

Cr(VI) Formation via Oxyhalide-Induced Oxidative Dissolution of Chromium Oxide/Hydroxide in Aqueous and Frozen Solution

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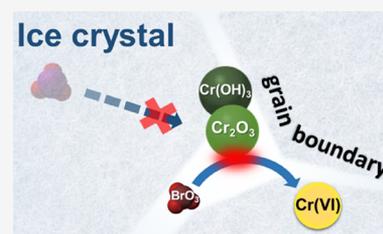
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ABSTRACT: The oxidative dissolution of Cr(III) species (Cr_2O_3 and $\text{Cr}(\text{OH})_3$) by oxyhalide species, which produces hexavalent chromium (Cr(VI)), was studied in aqueous and frozen solution. The oxyhalide-induced oxidation of Cr(III) in frozen solution showed a different trend from that in aqueous solution. Cr(VI) production was higher in frozen than aqueous solution with hypochlorous acid (HOCl) and bromate (BrO_3^-) but suppressed in frozen solution with hypobromous acid (HOBr) and periodate (IO_4^-). In particular, bromate markedly enhanced Cr(VI) production in frozen solution, whereas it had a negligible activity in aqueous solution. On the contrary, periodate produced Cr(VI) significantly in aqueous solution but greatly suppressed it in frozen solution. Bromate was found to be much more concentrated in the ice grain boundary than periodate according to both chemical and Raman spectral analyses. The oxidative transformation of Cr(III) to Cr(VI) was accompanied by the concurrent and stoichiometric reduction of oxyhalide species. Dissolved O_2 had little effect on the oxidative dissolution, but dissolved organic matter retarded the oxidation of Cr_2O_3 in both aqueous and frozen conditions. This study proposes that the oxyhalide-induced oxidation of Cr(III) (particularly by bromate) in frozen conditions might have a significant effect on the generation of Cr(VI) in the frozen environment.



INTRODUCTION

Chromium as a ubiquitous element (21st abundant in Earth's crust) has been widely used in various applications such as painting, coating, metal, pigment, tanning, etc., which is eventually released into the environment. However, chromium is considered as potentially hazardous in the ecosystem due to the toxicity of hexavalent chromium. Therefore, understanding the chemical fate of chromium in the environment is important. The common oxidation states of chromium found in nature are trivalent (Cr(III)) and hexavalent (Cr(VI)). While Cr(III) is an essential nutrient with low toxicity for living organisms, Cr(VI) is a severe toxicant for most of the organisms.^{1,2} Therefore, the oxidation of Cr(III) to Cr(VI) is an important chemical transformation in the environment. Manganese oxides in various forms were often studied for Cr(III) oxidation in the environment, and the reaction mechanisms were extensively studied for the effects of pH, surface passivation of manganese oxide, and other metal ions.^{3–6} Accordingly, a close relation between the content of manganese oxide and the proportion of Cr(VI) in a soil layer/sediment has been reported.^{7,8} However, other potential oxidants for Cr(III) oxidation have not been thoroughly studied yet.

Oxyhalide species may serve as an oxidant in many environmental processes. Hypochlorous acid (HOCl) is often used as a water disinfectant in water treatment plants, swimming pool, ballast water, etc.^{9–12} During the chlorination process, active chlorine species can oxidize other halides in water and produce oxyhalides such as chlorate (ClO_3^-),

bromate (BrO_3^-), and possibly periodate (IO_4^-).^{12–14} Furthermore, residual chlorine may react with halides in natural waters even after the discharge of the disinfected water.¹⁴ Another disinfection method, ozonation, can produce oxyhalide byproducts such as hypobromous acid (HOBr) and bromate (BrO_3^-).¹⁵ As the water disinfection industry grows, the emission of oxyhalide species into the aquatic environment would increase gradually. Although HOCl was studied for the oxidation of Cr(III),^{16–18} other oxyhalides have not been studied for Cr(III) oxidation.

Chemical reactions are usually slowed down as temperature decreases. However, it was found that some chemical reactions of environmental relevance are remarkably accelerated in frozen solution.^{19–31} This has great environmental significance since the frozen environmental media such as ice and snow are ubiquitous in nature. When the solution is frozen between the freezing and eutectic points, a minute portion of water remains unfrozen in the ice crystal grain boundary region where the solutes are highly concentrated. This liquid-like layer between ice crystals has properties that are very different from those of aqueous solution such as solute concentration, ionic strength,

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and pH.^{32–36} This induces unique chemical reactions in frozen solutions, which could have environmental impacts.

This study aims to understand the oxidative dissolution behaviors of chromium oxide/hydroxide in the presence of different oxyhalide species in aqueous and frozen solutions. Cr₂O₃(s) that is well-known for its high stability³⁷ is employed as the main Cr(III) source, and Cr(OH)₃(s) and Cr³⁺(aq) ions are also compared for their oxidation by oxyhalide species. The oxyhalide-induced oxidations of Cr(III) species in frozen solution show behaviors that are very different from the corresponding aqueous reactions. The freezing effects on the oxidative dissolution of chromium oxide/hydroxide and the mechanisms involving oxyhalide species as an oxidant are investigated and discussed in detail. The unusual reactions in frozen environments may provide a previously unrecognized source of Cr(VI).

METHODS

Materials. Chemicals and reagents used in this study were as follows: chromium oxide (Cr₂O₃, JUNSEI), chromium chloride (Cr(III)Cl₃, Sigma-Aldrich), sodium hypochlorite (NaClO 5% in solution, WAKO), sodium hypobromite (NaBrO 9% in solution, KANTO CHEMICAL), sodium bromate (NaBrO₃, Aldrich), sodium periodate (NaIO₄, JUNSEI), sodium chlorate (NaClO₃, Sigma-Aldrich), sodium perchlorate (NaClO₄, Sigma-Aldrich), sodium iodate (NaIO₃, Sigma-Aldrich), sulfuric acid (H₂SO₄, Sigma-Aldrich), sodium dichromate dihydrate (Na₂Cr₂O₇·2H₂O (Cr(VI)), Aldrich), diphenyl-carbazide (Aldrich), acetone (JUNSEI), sodium chloride (NaCl, Sigma-Aldrich), sodium bromide (NaBr, Aldrich), and sodium iodide (NaI, SHINYO PUER CHEMICALS). All chemicals were of analytical grade unless specified otherwise. Suwannee river fulvic acid (SRFA) was purchased from the International Humic Substances Society (<https://ihss.humicsubstances.org/>). The deionized water used in the experiments was of ultrapure (18 MΩ·cm) grade and was prepared using a Barnstead purification system.

