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1 IN-CLOUD PROCESSING AS A POSSIBLE SOURCE OF ISOTOPICALLY LIGHT IRON
2 FROM ANTHROPOGENIC AEROSOLS: NEW INSIGHTS FROM A LABORATORY STUDY

3

4

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26

27 **Abstract**

28 Wet atmospheric deposition can account for up to 50% of the total iron input to surface waters, so
29 establishing the extent to which kinetic and equilibrium isotope effects can influence aerosol soluble
30 $\delta^{56}\text{Fe}$ values is imperative to trace and constrain aerosol sources using Fe isotopes and to understand
31 the differences found between $\delta^{56}\text{Fe}$ values for bulk and soluble phases of aerosols. In this context,
32 changes in iron solubility and isotopic composition of dissolved Fe during simulated atmospheric
33 processing of industrial ash was investigated. Kinetic and equilibrium experiments were performed
34 under UV/VIS light using ash from a Fe–Mn alloy metallurgical plant and a synthetic solution that
35 mimics cloud water chemistry. The nature of the Fe species of the industrial ash was investigated by
36 Mössbauer Spectroscopy, whereas ash and dissolved $\delta^{56}\text{Fe}$ values were measured by MC-ICP-MS.
37 Mössbauer Spectroscopy revealed that α -hematite, magnetite, and poorly crystallized manganoferrite
38 nanoparticles are the main Fe species. In the early-stage dissolution (until 60 min) a Fe isotope
39 fractionation ($\Delta^{56}\text{Fe}_{\text{solution-bulk ash}}$) of $-0.284 \pm 0.103\text{‰}$ was found at the minimum contact time
40 evaluated herein (i.e., 5 min.) due to kinetic isotopic effects. In the late-stage dissolution (after 60
41 min) a $\Delta^{56}\text{Fe}_{\text{solution-ash}}$ of $0.227 \pm 0.091\text{‰}$ was found due to equilibrium isotopic effects. The kinetic
42 isotope effect within one ash surface monolayer was modeled with an enrichment factor (ϵ) of -1‰
43 in $^{56}\text{Fe}/^{54}\text{Fe}$ ratio. Iron fractional dissolution undergone during different atmospheric processing time
44 scales may release Fe with contrasted isotope compositions to solution, changing the original soluble
45 Fe isotope signature (which is linked to its source). This might be especially important when the
46 dissolution process goes from kinetic to near-equilibrium conditions, in which higher amounts of Fe
47 are progressively released from ash surface.

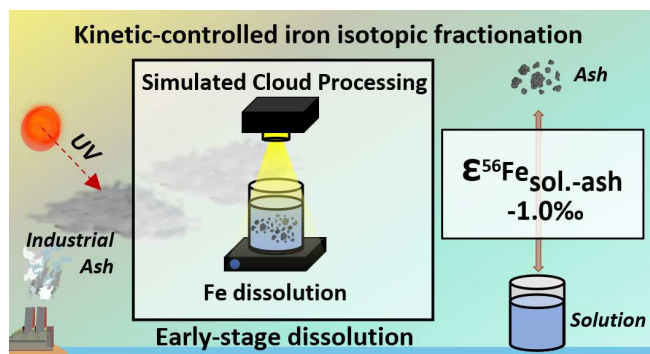
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49 **Keywords:** iron isotope; iron dissolution; aerosol; cloud processing; isotope fractionation; iron oxide

50

51

52 **Graphical Abstract**



53

54

55 1. INTRODUCTION

56 Iron is a key micronutrient that limits primary productivity over vast areas of oceans due to its
57 low solubility in seawater and, therefore, it has strongly impacted the world's fixation of carbon
58 dioxide (Field et al., 1998; Boyd and Ellwood, 2010; Tagliabue et al., 2017) and global nitrogen
59 fixation (Geider and La Roche, 1994). Iron is added to oceans by three main pathways known as
60 margin sediment dissolution, atmospheric dust dissolution, and hydrothermal dispersion (e.g.,
61 Jickells et al., 2005; Tagliabue et al., 2010; Radic et al., 2011). Regionally variable dust from arid
62 and semi-arid regions dominates the global total Fe aeolian dust cycle and has long been considered
63 as an important external input of Fe source to the ocean's surface waters (Mahowald et al., 2005),
64 particularly in regions such as the North Atlantic due to its proximity to the Saharan dust source
65 (Conway and John, 2014). Recent studies showed that noncrustal sources arising from anthropogenic
66 activities such as industrial emissions and fossil, biofuel and biomass burning (i.e. pyrogenic
67 particles) emissions may also be important Fe sources, especially due to their high soluble Fe
68 concentrations (e.g., Sedwick et al., 2007; Luo et al., 2008; Sholkovitz et al., 2009; Ito et al., 2019;
69 Rodríguez et al., 2021 and references therein). Anthropogenic Fe-bearing aerosols display solubility
70 several orders of magnitude higher than the primary natural source of atmospheric Fe to oceans
71 (Sedwick et al., 2007). Therefore, variations in the atmospheric soluble Fe input into the oceans
72 induced by anthropogenic activities likely exert strong influence on marine phytoplankton carbon
73 uptake and storage, playing an important role in the global CO₂ budget and eventually in climate
74 change (Kohfeld et al., 2005; Martínez-García et al., 2011).

75 To provide a reliable mass balance of reactive Fe in the global ocean, the isotope fingerprint
76 technique might be relevant if the isotope composition of the sources and the process undergone in
77 the aerosol atmospheric lifetime have been well addressed (Chen et al., 2020). Bulk natural aerosol
78 dust has been assigned to yield a near-crustal $\delta^{56}\text{Fe}$ value of +0.1‰ (Poitrasson, 2006; Waeles et al.,
79 2007; Mead et al., 2013), whereas the Fe isotope compositions of anthropogenic endmembers are

80 highly fractionated with $\delta^{56}\text{Fe}$ values ranging from -3 to +0.3‰ (Majestic et al., 2009; Mead et al.,
81 2013; Kurisu et al., 2016a, 2016b). Recent studies linked aerosols yielding light $\delta^{56}\text{Fe}$ values with an
82 anthropogenic component (*e.g.*, Kurisu et al., 2016; Conway et al., 2019) based on their proximity to
83 combustion sources (Majestic et al., 2009; Mead et al., 2013; Kurisu et al., 2016). While these light
84 isotope signatures can be linked to a primary anthropogenic source, the presence of a lighter-than-
85 bulk soluble $\delta^{56}\text{Fe}$ may also be indicative of kinetic isotope effects undergoing Fe partial dissolution
86 during atmospheric processing (Revels et al., 2015; Chen et al., 2020).

87 Iron isotopes are known to fractionate through kinetic and equilibrium effects in earth surface
88 low temperature environments (Beard, 2003; Wiesli et al., 2004) and might be a prominent tool to
89 better understand the aqueous-phase reactions between aerosol Fe and cloud water. Previous studies
90 (Wiederhold et al., 2006; Chapman et al., 2009; Kiczka et al., 2010) showed that ligand-promoted
91 and reductive dissolution of goethite and silicates caused the preferential release of isotopically light
92 Fe in the early fraction released from the mineral surface, due to kinetic isotope effects undergone in
93 early-stage dissolution. Together with proton-promoted dissolution, these processes are among the
94 most relevant mechanisms that enhance solubility of Fe-bearing aerosol particles during cloud
95 processing (Chen and Grassian, 2013). Therefore, establishing the extent to which kinetic and
96 equilibrium isotope effects can influence aerosol soluble $\delta^{56}\text{Fe}$ values is imperative to trace and
97 constrain aerosol sources using Fe isotopes, and understand the differences between $\delta^{56}\text{Fe}$ values
98 found for bulk and soluble phases of aerosols, such as those reported for near-source aerosols found
99 at Hiroshima, Japan (Kurisu et al., 2016) and open ocean North Atlantic airborne particles (Conway
100 et al., 2019). This is all the more necessary since wet atmospheric deposition can account for up to
101 50% of the total iron input to surface waters, for example in the subtropical North Atlantic (López-
102 García et al., 2021).

103 The present study investigated changes in iron solubility and dissolved Fe isotopic composition
104 leached from pyrogenic particles (an industrial ash collected from a Fe-Mn alloy company), during

105 simulated atmospheric processing using leaching solutions that mimic cloud water chemistry. The
106 "coke + ore" sintering process is widespread in the field of metallurgy and in the iron and steel
107 industry and the particles emitted are therefore representative of the emissions of this type of
108 production unit which is, moreover, known to be the most emissive among all the units constituting a
109 metallurgy or iron and steel plant. Lab-scale experiments were performed aiming to: (i) evaluate the
110 kinetic and equilibrium mechanisms involved in Fe dissolution; (ii) understand the effect of
111 dissolution on the isotopic composition of the remaining dissolved Fe phase; and (iii) understand the
112 mechanisms controlling Fe isotopic fractionation during cloud processing experiments. The results
113 reported herein can be used to better understand the integrated in-cloud chemical processes during
114 atmospheric transport of aerosols collected in different Earth surface pools and support the
115 identification of possible sources of the airborne particles.

