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# Subaerial volcanism is a potentially major contributor to oceanic iron and manganese cycles

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## Abstract

Surface ocean availability of the micronutrients iron and manganese influences primary productivity and carbon cycling in the ocean. Volcanic ash is rich in iron and manganese, but the global supply of these nutrients to the oceans via ash deposition is poorly constrained. Here, we use marine sediment-hosted ash composition data from ten volcanic regions, and subaerial volcanic eruption volumes, to estimate global ash-driven nutrient fluxes. Using Monte Carlo simulations, we estimate average fluxes of dissolved Iron and Manganese from volcanic sources to be between 50 – 500 (median 180) and 0.6 – 3.2 (median 1.3) Gmol yr<sup>-1</sup>, respectively. Much of the element release occurs during early diagenesis, indicating ash-rich shelf sediments are likely important suppliers of aqueous iron and manganese. Estimated ash-driven fluxes are of similar magnitude to aeolian inputs. We suggest that subaerial volcanism is an important, but underappreciated, source of these micronutrients to the global ocean.

## 26 **Introduction**

27 Primary production in the oceans is a major driver of the biogeochemical carbon cycle<sup>2,3</sup>, largely  
28 controlling carbon dioxide (CO<sub>2</sub>) exchange between oceanic and atmospheric carbon pools. The  
29 drawdown of atmospheric CO<sub>2</sub> via photosynthetic phytoplankton represents one of the largest  
30 atmospheric carbon sinks in the Earth System today, removing approximately 50 gigatons (Gt) carbon  
31 per year<sup>4</sup>. The importance of micronutrients, and in particular iron (Fe), in controlling levels of primary  
32 production has long been recognised<sup>5,6</sup>, with Fe essential to many biological processes<sup>5</sup>. Manganese  
33 (Mn) is also essential for phytoplankton photosynthesis<sup>7</sup>, with evidence it may act as a co-limiting  
34 nutrient<sup>8</sup>, especially in parts of the ocean containing low levels of dissolved Fe<sup>9</sup>.

35 There are multiple ways through which volcanoes may affect the climate on a range of timescales from  
36 hours to millions of years<sup>10,11</sup>. Volcanism can induce global climatic cooling via radiative forcing from  
37 sulfate injection<sup>12</sup>, but also potentially by oceanic fertilisation associated with the input of nutrient-rich  
38 ash<sup>13–16</sup>. Although experimental evidence demonstrates the release of nutrients from freshly-deposited  
39 ash (defined as all airborne volcanic particles under 2 mm in diameter) in surface seawater<sup>17</sup>, the impacts  
40 of this process appear to be restricted to transient algal blooms observed directly after eruptions<sup>18,19</sup>. In  
41 these cases, discrete eruptions may briefly alleviate nutrient deficiencies by providing a source of  
42 dissolved Fe<sup>11,18,20</sup>. Manganese supply from ash may also contribute to increases in productivity, with  
43 the addition of both Fe and Mn appearing to relieve Mn co-limitation after ash deposition<sup>21</sup>.

44 The major well-established routes by which dissolved Fe and Mn are delivered to the oceans are  
45 dissolved fluvial outflow, hydrothermal venting and desert dust deposition<sup>5,22,23</sup>. Although ash  
46 deposition has been invoked as a source of nutrients locally<sup>17,23</sup>, it is not generally considered in models  
47 of oceanic trace metal cycling<sup>22,24</sup>. Olgun et al.<sup>20</sup> compiled volcanic eruption rate data and undertook  
48 experimental studies of the amount of dissolved Fe released (over the course of 60 mins) by different  
49 types of fresh volcanic ash. This study concluded that 128–221 x 10<sup>12</sup> g yr<sup>-1</sup> of ash is delivered to the  
50 Pacific Ocean, releasing 0.003–0.075 Gmol yr<sup>-1</sup> of dissolved Fe to surface waters. This flux is  
51 comparable to the flux of dissolved Fe delivered to the Pacific Ocean by non-volcanic mineral dust  
52 (0.001–0.065 G mol yr<sup>-1</sup>)<sup>25</sup>.