Chromium Hydroxide (Cr(OH)₃) Synthesis. The synthetic process followed the literature method.³⁸ Cr(III) stock solution of 60 mM was prepared and subsequently purged with Ar gas. Then, the pH was adjusted to 9.0–9.5 by adding an aliquot of NaOH (1.0 M). Dark greenish Cr(OH)₃ was precipitated at pH > 9. The suspension was aged for 4 h under stirring and Ar gas purging. After aging, synthesized Cr(OH)₃ was recovered by centrifugation and washed with deionized water several times until the suspension pH becomes close to 8.0. Cr(OH)₃ concentration of the suspension was measured gravimetrically after completely drying the suspension in a vial. The suspension was stored in a refrigerator before experiments.

Experimental Procedure. Chemical reagent stock solutions were prepared weekly. Ten milliliters of sample solution was transferred into a 15 mL conical tube, and the sample pH was adjusted with sulfuric acid solution. The samples were frozen by immersing in a constant-temperature ethanol bath maintained at –20 °C. After certain reaction time, the frozen samples were taken out from the ethanol bath and melted in warm water (40 °C). After completely thawing, the sample was filtered with a 0.45 μm syringe filter. The procedure was the same for aqueous phase experiments except that the ethanol bath temperature was kept at 20 °C. For the dissolved oxygen control, the sample solution (10 mL) was purged with Ar or O₂ gas for 10 min before freezing in the ethanol bath.

Analysis. The amount of generated Cr(VI) was determined by using the DPC (1,5-diphenylcarbazide) method.³⁹ The DPC reagent solution was daily made by adding 250 μL of sulfuric acid and 0.05 g of DPC into 25 mL of acetone. The filtered sample solution (0.5 mL) was transferred into a 5 mL conical tube with 2.5 mL of deionized water. Then, 100 μL of the DPC reagent was added and well mixed. After 30 min, the absorption spectra were measured with a UV/Visible spectrophotometer (Agilent 8453). The absorbance peak at 540 nm was used for measuring Cr(VI) concentration. Anion species such as chloride (Cl[–]), chlorate (ClO₃[–]), bromide (Br[–]), bromate (BrO₃[–]), iodide (I[–]), and iodate (IO₃[–]) were measured using an ion chromatograph (IC, Dionex ICS-2100) with a Dionex IonPac AS 18 column (4 mm × 250 mm) and a conductivity detector. KOH solution was used as the eluent. The amount of hypochlorous acid (HOCl) and hypobromous acid (HOBr) was determined colorimetrically using an ABTS (2,2-azino-bis(3-ethylbenzothiazoline)-6-sulfonic acid-diammonium salt) reagent.⁴⁰ A filtered sample (5 mL) was transferred into a 15 mL conical tube. Then, 0.5 mL of ABTS solution (1 g/L), 0.5 mL of sulfuric acid solution (0.05 M), and 4 mL of deionized water were added. For HOBr measurement, the absorbance spectra were measured (Agilent 8453) right after addition of the ABTS solution, while the solution was equilibrated for 10 min before HOCl measurement. The concentration was calculated using the molar absorptivity ($\epsilon = 31,600 \text{ M}^{-1} \text{ cm}^{-1}$) at 405 nm for both HOCl and HOBr. Periodate (IO₄[–]) was also measured colorimetrically using iodide. The filtered sample solution (7 mL) was added with 2 mL of pH 6 phosphate buffer and 1 mL of 0.15 M iodide solution. After 3 min, the absorbance at 352 nm was measured with a UV/Visible spectrophotometer (Agilent 8453).

Estimation of Oxyhalide Distribution between the Ice Surface and Ice Bulk. The distribution of oxyhalide species between the ice surface and the ice bulk region was very roughly estimated by following the previous method.^{41,42} Briefly, the solution of specific oxyhalide in a 15 mL conical tube was frozen in an ethanol bath at –20 °C. After complete freezing, the frozen ice was taken out of the conical tube and transferred to a cooled plate whose surface temperature was maintained at 0 °C by a cold stand connected to an ethanol circulator. The surface temperature of the plate was monitored with an infrared thermometer. The bulk frozen ice was crushed into fine ice particles for 1 min, and then, cold deionized water (0 °C) washed the crushed ice particles away for 3 min to preferentially dissolve the surface layer of ice particles. The washed solution was recovered from the cold plate, and the remaining ice particles were fully thawed to obtain another sample. The concentrations of the oxyhalide species in both samples (one melted from the ice particle surface region, and the other melted from the bulk ice particle) were then analyzed. The experiments were repeated many times until the result became reproducible.

For in situ measurement of oxyhalide species in the ice grain boundary and ice crystal, a confocal Raman microscope (inVia Qontor confocal Raman microscope, Renishaw) equipped with a 532 nm edge laser was used. A Linkam stage (THMS 600, Linkam) was used for freezing the sample solution. A sample solution drop (50–100 μL) put on the Linkam stage was cooled down gradually (–1 °C/min) to –20 °C.

RESULTS AND DISCUSSION

Chromium Oxide (Cr₂O₃) Oxidation by Oxyhalide.