116

117 2. MATERIAL AND METHODS

118 2.1. *Nature of the industrial ash particles*

119 The industrial ash used by the present study belongs to a Fe – Mn alloy metallurgical plant
120 located at Dunkerque in northern France. The particles were collected in the chimney filter of the
121 industry sintering working unit where the raw ore is transformed into an intermediate grade material
122 using anthracite as the reducing agent (Marris et al., 2013). The industrial ash consists of a mixture
123 of metallic, aluminosilicate and aluminosilicate-metallic particles (irrespective of their sizes),
124 containing approximately 76-89% of Mn oxides (Marris et al., 2013) and 6.2 wt.% of Fe (Table S1 in
125 Supplementary Material).

126

127 2.2. *Synthetic cloud water composition*

128 Iron dissolution experiments were performed using solutions that mimic cloud water chemical
129 composition to simulate the atmospheric aerosol dissolution processes as closely as possible. The

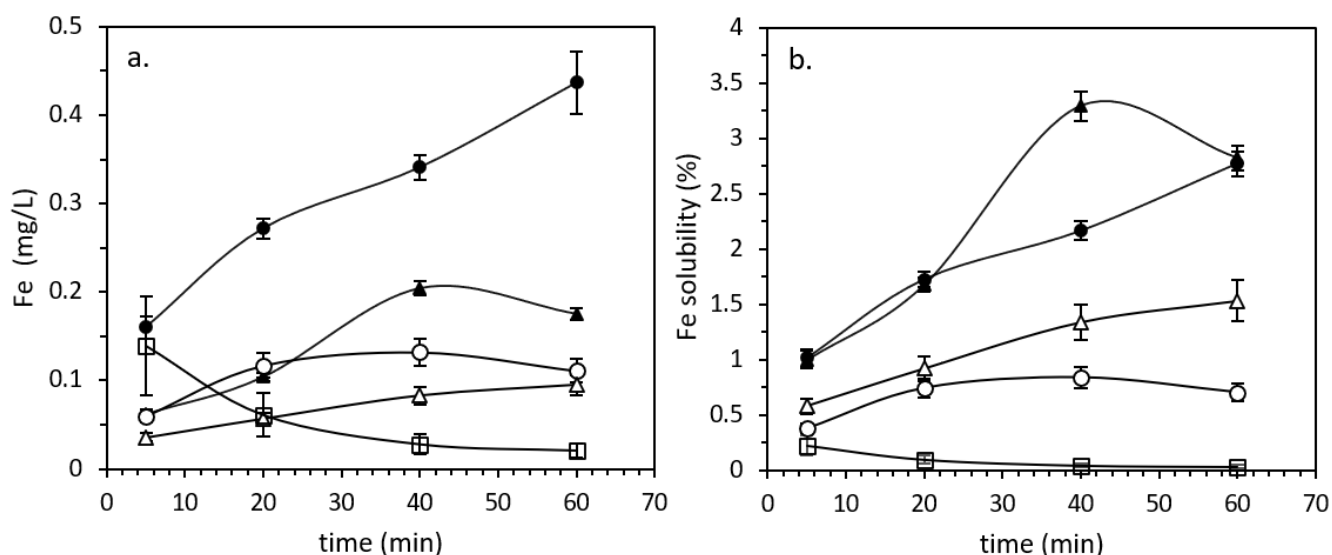
130 concentrations of dissolved major ions (Ca^{2+} , Mg^{2+} , NH_4^+ , K^+ , Na^+ , Cl^- , NO_3^- , and SO_4^{2-}), and
131 organic compounds (formate, acetate, oxalate, malonate, and tartrate) were set in agreement with
132 average values calculated from cloud water composition collected in different regions worldwide, as
133 reported by Guo et al. (2012), Paris and Desboeufs (2013) and the references therein. Synthetic cloud
134 water solutions were prepared using reagents of analytical grade and ultrapure water ($\geq 18.2 \text{ M}\Omega \text{ cm}$).
135 The synthetic cloud water was prepared using NaCl , CaSO_4 , $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, KNO_3 , $\text{CH}_3\text{CO}_2\text{NH}_4$,
136 $\text{CH}_3\text{CO}_2\text{NH}_4$ and HCO_2NH_4 Merk Suprapur[®] salts, and HCl , HNO_3 and H_2SO_4 distilled acids, which
137 were also applied to decrease solution pH. The concentrations of the inorganic compounds
138 introduced in the synthetic cloud water were verified by Ionic Chromatography using a Dionex ICS-
139 5000 Ion Chromatography System, whereas the concentrations of the organic compounds were
140 estimated through stoichiometric calculations. The measured and estimated concentrations of the
141 synthetic cloud water used herein are shown in Tables S2 and S3. Before starting the experiments,
142 solution pH was adjusted to 2 using few drops of conc. HClO_4 , since perchlorates are a weak ligand
143 capacity in low ionic strength solutions (Johansson and Yokoyama, 1990) and do not form Fe
144 complexes.

145

146 2.3. *Iron dissolution experiments*

147 The Fe dissolution experiments performed under UV/VIS irradiation evaluated herein were
148 similar to that of Wiederhold et al. (2006), but to be representative of the dissolution mechanisms
149 occurring during the atmospheric transport of pollution aerosols, the concentration range of organic
150 ligands was adjusted to values commonly found in cloud waters and the experiment duration was
151 adapted to the lifetime of cloud droplets, i.e. a few hours (Flossmann and Wobrock, 2019). A
152 maximum ash and solution contact time of 120 min was established, since it is consistent with
153 aerosol processing between cloud droplet formation and precipitation (Warneck, 1988) and agrees
154 with the dissolution time performed by previous studies (e.g., Paris and Desboeufs, 2013). The ash

155 concentration was defined according to preliminary dissolution experiments that showed faster
 156 dissolution rates and higher final dissolved Fe concentrations in more acidic solutions with an ash
 157 concentration of 250 mg/L (Figure 1a,b). A higher ash concentration (1000 mg/L) possibly created
 158 experimental or filtration artifacts and reduced Fe solubility towards higher contact times (Figure
 159 1b). The dissolution experiments performed to evaluate iron isotope fractionation used pH 2
 160 synthetic cloud water solutions with an ash concentration of 250 mg/L to improve signal intensity
 161 during Fe isotope measurements due to the higher concentration of dissolved Fe in the final solution
 162 (Figure 1a). The dust concentrations reported herein were in agreement with those found in cloud
 163 water, which usually range from 100 $\mu\text{g/L}$ to 1 g/L (Shi et al., 2012 and references therein).



164
 165 **Figure 1:** Dissolved Fe concentrations (a) and Fe solubility (b) during simulated atmospheric
 166 processing of industrial ash in pH 2 solutions (black circles and triangles) and pH 3 solutions (open
 167 circles, triangles, and squares) with industrial ash concentrations of 100 mg/L (black and open
 168 triangles), 250 mg/L (black and open circles), and 1000 mg/L (open squares). Error bars represent
 169 two standard deviations ($\pm 2\text{SD}$) of the experimental data.

170
 171 Independent experiments were conducted in Savillex® Teflon vessels during a contact time
 172 between ash and solutions of 5, 30, 60, 90 and 120 min at $\sim 25^\circ\text{C}$ with constant UV/VIS irradiation
 173 promoted by a Newport® Oriel Sol11A, Class ABB solar simulator. An amount of 7 mg of industrial
 174 ash was precisely weighted on a previously 1M HCl cleaned plastic weighing boat using a Mettler

175 Toledo microbalance (XP6 model). The ash was transferred to a 30 mL Savillex Teflon vessel
176 containing 23 mL of synthetic cloud solution and the weighing boat was rinsed with 5 mL of
177 synthetic cloud water to ensure that all ash particles were transferred to the Teflon vessel, making up
178 a final volume of 28 mL and an ash concentration of 250 mg/L. The Savillex was immediately
179 placed over a magnetic stirrer under constant UV/VIS irradiation. After the predefined contact time,
180 the vessel was removed from the stirrer and the solution was immediately filtered using a Millipore
181 cellulose acetate membrane with 0.45 μm pore size previously rinsed with 2% HNO_3 . Aliquots of \approx
182 10 and 20ml of the filtered solution were acidified using conc. HNO_3 for further Fe concentration
183 and isotopic composition measurements, respectively. Analysis of the cloud water showed it had an
184 Fe concentration of 4.2 $\mu\text{g/L}$, which is less than 3% of the minimum amount of dissolved Fe
185 measured in samples collected from the dissolution experiments. To verify the reproducibility of the
186 results, the experiments were performed three times. Control experiments were performed to
187 investigate the role of colloidal Fe in the dissolved Fe isotope signature and evaluated possible Fe
188 precipitation. These independent dissolution experiments were performed with the same solution pH,
189 ash concentration and duration as the ones performed for isotope measurements, but the final
190 solutions were first filtered with membranes with 0.45 μm pore size and subsequently filtered with a
191 Macrosep Centrifugal Filter with 100 KDa pore size. Iron concentrations measured in the $<0.45\mu\text{m}$
192 and $<100\text{KDa}$ fractions were identical. Images from the 100KDa membranes performed by Scanning
193 Electron Microscopy did not show colloidal Fe phases. Together, these observation showed that Fe is
194 mainly present as truly dissolved metal, due to the acidic solution pH, and complexed with organic
195 ligands, e.g. $\text{Fe}(\text{C}_2\text{O}_4)_n$ due to the presence of oxalate.

