

Iron solubility and isotope fractionation of industrial particles during simulated cloud processing

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1. Context and objectives

Iron (Fe) plays an important role in many environmental processes including ocean biogeochemistry and thereby the global carbon cycle. Specifically, Fe is an essential micronutrient for marine phytoplankton, and low dissolved Fe concentrations in seawater limit primary production in >30% of the surface ocean. Iron sources to these so-called High Nutrient Low Chlorophyll (HNLC) regions include inputs from atmospheric deposition, continental margin sediments and hydrothermal vents (Conway & John, 2014).

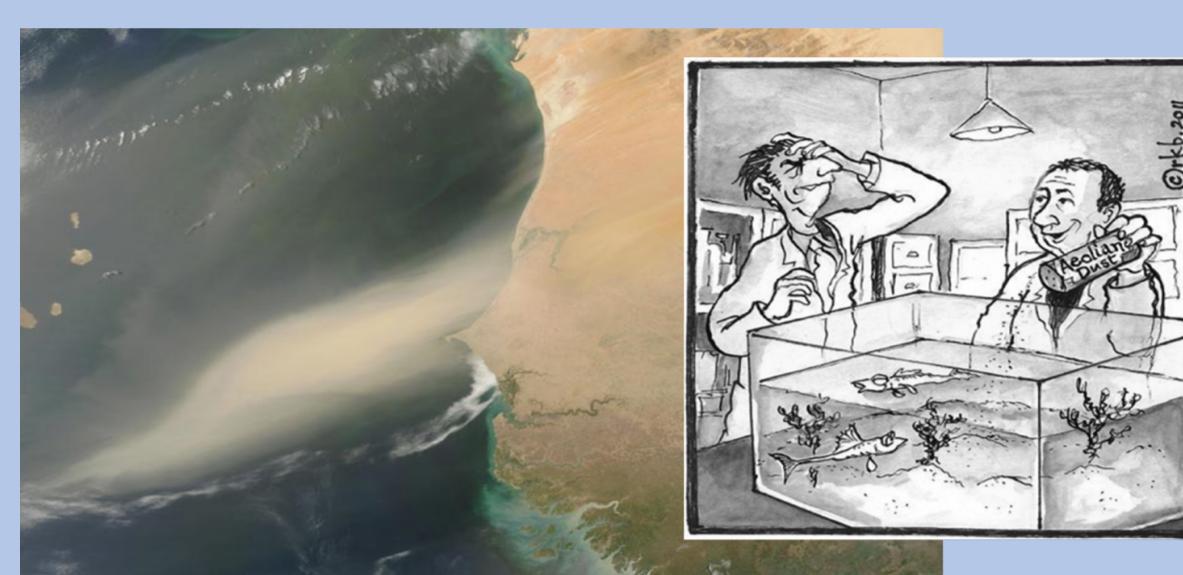


Figure 1. Sahel dust over the mid Atlantic Ocean (NASA, 2003)

While mineral dust is often regarded as the primary source of atmospheric Fe to the ocean (Fig.1), anthropogenic particles typically display much higher Fe solubility by up to an order of magnitude compared to that of dust (<1 wt.%) (Takahashi et al., 2013).

For Ito and Shi (2016) anthropogenic atmospheric Fe contribute to ≈ 50% of the soluble Fe supply to the oceans, in the Northern Hemisphere. However, large uncertainties remain in the deposition fluxes and fractional Fe solubilities of these natural and anthropogenic particles (Mahowald et al., 2009).

Iron isotopes have emerged as powerful tool for tracing natural and anthropogenic Fe sources in the environment (Majestic et al., 2009), due to analytical advances which have now made it possible to measure small differences in its stable isotopes (^{54}Fe , ^{56}Fe , ^{57}Fe , ^{58}Fe). However, airborne particles are subjected to various physicochemical processes (e.g., acidification, photochemistry) before fallout and while such 'atmospheric processing' is recognized to enhance Fe solubility (Nickovic et al., 2013), its effect on the Fe isotopic signature of the particles remains unknown.

The present study investigates changes in iron solubility and isotopic composition of industrial ash (one of the main component of Fe-rich anthropogenic aerosols), collected from a Fe – Mn alloy company, during simulated atmospheric processing using leaching solutions that mimics cloud water chemistry aiming to: (i) evaluate the kinetic and equilibrium mechanisms involved in Fe short and long-term dissolution and (ii) understand the effect of dissolution on the isotopic composition of the remaining soluble Fe phase.

3. Results

Iron kinetic dissolution of the industrial ash particles presented different rates when comparing solutions with different pH values and ash concentrations as shown in Figure 3. Faster dissolution rates and higher Fe solubility were achieved in more acidic solutions (i.e., pH=2) with higher ash concentrations.

