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Supplement of

Delivery of anthropogenic bioavailable iron from mineral dust and combustion aerosols to the ocean

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This supplementary document contains detailed descriptions of the methodologies for iron (Fe) dissolution scheme.

1 Recent global modeling studies of oxalate-promoted Fe dissolution from dust aerosols

Increased attention has been given to the organic acids for promoting Fe dissolution from mineral dust aerosols in global models (Luo and Gao, 2010; Johnson and Meskhidze, 2013; Myriokefalitakis et al., 2015). Luo and Gao (2010) prescribed pH and oxalate/hematite ratio dependent dissolution rates of hematite for mineral dust based on laboratory experiments by Xu and Gao (2008). They also prescribed the molar ratio of oxalate to sulfate (2%) to estimate the oxalate concentration in mineral dust, based on observations ranging from 0.46% to 5% (Yu et al. 2005). Note that the observed oxalate refers to the sum of oxalic acid and oxalate in aerosol particles, since ion chromatography allows quantification of oxalate independent of its chemical form (here referred to oxalate unless specified). Furthermore, laboratory measurements suggested that different oxalate species in solution (i.e., $HC_2O_4^-$ and $C_2O_4^{2-}$) formed similar surface complexes (Yoon et al., 2004), increasing the activities of oxalate (hydrogen oxalate + oxalate) in solution at high oxalate concentration did not cause any significant increase in the surface concentration of oxalate, and hence on dissolution rate (Cama and Ganor, 2006). Johnson and Meskhidze (2013) used a linear relationship between oxalate-promoted dissolution rate and oxalate concentration in solution, based on the initial Fe release rates of Fe oxides and aluminosilicates at pH = 4.7 in one hour under cloud water conditions (Paris et al., 2011). Myriokefalitakis et al. (2015) applied the same equation to model-calculated oxalate concentration ($[C_2O_4^{2-}]$) in cloud water only (Johnson and Meskhidze, 2013; Paris et al., 2011).

2 Materials and methodology in laboratory experiments

The dust sample collected from a dry riverbed draining the Tibesti Mountains (South Libya; N25°35′ E16°31′; hereafter termed Tibesti) was first dry-sieved to <63 μm and then wet-sieved to <20 μm (Tibesti-PM_{20}) with ~50 mL of Milli-Q water (18.2 MΩ). The sample suspensions were freeze dried and later were gently disaggregated before further experimentation. This procedure has been shown to have little impact on the Fe speciation and dissolution behavior at acidic pH (Shi et al., 2011). All experiments were performed at room temperature (~298 K) under constant stirring (~50 rpm) and in dark conditions (wrapped in aluminium foil).

3 Effects of inorganic anions on Fe dissolution

Fig. S1 demonstrated that Fe solubility in solutions with 0.1 mol L^{-1} H^+ (as HCl) and 3 mol L^{-1} NH_4Cl (red triangles) is higher than that in sulfuric acid solution at a dust/liquid ratio of 1 g L^{-1} (blue squares). This is consistent with higher H^+ activity in 3 mol L^{-1} NH_4Cl solution (larger than 1 and so the predicted pH is 0.9). However, the measured Fe solubility in HCl is lower than that measured at a dust/liquid ratio of 60 mg L^{-1} ($[H^+]$ = 0.1 mol L^{-1}) in sulfuric acid solution only (black circles). Thus the dissolution of Fe minerals is suppressed at higher dust/liquid ratio (1 g L^{-1}), likely due to weak complex of Cl^- with Fe^{3+} (Meskhidze et al., 2005; Hsu et al., 2007). This is consistent with previous laboratory measurements (Hamer et al., 2003; Shi et al., 2011).

4 Comparison of Fe dissolution for illite

When dissolution rates are normalized to Brunauer, Emmett and Teller (BET) specific surface areas of minerals, the dissolution rates of chlorite are more than an order of magnitude higher than those for smectite and illite (Zysset and Schindler, 1996; Bauer and Berger, 1998; Brandt et al., 2003; Köhler et al., 2003; Amram and Ganor, 2005; Lowson et al., 2005; Golubev et al., 2006; Rozalén et al., 2008). However, the BET surface area does not represent the reactive surface area of nano-sized Fe oxides and phyllosilicate minerals (Brandt et al., 2003; Rozalén et al., 2008; Lanzl et al., 2012). A weak correlation ($R = 0.27$) between the total dissolved Fe and BET surface area was also found for the Fe dissolution experiment of combustion aerosols (Chen and Grassian, 2013). The similarity in the dissolution rates normalized to mass of the aluminosilicates suggests that similar clay structures dissolve by similar mechanisms (see Fig. 10 in Rozalén et al., 2008). To examine whether our Fe dissolution scheme can reproduce the Fe release rates measured for illite (Shi et al., 2011), a comparison of the Fe solubility for illite at pH = 2 under dark conditions due to proton-promoted Fe dissolution is shown in Fig. S2. The comparison exercise reveals that both the calculations using the Fe release rate for mineral dust in this work (red squares) and that for illite in Ito and Xu (2014) (blue squares) reproduce the Fe solubility change with time on the timescale of aerosol lifetime. In Ito and Xu (2014), illite dissolution rate at stage III was calculated using potassium (K) release rate between 144 and 840 hours of reaction time (Nagy, 1995). Because of the high initial release rate of K at pH = 2 before reaching a steady state, the Fe dissolution from illite used in Ito and Xu (2014) is significantly faster than that from structural Fe under steady state conditions (Journet et al., 2008; Bibi et al., 2011).