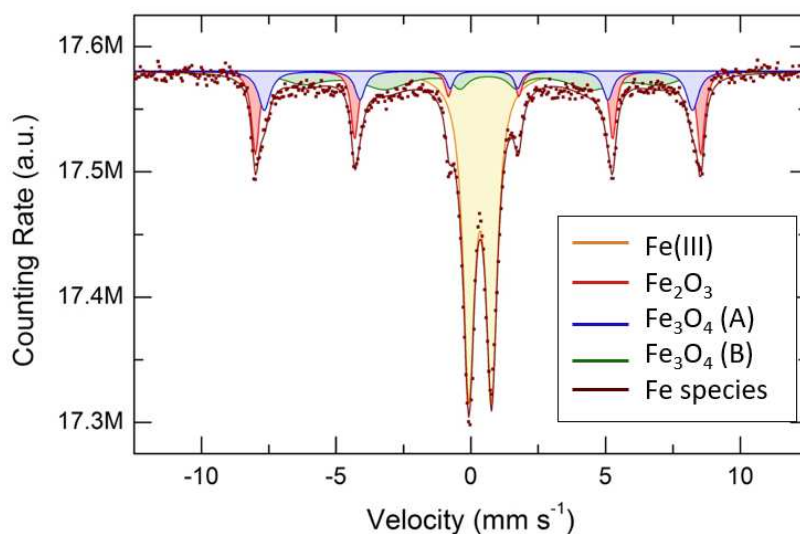
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197 2.4. *Mossbauer Spectroscopy*

198 The typical room-temperature ^{57}Fe Mössbauer spectrum of industrial ash particles is shown in
199 Figure 2. The spectrum shows a quadrupole doublet (i) and at least three magnetically-split Zeeman

200 patterns (ii), corresponding to the Fe(III) ions and the iron oxide form, respectively. The results of a
201 least-square fit using the Lorentzian line shape are collected in Table S4 in SI. These paramagnetic
202 (i) and magnetically (ii) forms are present in comparable proportions, *i.e.*, 47.7% and 52.3%,
203 respectively. The isomer shifts IS are given relative to α -Fe, and the quadrupole splitting QS,
204 hyperfine magnetic field H_{eff} and line width W are also shown. The sextet with the largest $H_{\text{eff}} =$
205 51.4 T (red lines in Figure 2) corresponds to hematite α -Fe₂O₃. Hematite is rather well crystallized
206 with the narrowest spectral lines for the studied sample, $0.30 \leq W \leq 0.35 \text{ mm s}^{-1}$. Small quadrupole
207 splitting $QS = 0.21 \text{ mm s}^{-1}$ indicates a slight distortion of the iron local environment in the
208 rhombohedral α -Fe₂O₃ lattice. The hyperfine interaction parameters of the two remaining sextets are
209 similar to those in magnetite Fe₃O₄. Pure magnetite crystallizes in the inverse spinel structure in
210 which Fe²⁺ and Fe³⁺ ions are distributed over tetrahedral A and octahedral B sites: (Fe³⁺)_A(Fe²⁺
211 Fe³⁺)_BO₄. Tetrahedral Fe³⁺ ions exhibit a magnetically split pattern with $H_{\text{eff}} = 49.4 \text{ T}$ (blue lines in
212 Figure 2). A fast electronic exchange at room temperature between octahedral Fe²⁺ and Fe³⁺ ions
213 compared to ⁵⁷mFe nuclear lifetime ($t_{1/2} = 100 \text{ ns}$) does not allow one to distinguish two different
214 iron oxidation states in magnetite. Consequently, the average Zeeman pattern with intermediate IS
215 between limiting values of Fe³⁺ (0.37 mm s^{-1}) and Fe²⁺ (1.0 mm s^{-1}) is observed. Magnetite is
216 clearly ill-crystallized and impure. Both A and B sites are disordered, characterized by large line
217 widths: $0.38 \leq W_A \leq 0.54 \text{ mm s}^{-1}$, and $0.7 \leq W_B \leq 2.1 \text{ mm s}^{-1}$. In particular, the B-sublattice appears
218 to be highly disordered, suggesting a partial occupation of iron sites by metallic cations of similar
219 size (Mn²⁺, Ca²⁺, etc.). The most intense quadrupole doublet (47.7% of the total resonance pattern)
220 corresponds to high-spin Fe³⁺ species in oxide environment. Similar hyperfine interaction
221 parameters are observed for a number of highly dispersed pure and mixed iron oxides and
222 hydroxides. The absence of magnetic ordering at room temperature suggests the average size of iron

223 oxide particles to be below 10 nm. An increased line width for the quadrupole doublet (0.50 mm s^{-1})
224 is consistent with this hypothesis.



225
226 **Figure 2:** Room-temperature ^{57}Fe -Mössbauer spectrum of industrial ash sample measured in
227 absorption geometry. Red square dots are the experimental measurements and coloured lines result
228 from the deconvolution procedure.

229

230 2.5. Iron concentration and isotope measurements

231 The filtered solutions obtained from the industrial ash dissolution experiments were evaporated
232 at 120°C , re-dissolved in 2 ml of conc. sub-boiled HNO_3 and dried at 120°C . The final residues were
233 subsequently solubilized by 1 mL of sub-boiled 6M HCl and stored in the refrigerator until Fe
234 purification through anion exchange chromatography in an HCl medium took place. The Fe
235 purification procedure used 1.6 ml of Bio-Rad AG1 X-8, 100-200 mesh resin loaded in Bio-Rad
236 Poly-Prep columns, both cleaned with 6M sub-boiled HCl, 1M sub-boiled HNO_3 and ultrapure water
237 ($\geq 18.2 \text{ M}\Omega \text{ cm}$). The cleaned resins were preconditioned with 10 ml of 6M sub-boiled HCl, prior to
238 the introduction of 2 ml of the sample previously dissolved in 6M sub-boiled HCl. The matrix was
239 eluted in 30 ml of 6M sub-boiled HCl, whereas the Fe was collected with 20 ml of 0.5M sub-boiled
240 HCl. The solutions containing the purified Fe were dried and re-dissolved with sub-boiled 0.05M
241 HNO_3 for Fe isotope measurements.

242 Iron isotope measurements were carried out at the Université Libre de Bruxelles (Laboratoire G-
243 Time) with a Nu Plasma II Multi-Collector Inductively Coupled Plasma Mass Spectrometer (MC-
244 ICP-MS) from Nu Instruments (Wrexham, UK). An Aridus-II desolvating sample introduction
245 system from Cetac Technologies was used to reduce the predominant $^{40}\text{Ar}^{14}\text{N}$, $^{40}\text{Ar}^{16}\text{O}$ and
246 $^{40}\text{Ar}^{16}\text{O}^1\text{H}$ interferences on iron isotopes 54, 56 and 57, respectively. The instrument was further
247 operated in pseudo-high-resolution mode ($R \sim 1600$), to partially resolve the abovementioned
248 polyatomic argon-based interferences from the Fe masses. This is achieved by reducing the width of
249 the source-defining slit using a selectable slit mechanism and then reducing the width of the alpha
250 slit located before the ESA (Electrostatic Analyzer) to enhance the peak shape by reducing any
251 image aberration, resulting in a flat-topped section of resolved peak for isotopic ratio measurements
252 (Figure S1). In addition to the Fe masses, ^{53}Cr was also monitored and an online Cr correction was
253 applied to account for any iso-baric interference from ^{54}Cr on mass ^{54}Fe . This correction was either
254 negligible or non-existent due to the effective separation of Fe from Cr during column chemistry.

255 Instrumental mass bias was corrected by external normalization with Ni added to standards and
256 samples, applying the exponential law in combination with standard-sample bracketing. Both sample
257 and standard solutions were run at 1 ppm Fe doped with 1 ppm Ni in 0.05M HNO_3 , giving a total Fe
258 beam intensity of $\sim 25\text{V}$ and a total Ni beam intensity of $\sim 20\text{V}$. Two isotopic ratios were measured
259 ($^{56}\text{Fe}/^{54}\text{Fe}$, $^{57}\text{Fe}/^{54}\text{Fe}$) in the analytical sessions, but only $^{56}\text{Fe}/^{54}\text{Fe}$ ratios were reported since samples
260 plot on a single mass dependent fractionation line. The results are reported using delta notation
261 relative to international Fe standard IRMM-014 (European Commission Institute for Reference
262 Materials and Measurements), as described by Equation 1.

263
$$\delta^{56}\text{Fe} (\text{‰}) = [(^{56}\text{Fe}/^{54}\text{Fe})_{\text{sample}} / (^{56}\text{Fe}/^{54}\text{Fe})_{\text{IRMM14}} - 1] \times 10^3 \text{ (Eq. 1)}$$

264 Accuracy and reproducibility were assured by analyzing an in-house quality control standard
265 called "MIX". The MIX standard contains Fe extracted and purified by ion chromatography from
266 Ammonitico Rosso carbonates (Préat et al., 2008). The $\delta^{56}\text{Fe}$ values found herein for the in-house

267 MIX standard was $-1.58 \pm 0.10\text{‰}$ (2SD, $n = 5$), in agreement with the long-term measurement
268 average value obtained on this instrument (Table S5). The accuracy of the MIX in-house standard
269 reference material had been verified prior to this study by concomitant analysis of two reference
270 materials from the Swiss Federal Institute of Technology (ETH, Zürich) with well-established
271 consensus values: ETH Hematite and ETH Fe Salt. Our results (Table S5) were in good agreement
272 with the reported values from expert laboratories equipped with various types of MC-ICP-MS
273 instruments (Dideriksen et al., 2008; Teutsch et al., 2005; Williams et al., 2004; Poitrasson and
274 Freydier, 2005).

