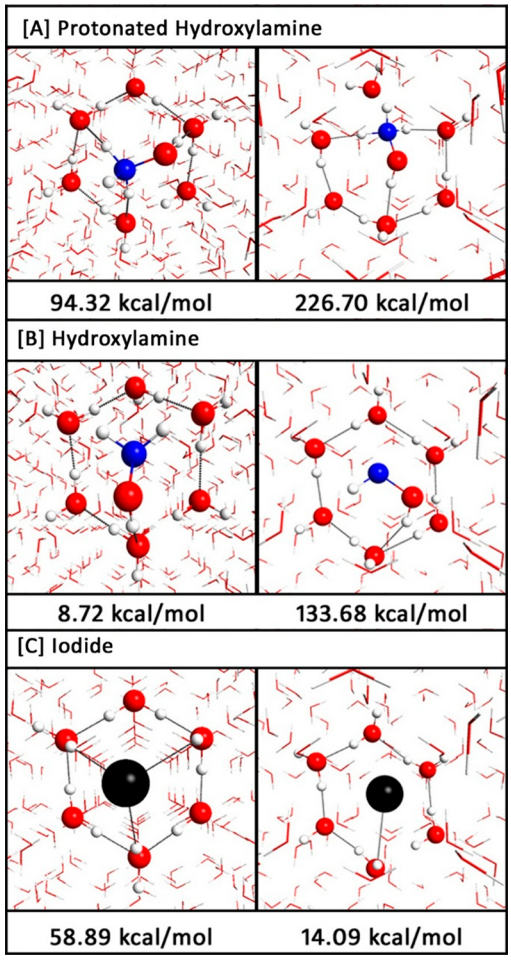

Figure 5. Theoretically optimized structures and binding energies of (A) protonated hydroxylamine, (B) neutral hydroxylamine, and (C) iodide on the ice surface (left) and in the bulk ice lattice (right). The colored balls represent O (red), H (white), N (blue), and I (black).

energies of protonated hydroxylamine (A), neutral hydroxylamine (B), and iodide (C) on the ice surface (left) and in the bulk ice (right) are compared in Figure 5. As shown in the hydroxylamine case, both the protonated and neutral forms are more stable in the bulk ice lattice. However, neutral hydroxylamine has a much lower relative surface preference (8.72/133.68 = 0.065) than protonated hydroxylamine (94.32/226.70 = 0.42), which implies that neutral hydroxylamine should be more easily incorporated into the ice lattice than its protonated form. When more hydroxylamine molecules (reductants) are incorporated within the ice lattice, they should have less contact with the iron oxide particles in the grain boundary (surface) region and, hence, less reductive dissolution of iron oxide. This calculation result is in good agreement with the observed pH-dependent dissolution of iron oxides with hydroxylamine, which exhibited the freezing-enhanced dissolution in pH 3 (where protonated hydroxylamine should be dominant on the surface region) but the freezing-suppressed dissolution at higher pH (where the fraction of protonated forms on the surface region is lowered) (see Figure 3B). On the other hand, iodide ion strongly prefers the ice surface region (58.89/14.09 = 4.18), and therefore, its concentration in the ice surface region should be higher than that in the bulk ice. This explains why iodide-induced dissolution of iron oxide is consistently higher in frozen solution than in aqueous solution, regardless of pH, unlike the case of ascorbic acid and hydroxylamine, in which the relative effect on the iron oxide dissolution in frozen solution is dependent upon pH (see Figure 3).

3.4. Effects of Other Factors on the Iron Oxide Dissolution. According to the previous discussion, the ligands that are preferentially included in the ice bulk (e.g., ascorbic acid) are expected to have less freeze concentration effect than the ligands such as iodide[9,26] and protonated hydroxylamine that prefer the ice surface region. To investigate this further, the temperature-dependent production of ferrous ions from goethite dissolution induced by ascorbic acid, hydroxylamine, and iodide was measured and compared in Figure 6. The iron

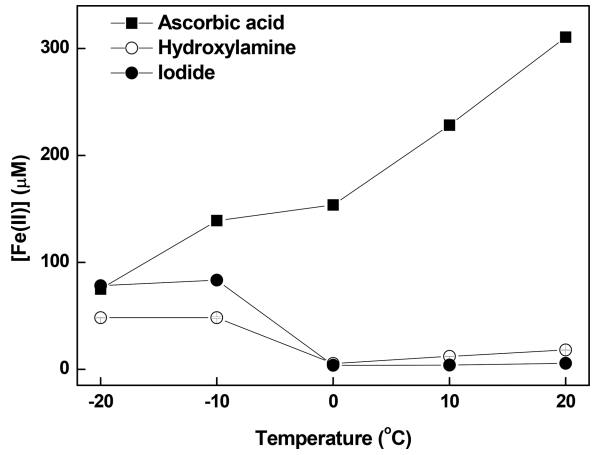

Figure 6. Temperature effect on the production of Fe(II) dissolved from goethite in the presence of ascorbic acid, iodide, and hydroxylamine. Experimental conditions: [goethite], 0.2 g/L; [ligand], 1 mM; reaction time, 24 h; and pH, 3 (the error bars are smaller than the symbol size).

oxide dissolution by ascorbic acid monotonously decreased with a decreasing temperature (from 20 to −20 °C), and there is no sign of enhancement below the freezing point, which implies the absence of the freeze concentration effect. On the other hand, hydroxylamine and iodide showed a clear sign of enhancement in the iron oxide dissolution below 0 °C, which supports the freeze concentration of the ligands.