Hexavalent chromium (Cr(VI)) was produced from the oxidation of trivalent chromium (Cr(III)) in chromium oxide (Cr₂O₃). Figure 1 shows the time profiles of the Cr(VI)

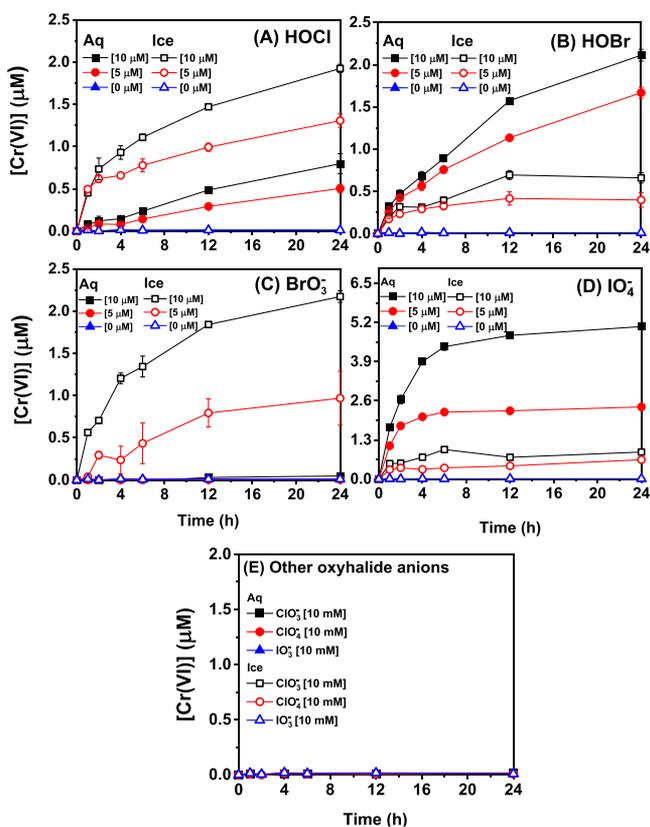


Figure 1. Time profiles of [Cr(VI)] dissolved from chromium oxide (Cr₂O₃) that was oxidized by (A) hypochlorite (HOCl), (B) hypobromite (HOBr), (C) bromate (BrO₃⁻), (D) periodate (IO₄⁻), and (E) other oxyhalide anions (ClO₃⁻, ClO₄⁻, and IO₃⁻) under aqueous (20 °C) and frozen (-20 °C) solutions. Experimental conditions: pH_i = 4, [Cr₂O₃]₀ = 0.2 g/L, and [oxyhalide]₀ = 0, 5, and 10 μM (for A–D) or 10 mM (for E) in dark conditions.

formation in aqueous and frozen solutions in the presence of oxyhalide species: hypochlorous acid (HOCl), chlorate (ClO₃⁻), perchlorate (ClO₄⁻), hypobromous acid (HOBr), bromate (BrO₃⁻), iodate (IO₃⁻), and periodate (IO₄⁻). Four types of oxyhalide species (HOCl, HOBr, BrO₃⁻, and IO₄⁻) were capable of oxidizing Cr(III) into Cr(VI). On the other hand, the other oxyhalide species (ClO₃⁻, ClO₄⁻, and IO₃⁻) were not active at all for the oxidation of Cr(III) even with 10⁻³-fold higher concentration (10 mM) in both aqueous and ice phases (see Figure 1e). This is consistent with the fact that these oxyhalide species (ClO₃⁻, ClO₄⁻, and IO₃⁻) have less oxidizing power than the others and do not have enough driving force to oxidize Cr(III) to Cr(VI) (see Table 1).

In aqueous conditions, IO₄⁻ was the most active in producing Cr(VI) (Figure 1). The order of Cr(VI) production by oxyhalide species was IO₄⁻ > HOBr > HOCl > BrO₃⁻ in the aqueous phase. However, in frozen solution, the amount of Cr(VI) produced by oxyhalide species was in a totally different order (BrO₃⁻ > HOCl > HOBr and IO₄⁻). BrO₃⁻ and HOCl induced much enhanced formation of Cr(VI) in frozen than in aqueous solution, while HOBr and IO₄⁻ suppressed the production of Cr(VI) in frozen solution compared with that in aqueous solution. In particular, it should be noted that the presence of BrO₃⁻ does not induce Cr(VI) formation at all in the aqueous phase but dramatically enhanced it in ice. Such a freezing-induced enhancement of BrO₃⁻ reaction was also observed for its reductive transformation,⁴³ which has been ascribed to the freeze-concentration effect.

In the previous studies,^{16,44} the oxidation of Cr(III) species accompanied the transformation of the oxidants into the reduced form with a specific stoichiometric ratio (e.g., Cl⁻ and Br⁻ from HOCl and HOBr). Table 2 compares the halogen species produced from the oxidation of Cr₂O₃ and Cr(OH)₃ in aqueous and frozen solution. In all cases, the total halogen mass balance was well-matched. In HOCl and HOBr cases, the product was Cl⁻ and Br⁻, respectively (eqs T3 and T6) while oxidizing Cr₂O₃ to Cr(VI). The balanced redox reactions for Cr(III)/HOCl and Cr(III)/HOBr systems (eqs 1 and 2) (≡ Cr³⁺(s) indicates the surface Cr(III) species on Cr₂O₃ and Cr(OH)₃) show the stoichiometric product ratio of [X⁻]/[Cr(VI)] = 1.5, which is close to the experimentally observed ratio (see Table 2). The ratio ([X⁻]/[Cr(VI)]) was 1.6 and 1.4