275 The magnitude of the isotope fractionation ($\Delta^{56}\text{Fe}_{\text{solution-bulk ash}}$) was calculated using Equation 2
276 by comparing the Fe isotope compositions of the solutions with the initial bulk industrial ash, as also
277 proposed by Wiederhold et al. (2006). The isotope composition of the industrial ash used herein was
278 first measured and reported by Maters et al. (2017) with a $\delta^{56}\text{Fe}$ value of $-0.12 \pm 0.08\text{‰}$.

$$279 \quad \Delta^{56}\text{Fe}_{\text{solution-bulk ash}} = \delta^{56}\text{Fe}_{\text{solution}} - \delta^{56}\text{Fe}_{\text{buk ash}} \quad (\text{Eq. 2})$$

280

281 3. RESULTS AND DISCUSSION

282 3.1. Ash particle composition

283 The industrial ash collected from a Fe-Mn alloy company consists of a mixture of metallic,
284 aluminosilicate, and, mainly, of internally mixed “aluminosilicate-metallic” particles (Marris et al.
285 2012 and Marris et al. 2013). Mössbauer measurements shown herein evidenced the presence of α -
286 hematite and magnetite particles (Fig. 2), also shown by automated SEM-EDX analyses performed
287 by Marris et al. (2013). But, in relation to their size, 44 to 60% of the analyzed particles consist of an
288 internal mixture of aluminosilicates with Fe- and Mn-oxides (e.g., hausmannite, bixbyite). The high-
289 spin Fe^{3+} species in an oxide environment, evidenced in Mössbauer measurements (section 2.5),
290 responsible for the most intense quadrupole doublet (Figure 2), are linked with a heterogeneous
291 metal distribution inside these particles. In summary, the most prevalent Fe-rich particle type in ash

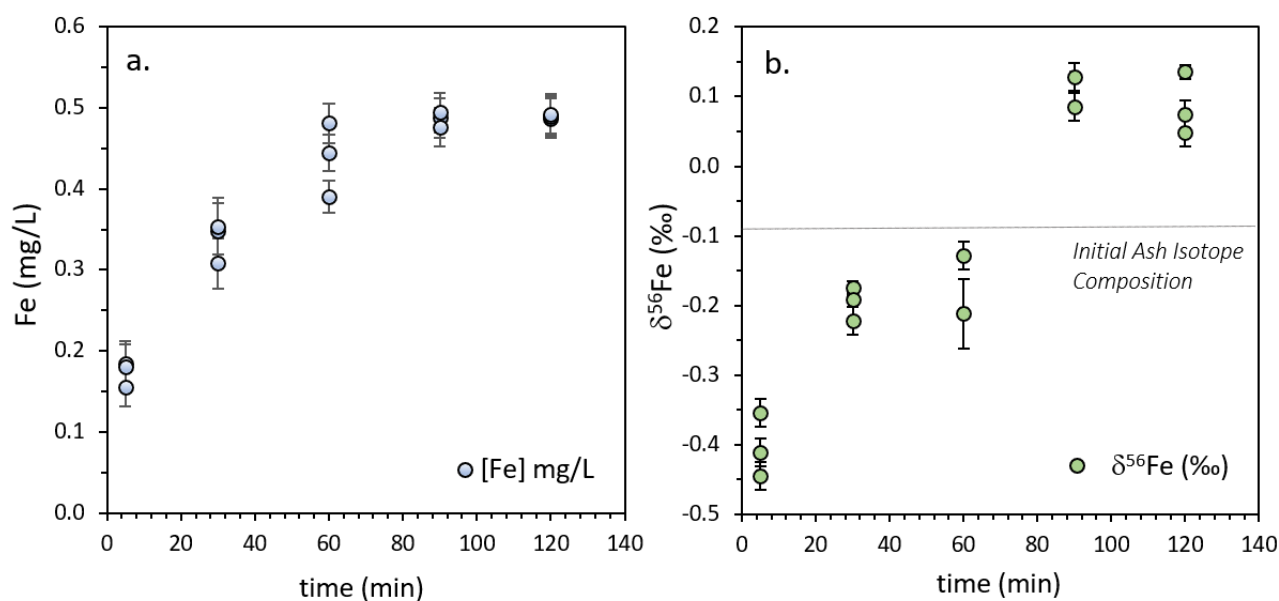
292 (up to 60%), consist of a set of poorly crystallized manganoferrite nanoparticles, with a grain size up
293 to 10 nm, that could explain the most intense Mössbauer signal. A detailed interpretation and
294 discussion of the Mössbauer analysis are available in the Supplementary Material.

295

296 3.2. Dissolved iron isotope composition

297 Dissolved iron average concentrations increased from 155 to 397 $\mu\text{g/L}$ from 5 to 120 min, which
298 represents a solubility ranging from 1 to 2.5% (Figure 3a and Table S6). The dissolution process of
299 the industrial ash as a function of time (Figure 3b) can be divided into two stages based on the
300 dissolved Fe isotopic composition ($\delta^{56}\text{Fe}$), i.e.: (i) early-stage dissolution (until 60 min), and (ii) late-
301 stage dissolution (after 60 min), as also proposed by Wiederhold et al. (2006) during the dissolution
302 of goethite under controlled experimental conditions. In the early stage, the preferential dissolution
303 of light Fe isotopes occurs, with a minimum measured $\delta^{56}\text{Fe}_{\text{solution}}$ value of $-0.45 \pm 0.07\text{‰}$ at 5
304 minutes dissolution time. As the dissolution contact time increases, Fe isotope composition becomes
305 heavier, toward the values of the bulk industrial ash (i.e., $-0.12 \pm 0.08\text{‰}$, Maters et al., 2017). At the
306 late-stage dissolution, dissolved Fe isotope composition becomes heavier than the bulk industrial ash,
307 achieving a measured $\delta^{56}\text{Fe}_{\text{solution}}$ value of $+0.09 \pm 0.07\text{‰}$ at maximum Fe dissolution.

308



309
 310 **Figure 3:** (a) Dissolved Fe concentration and (b) isotopic composition during dissolution
 311 experiments of the industrial ash. The horizontal dashed line corresponds to the initial ash isotope
 312 composition ($\delta^{56}\text{Fe}_{\text{bulk ash}}$).
 313

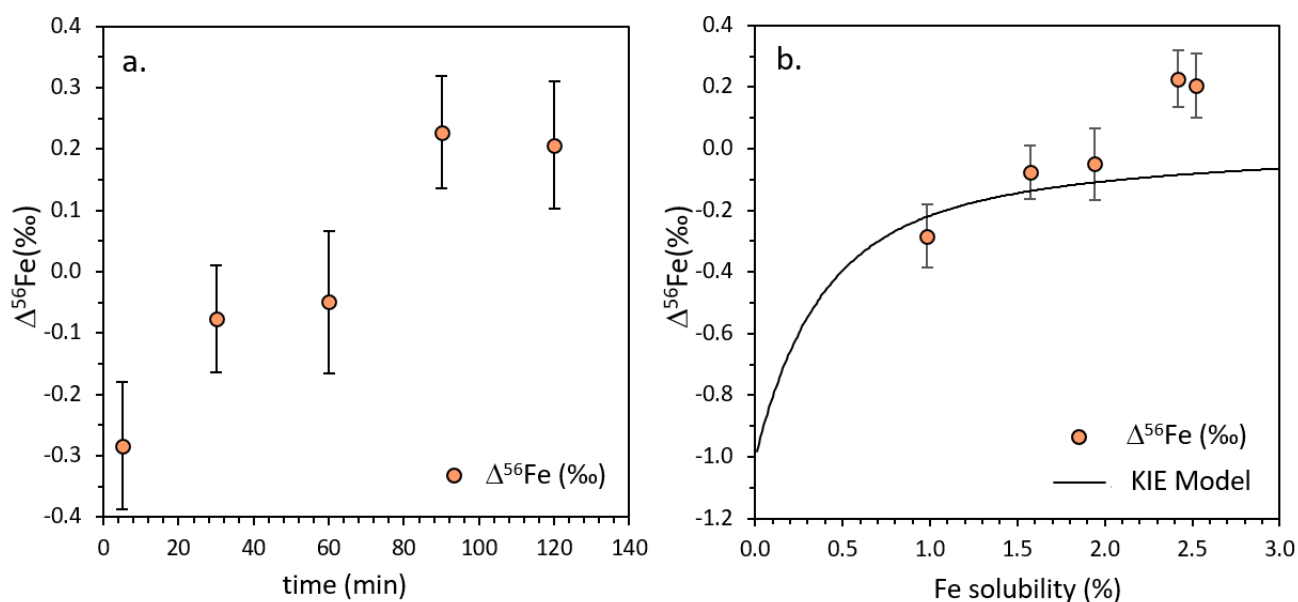
314 3.3. Mechanism controlling dissolved iron isotope fractionation

