

Interactive comment on “Iron dissolution kinetics of mineral dust at low pH during simulated atmospheric processing” by Z. Shi et al.

Z. Shi et al.

z.shi@leeds.ac.uk

Received and published: 2 January 2011

General response:

We have addressed all the specific comments as shown below. We have also expanded our discussion somewhat by discussing our data in the context of those published in Machie et al. (2005) as well as in Cwiertny et al. (2008) and Fu et al. (2010) in section 3.6.

Comment 1: p. 26610, l.16: It might be appropriate to cite Journet et al. (2008) between the sentences, although it is noted in p.26617. It might be also noted that recent modelling study has shown the sensitivities of Fe depositions to the dust Fe mineralogy (Ito and Feng, 2010), although it is cited in l. 17. These studies may

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



support the necessity of the kinetically-controlled dissolution rate of Fe in dust.

Response: We agree with the reviewer and have added two sentences at the end of the mentioned paragraph. They are: "Journet et al. (2008) also showed that different types of Fe-containing minerals exhibit distinct reactivities in term of Fe dissolution. A more recent modelling study suggested that the predicted Fe solubility is sensitive to the chemical specification of Fe-containing minerals (i.e., hematite or illite) in dust (Ito and Feng, 2010)."

Comment 2: p. 26611: The pH-dependence of iron dissolution rate has been shown in previous studies. Although the references are listed in p.26625, it would be helpful for the reader if you summarize how earlier studies related the variables to iron dissolution rate in introduction. This may help to explain how the data obtained in this study are useful for the modeling studies.

Response: These references have been included in the introduction. We modified the last few sentences in paragraph 5 to: "On the other hand, factors affecting Fe dissolution in dust or soils for 12 h to a few days have been investigated. For example, Machie et al. (2005) reported Fe dissolution in Australian dust from pH 2.15 to pH 7.1 and found that Fe is significantly mobilized below a threshold of pH $\sim$ 3.6; Cwiertny et al. (2008) showed that soil samples of different origins have significantly different Fe dissolution behaviour at low pHs and the Fe solubility measured after 24 h does not scale with either the specific surface area or the total Fe content of the samples; Fu et al. (2010) demonstrated that pH, photo-radiation, temperature and types of acids all affect Fe dissolution in soil dust samples. However, a fundamental understanding of the kinetics of Fe dissolution in real dust samples has not been developed yet. Such studies need to be carried out under experimental conditions relevant to and as representative as possible of atmospheric processes. "

Comment 3: p. 26611, l.11: Please define a dust/liquid ratio. Response: We have now defined this term

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



Comment 4: p. 26613, l.18: Please explain why there was no dissolution data of Tibesti at pH 3.

Response: The purpose of the data of Beijing dust sample at pH 3 was to show that at higher pH, Fe dissolution is slower. We believe that the data are adequate for this purpose and therefore we chose not to conduct additional experiments on the Tibesti samples which we expect would show the same results and which take more than one month.

Comment 5: p. 26613, l.21: Please explain why there was no dissolution data at various dust/liquid ratios over 24 hours.

Response: Our results here show that the dust/liquid ratio is an important variable in this system. For this purpose 24 h Fe dissolution is adequate. It is planned to conduct such experiments in the future to examine this variable in much more detail.

Comment 6: Fig.7: How did you estimate the total Fe concentrations for various dust/solution ratios?

Response: The total mass of Fe for 60mg L⁻¹ is calculated as $60 \times 3.5 / 100 = 2.1$ mg = 37.5 μ mol in which 3.5% is the FeT in the Beijing dust. Total Fe concentration would be 37.5 μ mol L⁻¹. Its log value is 4.4. We have added (μ mol L⁻¹) after total Fe concentrations to make it easier to understand.

Comment 7: p. 26624, l.1: Fe dissolution calculated from rate constants used in Meskhidze et al. depends on pH, so the figure should be separated into two (i.e., pH 1 and pH 2). Please show all variables (i.e., K, T, a(H⁺), f(G), and W) in the calculation of the Fe dissolution using rate constants in Meskhidze et al., which may correspond to some portions of the slow Fe pool. Presumably, you used the rate constant for the first 0-0.8% of the total Fe in the dust, but it should depend on the total amount of the Fe dissolved. The modelling studies also assume an extractable Fe pool, which may correspond to FeA. What if the three-stage kinetic process is considered for specification

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



of the dissolution constant (Meskhidze et al., 2005), using FeA as the initial condition for the soluble iron fraction?

Also, what if the dissolution rate of illite is used for the dissolution (Ito and Feng, 2010), using FeA as the initial condition for the soluble iron fraction?