Table 1. Reduction Potentials^{64–67}

reduction equation		$E^0(V_{\text{NHE}})^a$	$E(V_{\text{NHE}})^b$	$E(V_{\text{NHE}})^c$
$\text{HCrO}_4^- + 7\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{Cr}^{3+} + 4\text{H}_2\text{O}$	(eq. T1)	1.35 ⁶⁴	0.80	0.88
$2\text{HCrO}_4^- + 8\text{H}^+ + 6\text{e}^- \rightleftharpoons 2\text{Cr}_2\text{O}_3 + 5\text{H}_2\text{O}$	(eq. T2)	1.41 ^{64,65}	0.98	1.04
[Chlorine]				
$\text{HOCl} + \text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Cl}^- + \text{H}_2\text{O}$	(eq. T3)	1.48 ⁶⁴	1.36	1.38
$\text{ClO}_3^- + 3\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{HClO}_2 + \text{H}_2\text{O}$	(eq. T4)	1.21 ⁶⁴	0.85	0.91
$\text{ClO}_4^- + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{ClO}_3^- + \text{H}_2\text{O}$	(eq. T5)	1.19 ⁶⁴	0.95	0.99
[Bromine]				
$\text{HOBr} + \text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Br}^- + \text{H}_2\text{O}$	(eq. T6)	1.33 ⁶⁴	1.21	1.23
$\text{BrO}_3^- + 5\text{H}^+ + 4\text{e}^- \rightleftharpoons \text{HOBr} + 2\text{H}_2\text{O}$	(eq. T7)	1.45 ⁶⁶	1.15	1.20
$\text{BrO}_3^- + 6\text{H}^+ + 6\text{e}^- \rightleftharpoons \text{Br}^- + 3\text{H}_2\text{O}$	(eq. T8)	1.42 ⁶⁶	1.18	1.22
[Iodine]				
$\text{IO}_3^- + 5\text{H}^+ + 4\text{e}^- \rightleftharpoons \text{HOI} + 2\text{H}_2\text{O}$	(eq. T9)	1.13 ⁶⁴	0.83	0.88
$\text{IO}_4^- + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{IO}_3^- + \text{H}_2\text{O}$	(eq. T10)	1.59 ⁶⁷	1.35	1.39
$\text{H}_4\text{IO}_6^- + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{IO}_3^- + 3\text{H}_2\text{O}$	(eq. T11)	1.60 ⁶⁴	1.36	1.40

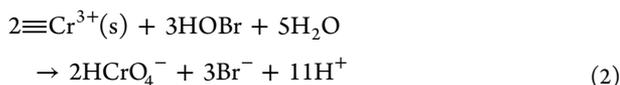
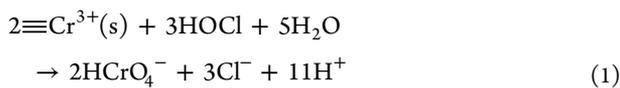
^aStandard reduction potentials. ^bReduction potentials corresponding to actual experimental conditions at 25 °C: pH = 4.0, [Cr species] = 1 μM, and [oxyhalide, halide] = 10 μM. ^cReduction potentials corresponding to actual experimental conditions at -20 °C.

Table 2. Concentrations (μM) of Cr(VI) and Other Halogen Species Produced from the Oxidation of Cr_2O_3 and $\text{Cr}(\text{OH})_3$ in the Aqueous and Ice Phase with Different Oxyhalides as an Oxidant^a

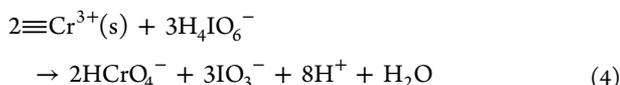
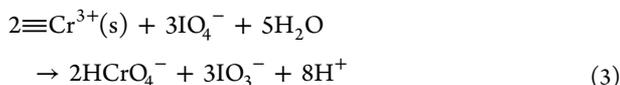
		oxidant	[Cr(VI)]	[X ⁻] ^b	[XO ⁻] ^b	[XO ₃ ⁻] ^b	[XO ₄ ⁻] ^b	[X total] ^b
Cr_2O_3	aq	HOCl	0.5 ± 0.0	0.8 ± 0.2	8.9 ± 0.5			9.7 ± 0.6
		HOBr	1.2 ± 0.2	1.9 ± 0.4	7.6 ± 0.3			9.5 ± 0.6
		BrO_3^-	0.0	0.0	0.0	9.9 ± 0.6		9.9 ± 0.6
		IO_4^-	5.1 ± 0.0			8.0 ± 0.2	1.8 ± 0.1	9.8 ± 0.1
	ice	HOCl	1.7 ± 0.2	2.4 ± 0.0	7.5 ± 0.3			9.9 ± 0.3
		HOBr	0.7 ± 0.2	1.2 ± 0.0	9.0 ± 0.5			10.2 ± 0.5
		BrO_3^-	2.5 ± 0.4	1.1 ± 0.1	0.3 ± 0.2	8.7 ± 0.2		10.0 ± 0.2
		IO_4^-	1.0 ± 0.1			1.7 ± 0.2	8.2 ± 0.8	9.8 ± 0.6
$\text{Cr}(\text{OH})_3$	aq	HOCl	0.9 ± 0.8	1.3 ± 0.2	8.7 ± 1.1			10.0 ± 0.9
		HOBr	1.5 ± 1.3	2.1 ± 0.6	7.7 ± 2.2			9.8 ± 1.6
		BrO_3^-	0.0	0.0	0.0	9.9 ± 0.5		9.9 ± 0.5
		IO_4^-	5.8 ± 1.4			8.1 ± 1.7	1.6 ± 0.4	9.7 ± 1.2
	ice	HOCl	1.5 ± 0.5	2.1 ± 0.3	7.6 ± 0.6			9.7 ± 0.9
		HOBr	0.2 ± 0.2	0.3 ± 0.3	9.4 ± 2.2			9.7 ± 1.9
		BrO_3^-	1.5 ± 0.9	0.5 ± 0.1	0.3 ± 0.1	9.2 ± 0.2		10.0 ± 0.2
		IO_4^-	2.1 ± 1.4			3.1 ± 0.5	7.8 ± 2.9	10.9 ± 3.4

^aExperimental conditions: $[\text{Cr}_2\text{O}_3, \text{Cr}(\text{OH})_3] = 0.2 \text{ g/L}$, $[\text{oxidant}]_0 = 10 \mu\text{M}$, $\text{pH}_i = 4$, reaction time of 24 h, and in aqueous (20 °C) and ice (-20 °C) conditions. ^bX = Cl (for HOCl), Br (for HOBr and BrO_3^-), and I (for IO_4^-).