315 To evaluate the extent to which the kinetic isotope effect controls the evolution of the dissolved Fe
 316 isotope composition, the experimental $\Delta^{56}\text{Fe}_{\text{solution-bulk ash}}$ data were compared with the Wiederhold's
 317 kinetic effect model (Wiederhold et al., 2006). This empirical model has been well applied to explain
 318 the early-stage dissolution process within one surface monolayer of Fe-bearing minerals in which the
 319 preferential depletion of isotopically light Fe occurs. Density Functional Theory (DFT) provides an
 320 alternative to empirical models to explain observed fractionations. However, when applied to the
 321 same system studied by Wiederhold et al. (2006), i.e. goethite dissolution in oxalate aqueous
 322 solutions, these DFT predictions resulted in significant disagreement as to the magnitude of the
 323 fractionation reached at equilibrium ($1.91 < \Delta^{56}\text{Fe}_{\text{solution-goethite}} < 2.18\text{‰}$, vs. $\cong 0.30\text{‰}$ for experimental
 324 measurements (Domagal-Goldman and Kubicki, 2008)). Furthermore, the DFT results do not give
 325 any information on the temporal evolution of the fractionation and we have therefore chosen the
 326 empirical model of Wiederhold to guide our interpretation of the experimental results obtained here.
 327 A detailed description of our calculations is provided in Appendix A and model outputs are presented

328 in Figure 4b. Two fitting parameters are used, i.e.: (i) the fractionation constant, converted to the
 329 enrichment factor ϵ (Wiederhold et al., 2006); and (ii) the surface site density of Fe atoms (SSD – see
 330 Appendix A), used in the calculation of the fraction of iron atoms (ρ , in % of the total number of Fe
 331 atoms) that belong to the reactive surface site pool (rss).

332 In the early-stage dissolution (Fig. 3), the maximum Fe isotope fractionation was observed at 5
 333 min with a $\Delta^{56}\text{Fe}_{\text{solution-bulk ash}}$ of $-0.28 \pm 0.10\text{‰}$, whereas in the late-stage dissolution the maximum Fe
 334 isotope fractionation occurred at 90 min with a $\Delta^{56}\text{Fe}_{\text{solution-bulk ash}}$ of $+0.23 \pm 0.09\text{‰}$. Applying the
 335 kinetic isotope effect model to the experimental data (Figure 4b), the best fit was obtained for a SSD
 336 of 2 sites/nm², close to the minimum value proposed by Koretsky et al. (1998) for pure crushed
 337 hematite (4.5 sites/nm²). It results in a fraction of Fe atoms that belongs to the reactive surface site ρ
 338 = 0.22%, and an enrichment factor $\epsilon = -1\text{‰}$, close to the value of -1.7‰ , corresponding to the best
 339 fit value for the $^{56}\text{Fe}/^{54}\text{Fe}$ data obtained for goethite by Wiederhold et al. (2006).

340



341 **Figure 4:** (a) Variation of Fe isotope fractionation over ash-solution contact time periods at room
 342 temperature, with UV/VIS irradiation ($\Delta^{56}\text{Fe}$ is reported relative to the bulk ash – Eq. 2). (b) Kinetic
 343 Isotope Effect (KIE) Model output vs. experimental data (± 2 S.D. reported as error bars) obtained
 344 for isotope fractionation during industrial-ash dissolution in cloud water simulation experiments
 345

346

347 The model succeeded in describing the kinetic-controlled isotope fractionation process at the
348 early-stage dissolution of Fe-bearing aerosols in which the faster breakage of energetically weaker
349 $^{54}\text{Fe-O}$ surface bonds occurs, but it was not able to describe the late-stage dissolution due to near-
350 equilibrium conditions in which equilibrium isotope effects prevail. The good agreement between the
351 experimental data found during the early-stage dissolution and the model data suggests that kinetic
352 isotope effect is a significant mechanism controlling the isotope signatures of dissolved Fe during the
353 atmospheric processing of an anthropogenic aerosol. However, Revels et al. (2015) showed that an
354 argumentation based on a simple data fit to a kinetic isotope effect model is not robust enough to
355 suggest kinetic isotope fractionation as the only mechanism controlling the isotopic evolution of the
356 $\delta^{56}\text{Fe}$ values over time. These authors showed that the evolution of dissolved Fe isotope composition
357 over ash and solution contact time periods can be attributed to (i) the mixing of leached fractions
358 from two phases (i.e., poorly and well crystallized Fe oxides) yielding different labilities and isotope
359 compositions without isotope fractionation of either phases, according to a two-phases mixing
360 model; and (ii) a kinetic-controlled isotope fractionation due to the faster breakage of $^{54}\text{Fe-O}$ bonds
361 from Fe oxides on the ash surface, according to a kinetic isotope effect model, highlighting the
362 complexity of determining the mechanism controlling the leached $\delta^{56}\text{Fe}$ values evolution during ash
363 dissolution by cloud processing.

364 Analyzing the isotopic composition of each separate Fe phase (i.e., poorly and well crystallized
365 Fe oxides) can be an attractive approach for evidencing if the two-phases mixing process is an
366 important mechanism controlling the evolution of dissolved Fe and $\delta^{56}\text{Fe}$ values. However, there is a
367 lack of consensus on the appropriate method for extracting the reactive phase for Fe isotope
368 determination (Chen et al., 2020), especially for the extraction of poorly crystallized and amorphous
369 Fe oxides. The most efficient selective methods for the separation of poorly-crystallized and
370 amorphous Fe oxides are the ascorbic acid (Raiswell et al., 2010) and hydroxylamine hydrochloride
371 (Berger et al., 2008) methods. However, they also induce Fe kinetic and equilibrium isotope effects

372 through ligand and proton promoted dissolution and redox reactions according to particle mineral
373 assemblage composition (Brantley et al., 2004; Wiederhold et al., 2006; Chapman et al., 2009;
374 Kiczka et al., 2010). Information on the isotope composition differences between poorly and well
375 crystallized oxides should come from a different approach. For instance, Flament et al. (2008) showed
376 that the high-temperature sintering operation tends to standardize the isotope composition of the Fe
377 phases presented therein, since the collected dust had $\delta^{56}\text{Fe}$ values ranging only from +0.53 to +0.86
378 ‰, which are much more homogeneous than the ore used in the sintering process ($\delta^{56}\text{Fe}$ values
379 ranging only from -0.16 to +1.19). The referred work was carried out in a steel industry close to the
380 one in which the dust was collected by the present study, both with same sintering process (e.g.,
381 temperature, ores, and reducing and melting agents). Additionally, Chen et al. (2020) showed that
382 differences between Fe isotope signatures of amorphous Fe (hydro)oxides, ferrihydrite, and more
383 crystallized goethite and hematite are small, based on the homogeneity of the isotopic signatures
384 generally observed for dust Fe mineral phases, despite the high variability of the poorly and well
385 crystallized Fe oxides concentrations. Therefore, a two-phases mixing process may not be so relevant
386 to explain the evolution of Fe isotope composition found herein, since the differences of the Fe
387 isotope composition of such particles are small, irrespective of their crystallinity. Therefore, kinetic
388 isotope effects are likely to be the most important process controlling the evolution of $\delta^{56}\text{Fe}$ values
389 over time during ash dissolution.

390 391 *3.4. Mechanisms of Fe isotope fractionation during cloud processing*

392 The good agreement of the experimental data with the kinetic fractionation model shows the
393 faster release of ^{54}Fe at the onset of the ligand-controlled dissolution process, due to the faster
394 breakage of the ^{54}Fe -O surface bond, by comparison with bonds involving heavier isotopes, as it is
395 generally accepted on a theoretical basis (Schauble et al., 2001). Ligand-controlled dissolution occurs
396 through the formation of strong surface complexes, which weaken the bonds between Fe atoms and

397 the coordinating oxygen atoms in the particle lattice surface (Stumm, 1995). This process is prone to
398 cause significant isotope fractionation, due to the faster breakage of the energetically weaker $^{54}\text{Fe-O}$
399 bond, forming aqueous species such as $\text{Fe}(\text{C}_2\text{O}_4)_n$ due to the presence of oxalate. Previous studies
400 showed that ligand-controlled dissolution causes Fe isotope fractionation of goethite, granite, basalts
401 and phyllosilicates in experiments containing oxalic acid (Wiederhold et al., 2006; Chapman et al.,
402 2009). Organic ligands also promote ligand-to-metal electron transfer in the organo-Fe(III) surface
403 complexes under the irradiation of UV/VIS light, causing Fe solubilization as aqueous Fe(II) species
404 (Chen and Grassian, 2013). This process, known as reductive ligand-promoted dissolution, can also
405 cause isotope fractionation of Fe oxides with a measured $\Delta^{56}\text{Fe}_{\text{solution-goethite}}$ of -1.67‰ . Conversely,
406 previous studies investigating Fe dissolution from hematite and ferromanganese nodules showed that
407 proton-promoted dissolution has a limited effect on Fe isotope fractionation, although known as the
408 most important process to cause Fe oxides dissolution in acidic conditions, due to the breakage of Fe-
409 O lattice bonds, during protonation of oxyhydroxides surface sites.

410 The role of organic ligands in Fe dissolution is also evidenced at the late-stage dissolution, in
411 which equilibrium isotope effects are observed. The depletion in ^{54}Fe of the leached layer leads to the
412 breaking of higher energy bonds and to the relative ^{56}Fe enrichment of the solution, inducing lower
413 isotope fractionation rates, on the time scale considered here. For dissolved Fe fractions $> 2\%$ an
414 enrichment of the cloud water in ^{56}Fe ($\Delta^{56}\text{Fe} > 0$) is even observed. Wiederhold et al. (2006),
415 concluded that such results confirmed ligand-controlled dissolution processes, giving rise to the
416 formation in solution of Fe-complexes, with a strong bond energy. Even if the leached solid surface
417 layer becomes enriched in heavy Fe isotopes, these Fe-O bonds are weaker than bonds existing in
418 aqueous Fe-complexes leading to heavy Fe isotopes enrichment in the solution.

419

420 4. IMPLICATIONS

421 The present study is part of current attempts to improve geochemical models of anthropogenic
422 Fe aerosols deposition to the oceans. It is based on a simplified description of the phenomena taking
423 place during the incorporation of pyrogenic particles within the cloud masses. The results presented
424 herein showed that atmospheric processing of pyrogenic particles, as an industrial ash, can generate
425 Fe isotope fractionation with different magnitudes and directions, according to the ash solution
426 contact time (i.e., atmospheric processing time scale) and the fraction of Fe dissolved from the
427 airborne particles. This indicates that atmospheric processes and especially the incorporation of the
428 particles within the cloud masses, complicate the analysis of the origin of the iron aerosols, in the
429 sense that the partial solubilization of these particles induces an Fe isotope fractionation of variable
430 extent. If the particles are dry deposited near the sources, in the epicontinental oceanic zones, the
431 initial soluble Fe isotopically light signatures of anthropogenic particles are probably preserved. On
432 the other hand, if the residence time within the troposphere is longer, as shown by Rodríguez et al.
433 (2021), the solubility of iron increases with the multiplication of evaporation and condensation
434 cycles (atmospheric processing). Iron fractional dissolution undergone during different atmospheric
435 processing time scales may release Fe with contrasted isotope compositions (Fig. 4) to solution,
436 changing the original soluble Fe isotope signature (which is linked to its source). This might be
437 especially important when the dissolution process goes from kinetic to near-equilibrium conditions,
438 in which higher amounts of Fe are progressively released from ash surface. These findings shows
439 that it is then necessary to be able to distinguish between what comes from short-term atmospheric
440 processes (on the scale of the lifetime of a cloud droplet) and what is part of longer processes, since
441 the impact of atmospheric processing on soluble Fe isotope compositions can be significant. The
442 different behavior of natural dust, less soluble and therefore less sensitive to the effect of
443 atmospheric processing, will likely facilitate the determination of their isotopic signature at the time
444 of their oceanic deposition. However, this observation must be relativized when the atmospheric
445 residence time of these dust increases, since it increases the possibility that they are mixed with

446 pyrogenic particles within the cloud droplets, which should lead to an increase of their solubility. The
447 situation will be different for pyrogenic particles, because of their highly variable initial solubility,
448 depending on the source considered (Rodríguez et al., 2021 and references therein) and also because
449 of their greater sensitivity to atmospheric processes. Conclusively, despite the simplifications
450 intrinsic to laboratory studies, the fractionations measured here are consistent with those obtained on
451 real aerosols by Conway et al. (2019), results that allowed these authors to refine the quantification
452 of soluble iron deposition to the oceans. The present study shows that cloud processing should be
453 considered and investigated while using $\delta^{56}\text{Fe}$ values to constrain anthropogenic and natural Fe in
454 near-source and open-ocean aerosols, and, ultimately when it comes to defining the isotopic
455 composition of the atmospheric source term, in studies concerned with the identification of processes
456 and fluxes of key elements in ocean biogeochemistry, as well as their evolution in response to
457 changes in climatic and environmental conditions. Other studies evaluating the effects of cloud
458 processing on Fe isotope fractionation are highly encouraged, especially those performed at lower
459 dust concentrations (which better represents the concentrations commonly found in cloud water),
460 since it effects Fe solubility and might play an important role controlling the magnitude of the Fe
461 isotope fractionation.

462

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473

474

APPENDIX A

475 Our simulation of the behavior of iron isotopes during the dissolution of Fe-bearing particles is based on
 476 the description of the kinetic fractionation model developed in the Supporting Information in Wiederhold et
 477 al.(Wiederhold et al., 2006). The model distinguishes the iron atoms according to their atomic mass number
 478 $A \in \{54,56,57,58\}$ and is based on their location: in the bulk mineral, in its reactive surface site (*rss*) pool or
 479 in the solution surrounding the mineral. The number of ${}^A_{26}\text{Fe}$ atoms in solution is labeled $N_{solution}^{Fe-A}$ with
 480 equivalent notations for the bulk and the *rss* pool. The total number of iron atoms in solution is $N_{solution}^{Fe-*} =$
 481 $N_{solution}^{Fe-54} + N_{solution}^{Fe-56} + N_{solution}^{Fe-57} + N_{solution}^{Fe-58}$ and N_{tot} is the total number of iron atoms in the system. The
 482 reaction progress variable is defined as the number of iron atoms in solution: $\xi = N_{solution}^{Fe-*}$, and the
 483 dissolved fraction is equal to: $100 \frac{N_{solution}^{Fe-*}}{N_{tot}}$ (in %). The fraction of a given isotope *A* in the mineral before
 484 dissolution is X_A .

485 According to Wiederhold et al.(Wiederhold et al., 2006), the evolution of the number of iron isotopes in
 486 the reactive surface site pool is driven by two contributions:

$$487 \frac{dN_{rss}^{Fe-A}}{d\xi} = - \frac{(1+f_A)N_{rss}^{Fe-A}}{(1+f_{54})N_{rss}^{Fe-54} + (1+f_{56})N_{rss}^{Fe-56} + (1+f_{57})N_{rss}^{Fe-57} + (1+f_{58})N_{rss}^{Fe-58}} + \left(1 - \frac{N_{solution}^{Fe-*}}{N_{tot}}\right) X_A. \quad (A1)$$

488 The first term on the right-hand side of the equation is the contribution of iron atoms moving with
 489 isotope fractionation from the *rss* pool to the solution, while the second term describes iron atoms going
 490 from the bulk to the *rss* pool without any fractionation. If a fixed percentage of atoms in the mineral goes
 491 from the bulk to the *rss* pool during the dissolution, it is expected that the number of atoms arriving to the
 492 *rss* pool decreases with time, this is modeled via the coefficient $\left(1 - \frac{N_{solution}^{Fe-*}}{N_{tot}}\right)$ in front of X_A . The coefficients

493 f_n (for example): $f_{56} = \frac{md_{56}}{1000(md_{56} - md_{54})} \epsilon$) depend on the enrichment factor ϵ (ϵ in ‰). The constants

494 md_n are the mass differences for the iron isotopes relative to that of natural Fe and are tabulated in Table
 495 S3 (IRMM-014) of the Supporting Information in Wiederhold et al.(Wiederhold et al., 2006).

496 We extend the set of differential equations of Wiederhold et al.(Wiederhold et al., 2006) by considering
 497 the evolution of the number of iron isotopes in the solution as well:

$$498 \quad \frac{dN_{solution}^{Fe-A}}{d\xi} = \frac{(1+f_A)N_{rSS}^{Fe-A}}{(1+f_{54})N_{rSS}^{Fe-54} + (1+f_{56})N_{rSS}^{Fe-56} + (1+f_{57})N_{rSS}^{Fe-57} + (1+f_{58})N_{rSS}^{Fe-58}} \quad (A2)$$

499
 500 The fraction of iron atoms (ρ , in%) that belong to the reactive surface site pool is

$$501 \quad \rho = 100 \cdot SSD \cdot SA \cdot M_{mineral} / N_A \quad (A3)$$

502 where: (i) $SA = 3.7 \text{ m}^2/g$ is the measured (B.E.T. method) surface area of the industrial ash (table S1 in SI);
 503 (ii) $N_A = 6.02 \cdot 10^{23} \text{ mol}^{-1}$ is the Avogadro number; (iii) $SSD = 2 \text{ sites/nm}^2$ is the surface site density of
 504 iron atoms, based on the range of values proposed by Koretsky et al.(Koretsky et al., 1998) for crushed
 505 hematite; and (iv) $M_{mineral} = 177.14 \text{ g/mol}$ is the *ash equivalent molar mass*, obtained from a linear
 506 combination of the molar masses of pure phases identified from X-ray diffraction and Mössbauer
 507 spectroscopy measurements (sections 2.5 and 3.1). The contributions of pure phases are arbitrarily set to 20
 508 wt.% for $\alpha\text{-Fe}_2\text{O}_3$ ($M = 159.69 \text{ g/mol}$), 25 wt.% for Fe_3O_4 ($M = 231.50 \text{ g/mol}$) and 55 wt.% for FeMnO_3 (158.78
 509 g/mol).