53 Given the potential importance of volcanism for oceanic nutrient availability, we have sought to  
54 constrain the magnitude of the global dissolved Fe flux from a different perspective. We compare the  
55 composition of fresh ash from 10 active volcanic regions globally (Fig. 1) with the composition of ash  
56 recovered from marine sediments of various ages (Supplementary Fig. 1), to estimate the loss of Fe and  
57 Mn over a longer timescale than permitted in experimental studies (cf. ref.<sup>20</sup>). We combine this  
58 approach with the most recently available constraints on global volcanism rates derived from the Global  
59 Volcanism Program<sup>1</sup> to provide estimates of global volcanogenic Fe and Mn supply. The longer  
60 timescale approach is analogous to studies of dissolved and colloidal Fe released from shelf sediments  
61 during long-term diagenesis, which is known to be an important source of Fe to surface waters where  
62 it can stimulate phytoplankton growth<sup>26</sup>.

## 63 **Results and Discussion**

### 64 Diagenetic release of Fe and Mn from ash

65 Depletion factors, representing the difference between unaltered and altered ash metal contents (see  
66 Methods), for Fe (median 45% depletion) and Mn (median 20% depletion) suggest that a large  
67 proportion of these elements in ash is available to be released into seawater during particle settling and  
68 early diagenesis (Fig. 2). These Fe depletion factors are higher than those observed under laboratory  
69 conditions<sup>20</sup>. This is likely because Fe and Mn release continues much longer than the duration of such  
70 experiments, as a consequence of diagenetic processes once ash settles to the seafloor<sup>15,27</sup>.

71 While experimental work suggests that basaltic ash releases higher absolute Fe concentrations during  
72 dissolution than silicic ash<sup>28</sup>, the results from our study suggest that the rhyolitic ashes from the Taupo  
73 and Aleutian arcs proportionally (and counterintuitively) release the most Fe and Mn (Fig. 2). This  
74 unexpected relationship may be due to a higher ratio of surface-bound Fe to intra-silicate Fe in these  
75 samples<sup>29</sup>, and may not be indicative of greater absolute Fe and Mn release. Alternatively, this  
76 discrepancy may be linked to variations in secondary clay precipitation, a process which is controlled  
77 by a range of mineralogical and compositional factors, resulting in differing rates of ash alteration<sup>30</sup>.

78 Another factor that likely determines the rates of Fe and Mn release and depletion factor differences is  
79 grain size variations. Basaltic ash generally contains fewer very fine (<30 to 60  $\mu\text{m}$ ) particles (<1 – 4  
80 %) than rhyolitic and silicic ash (30 – >50 %) due to their eruption characteristics<sup>31</sup>. Thus, rhyolitic  
81 ashes (such as those from the Taupo arc) likely contain a greater proportion of fine particles, with a  
82 greater surface area/volume ratio, that react more extensively with seawater<sup>11</sup>.

83 Ashes from the Central American Volcanic Arc (Fig. 1a) show a distinctive behaviour from the other  
84 sites, with a large range of Fe depletion factors, and a number of ash layers demonstrating net adsorption  
85 of Fe (Fig. 2). The uptake of Fe and Mn by the ash may arise from the high nutrient supply in this area,  
86 as a result of equatorial upwelling of nutrient-rich Southern Ocean waters<sup>32–34</sup>. Pore water measurements  
87 from the region show that Mn (and Fe) are concentrated in the uppermost sedimentary layers, a result  
88 of the diffusive flux of these elements from deeper, suboxic sediment<sup>35</sup>.