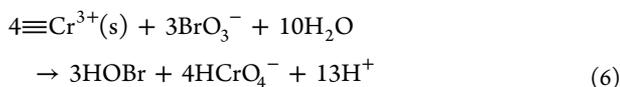
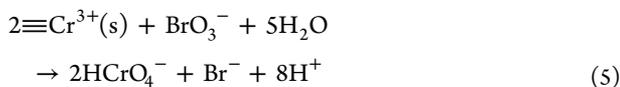
for $[\text{Cl}^-]/[\text{Cr}(\text{VI})]$ and 1.6 and 1.7 for $[\text{Br}^-]/[\text{Cr}(\text{VI})]$ in aqueous and frozen solution, respectively, which should match the stoichiometric ratio within the experimental errors resulting from the adsorbed amount of X⁻ and Cr(VI) on $\text{Cr}_2\text{O}_3/\text{Cr}(\text{OH})_3$.



When IO_4^- was used as an oxidant, IO_3^- was the only product. As IO_3^- cannot oxidize Cr_2O_3 at all (see Figure 1e), the in situ generated IO_3^- cannot be further reduced to iodide. The ratio of $[\text{IO}_3^-]/[\text{Cr}(\text{VI})]$ was 1.6 and 1.7 for aqueous and frozen conditions, respectively. This is close to the stoichiometry of the balanced reaction of IO_4^- and chromium oxide (eqs 3 and 4).



For the BrO_3^- case, Br^- and HOBr were formed from the reduction of BrO_3^- only in frozen solution, whereas there was no reaction in aqueous solution. The balanced redox reactions between chromium oxide and bromate (eqs 5 and 6) indicated the stoichiometry of $[\text{Cr}(\text{VI})] = 2[\text{Br}^-] + 4/3[\text{HOBr}]$, which is consistent with what was observed (see Table 2).



The above described oxyhalide-specific dissolution of Cr_2O_3 that was observed at $\text{pH}_i = 4$ (Figure 1) was consistently observed at other pH conditions (Figure 2). The Cr(VI) production was higher in frozen than aqueous solution for

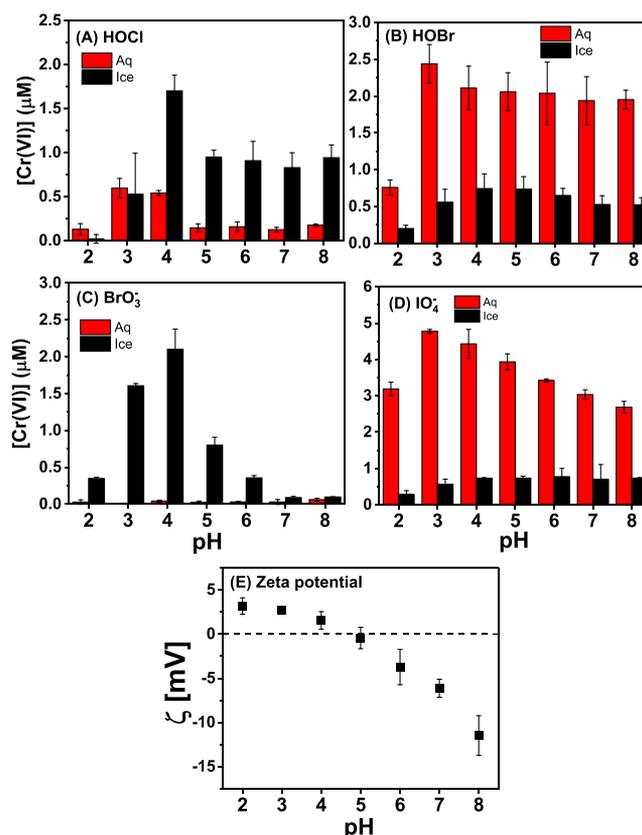


Figure 2. pH-dependent Cr(VI) production from the oxidative dissolution of chromium oxide (Cr_2O_3) in frozen (-20 °C) and aqueous (20 °C) solutions in the presence of oxyhalide species; (A) HOCl, (B) HOBr, (C) BrO_3^- , and (D) IO_4^- . (E) pH-dependent zeta potential of Cr_2O_3 . Experimental conditions: $[\text{Cr}_2\text{O}_3]_0 = 0.2 \text{ g/L}$, $[\text{oxyhalide}]_0 = 10 \mu\text{M}$, and dark reaction for 24 h.

HOCl and BrO_3^- , while it was the opposite for HOBr and IO_4^- in the tested pH range of 2–8. The pH dependence of Cr_2O_3 oxidation is more clearly observed for BrO_3^- and IO_4^- than for HOCl and HOBr. This might be related with the pH-dependent surface charge of Cr_2O_3 ($\text{pH}_{\text{zpc}} \sim 5$) (see Figure 2E) as the adsorption of an oxidant on the Cr_2O_3 surface is necessary for the oxidative dissolution reaction.⁴⁵ Since the surface charge becomes gradually more negative with increasing pH, more anions (e.g., BrO_3^- and IO_4^-) are electrostatically repelled from the surface of Cr_2O_3 at higher pH. This subsequently should retard the Cr_2O_3 oxidation reaction as pH increases, which is consistent with the case of BrO_3^- and IO_4^- . HOCl and HOBr exhibit weaker pH dependence since they are neutral molecules. On the other hand, the production of Cr(VI) was significantly suppressed at pH 2 regardless of the kind of oxyhalide species probably because all the oxyhalide-induced oxidation reactions of Cr_2O_3 (eqs 1–6) are not thermochemically favored at acidic conditions. The optimal oxyhalide-induced oxidative dissolution of Cr_2O_3 should be balanced between the acidic condition favored for the adsorption of oxyhalide anions and the alkaline condition favored for the higher thermodynamic driving force.