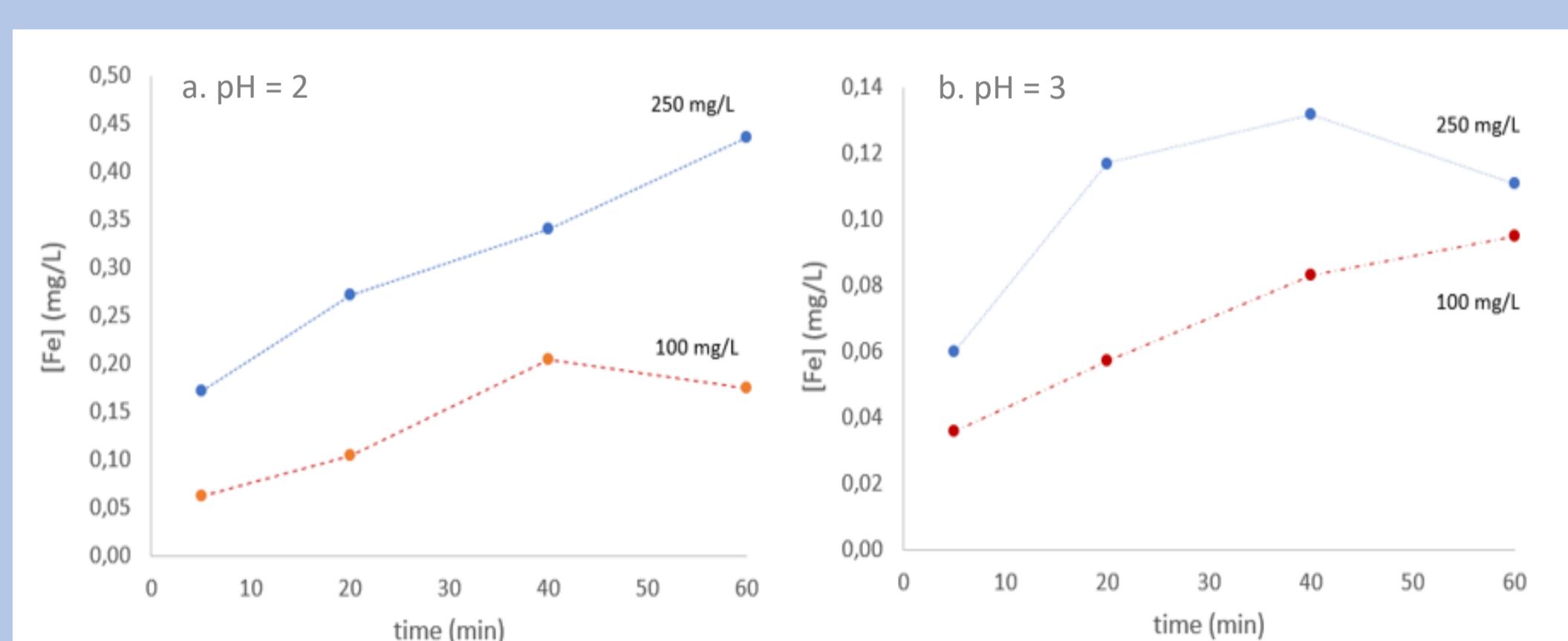


Figure 3. Iron dissolution kinetic during cloud processing experiments using synthetic cloud water solutions adjusted to pH 2 (a.) and 3 (b.). The experiments were conducted under solar irradiation at ~25 °C with different ash concentrations.

According to Figure 4a, the dissolution process can be divided in two stages based in the soluble Fe isotopic composition, as also proposed by Wiederhold et al. (2006). In the early-stage dissolution (until 60 min), the preferential dissolution of light Fe isotopes occurs with a minimum $\delta^{56}\text{Fe}$ value of -0.45‰ at 5 minutes of dissolution time. As the dissolution contact time increase, Fe isotope composition becomes heavier toward the values of the bulk industrial ash (i.e., -0.12‰). At the late-stage dissolution (after 60 min), soluble Fe isotopic composition becomes heavier than the bulk industrial ash.