#### 89 Global annual flux of Fe and Mn from ash diagenesis

90 The overall trends of depletion of Fe and Mn in ash recovered from marine sediments indicate that ash  
91 may be an important source of these nutrients to oceanic environments. Using a Monte Carlo modelling  
92 approach, we probabilistically estimated the most likely values for global annual input of Fe and Mn to  
93 the oceans arising from this process (see Methods). We employed well-constrained ranges of variables,  
94 which include annual ash production rates; ash geochemistry; ash density; and ash dispersal, to estimate  
95 overall Fe and Mn supply rates. The main aim of this exercise is to determine the net fluxes of dissolved  
96 Fe and Mn arising from the alteration of ash, rather than to study the specific geochemical and  
97 mineralogical processes that control these fluxes.

98 As we consider estimates of numerous variables in the construction of our model, each characterised  
99 by their own error, the use of a probabilistic approach is considered the most suitable. For example, the  
100 depletion factor values developed here are considered to represent the full range of feasible volcanic  
101 ash compositions, and thus, the mean and standard deviation of the dataset represent a credible range  
102 of values. As such, this variable is likely well-constrained. However, variables such as the amount of  
103 ash entering the ocean from each volcanic province (see Methods), which despite being based on a

104 method developed that considers prevailing winds and the weathering and post-depositional transport  
105 (via waterways and re-suspended material) of subaerially deposited ash<sup>20,36</sup>, is still uncertain. To tackle  
106 this problem, we apply additional error estimates to those values resulting in higher standard deviations,  
107 which help represent the inherent uncertainty of these variables.

108 Models of the biogeochemical Fe cycle typically consider four main sources of dissolved Fe;  
109 atmospheric deposition (comprising dust, fire and industrial sources), dissolved fluvial input, marine  
110 sediment diagenesis, and hydrothermal venting<sup>23,37</sup> (Table 1). Our simulations suggest a net flux of  
111 between 90 – 500 Gmol Fe yr<sup>-1</sup> (representing median values of the ‘small’ and ‘large’ ash volume  
112 scenarios; see Methods) to the oceans from ash deposition, dissolution, and diagenesis (Fig. 3). The  
113 median value derived from the ‘medium’ ash scenario (180 Gmol Fe yr<sup>-1</sup>) is higher than estimates of  
114 global dissolved fluvial Fe flux (27 Gmol Fe yr<sup>-1</sup>) and greater than the authigenic Fe flux (90 Gmol Fe  
115 yr<sup>-1</sup>) and that related to coastal erosion (140 Gmol Fe yr<sup>-1</sup>; refs.<sup>6,38</sup>). They are on the same order as  
116 postulated dust inputs, but this value does not consider the solubility of Fe in dust, estimated to be <1-  
117 4% (refs.<sup>23,39</sup>). Hence, the available Fe from dust sources (calculated as 3 – 11 Gmol Fe yr<sup>-1</sup>) is likely  
118 lower than our estimates of ash diagenesis input.

119 We now consider Mn fluxes related to this process. In current models of the Mn biogeochemical cycle,  
120 oceanic inputs are thought to derive predominantly from dissolved fluvial inputs (0.3 Gmol Mn yr<sup>-1</sup>),  
121 dust (5.6 Gmol Mn yr<sup>-1</sup>) and hydrothermal activity (102 Gmol Mn yr<sup>-1</sup>; ref.<sup>22</sup>). Our simulations suggest  
122 a likely net flux from ash diagenesis of 0.6 – 3.2 Gmol Mn yr<sup>-1</sup>, (Fig. 3), with the median value from  
123 the ‘medium’ scenario of 1.3 Gmol Mn yr<sup>-1</sup> comparable with both dissolved fluvial flux and atmospheric  
124 deposition, but smaller than the hydrothermal Mn flux (Table 1) and particulate fluvial flux<sup>40</sup>.