These oxyhalide-specific and medium-specific reactions of Cr(VI) production imply that the freeze-concentration effect of oxyhalide should be different depending on the kind of oxyhalide. When a solution freezes, solutes are expelled from the ice crystals and concentrated in the liquid-like ice grain boundary region where water could remain as a liquid far below the freezing point (down to 250 K).⁴⁶ This accelerates the chemical reactions of various organic and inorganic compounds.^{19–24} However, it has been found out that some solutes are not preferentially concentrated in the ice grain boundary,^{41,42} and they do not induce freezing-accelerated reactions. HOBr and IO_4^- seem to be such a case. The different freezing effects of oxyhalide species on the oxidative dissolution of chromium oxide might be related with the species-specific distribution of oxyhalide species between the ice grain boundary and bulk ice crystal. To investigate this, the distribution of oxyhalide between the ice surface and ice bulk was estimated as described in the method section and in the previous studies.^{41,42} Although the method was rough and may induce large errors, the different tendencies of the solute distribution upon freezing could be clearly differentiated among the tested oxyhalide species (HOCl, HOBr, BrO_3^- , and IO_4^-). Note that the ice samples were prepared under the same experimental condition, and the ice formation process should be the same for all the tested oxyhalides. Table 3 shows the percentage of oxyhalide anions in the ice surface region and the ratio of the Cr(VI) production between the frozen and

Table 3. The Proportion of Oxyhalide Species in the Ice Surface Region and the Ratio of Produced [Cr(VI)] from Cr_2O_3 Oxidation between Ice and Aqueous Phases

oxidants (Ox)	[Ox(ice surf)]/[Ox(tot)] (%)	[Cr(VI)] _{ice} /[Cr(VI)] _{Aq} ^{a,b}
HOCl	66.8 (±2.0)	6.1
HOBr	42.6 (±7.1)	0.7
BrO_3^-	87.6 (±4.6)	51.2
IO_4^-	32.1 (±3.4)	0.2

^aExperimental conditions: $[\text{Cr}_2\text{O}_3] = 0.2 \text{ g/L}$, $[\text{oxidant}]_0 = 10 \mu\text{M}$, $\text{pH} = 4$, reaction time of 2 h, and in aqueous (20 °C) and ice (−20 °C) conditions. ^bData from Figure 1.

aqueous solutions. The proportions of the oxidants in the ice surface region were in the order of $\text{BrO}_3^- > \text{HOCl} > \text{HOBr} > \text{IO}_4^-$, which is in the same order of the ratio of produced [Cr(VI)] from Cr_2O_3 oxidation between ice and aqueous phases, $[\text{Cr(VI)}]_{\text{ice}}/[\text{Cr(VI)}]_{\text{Aq}}$ (taken from Figure 1). It is noted that HOBr and IO_4^- , which suppressed the production of Cr(VI) in ice (i.e., $[\text{Cr(VI)}]_{\text{ice}}/[\text{Cr(VI)}]_{\text{Aq}} < 1.0$), are markedly less concentrated in the ice surface region than HOCl and BrO_3^- . When HOBr and IO_4^- are not much available (not freeze-concentrated) in the ice grain boundary, the oxidative dissolution of Cr_2O_3 by the oxyhalide species within the ice grain boundary region can be retarded. Such species-specific freeze-concentration behaviors of various organic and inorganic species were observed and discussed in our previous studies^{41,42} although the reason for such behaviors remains to be further investigated.

The different distributions of oxyhalide species in frozen solution were also observed in situ using a confocal Raman microscope. Figure 3 shows the Raman spectra and chemical

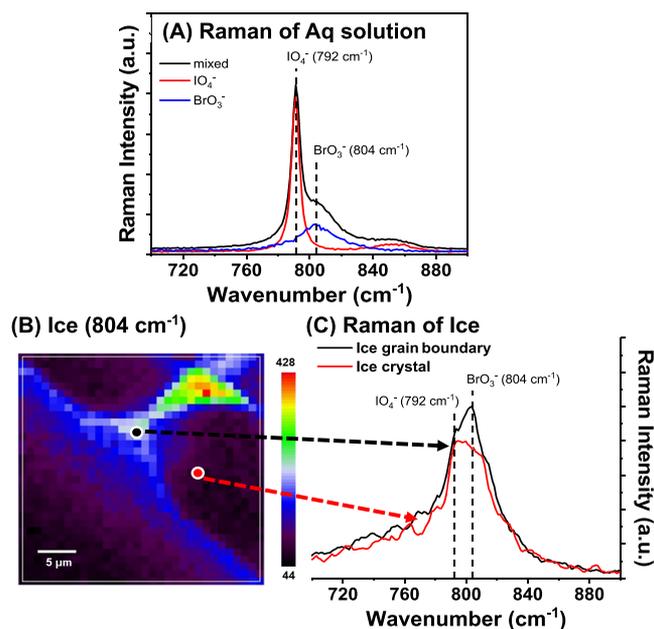


Figure 3. (A) Raman spectra of IO_4^- (0.5 M), BrO_3^- (1.0 M), and mixed solutions. (B) Mapping of Raman signals at 804 cm^{-1} and (C) Raman spectra of the frozen solution with IO_4^- (0.5 M) and BrO_3^- (1.0 M) that were obtained from the ice grain boundary (black circle spot in (B)) and ice crystal bulk (red circle spot in (B)). The sample solution was frozen at 253.2 K (−20 °C).

mapping image of aqueous and frozen solution with BrO_3^- and IO_4^- . In aqueous solution, the specific peaks appeared at 792 cm^{-1} for IO_4^- and 804 cm^{-1} for BrO_3^- , which matches the literature values.^{47,48} Since the peaks were adjacent to each other, the aqueous solution containing both oxyhalide anions exhibited two peaks partially overlapped. The mapping of a BrO_3^- (804 cm^{-1}) peak clearly shows that the oxyhalide anions are localized in the ice grain boundary region (see Figure 3b). In aqueous conditions, the peak of IO_4^- (792 cm^{-1}) was much higher than the BrO_3^- (804 cm^{-1}) peak because of the higher Raman sensitivity of IO_4^- (see Figure 3a). However, when the solution was frozen, the IO_4^- peak in the ice grain boundary region became lower than the BrO_3^- peak (see Figure 3c). This is consistent with the observation

that the concentration of IO_4^- in the ice grain boundary region is significantly lower than that of BrO_3^- (Table 3). Additionally, the relative peak intensities in the ice bulk crystal region are reversed from those in the ice grain boundary. This clearly indicates that BrO_3^- anions relatively favor the ice grain boundary, whereas IO_4^- anions favor the ice bulk region.

