

Interactive comment on “Atmospheric Processing of Iron in Mineral and Combustion Aerosols: Development of an Intermediate-Complexity Mechanism Suitable for Earth System Models” by Rachel A. Scanza et al.

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Referee comments are in black and the authors responses are in red. When text from the manuscript is quoted, new text is in bold face.

Referee 2: Interactive comment on “Atmospheric Processing of Iron in Mineral and Combustion Aerosols: Development of an Intermediate-Complexity Mechanism Suitable for Earth System Models” by Rachel A. Scanza et al.

This paper, develop an iron dissolution scheme of intermediate complexity that can

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be used in Earth system models. The overall presentation of the article is clearly structured, and the description of tests and calculations is also complete. However, there are some problems you should clearly explain and corrected before this paper is accepted.

We thank the referee for the careful evaluation and helpful comments to improve the quality of the manuscript. We revise the text to clarify and address the referee's comments.

Page 3, line 18, you said, "We simulate four types of iron (readily-released Fe, medium soluble Fe, slow soluble Fe and combustion Fe)". But on page 5, line 24, you have said "Three types of dust Fe are simulated in the model: readily-released iron (FeRR), medium-soluble iron (Femed) and slow-soluble or refractory iron (Feslow)". There are some confusions, please explain clearly. We account for three types of iron from dust and one type from combustion. We modify the text on page 3, line 17-18: "We simulate four types of iron, three for mineral dust (readily-released Fe, medium soluble Fe and slow-soluble Fe) and one for combustion aerosols (combustion Fe). "

2. Page 6, line 13, it is recommended that "FeRR, Femed and Feslow" should be enclosed in parentheses.

We modify the text on page 6: "...three types of iron in dust (FeRR, Femed, and Feslow)."

3. In equation (1), R should be constant. However there is no explanation in the following text, please explain clearly. In Eq. (1), R is a function of temperature. $R_{Fe} = K(T) \times a(H)^m \times f(\hat{\Delta}GG) \times A \times MW$ where,

$K(T)$ is a function of temperature and has units of (mol m⁻² s⁻¹)

We add the following text on page 6: "where R_{Fe_i} is a function of temperature and has units (s⁻¹), i represents either medium or slow soluble Fe, $K_i(T)$ in units of (moles m⁻² s⁻¹) is the temperature dependent rate coefficient (Table 8, Meskhidze et al., 2005),

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$a(\text{H}^+)$ is the proton concentration with an empirical reaction order m_i , $f(\hat{\Delta}G_r)$ accounts for the change in the dissolution rate with variation from equilibrium (and equals 1 for simplicity (Luo et al., 2008)), A_i is the specific surface area of mineral i in units of $\text{m}^2 \text{g}^{-1}$ and MW_i is the molecular weight in units of g mol^{-1} for mineral i .”

4. In equation (1), please explain how to calculate R .

$R = K(T) \times a(\text{H}^+)^{m_i} \times f(\hat{\Delta}G_r) \times A_i \times MW_i$ For example, $K(T)$ utilizes Tables 8 in Meskizze et al., 2005 for illite and hematite (stage II) (Ito and Xu, 2014), $a(\text{H}^+)^{m_i}$ is the pH, $f(\hat{\Delta}G_r)$ is set to 1 following Luo et al., 2008, A_i is the specific surface area of illite (Femed), hematite (Feslow) and MW_i is simply the molecular weight of either illite or hematite, depending on which dissolution rate you are calculating.

5. In equation (2), please explain the significance of each physical quantity.

In Eq. (2), $[\text{C}_2\text{O}_4^{2-}]$ is the concentration of oxalate in each atmospheric gridbox. $[\text{OC}]$ and $[\text{SOA}]$ are the organic carbon and secondary organic aerosol concentrations (mass mixing ratio) in each gridbox, and these species are included in the release version of CESM. The denominator is the maximum of the sum of global averaged mass mixing ratios for OC & SOA, to ensure that the highest possible oxalate concentration is $15 \mu\text{mols L}^{-1}$, this factor was chosen to best match observations of fractional iron solubility and the spatial distribution of oxalate from Myriokefalitakis et al., 2011. We've added the following text on page 7, lines 10-13: “In choosing our reference case, multiple simulations were conducted to best match observations of fractional iron solubility and the surface distribution of oxalate (Figure 2a,c, Myriokefalitakis et al., 2011); the factor of 15 in Eq. (2) yielded the best results.”