510 With the above values we obtain $\rho = 0.22\%$.

511 Initially, there are no atoms in the solution and the vector of initial conditions is:

512

$$\begin{pmatrix} N_{rss}^{Fe-54}(0) \\ N_{rss}^{Fe-56}(0) \\ N_{rss}^{Fe-57}(0) \\ N_{rss}^{Fe-58}(0) \\ N_{solution}^{Fe-54}(0) \\ N_{solution}^{Fe-56}(0) \\ N_{solution}^{Fe-57}(0) \\ N_{solution}^{Fe-58}(0) \end{pmatrix} = \frac{\rho}{100} N_{tot} \begin{pmatrix} X_{54} \\ X_{56} \\ X_{57} \\ X_{58} \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}.$$

513

514 We arbitrarily choose $N_{tot} = 10000$ to numerically solve the system of coupled differential equations with
 515 Maple 2019 and compute $\delta^{56}Fe_{solution}(\xi)$ as:

516

$$\delta^{56}Fe_{solution}(\xi) = 1000 \left(\frac{\frac{N_{solution}^{Fe-56}(\xi)}{N_{solution}^{Fe-54}(\xi)}}{\frac{X_{IRMM}^{Fe-56}}{X_{IRMM}^{Fe-54}}} - 1 \right).$$

517 We then obtain $\Delta^{56}Fe_{solution}(\xi)$ through the relation $\Delta^{56}Fe_{solution}(\xi) = \delta^{56}Fe_{solution}(\xi) + 0.12\text{‰}$.

518

519 REFERENCES

520

521 Beard, B., 2003. Application of Fe isotopes to tracing the geochemical and biological cycling of Fe.
 522 Chem. Geol. 195, 87–117. [https://doi.org/10.1016/S0009-2541\(02\)00390-X](https://doi.org/10.1016/S0009-2541(02)00390-X)

523 Berger, C.J.M., Lippiatt, S.M., Lawrence, M.G., Bruland, K.W., 2008. Application of a chemical
 524 leach technique for estimating labile particulate aluminum, iron, and manganese in the
 525 Columbia River plume and coastal waters off Oregon and Washington. J. Geophys. Res. 113, 1–
 526 16. <https://doi.org/10.1029/2007jc004703>

527 Boyd, P.W., Ellwood, M.J., 2010. The biogeochemical cycle of iron in the ocean. Nat. Geosci. 3,
 528 675–682. <https://doi.org/10.1038/ngeo964>

529 Chapman, J.B., Weiss, D.J., Shan, Y., Lemburger, M., 2009. Iron isotope fractionation during
 530 leaching of granite and basalt by hydrochloric and oxalic acids. Geochim. Cosmochim. Acta 73,
 531 1312–1324. <https://doi.org/10.1016/j.gca.2008.11.037>

532 Chen, H., Grassian, V.H., 2013. Iron dissolution of dust source materials during simulated acidic
 533 processing: The effect of sulfuric, acetic, and oxalic acids. Environ. Sci. Technol. 47, 10312–
 534 10321. <https://doi.org/10.1021/es401285s>

535 Chen, T., Li, W., Guo, B., Liu, R., Li, G., Zhao, L., Ji, J., 2020. Reactive iron isotope signatures of
 536 the East Asian dust particles: Implications for iron cycling in the deep North Pacific. Chem.
 537 Geol. 531, 119342. <https://doi.org/10.1016/j.chemgeo.2019.119342>

- 538 Conway, T.M., Hamilton, D.S., Shelley, R.U., Aguilar-Islas, A.M., Landing, W.M., Mahowald,
539 N.M., John, S.G., 2019. Tracing and constraining anthropogenic aerosol iron fluxes to the North
540 Atlantic Ocean using iron isotopes. *Nat. Commun.* 10, 1–10. [https://doi.org/10.1038/s41467-](https://doi.org/10.1038/s41467-019-10457-w)
541 019-10457-w
- 542 Conway, T.M., John, S.G., 2014. Quantification of dissolved iron sources to the North Atlantic
543 Ocean. *Nature* 511, 212–215. <https://doi.org/10.1038/nature13482>
- 544 Dideriksen, K., Baker, J. a., Stipp, S.L.S., 2008. Equilibrium Fe isotope fractionation between
545 inorganic aqueous Fe(III) and the siderophore complex, Fe(III)-desferrioxamine B. *Earth Planet.*
546 *Sci. Lett.* 269, 280–290. <https://doi.org/10.1016/j.epsl.2008.02.022>
- 547 Domagal-Goldman, S.D., Kubicki, J.D., 2008. Density functional theory predictions of equilibrium
548 isotope fractionation of iron due to redox changes and organic complexation. *Geochim.*
549 *Cosmochim. Acta* 72, 5201–5216. <https://doi.org/10.1016/j.gca.2008.05.066>
- 550 Field, C.B., Behrenfeld, M.J., Randerson, J.T., Field, C.B., Behrenfeld, M.J., Randerson, J.T., 1998.
551 Primary Production of the Biosphere : Integrating Terrestrial and Oceanic Components
552 Published by : American Association for the Advancement of Science Stable URL :
553 <http://www.jstor.org/stable/2896014> Linked references are available on JSTOR for this arti.
554 *Science* (80-.). 281, 237–240.
- 555 Flament, P., Mattielli, N., Aimo, L., Choël, M., Deboudt, K., Jong, J. de, Rimetz-Planchon, J.,
556 Weis, D., 2008. Iron isotopic fractionation in industrial emissions and urban aerosols.
557 *Chemosphere* 73, 1793–1798. <https://doi.org/10.1016/j.chemosphere.2008.08.042>
- 558 Flossmann, A.I., Wobrock, W., 2019. Cloud processing of aerosol particles in marine stratocumulus
559 clouds. *Atmosphere (Basel)*. 10. <https://doi.org/10.3390/atmos10090520>
- 560 Geider, R.J., La Roche, J., 1994. The role of iron in phytoplankton photosynthesis, and the potential
561 for iron-limitation of primary productivity in the sea. *Photosynth. Res.* 39, 275–301.
562 <https://doi.org/10.1007/BF00014588>
- 563 Guo, J., Wang, Y., Shen, X., Wang, Z., Lee, T., Wang, X., Li, P., Sun, M., Collett, J.L., Wang, W.,
564 Wang, T., 2012. Characterization of cloud water chemistry at Mount Tai, China: Seasonal
565 variation, anthropogenic impact, and cloud processing. *Atmos. Environ.* 60, 467–476.
566 <https://doi.org/10.1016/j.atmosenv.2012.07.016>
- 567 Ito, A., Myriokefalitakis, S., Kanakidou, M., Mahowald, N.M., Scanza, R.A., Hamilton, D.S., Baker,
568 A.R., Jickells, T., Sarin, M., Bikkina, S., Gao, Y., Shelley, R.U., Buck, C.S., Landing, W.M.,
569 Bowie, A.R., Perron, M.M.G., Guieu, C., Meskhidze, N., Johnson, M.S., Feng, Y., Kok, J.F.,
570 Nenes, A., Duce, R.A., 2019. Pyrogenic iron: The missing link to high iron solubility in
571 aerosols. *Sci. Adv.* 5, eaau7671. <https://doi.org/10.1126/sciadv.aau7671>
- 572 Jickells, T.D., An, Z.S., Andersen, K.K., Baker, A.R., Bergametti, G., Brooks, N., Cao, J.J., Boyd,
573 P.W., Duce, R.A., Hunter, K.A., Kawahata, H., Kubilay, N., laRoche, J., Liss, P.S., Mahowald,
574 N., Prospero, J.M., Ridgwell, A.J., Tegen, I., Torres, R., 2005. Global Iron Connections
575 Between Desert Dust, Ocean Biogeochemistry, and Climate. *Science* (80-.). 308, 67 LP – 71.
576 <https://doi.org/10.1126/science.1105959>
- 577 Johansson, G., Yokoyama, H., 1990. Inner- and outer-sphere complex formation in aqueous erbium
578 halide and perchlorate solutions. An x-ray diffraction study using isostructural substitution.
579 *Inorg. Chem.* 29, 2460–2466. <https://doi.org/10.1021/ic00338a015>
- 580 Kiczka, M., Wiederhold, J.G., Frommer, J., Kraemer, S.M., Bourdon, B., Kretzschmar, R., 2010.