Oxidation of $\text{Cr}(\text{OH})_3(\text{s})$ and $\text{Cr}^{3+}(\text{aq})$ by Oxyhalide.

The oxyhalide-induced oxidation of other Cr(III) species was also investigated. Chromium hydroxide ($\text{Cr}(\text{OH})_3$) and Cr^{3+} ions were tested and compared with Cr_2O_3 for the oxidative transformation to Cr(VI) (Figure 4). Since $\text{Cr}(\text{OH})_3$ is a more

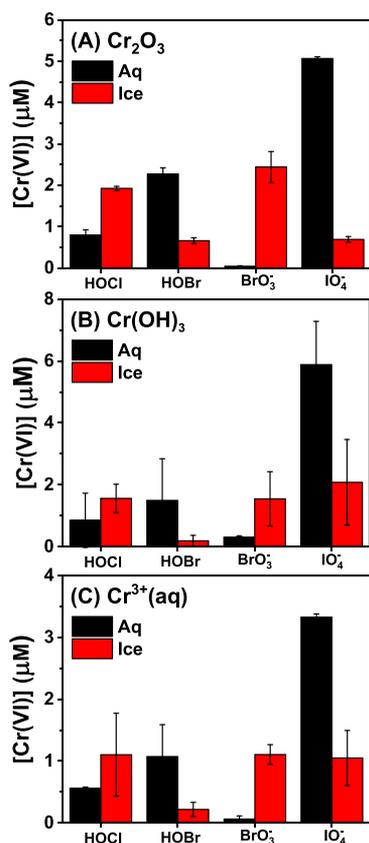


Figure 4. Cr(VI) production from (A) $\text{Cr}_2\text{O}_3(\text{s})$, (B) $\text{Cr}(\text{OH})_3(\text{s})$, and (C) $\text{Cr}^{3+}(\text{aq})$ oxidation by oxyhalide in aqueous (20 °C) and frozen (−20 °C) solution. Experimental conditions: $\text{pH}_i = 4$, (A,B) $[\text{Cr}_2\text{O}_3]$ and $[\text{Cr}(\text{OH})_3]_0 = 0.2 \text{ g/L}$, (C) $[\text{Cr}(\text{III})]_0 = 1 \text{ mM}$, $[\text{oxyhalide}]_0 = 10 \text{ } \mu\text{M}$, and dark reaction for 24 h.

common form of Cr(III) than Cr_2O_3 in nature,⁴⁹ the reaction of oxyhalide with $\text{Cr}(\text{OH})_3$ should be more environmentally relevant. The oxyhalide can oxidize $\text{Cr}(\text{OH})_3(\text{s})$ and $\text{Cr}^{3+}(\text{aq})$ as well, and the Cr(VI) production by oxyhalide exhibits similar behaviors among $\text{Cr}_2\text{O}_3(\text{s})$, $\text{Cr}(\text{OH})_3(\text{s})$, and $\text{Cr}^{3+}(\text{aq})$. As in the case of Cr_2O_3 , the production of Cr(VI) from $\text{Cr}(\text{OH})_3(\text{s})$ and $\text{Cr}^{3+}(\text{aq})$ in frozen solution was enhanced when HOCl and BrO_3^- were oxidants but was suppressed in the presence of HOBr and IO_4^- compared with that in aqueous solution. The stoichiometry of $\text{Cr}(\text{OH})_3$ oxidation by oxyhalide species was similar with that of Cr_2O_3 oxidation, and the ratio between the produced halogen species and Cr(VI) were almost the same (see Table 2).

Effect of Dissolved Oxygen and Dissolved Organic Matter (DOM). The effect of dissolved oxygen on the oxidation of Cr(III) in Cr_2O_3 by oxyhalide species was

investigated. The solutions with different oxyhalide species and Cr_2O_3 were purged with argon (Ar), air, or dioxygen (O_2) gas in aqueous solution or presaturated with each gas prior to freezing. Figure 5 compares the amount of Cr(VI) production

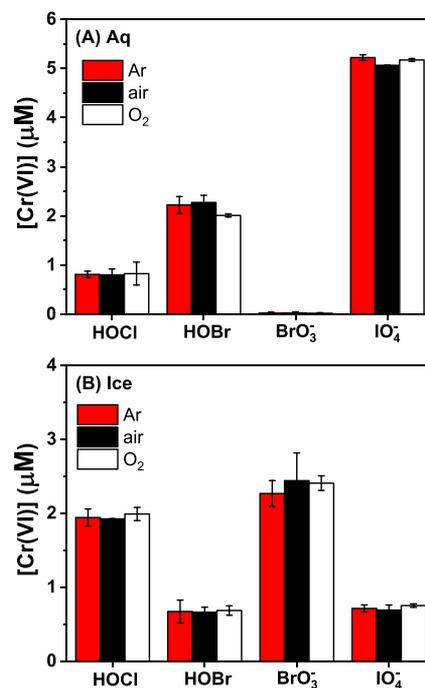


Figure 5. Effects of dissolved gas (Ar, air, and O_2) on the oxidative dissolution of Cr(VI) from chrome oxide in (A) aqueous (20 °C) and (B) frozen (−20 °C) solution. A prepurged solution was frozen. Experimental conditions: $[\text{Cr}_2\text{O}_3]_0 = 0.2 \text{ g/L}$, $[\text{oxyhalide}]_0 = 10 \text{ } \mu\text{M}$, and dark reaction for 24 h.

