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Discussions

Interactive comment on "Accelerated dissolution of iron oxides in ice" *by* D. Jeong et al.

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We would like to thank N. Takenaka for the careful consideration of our manuscript, and welcome the opportunity to respond to the comments and integrate the suggestions into the revised manuscript.

Freezing is ubiquitous phenomenon in the world and the effect of freezing aqueous solution on the environment is hardly understood. In this sense, this article is a very important study, and the results are very interesting. There are some comments described below.

Major comments; Comment) The dissolution of iron is equilibrium phenomenon. What is the equilibrium concentration of Fe(3+)? In ice, the authors mentioned that the pH

decreased. This means that the equilibrium is established at lower pH in ice. When the sample is thawed, the equilibrium moves to the original pH. If this is true, the results could depend on the time from thawing the sample to the measurements. Please state the view point of equilibrium in the text.

Response) This is what we have not thought about. Interesting comment. However, the re-precipitation of dissolved Fe3+ ions is very slow at the acidic condition and the time-dependency of the measurement may not be important. Anyway, we carried out an additional control experiment and the following sentence was added.

(p. 20117) "To check out the possibility that some dissolved iron may re-precipitate before the analysis, the samples were also kept in dark for 24 h before measurement. The analysis result was not different from that obtained right after thawing."

Minor comments; Comment 1) Unit: the SI unit is favorite to use. For example, l should be cmËĘ3. In this case, oC can be used because freezing aqueous solution can be easily understood by using Celsius.

Response) cmËĘ3 may be more formal but l is also an acceptable and common notation.

Comment 2) 2.2 Experimental procedure: the temperatures are wrong. "10 oC, -20 oC, and 30 oC " and "70 oC " and "196 oC" are "-10 oC, -20 oC, and -30 oC " and "-70 oC " and "-196 oC"

Response) Corrections have been made.

Comment 3) In Figure 2, the authors compare the reaction rate. However, the initial condition is g/ L. It is difficult to compare. The reaction rates depend on M but not g/L. Furthermore, the authors discuss about the surface area. If the authors want to discuss the surface area, show the dependence of surface area by using all data or one material with different surface areas.

Response) To our knowledge, the concentrations of solid materials in dissolution studies are usually expressed as the mass-based concentration, not molar concentration. Of course, it should be better to compare the dissolution rates of a single type of iron oxide with different surface areas. We will carry out dissolution experiments by controlling the surface area of a single type of iron oxide in future studies. Instead, to show the effect of surface area on the dissolution, the dissolution rates (in Table 2) in the absence of organic ligands are also shown with the values normalized by the BET SA. And the following parts were rewritten to address this issue. (p. 20119) “For the dissolution rates in the absence of organic ligands, the values normalized by the surface area are also compared (numbers in the parentheses). It is noted that the surface area-normalized dissolution rates much less vary among the different iron oxides than the apparent dissolution rates do: the apparent dissolution rate of goethite and hematite in ice is 187 vs 3.9 while its surface area-normalized counterpart is 5.3 vs 2.4. Therefore, the key parameter that determines the dissolution rate of iron oxides in ice should be the surface area, not the crystallinity.”

Comment 4) Figure 4 is difficult to understand. The order of the concentrations are very different. For acetic acid, the authors investigated at mM level but for DFOB, it was μM level. In the case of DFOB, the production of Fe(tot) may decrease in mM level. These are not good example to discuss. Furthermore, if we consider the reaction kinetics, the reaction rates must increase at higher concentration. Please discuss in the text.

Response) Since the solubilities of DFOB and acetic acid are greatly different, their concentration levels cannot be the same. The solubility of DFOB in water is limited (< 9 mM) and we could not test extremely high concentrations. The concentrations of DFOB (50 μM) and other organic acids (6 mM) used in the study were determined based on the past studies (Borer et al., 2005; Pehkonen et al., 1993; Siefert et al., 1994). What we tried here is to show that the dissolution of iron oxides can differ depending on the concentration and type of organic matters.

Comment 5) At low pH(around 2), Fe(2+) becomes more stable than Fe(3+) and is dissolve in water. This does not relate to the results?

Response) As shown in Figure 3, the production of Fe2+ ions was insignificant in the present experimental condition.

Comment 6) Page 20120, lines 7 - ; The thickness of the liquid-like layer in the ice decrease with decreasing temperature. Yes, this is true, but the amounts of substances are the same and the concentration increases. The reaction rate depends on the concentration and temperature. So, it is not enough to discuss with only the thickness of the liquid-like layer in the ice.

Response) We did not discuss only in terms of the liquid-like layer thickness. We also discussed the effect of freezing rate that depends on temperature. The following sentences were added to discuss this point.

(p. 20120) “Overall, lowering freezing temperature influences the dissolution of iron oxides in ice in a complex way. It may enhance the freeze concentration effect by reducing the liquid content in the grain boundaries whereas it may cause an opposite effect by retarding the migration of the solutes during the freezing process. Judging from the result of Figure 5, the latter effect seems to prevail.”

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 20113, 2012.