## 125 Implications for modern Fe and Mn cycles and the carbon cycle

126 Our estimates of the Fe (and to a lesser extent Mn) supply to the oceans from ash diagenesis are of the  
127 same order of magnitude as other sources (e.g. atmospheric deposition and dissolved riverine flux) and  
128 highlights the need to include this process in global budgets<sup>20</sup>. However, while most other Fe sources  
129 are not expected to show rapid changes in magnitudes over geologically short intervals, explosive

130 subaerial volcanic activity can show large (and apparently stochastic) variations over short time  
131 intervals. For example, while the global annual average eruption rate of ash is  $\sim 1 \text{ km}^3$  ash Dense Rock  
132 Equivalent (DRE), the eruption of Mount Pinatubo in 1991 (Volcanic Explosivity Index (VEI) 6)  
133 released more than  $5 \text{ km}^3$  of ash within a matter of days. Much of this ash was rapidly deposited in the  
134 ocean, covering roughly  $4 \times 10^6 \text{ km}^2$  of the South China Sea<sup>41</sup>.

135 Furthermore, the nature of ash supply to the oceans may mean that a large proportion of the nutrients  
136 are released in the upper ocean. Firstly, most volcanoes are located close to the oceans (Fig. 1), and ash  
137 will be supplied directly to the upper ocean and may be directly bioavailable. To provide an approximate  
138 estimate of bioavailability, we use the experimental data of ref.<sup>36</sup>, wherein ash from Montserrat  
139 (Caribbean Sea) was exposed to seawater to simulate dissolution for 6 months. We calculate that during  
140 this period,  $\sim 0.4\%$  of the total Fe, and  $\sim 14\%$  of the total Mn originally hosted in the ash was released  
141 (Supplementary Fig. 2), but that the reaction was still ongoing. These proportions appear small but  
142 when scaled up using our models, correspond to between  $0.82 - 4.43 \text{ Gmol Fe yr}^{-1}$ , on the same order  
143 of magnitude as aeolian dust supply<sup>6</sup> (Table 1). For Mn, the loss of 14% of the original ash content  
144 corresponds to between  $0.18 - 0.99 \text{ Gmol Mn yr}^{-1}$  being released in the upper ocean. The value of 14%  
145 Mn loss in the early stages of transport and burial represents 65% of total Mn depletion and suggests  
146 the bulk of Mn release occurs in this period (Supplementary Figs. 2, 3).

147 Most of the ash deposited in the oceans settles on continental shelves (Fig. 1, ref.<sup>42</sup>), which represent an  
148 important source of Fe to the ocean system<sup>43</sup>. Once sediment is deposited on the shallow seafloor,  
149 diagenetic processes (e.g. biological action and redox reactions) and wave action result in the flux of  
150 soluble and colloidal fractions of  $\text{Fe}^{2+}$  (and  $\text{Mn}^{2+}$ ) to the overlying water column<sup>44</sup>. These Fe- and Mn-  
151 enriched waters may then be advected into the open ocean<sup>26</sup>, as evidenced by the positive relationship  
152 between dissolved Fe concentrations of ocean water and proximity to continental shelves<sup>45</sup>. As a large  
153 proportion of Fe release likely occurs during early diagenesis on continental shelves, volcanic ash  
154 dissolution may be a component of boundary exchange of dissolved Fe, a mechanism for transporting  
155 shelf-hosted nutrients out to the open ocean<sup>46,47</sup>. This is supported by studies showing high Fe content  
156 in some water masses affected by high volcanogenic sediment supply<sup>48-50</sup>. Analysis of the Fe isotopic

157 composition of one such location, offshore of the Crozet Islands, indicates a volcanic signature of the  
158 dissolved Fe, related to volcanogenic sediment diagenesis and weathering<sup>51,52</sup>. This is supported by Fe  
159 isotope evidence from the western Pacific Ocean<sup>53,54</sup> and the Southern Ocean<sup>55</sup>, where isotopically  
160 heavy Fe is linked to non-reductive dissolution of shelf-sediment Fe-bearing phases. In view of this  
161 evidence, it appears that much of the Fe (and some of the Mn) added to the oceans via ash deposition  
162 may have previously been included in estimates of the overall sedimentary fluxes, rather than  
163 representing an entirely new flux (Table 1). Estimates of the magnitude of Fe release during diagenesis  
164 of shelf sediments vary widely. For example, in a recent sedimentary flux model comparison, estimates  
165 of Fe supply varied between 0.6 – 194 Gmol yr<sup>-1</sup><sup>24</sup>. This highlights the need for further investigation  
166 into benthic fluxes on a shelf-by shelf basis, to provide quantitative estimates of Fe supply via  
167 weathering, followed by assessments of exactly how much of this flux is ash-related. Our work also  
168 indicates the need for models of biogeochemical cycling to consider the input of large, apparently  
169 stochastic events such as volcanic eruptions on Fe and Mn cycles. Such work may help indicate the  
170 impact of individual events which supply a large amount of nutrients to certain area of the oceans, and  
171 how internal marine processes may act to cycle these inputs.