6. Page 7, line 15, you said “There tends to be more oxalate in the model simulations in tropical regions (Figure 2 from Myriokefalitakis et al., 2011) which is better captured in our model simulations using the OC+SOA versus the sulfate proxy for modeled oxalate concentrations. Have you verified it? Please explain this.

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Visually comparing Figure 2 in this study with Figure 2 (a) and (c) in Myriokefalitakis et al., it should be clear that the spatial distribution of oxalate using the OC+SOA (a) vs the sulfate (b) proxy is a better match to Myriokefalitakis et al., 2011.

7. Page 11, line 28, you have said “While the oxalate mechanism derived from the sulfate proxy (SS2) have marginally stronger correlations compared to the reference casem the difference between these is not statistically significant”. Please explain the statistical relevance and variability mentioned.

We remove this sentence as the correlation coefficients for all cases are poor.

8. Page 13, line 6, you said, “Again, however, the fractiona; iron solubility is inversely related to total and soluble iron deposition, a result consistent with theory and observations”. Please explain in detail the theories and observations mentioned in the text.

Many studies assume that OPP requires bioavailable iron and report increased iron liberation from ferric oxides with decreasing pH acidic species (Duce and Tindale, 1991;Zhu et al., 1997;Zhuang et al., 1992;Jickells and Spokes, 2001;Desboeufs et al., 2001;Meskhidze et al., 2003). (Chen and Siefert, 2004) and (Baker and Jickells, 2006) find decreasing fractional iron solubility with mineral dust concentrations for different atmospheric environments, concluding that solubility is partially a function of particle size (Baker and Croot, 2010). Smaller particles have longer atmospheric lifetimes and thus higher probabilities of undergoing chemical reduction. Additionally, combustion aerosols whose fractional iron solubility is higher are generally small particles Particle size has been implicated in the bioavailable iron problem with many studies finding that smaller particles with a larger surface area to volume ratio have increased dissolution (Baker and Jickells, 2006). This observation could result because smaller particles dominate long-range transport as larger particles are preferentially removed due to gravity. For example, (Hand et al., 2004) finds that soluble iron is several times greater in the fine dust mode than the coarse mode without including a surface area effect. More recently however, iron solubility increasing with decreasing particle size

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has been disputed (Shi et al., 2012; Buck et al., 2010), indicating that particle size can only partially account for the differences in solubility. The implication that particle size enhances solubility does not take into account that the mineralogy of the dust distribution changes during transport, with clay enrichment due to the larger particles sizes of quartz and feldspar (Glaccum and Prospero, 1980). The mineralogy of dust is important with different minerals contributing different forms of iron (i.e. iron oxides, nanoparticle coating, aluminosilicate substitutions) (Journet et al., 2008; Ito and Xu, 2014; Meskhidze et al., 2005). Observations from Sholkovitz et al., 2012 show a trend of increasing iron solubility with decreasing total iron concentration and conclude that much of this is due to the smaller particle size distribution of combustion aerosols and their ability to enhance dust iron dissolution. Mahowald et al, in press, show using a simple 1-d plume model, that either differential solubility in emissions of combustion aerosols, or atmospheric processing of dust iron can match the observed relationship described above. At emission, combustion aerosols are typically smaller and thus remain suspended in the atmosphere longer than the larger dust aerosols. In addition, since combustion aerosols appear to have higher Fe solubility, the plume will increase in solubility as it is transported downwind from continental sources. Alternatively, if only dust aerosols are considered to be sources of iron, but are atmospherically processed downwind from source regions, one will see lower values of iron in the aerosols, as particles fall out yet the remaining iron will be more soluble (longer atmospheric processing). Quantitative comparison of this simple plume model indicates that either of these two cases can match observations (Mahowald et al., in press).

We include the following text on page 2: “Observations from Sholkovitz et al., 2012 show a trend of increasing iron solubility with decreasing total iron concentration and conclude that much of this is due to the smaller particle size distribution of combustion aerosols and their ability to enhance dust iron dissolution. Mahowald et al, in press, show using a simple 1-d plume model, that either differential solubility in emissions of combustion aerosols, or atmospheric processing of dust iron can match the observed relationship described above. At emission, combustion aerosols are typically smaller

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