Response: We agree with the reviewer that data from pH 1 and pH 2 should not be in the same figure. In the original figure, we calculated Fe dissolution based on pH 2 parameters from Meskhidze et al. (2005). To response to this comment, we now removed the data of Tibesti-PM20 at pH 2 and only showed data and calculations at pH 1 for convenience of comparison (since Fan et al. (2006) assumed the dissolution rate under the conditions of $\text{pH} < 2$). Since the purpose of this figure is simply to compare the predicted with actually measured data, we did not add another figure at pH 2. We have also added the equations and all the parameters used to calculate Fe dissolution for Meskhidze et al. (2005) and Fan et al. (2006) parameterization in the figure caption now. Using the parameters from Meskhidze et al. (2005), less than 0.8% of Fe would be dissolved in 72 hours and therefore for this figure, only the first stage dissolution rate was used.

We cannot directly apply our three-stage kinetic model parameters to the existing equation in Meskhidze et al. (2005) because these authors' equation would need dissolution rate in unit of mole dissolved/ m^2 of mineral/s (zero-order). Similarly, in Ito and Feng (2010), a zero-order dissolution rate is assumed for illite with a unit of mole dissolved/ m^2 of mineral/s. The reviewer raised two important issues which require new modelling works with small modifications of the parameterization (for example switching from zero-order to first-order dissolution kinetics of illite). We expect to see such works in the near future.

Comment 8: p. 26624, l.10: If you mean the effect of the solution saturation state on dissolution rates (p. 26621), the model uses a function of Gibbs free energy change of a particular mineral dissolution reaction. However, it is unlikely to reach true thermody-

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



dynamic equilibrium in the atmosphere, as you mentioned in p. 26611. Could you specify which effect was not considered in the model?

Response: Meskhidze et al. (2005) did not mention whether they assigned $f(\Delta Gr)$ to be 1. However, since the dissolution of iron-containing minerals was assumed to be very slow, and the system consistently remained far from reaching equilibrium under the experimental conditions (see Ito and Feng (2010)), it is expected that Meskhidze et al. (2005) did not consider the backward reaction (so $f(\Delta Gr)$ was assigned to be 1)). If this is true, then the solution saturation effect is still not considered in their model.

To address the reviewer's comments, the sentence has now been changed to: "...solution saturation effect at high dust/liquid ratio in real dust aerosols on the Fe dissolution was not considered in the present models."

Comment 9: p. 26624, l.13: Is this true in ambient atmospheric conditions? Is k independent of temperature, type of acids, and so on?

Response: The reviewer is right that ambient atmospheric conditions vary a lot. The rate of dissolution k is likely to be dependent on temperature, light, and type of acids etc. Therefore, to make our description more accurate, we have now modified this sentence to: "... k at low pHs can be calculated using equations (2)-(4) at similar conditions simulated in this study (e.g., temperature, type of acid, no-irradiation)."

Technical corrections

Comment 1: Correct 300 g/L to 1000 mg/L.

Response: We do not know where this comment specifically came from. We checked the places with 300g/L and we found that it should be 300 g/L, which may occur in actual aerosol conditions. 1000 mg/L is the dust/liquid ratio used in this study.

Comment 2: p. 26609, l.3: Boyd and Ellwood, 2010.

Response: We have now changed Boyd et al. 2010 to Boyd and Ellwood, 2010.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



Comment 3: p. 26614, l.11: at room temperature “(298 K)”.

Response: We now have changed this to “at room temperature (~ 298 K)”

Comment 4: p. 26615, l.7: Add "Lazaro et al., 2008" to the references.

Response: We have now added this paper to the reference list.

Comment 5: p. 26616, l.11 - p. 26617, l.14: Most of these may be moved to Appendix.

Response: We agree that this part could be removed to Appendix. However, since this section is relatively short, we tend to think it is not necessary to create an Appendix.

Comment 6: p. 26618, l.2: Show the unit for rate constant.

Response: The unit now has been added.

Comment 6: p. 26619, l.26: The “equilibrium” Fe concentration may need to be rephrased, because the result for the Beijing dust does not represent the thermodynamic “equilibrium” condition.

Response: We agree and now have re-phrased the sentence: “representing here the Fe concentration at equilibrium for the Beijing dust suspension at 60 mg L⁻¹, with the equilibrium Fe solubilities of a series of Fe oxides over a range of pH values (Fig. 7).”

Comment 7: p. 26622, l.22: the fact “that”.

Response: We have now changed “than” to “that”.

Comment 8: Fig.4: What is the red circle?

Response: It is a unidentified error in the original Origin figure. We have now changed the color.

Comment 9: Fig.6: Show the unit for rate constant.

Response: We have now added the unit.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



Interactive
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper