

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

D. Jeong et al.

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Received and published: 31 October 2012

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

Comment 1) Although the BET SAs for the iron oxide samples are quoted, there seems to be no indication of particle size or size dispersion which presumably is the key controlling factor for consideration of the dissolution rates/trends reported. The SAs are quoted with surprising precision i.e. single values, which would suggest monodisperse samples – this surely is not the case? To my knowledge, the commercial products stated usually come with a range of quoted values (and/or mean particle size) which reflect the inherent size dispersion. Page 5, line 24 states particles are ‘nanosized’, but

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can the authors define this further as 100s of nm or 10s of nm or a dispersion of both dimensions? Presumably it is the latter as deposition of particles was observed (page 4, line 24). Would it not be better to report dissolution rates (microM per hour) from Figure 2 normalised to the respective BET SA? In these terms, goethite has the lowest rate and magnetite the highest. How representative are the particle sizes/SAs used to 'real' iron-containing dust/soil samples?

Response) Whether the iron oxides used in the study represent 'real' iron-containing dust/soil samples is an important issue as the reviewer commented. It is difficult to determine a clear representativeness of the samples since the particle sizes/SAs of environmental iron oxides greatly vary (Schwertmann and Taylor, 1989). Of course, the commercial samples have variations in the size as well. The SA values represent the averages of many different particles and they do not mean the monodisperse samples. The properties of various iron oxide samples are summarized in Table 1, which is now added in the revised version. The dissolution rates (in Table 2) in the absence of organic ligands are also shown with the values normalized by the BET SA. The following parts were rewritten to address the above comment. (p. 20116) "The analyzed properties of iron oxide samples were summarized in Table 1. The iron oxides used in the study may represent the environmental samples well in terms of the particle size (< 100 nm) and surface area. The crystal size of soil iron oxides ranges from a few to several hundred nm and the surface area can be as small as < 1 m²g⁻¹ for massive crystals and as large as 100 m²g⁻¹ for fine crystals (Cornell, 1996)." (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."

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Comment 2) In the abstract (lines 9-10) and summary (page 10, lines 15-16), the authors state that there is a compositional/structural effect for the reported dissolution trends. I see no definitive evidence for this in the paper and, following from my first point, suggest the dissolution trends for experiments without organic binding to be predominantly a consequence of the varying particle sizes within samples of the different oxides. The trend of the oxide with the highest SA (i.e. contains the larger particles) having the highest dissolution rate, the one with the lowest SA, the lowest rate and those for which similar SAs are quoted have similar dissolution rates (bottom of page 6 / top of page 7) seems to indicate that, at best, the form of oxide plays only a relatively minor role in the dissolution behavior compared to particle size.

Response) We agree with the reviewer's opinion. The following parts were rewritten to reflect this point.

(abstract) "The extent of dissolved iron was greatly affected by the kind of organic complexing ligands and the surface area of iron oxides." (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."

(p. 20122) "The dissolution of iron oxides greatly increased when they were trapped in ice and the ice-enhanced effect depended on the kind of organic ligand, pH, and the type and surface area of iron oxides."

Comment 3) In both aqueous and frozen phases, another factor to be taken into consideration is that the particle dissolution rate is affected by the presence of surface defects (i.e. pits, cracks etc – see Jeschke and Dreybrodt, 2002; Geochim. Cosmochim.

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Acta, 66, 3055-), in which water can freeze and ions concentrate? These are likely to be more prevalent in the larger particles within samples. The role of such an 'inhomogeneous' dissolution process (even more important for 'real' dust particles which will have greater surface roughness than synthesised, commercial samples) would be more realistic than an idealised homogeneous dissolution at smooth outer surfaces as seemingly implicitly assumed by the authors. Maybe, any planned future studies could include TEM/SEM particle imaging of 'before and after' samples to answer this point.

Response) We agree with the reviewer that 'inhomogeneous' dissolution from iron oxide particles can better represent the real environmental process in terms of surface roughness and structural defects of the particles. To stress this point, the following sentences were added.

(p. 20123) "The dissolution process may be initiated inhomogeneously at the surface defect sites, which should be characterized at the molecular level. Careful control studies are required to understand the effect of each factor involved in the dissolution process and to verify the laboratory results for their implications in natural environmental conditions."

Comment 4) I think the previous points indicate the importance of studies on monodisperse samples if possible in future which would prevent any such uncertainties on the role of particle size dispersion. Is it not possible to grind/filter the initial samples accurately enough to produce monodisperse samples or at least reduce the likely size dispersion of sample prior to dissolution? Maybe the authors could try to produce their own samples in future as sol-gel synthesis of monodisperse iron oxide nanoparticles is well described in the literature (e.g. Matijevic, 1993; Chem. Mater., 5, 412-)

Response) We appreciate your suggestion. We will try to use synthesized monodisperse iron oxide particles in the future studies.

Comment 5) I'm sure spelling errors will be sorted out in the review process but I would highlight the inconsistent spelling of 'organic' i.e. page 7, line 6 and line 9

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Response) The spelling errors have been corrected.

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

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12, C8839–C8843, 2012

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