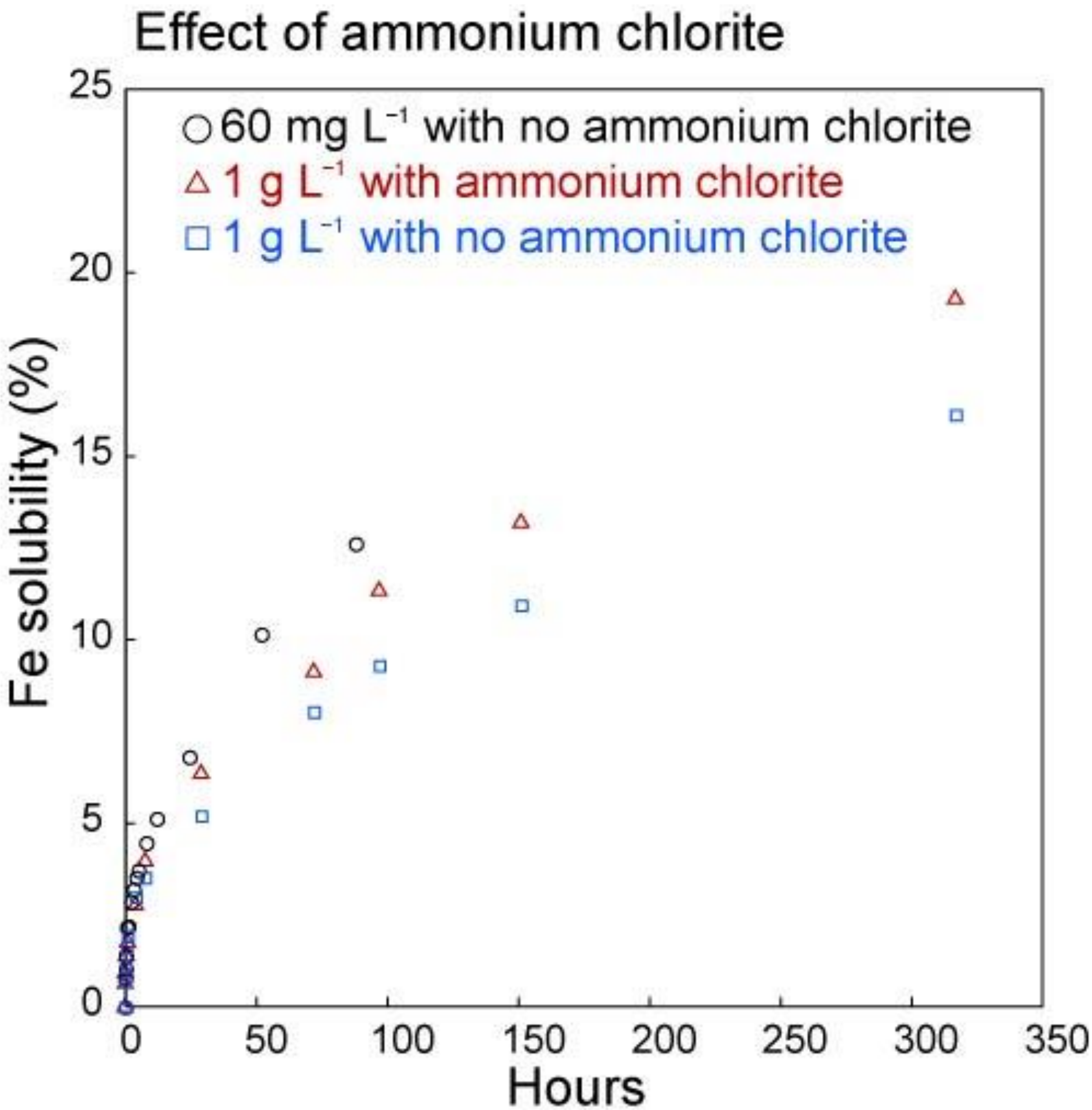

Fig. S1 Comparison of Fe solubility in solution (%) measured at a dust/liquid ratio of 1 g L^{-1} in 0.05 mol L^{-1} sulfuric acid solution (blue squares, pH =1.3, I = 0.15 mol L^{-1}), in 0.1 mol L^{-1} HCl solution with 3 mol L^{-1} NH_4Cl (red triangles, pH = 0.9, I = 3.2 mol L^{-1}), and at a dust/liquid ratio of 60 mg L^{-1} in 0.05 mol L^{-1} sulfuric acid solution (black circles, pH = 1) (Shi et al., 2011).