## 172 **Methods**

### 173 **Major and Trace Element Geochemistry**

174 We analysed ash layers from IODP Holes U1396C (Lesser Antilles) and U1339D (Aleutian Islands).  
175 Ash layers were identified visually (at macro- and microscopic scales) in the case of Hole U1339D, and  
176 via their relatively low CaCO<sub>3</sub> contents in Hole U1396C. To avoid inclusion of pelagic sediment, only  
177 samples located within the centre of ash layers were used. Such an approach also circumvents the  
178 potential impact of bioturbation. Bulk sample geochemistry for Holes U1396C and U1339D was  
179 determined via a closed vessel Aqua Regia digest (at 60°C), after which samples were dried, then further  
180 digested using a HF/HClO<sub>4</sub> mix (at 130°C), followed by a HClO<sub>4</sub> digest (at 130°C) before a final HCl  
181 dissolution. Digests were resuspended in 2% HNO<sub>3</sub> and analysed on a Thermo Scientific X-Series ICP-  
182 MS at the University of Southampton. Alongside samples, blanks and a reference material (HISS-1



183 marine sediment standard) were prepared and analysed using the same procedure (Supplementary Table  
184 1). Data from Hole U1396C were supplemented by previously published values<sup>56</sup>.

### 185 Chemical Depletion Factors

186 In addition to newly analysed ash layers from the Lesser Antilles and the Aleutian Islands, a database  
187 of previously published altered marine ash compositions was compiled from a selection of volcanic  
188 settings, from subduction zones (e.g. Aleutian Arc, Kamchatka), convergent margins (e.g. Taupo  
189 Volcanic Zone, Izu-Bonin Arc) and oceanic islands (e.g. Canary Islands) (Figure 1; Supplementary  
190 Table 2). Most of these data come from point-based geochemical methods (electron microprobe and  
191 laser ablation ICP-MS) of individual ash shards.

192 Unaltered protolith compositions were obtained from the GeoRoc database ([http://georoc.mpch-](http://georoc.mpch-mainz.gwdg.de)  
193 [mainz.gwdg.de](http://georoc.mpch-mainz.gwdg.de)) for volcanic material from the source regions for each of the published marine ash  
194 compositions. These data were filtered to remove data relating to non-outcropping subaerial samples,  
195 xenoliths, and any inclusion-based analyses, leaving only measurements of bulk igneous rock  
196 compositions. The database was used to reconstruct the most likely original composition of the erupted  
197 material prior to marine diagenesis. The comparison of bulk rock compositions to point-based glass  
198 shard analyses may result in an overestimation of depletion. This is because the glass in mafic ash will  
199 contain low Fe, but the accompanying minerals (for example pyroxenes) may have a high Fe content,  
200 but will not be considered in the measurements, leading to anomalously high depletion factors.  
201 However, glass typically makes up the majority of volcanic ash, and even in Fe rich minerals, Fe would  
202 not comprise the entirety of the material, so we believe our comparison is valid.