- 581 Iron isotope fractionation during proton- and ligand-promoted dissolution of primary
582 phyllosilicates. *Geochim. Cosmochim. Acta* 74, 3112–3128.
583 <https://doi.org/10.1016/j.gca.2010.02.018>
- 584 Kohfeld, K.E., Le Quéré, C., Harrison, S.P., Anderson, R.F., 2005. Role of marine biology in glacial-
585 interglacial CO₂ cycles. *Science* (80-.). 308, 74–78. <https://doi.org/10.1126/science.1105375>
- 586 Koretsky, C.M., Sverjensky, D.A., Sahai, N., 1998. A model of surface site types on oxide and
587 silicate minerals based on crystal chemistry; implications for site types and densities, multi-site
588 adsorption, surface infrared spectroscopy, and dissolution kinetics. *Am. J. Sci.* 298, 349–348.
- 589 Kurisu, M., Sakata, K., Miyamoto, C., Takaku, Y., Iizuka, T., Takahashi, Y., 2016a. Variation of
590 Iron Isotope Ratios in Anthropogenic Materials Emitted through Combustion Processes. *Chem.*
591 *Lett.* 45, 970–972. <https://doi.org/10.1246/cl.160451>
- 592 Kurisu, M., Takahashi, Y., Iizuka, T., Uematsu, M., 2016b. Very low isotope ratio of iron in fine
593 aerosols related to its contribution to the surface ocean. *J. Geophys. Res. Atmos.* 121, 11038–
594 11054. <https://doi.org/10.1002/2016JD024957>.Received
- 595 López-García, P., Gelado-Caballero, M.D., Patey, M.D., Hernández-Brito, J.J., 2021. Atmospheric
596 fluxes of soluble nutrients and Fe: More than three years of wet and dry deposition
597 measurements at Gran Canaria (Canary Islands). *Atmos. Environ.* 246.
598 <https://doi.org/10.1016/j.atmosenv.2020.118090>
- 599 Luo, C., Mahowald, N., Bond, T., Chuang, P.Y., Artaxo, P., Siefert, R., Chen, Y., Schauer, J., 2008.
600 Combustion iron distribution and deposition. *Global Biogeochem. Cycles* 22, 1–17.
601 <https://doi.org/10.1029/2007GB002964>
- 602 Mahowald, N.M., Baker, A.R., Bergametti, G., Brooks, N., Duce, R.A., Jickells, T.D., Kubilay, N.,
603 Prospero, J.M., Tegen, I., 2005. Atmospheric global dust cycle and iron inputs to the ocean.
604 *Global Biogeochem. Cycles* 19. <https://doi.org/10.1029/2004GB002402>
- 605 Majestic, B.J., Anbar, A.D., Herckes, P., 2009. Elemental and iron isotopic composition of aerosols
606 collected in a parking structure. *Sci. Total Environ.* 407, 5104–5109.
607 <https://doi.org/10.1016/j.scitotenv.2009.05.053>
- 608 Marris, H., Deboudt, K., Augustin, P., Flament, P., Blond, F., Fiani, E., Fourmentin, M., Delbarre,
609 H., 2012. Fast changes in chemical composition and size distribution of fine particles during the
610 near-field transport of industrial plumes. *Sci. Total Environ.* 427–428, 126–138.
611 <https://doi.org/10.1016/j.scitotenv.2012.03.068>
- 612 Marris, H., Deboudt, K., Flament, P., Grobéty, B., Gieré, R., 2013. Fe and Mn oxidation states by
613 TEM-EELS in fine-particle emissions from a Fe-Mn alloy making plant. *Environ. Sci. Technol.*
614 47, 10832–10840. <https://doi.org/10.1021/es400368s>
- 615 Martínez-García, A., Rosell-Melé, A., Jaccard, S.L., Geibert, W., Sigman, D.M., Haug, G.H., 2011.
616 Southern Ocean dust-climate coupling over the past four million years. *Nature* 476, 312–315.
617 <https://doi.org/10.1038/nature10310>
- 618 Maters, E.C., Flament, P., de Jong, J., Mattielli, N., Deboudt, K., 2017. Investigating Changes in Iron
619 Solubility and Isotopic Composition of Mineral Dust and Industrial Ash during Simulated
620 Atmospheric Processing, in: 2017 AGU Fall Meeting. New Orleans, Louisiana, pp. 11–15.
- 621 Mead, C., Herckes, P., Majestic, B.J., Anbar, A.D., 2013. Source apportionment of aerosol iron in
622 the marine environment using iron isotope analysis. *Geophys. Res. Lett.* 40, 5722–5727.
623 <https://doi.org/10.1002/2013GL057713>

- 624 Paris, R., Desboeufs, K. V., 2013. Effect of atmospheric organic complexation on iron-bearing dust
625 solubility. *Atmos. Chem. Phys.* 13, 4895–4905. <https://doi.org/10.5194/acp-13-4895-2013>
- 626 Poitrasson, F., 2006. On the iron isotope homogeneity level of the continental crust. *Chem. Geol.*
627 235, 195–200. <https://doi.org/10.1016/j.chemgeo.2006.06.010>
- 628 Poitrasson, F., Freydier, R., 2005. Heavy iron isotope composition of granites determined by high
629 resolution MC-ICP-MS. *Chem. Geol.* 222, 132–147.
630 <https://doi.org/10.1016/j.chemgeo.2005.07.005>
- 631 Pr eat, A.R., De Jong, J.T.M., Mamet, B.L., Mattielli, N., 2008. Stable iron isotopes and microbial
632 mediation in red pigmentation of the Rosso Ammonitico (mid-late Jurassic, Verona area, Italy).
633 *Astrobiology* 8, 841–857. <https://doi.org/10.1089/ast.2006.0035>
- 634 Radic, A., Lacan, F., Murray, J.W., 2011. Iron isotopes in the seawater of the equatorial Pacific
635 Ocean: New constraints for the oceanic iron cycle. *Earth Planet. Sci. Lett.* 306, 1–10.
636 <https://doi.org/10.1016/j.epsl.2011.03.015>
- 637 Raiswell, R., Vu, H.P., Brinza, L., Benning, L.G., 2010. The determination of labile Fe in
638 ferrihydrite by ascorbic acid extraction: Methodology, dissolution kinetics and loss of solubility
639 with age and de-watering. *Chem. Geol.* 278, 70–79.
640 <https://doi.org/10.1016/j.chemgeo.2010.09.002>
- 641 Revels, B.N., Zhang, R., Adkins, J.F., John, S.G., 2015. Fractionation of iron isotopes during
642 leaching of natural particles by acidic and circumneutral leaches and development of an optimal
643 leach for marine particulate iron isotopes. *Geochim. Cosmochim. Acta* 166, 92–104.
644 <https://doi.org/10.1016/j.gca.2015.05.034>
- 645 Schauble, E.A., Rossman, G.R., Taylor, H.P., 2001. Theoretical estimates of equilibrium Fe-isotope
646 fractionations from vibrational spectroscopy. *Geochim. Cosmochim. Acta* 65, 2487–2497.
647 [https://doi.org/10.1016/S0016-7037\(01\)00600-7](https://doi.org/10.1016/S0016-7037(01)00600-7)
- 648 Sedwick, P.N., Sholkovitz, E.R., Church, T.M., 2007. Impact of anthropogenic combustion
649 emissions on the fractional solubility of aerosol iron: Evidence from the Sargasso Sea.
650 *Geochemistry, Geophys. Geosystems* 8. <https://doi.org/10.1029/2007GC001586>
- 651 Shi, Z., Krom, M.D., Jickells, T.D., Bonneville, S., Carslaw, K.S., Mihalopoulos, N., Baker, A.R.,
652 Benning, L.G., 2012. Impacts on iron solubility in the mineral dust by processes in the source
653 region and the atmosphere: A review. *Aeolian Res.* 5, 21–42.
654 <https://doi.org/10.1016/j.aeolia.2012.03.001>
- 655 Stumm, W., 1995. The Inner-Sphere Surface Complex, in: Chin Pao Huang, Charles R. O'Melia,
656 J.J.M. (Ed.), *Aquatic Chemistry : Interfacial and Interspecies Processes*. American Chemical
657 Society, San Francisco, pp. 1–32. <https://doi.org/10.1021/ba-1995-0244.ch001>
- 658 Tagliabue, A., Bopp, L., Dutay, J.C., Bowie, A.R., Chever, F., Jean-Baptiste, P., Bucciarelli, E.,
659 Lannuzel, D., Remenyi, T., Sarthou, G., Aumont, O., Gehlen, M., Jeandel, C., 2010.
660 Hydrothermal contribution to the oceanic dissolved iron inventory. *Nat. Geosci.* 3, 252–256.
661 <https://doi.org/10.1038/ngeo818>
- 662 Tagliabue, A., Bowie, A.R., Boyd, P.W., Buck, K.N., Johnson, K.S., Saito, M.A., 2017. The integral
663 role of iron in ocean biogeochemistry. *Nature* 543, 51–59. <https://doi.org/10.1038/nature21058>
- 664 Teutsch, N., von Gunten, U., Porcelli, D., Cirpka, O.A., Halliday, A.N., 2005. Adsorption as a cause
665 for iron isotope fractionation in reduced groundwater. *Geochim. Cosmochim. Acta* 69, 4175–
666 4185. <https://doi.org/10.1016/j.gca.2005.04.007>

- 667 Waeles, M., Baker, A.R., Jickells, T., Hoogewerff, J., 2007. Global dust teleconnections: Aerosol
668 iron solubility and stable isotope composition. *Environ. Chem.* 4, 233–237.
669 <https://doi.org/10.1071/EN07013>
- 670 Warneck, P., 1988. *Chemistry of the natural atmosphere*. Academic Press, San Diego, CA.
- 671 Wiederhold, J.G., Kraemer, S.M., Teutsch, N., Borer, P.M., Halliday, A.N., Kretzschmar, R., 2006.
672 Iron isotope fractionation during proton-promoted, ligand-controlled, and reductive dissolution
673 of Goethite. *Environ. Sci. Technol.* 40, 3787–93.
- 674 Wiesli, R.A., Beard, B.L., Johnson, C.M., 2004. Experimental determination of Fe isotope
675 fractionation between aqueous Fe(II), siderite and “green rust” in abiotic systems. *Chem. Geol.*
676 211, 343–362. <https://doi.org/10.1016/j.chemgeo.2004.07.002>
- 677 Williams, H.M., McCammon, C.A., Peslier, A.H., Halliday, A.N., Teutsch, N., Levasseur, S., Burg,
678 J.P., 2004. Iron isotope fractionation and the oxygen fugacity of the mantle. *Science* (80-.). 304,
679 1656–1659. <https://doi.org/10.1126/science.1095679>
- 680
- 681