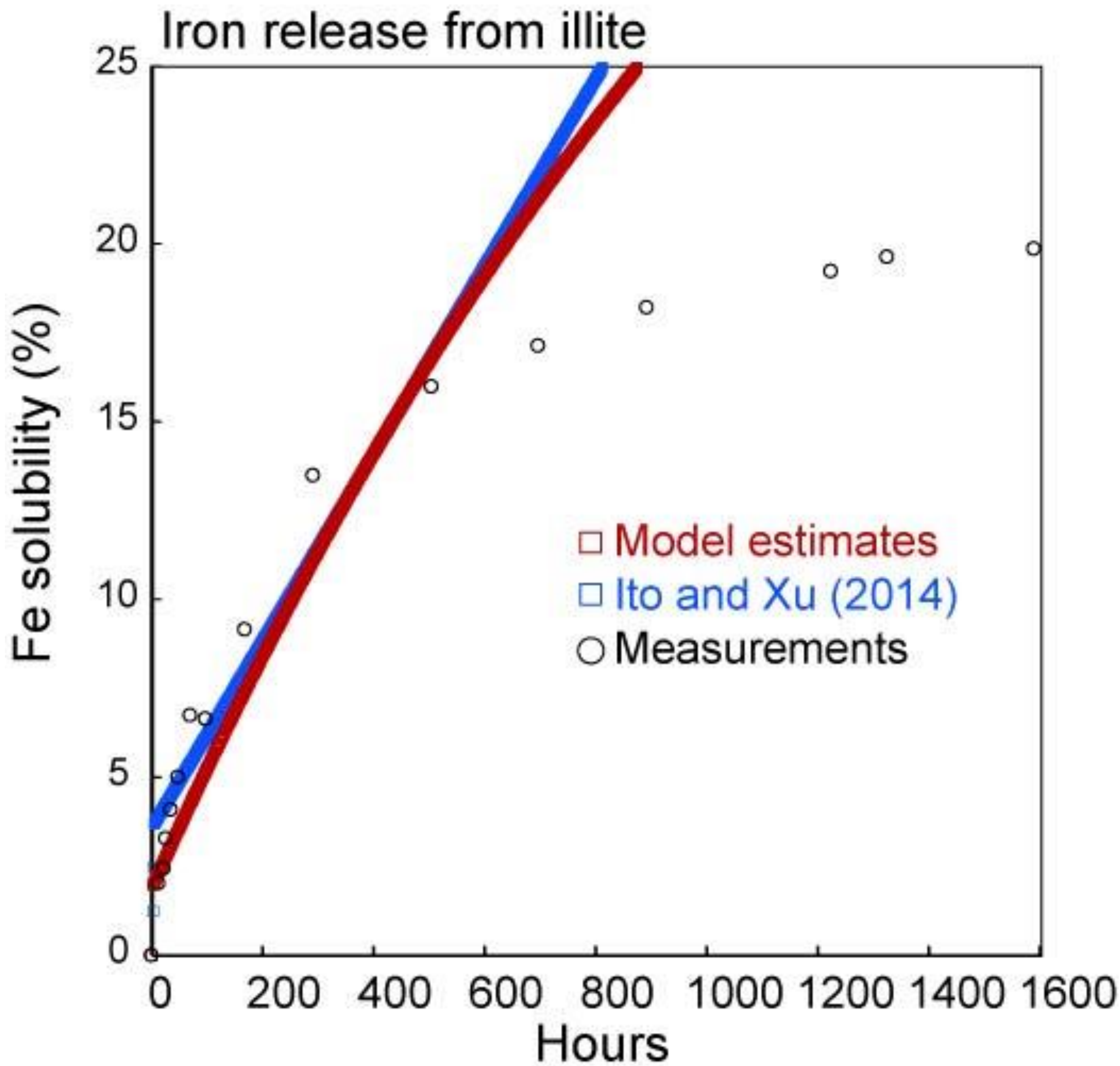

Fig. S2 Comparison of Fe solubility in solution (%) predicted using equation (1) with the measured Fe dissolution rates of illite at pH = 2. The red squares are calculated using equation (1) from rate constants for Fe-containing mineral dust used in this study at each hour. The blue squares are calculated using equation (1) from rate constants for illite used in Ito and Xu (2014). The black circles are the measured data for illite (Shi et al., 2011). The fraction of total dissolved Fe present as Fe(III) is prescribed at pH = 2 (0.2) in this calculation to emulate the experimental conditions, while the photochemical redox cycling between Fe(III) and Fe(II) in solution is explicitly simulated in our global model (Lin et al., 2014). The large fraction of Fe(II) in solution under the dark conditions is likely associated with the preferential Fe(II) release (Bibi et al., 2011).

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