The different freeze concentration behaviors of ascorbic acid and iodide can also be related with the different concentration dependences shown in Figure 7. Increasing the ascorbic acid concentration up to 1 mM gradually increased the iron dissolution in aqueous solution but reached the saturation above 0.1 mM in the case of frozen solution. This implies that ascorbic acids are not freeze-concentrated in the ice grain boundary. On the other hand, increasing the iodide concentration minimally increased the iron dissolution in aqueous solution but efficiently increased it in frozen solution, which implies that iodide ions are indeed freeze-concentrated in the ice grain boundary.[9,26] Both the temperature dependence (Figure 6) and the ligand concentration dependence (Figure 7) support that iodide ions are freeze-concentrated but ascorbic acids are not in frozen solutions. Such a difference causes their opposite effects on the iron oxide dissolution in frozen solutions (Figures 1 and 3).

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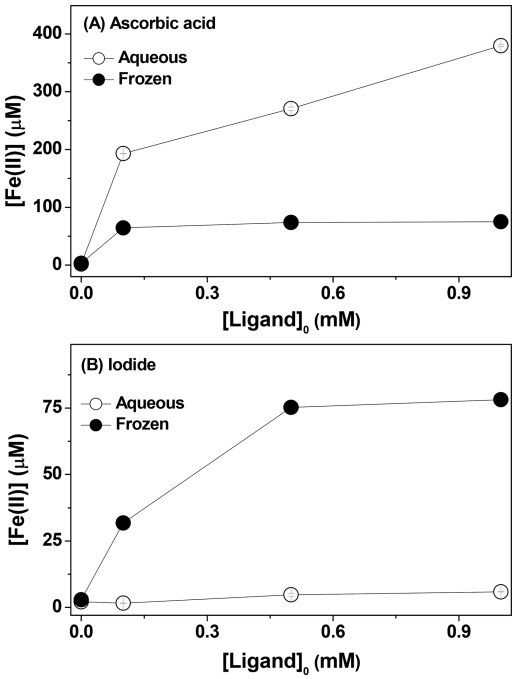

Figure 7. Dissolution of Fe(II) from goethite in aqueous and frozen solutions as a function of the ligand concentration: (A) ascorbic acid and (B) iodide. The ligand concentration indicates the aqueous concentration before freezing. Experimental conditions: [goethite], 0.2 g/L; reaction time, 24 h; and pH, 3 (the error bars are smaller than the symbol size).

4. ENVIRONMENTAL IMPLICATIONS

The present study found that the dissolution of iron oxide under a dark condition exhibits highly ligand-specific behavior. While all of the previous works on the dissolution of iron oxides in both dark and photo-irradiated conditions reported the enhancement of iron dissolution in frozen solutions compared to the aqueous counterpart,[7,26,27] this work found that some ligands, such as ascorbic acid, oxalic acid, citric acid, and neutral hydroxylamine, exhibit the opposite effect (freezing-suppressed dissolution). This could be ascribed to the ligand-specific distribution between the ice lattice (bulk) and the ice grain boundary (surface). While most solutes are thought to be freeze-concentrated in the ice grain boundary region upon freezing, some ligands that exhibit the freezing-suppressed dissolution of iron oxide are proposed to be preferentially incorporated in the ice bulk and not freeze-concentrated. The dust particles containing iron oxides can be trapped in an ice cloud in the upper atmosphere or deposited on snow and various ice media (sea ice and glacier) in the polar region. In particular, the iron oxide dissolution is more pronounced in acidic conditions, which can be often found in the environments such as marine aerosols and cloud droplets with pH < 3.5.[50] The present study shows that the dissolution rate of iron oxide particles trapped in frozen solutions can be sensitively influenced by the kind of organic and inorganic ligands present in various frozen media. Freezing in the presence of some compounds can accelerate the dissolution of iron oxide, while freezing with others may exhibit the opposite effect. As a result, freezing may cause an enhanced or suppressed dissolution of iron oxides depending upon the kind of ligands present in the environmental media. This study showing that the ligand-specific nature of iron oxide dissolution in frozen solutions should provide a better understanding of the iron bioavailability in cold environments.[7,27] The dissolution of iron oxides in environmental media (aqueous and frozen solutions) should be influenced by various parameters, such as the crystallinity and surface area of iron oxides, the kind and concentration of ligands, coexisting ions, pH, and temperature. In particular, this study found that the roles of ligands are complex and highly ligand-specific, which should explain the different dissolution behaviors between the aqueous and frozen conditions. It should also be recognized that the reality is even more complicated than the laboratory study. The composition of natural ice samples is far more complex than the controlled laboratory samples because of the coexistence of a wide variety of chemical species, including metal ions, inorganic ions, natural organic matters, etc. Furthermore, the pH-dependent behaviors in the iron oxide dissolution may complicate the problem. Therefore, applying the laboratory results to real environments requires more rigorous investigations.

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