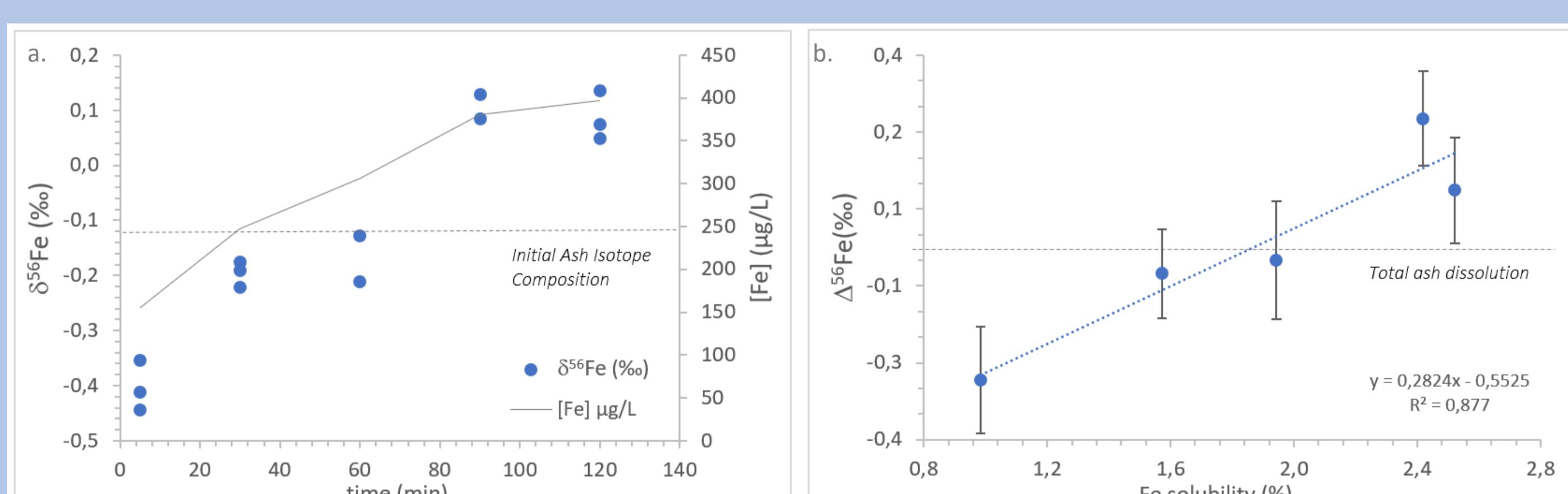


Figure 4. (a) Soluble Fe concentration and isotopic composition during the dissolution of the industrial ash. (b) Relationship between Fe isotope fractionation and Fe solubility.

The Fe-O bonds containing the lighter isotopes will be preferentially broken during the early-stage of the kinetic controlled isotope fractionation since they are energetically weaker when compared with the stiffer Fe-O bonds containing the heavier isotopes. As the dissolution contact time increases, the ash particle surface becomes more depleted in light Fe isotopes, leading to a gradual increase in the dissolution of heavier Fe isotopes. Once the late-stage dissolution is achieved, heavy Fe isotopes will be preferentially released due to the lack of light isotopes on the particle surface causing the enrichment of the solution with isotopically heavier Fe.

Figure 4b shows that the magnitude of Fe isotopic fractionation increases toward lower Fe solubility. Therefore, the dissolution of well crystallized and refractory Fe-bearing minerals might produce greater isotope fractionation in the early-stage dissolution due to their lower solubility rate.

2. Materials and Methods

The industrial ash used in the present study consisted of a mixture of metallic, aluminosilicate and aluminosilicate-metallic particles (irrespective of their sizes), containing approximately 76-89% of Mn oxides and 6.2 wt.% of Fe (Table 1).

Cloud water dissolution experiments (Fig.2) were performed at the LPCA Laboratory, Dunkerque, in an ISO 6 clean room. Industrial ash particles were introduced, at room temperature, in a Teflon PFA vessel, illuminated by a Newport® Oriel Sol1A, Class ABB solar simulator. During the kinetic survey, contact times between particles and the simulated cloud water vary between 5 and 120 min.

Industrial Ash Main Characteristics	
Fe abundance (wt. %)	6.2
Mean Particle Size (μm)	0.5
Specific Surface Area (m^2/g)	3.7