from Cr_2O_3 dissolution in different gas-saturated conditions. Unlike the previous study of the photoreductive dissolution of iron oxides,³⁰ oxidative dissolution of Cr_2O_3 was not affected at all by the presence of dissolved O_2 for each oxyhalide species in both aqueous and frozen solutions. This confirms that the main oxidant of Cr_2O_3 is the oxyhalide species, not the dissolved O_2 . It is also contrasted with the case of iodide photooxidation in the frozen solution where the dissolved O_2 in the ice grain boundary serves as a main oxidant with markedly accelerating the iodide oxidation.²⁷

Dissolved organic matter (DOM) is ubiquitous in nature and has major roles in geochemical processes. DOM working as an electron donor may hinder the oxyhalide-induced oxidation of chromium oxide. Figure 6 shows the time profiles of Cr(VI) production by BrO_3^- and IO_4^- in frozen and aqueous solutions in the presence of fulvic acid (Suwannee river) as DOM. The presence of DOM indeed suppressed Cr_2O_3 oxidation by oxyhalide anions in both aqueous and frozen solutions. With BrO_3^- in the frozen solution, the Cr(VI) production in 24 h was reduced by 59.6 and 80.5% with 1 and 3 ppm of DOM, respectively, while the formation of Cr(VI) was negligible in aqueous solution. As for IO_4^- , the inhibition by DOM was 37.9 and 54.7% with 1 and 3 ppm of DOM in aqueous solution, 71.5 and 85.1% in frozen solution, respectively. The prohibition effect was higher in frozen than aqueous conditions because DOM should be concentrated in the ice grain boundary under frozen conditions. DOM can be oxidized by oxyhalide anions and concurrently transform them

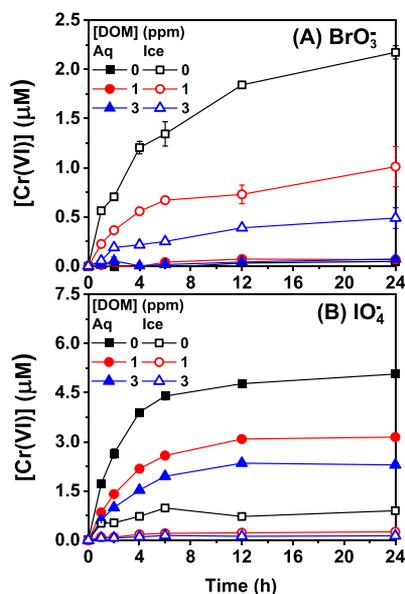


Figure 6. Time profiles of [Cr(VI)] dissolved from Cr_2O_3 that was oxidized by (A) bromate (BrO_3^-) and (B) periodate (IO_4^-) in the presence of dissolved organic matter (DOM) in frozen ($-20\text{ }^\circ\text{C}$) and aqueous ($20\text{ }^\circ\text{C}$) solution. Experimental conditions: $\text{pH}_i = 4$, $[\text{Cr}_2\text{O}_3]_0 = 0.2\text{ g/L}$, $[\text{oxyhalide}]_0 = 10\text{ }\mu\text{M}$, $[\text{fulvic acid}]_0 = 0, 1,$ and 3 ppm in dark conditions.

(e.g., to halide ions).^{43,50} Therefore, the oxyhalide anions would be consumed by DOM instead of Cr_2O_3 , which should prevent the formation of Cr(VI). On the other hand, the produced Cr(VI) might be reduced back to Cr(III) in the presence of highly concentrated DOM in the ice grain boundary. The fact that the DOM-induced prohibition effect was not proportional to DOM concentration (1 ppm vs. 3 ppm) implies that the oxidation and reduction of Cr species are in equilibrium in the ice grain boundary region in the presence of DOM.

Environmental Implications. Chromium-contaminated media such as acid mine drainage,^{51,52} contaminated soils,^{53–55} aerosols in industrial area,^{56–59} and industrial wastes⁶⁰ are found in acidic conditions. Furthermore, most of the natural samples contain significantly high percentage of the trivalent form (Cr(III)) (75–100%) than the hexavalent form (Cr(VI)) because of thermodynamic stability of Cr(III) in acidic conditions.¹⁷ Therefore, the Cr(III) oxidation behavior in acidic conditions needs to be studied to understand the generation of toxic Cr(VI) species. This study selected and tested various oxyhalide species as an oxidant of Cr(III) species such as $\text{Cr}_2\text{O}_3(\text{s})$, $\text{Cr}(\text{OH})_3(\text{s})$, and $\text{Cr}^{3+}(\text{aq})$ and found that the oxidative dissolution behaviors are very different between the aqueous and frozen solutions. Diverse oxyhalide species can be generated as byproducts from chemical disinfection processes. When those disinfection byproducts are discharged into the environment, they might induce the formation of toxic Cr(VI) from the oxidative dissolution of chromium oxide/hydroxide. The most prominent finding in this study is that the oxyhalide-induced oxidation of chromium oxide/hydroxide in frozen solution shows a different trend from that of the aqueous reaction. In particular, bromate induces the significant enhancement of Cr(VI) production in frozen solution, whereas it has a negligible activity in aqueous solution. Bromate is a common disinfection byproduct from the ozonation of water containing

bromide ions. It has been reported that ozone-treated water could have bromate over 100 ppb.^{61,62} As bromate is kinetically stable and recalcitrant,^{13,63} it persists for a long time in the environment. Therefore, if BrO_3^- is discharged to frozen environments, it may provide an unexpected source of Cr(VI) production by reacting with Cr(III)-containing minerals. The unusual reactions caused by the freeze-concentration effect in frozen environments could have significant impacts on the environment.

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Notes

The authors declare no competing financial interest.

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