203 The method follows that developed by ref.<sup>57</sup> to calculate metal mobility in Cretaceous ash layers, in  
204 which the elements of interest (M) are normalised to the Ti and Zr concentrations. These elements are  
205 largely immobile during diagenesis<sup>58</sup>, so variations in their concentrations in ash derived from a single  
206 source largely reflect magmatic differentiation processes<sup>13</sup>. The empirical relationship between Ti/Zr  
207 and M/Zr (as calculated from the GeoRoc database) can then be used to estimate the original  
208 composition of the unaltered volcanic protolith (Fig. 4). In each case, the empirical relationship is

209 represented by a linear or polynomial regression (Supplementary Table 2), and the equations are used  
 210 to back-calculate the unaltered protolith composition. The best fitting regression is determined by both  
 211 examination of the correlation coefficient, but also by determination of which fit best suits the altered  
 212 tephra dataset. For example, with Iceland we employ polynomial regression, due to the low Fe/Zr ratios  
 213 of most tephra compositions. Here, a linear relationship would not represent these data well, and lead  
 214 to underestimation of the depletion factor (Supplementary Figure 4). These compositions are then  
 215 compared to the marine ash data to calculate changes in composition during diagenesis<sup>13</sup> according to  
 216 Equation 1, which is shown here using Fe as the element of interest, as an example:

$$217 \quad Fe_D = \frac{M_{Fe}^L}{M_{Fe}^O} = 1 - \frac{\left(\frac{C_{Fe}^{re}}{C_{Zr}^{re}}\right)}{\left(\frac{C_{Fe}^O}{C_{Zr}^O}\right)} \quad (\text{Eq. 1})$$

218 The left side of the equation represents the fraction depleted, where  $M_{Fe}^O$  is the original mass of Fe in  
 219 the rock, and  $M_{Fe}^L$  what has been lost.  $C_{Fe}^{re}$  and  $C_{Zr}^{re}$  are the concentrations of Zr and Fe in the altered  
 220 ash, and so  $C_{Fe}^{re}/C_{Zr}^{re}$  represents the Fe/Zr ratio in the ash.  $C_{Fe}^O/C_{Zr}^O$  represents the Fe/Zr ratio in the  
 221 original rock, calculated using the GeoRoc-derived relationship between Fe/Zr and Ti/Zr (e.g., Fig. 4).  
 222 Graphs of M/Zr vs Ti/Zr for all locations are provided in Supplementary Figures 4-7.

223 To estimate annual inputs of Fe and Mn to the ocean from ash diagenesis, a Monte Carlo based  
 224 modelling approach (c.f.<sup>59</sup>) is applied using likely ranges of each of the pertinent parameters. For each  
 225 variable, the r package *rtruncnorm* was used to generate 10,000 random data points between two  
 226 boundaries assuming a normal distribution according to defined mean and standard deviation values  
 227 (Table 1).

228 Annual ash fluxes to the ocean are estimated from data derived from the Global Volcanism Program  
 229 database (GVP; ref.<sup>1</sup>). This database contains the location, style and intensity of volcanic activity  
 230 (Supplementary Tables 3, 4, 5), and was used in association with GeoRoc to estimate the elemental  
 231 composition of erupted ash (Fig. 1b-1e). In our analysis, we limit the data from GVP to eruptions from  
 232 the start of 1960 to the end of 2019, as before 1960 the knowledge of smaller eruptions becomes less