Table 1. Industrial Ash Main Characteristics

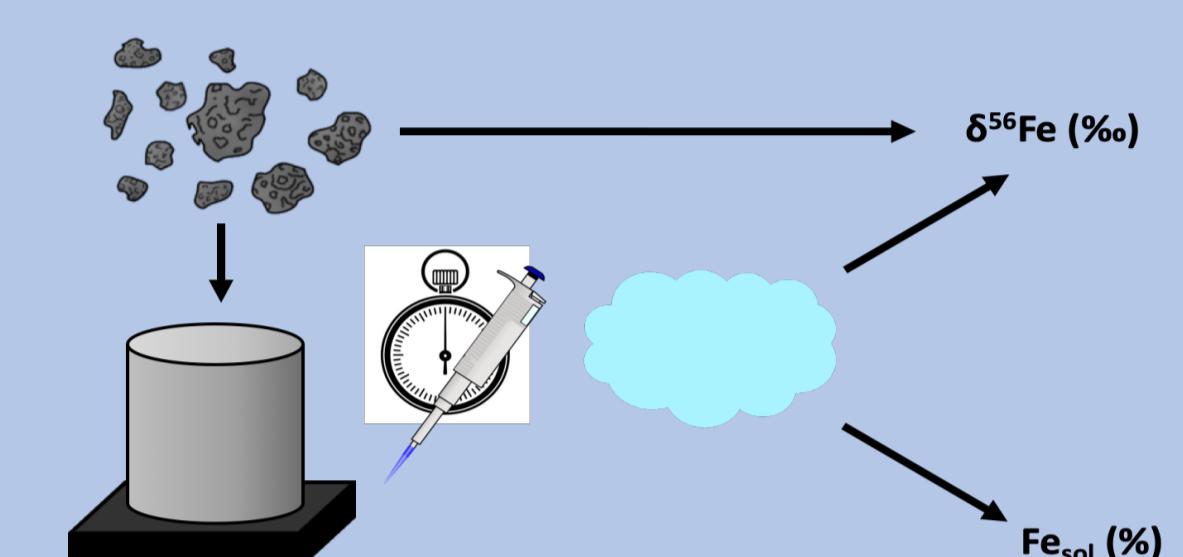


Figure 2. Schematic layout of the ash dissolution kinetic survey

Dissolution experiments were performed using a solution that mimics cloud water chemical composition (Table 2 and 3) to simulate, as close as possible, the atmospheric aerosol processes.

This study		Cloud water composition		
	Measured	Minimum	Maximum	Mean
Na^+	241.5	46	12,719	2,158
NH_4^+	3.752.2	2,646	21,870	2,646
K^+	414.3	36	1026	290
Mg^{2+}	138	61	2,977	467
Ca^{2+}	420.6	280	11,100	1,979
Cl^-	10,930.8	248	15,611	3,343
SO_4^{2-}	41,993.8	4,080	51,072	19,141
NO_3^-	46,081.5	4,898	55,800	16,306

Table 2. Concentrations of inorganic compounds measured in the synthetic cloud water solution (values reported in $\mu\text{g}/\text{L}$)

After the desired contact time, the solutions were filtered using Millipore cellulose acetate membranes with 0.45 μm pore size, previously rinsed with HNO_3 . Aliquots of 10ml and 20ml of the filtered solution were acidified using sub-boiled HNO_3 for further Fe concentration and isotopic composition measurements, respectively.

Fe concentrations were measured by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) at LPCA-Dunkerque.

Iron isotope measurements were performed with a Nu II Plasma MC-ICP-MS instrument (Free University Brussels, G-Time Laboratory), using high resolution entry slits to resolve polyatomic argon-based interferences and enable the full separation of Fe masses. Standard-sample bracketing and external normalization using Ni-doping were applied to correct the instrumental mass bias.

4. Implications

The evaporation and condensation cycles of cloud water during the lifetime of an airborne particle can cause strong disequilibria between soluble Fe phases and the Fe-bearing minerals during the early-stage dissolution.

The complete evaporation of the cloud water (i.e., relative humidity below the efflorescence point) in high temperature environments will cause the formation of highly reactive and soluble Fe species (e.g., ferrhydrite). If the cloud water is completely evaporated before dissolution equilibrium is achieved, the new formed ferrhydrites will have an isotope composition lighter than the original Fe aerosol.

Moreover, the water uptake by a wet aerosol particle will cause the rise of the solution pH during the transition of a wet aerosol particle into cloud droplets. Iron will start to precipitate as Fe nanoparticle as the solution pH rises to near-neutral values found in cloud water (i.e., pH between 4 and 6). If the transition of a wet aerosol into cloud droplets occurs before the equilibrium of the dissolution process is achieved, the neo-formed Fe nanoparticles will have an isotope composition lighter than the original aerosol due to kinetic controlled isotope fractionation.

The magnitude of the isotopic fractionation can be enhanced if the Fe species found in the original aerosol are well crystallized and refractory. Previous studies showed that the dissolution of a well crystallized goethite can produce an isotopic fractionation ($\Delta^{56}\text{Fe}_{\text{solution-goethite}}$) up to -1.67‰ in the presence of organic ligands and UV light. Therefore, the cloud processing undergoing during the evaporation and condensation cycles of cloud droplet can likely generate neo-formed Fe-species with an isotope composition as the ones found by Kurisu et al. (2016) in the soluble fraction of a fine marine aerosol, i.e., $\delta^{56}\text{Fe}$ values ranging from -3.91‰ to -1.87‰.

This study showed that kinetic isotopic fractionation can cause the release of isotopically light Fe during the early-stage dissolution of a wet aerosol. The dissolved Fe can be transformed during the condensation/evaporation cycles into highly reactive and bioavailable Fe nanoparticles yielding a low isotopic signature.

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