233 certain. Using the GVP's archive of VEI (Supplementary Table 5), we estimated the amount of ash  
234 erupted annually, by converting the VEI of eruptions into Dense Rock Equivalent (DRE) volume. Since  
235 small eruptions are unlikely to result in ash plumes and are insignificant in terms of ash delivery to the  
236 oceans, we do not consider any eruptions  $\leq$ VEI 2. As a VEI indicates a range of potential volumes (e.g.,  
237 VEI 5 is 1 – 10 km<sup>3</sup> DRE), for each eruption we produce three possible scenarios; a low (e.g., 1 km<sup>3</sup> for  
238 VEI 5), medium (e.g., 5 km<sup>3</sup> for VEI 5) and high (e.g., 10 km<sup>3</sup> for VEI 5) scenario. Wherever possible,  
239 we constrain larger eruption estimates using published data (see Supplementary Table 6). We use our  
240 'low', 'medium' and 'high' scenarios to attain three estimates of ash deposition for each year. We then  
241 sum and average the values of each scenario for each year, yielding three estimates of yearly ash input:  
242 a 'low' scenario of 0.47 km<sup>3</sup> yr<sup>-1</sup>, a 'medium' scenario of 1.07 km<sup>3</sup> yr<sup>-1</sup> and a 'high' scenario of 1.81  
243 km<sup>3</sup> yr<sup>-1</sup> (Fig. 1e), all of which are broadly consistent with an earlier estimate of 1 km<sup>3</sup> yr<sup>-1</sup> (ref.<sup>60</sup>). Using  
244 the average and standard deviation of each scenario, we run 10,000 simulations of ash volume per year,  
245 and use these values in our estimates of Fe and Mn supply, resulting in estimation of total Mn and Fe  
246 supply for three scenarios (Fig. 3, Supplementary Fig. 8).

247 One limitation of using the period 1960 – 2019 is that we do not include any eruptions >VEI 6, since  
248 the last was Tambora in 1815. To assess the impact of such an event on our estimates, we calculate  
249 (using the same approach as above), the ash flux for all eruptions between VEI 2 and VEI 4 from 1960  
250 – 2019, which yields a value of 0.57 km<sup>3</sup> yr<sup>-1</sup> (Supplementary Figure 9). Assuming this is representative  
251 of background ash flux (i.e. all eruptions smaller than VEI 5), we take this as a baseline value for flux  
252 back to 1800, and add in all larger eruptions, using published data for volumes wherever possible  
253 (Supplementary Figure 9; Supplementary Table 6). By averaging these data, we obtain an estimate of  
254 annual ash flux of 1.42 km<sup>3</sup> yr<sup>-1</sup>, greater than the estimate derived from the period 1960-Present  
255 (Supplementary Figure 9). This indicates how these periodic large events may play a controlling role in  
256 total ash volumes and indicating that our first approach may yield an underestimation. However, the  
257 incompleteness of eruption data prior to 1960 means we do not use this value in modelling.

258 To account for the composition of erupted ash, we categorise all eruptions according to their eruption  
259 style (Supplementary Tables 3,4) and assess the percentage contribution of each style of eruption (Fig.

260 1b). Using lithological data available through GeoRoc, we estimate the Fe and Mn concentrations in  
261 material supplied from each volcanic source, and using the percentage of eruptions from the GVP,  
262 convert this to absolute ranges in composition (Supplementary Tables 7 and 8). This exercise suggests  
263 that, on average, ash (i.e. a combination of all ash types, locations and eruptions styles) contains  $6 \pm 1$   
264 wt.% Fe and  $0.12 \pm 0.02$  wt.% Mn (Supplementary Table 9). To convert from volume to density we use  
265 an average ash density of  $1400 \text{ kg/m}^3$ , with a standard deviation of  $133 \text{ kg/m}^3$  (ref.<sup>61</sup>). Finally, we use  
266 the depletion factors derived above, to convert from absolute values of Fe and Mn to the amount  
267 released to the oceans during ash transport and diagenesis. For these values we use mean depletion  
268 factors, and the standard deviation of the entire dataset (Supplementary Table 10). To avoid  
269 unreasonable under- or over-estimation, we place boundaries derived from the 10% and 90% percentiles  
270 of the data to our simulations (Supplementary Table 10).

271 To ensure we do not include ash which does not fall into the ocean, we sort the GVP data by sub-region,  
272 and estimate the proportion of ash which falls into the ocean at each location (using prevailing wind  
273 directions and the position of the sub-region, cf. ref.<sup>20</sup>). In making these estimates, we directly consider  
274 published isopachs and examples of marine sedimentary deposition from each of the regions (see  
275 Supplementary Table 11). This approach relies upon several assumptions, namely that wind directions  
276 may not be in the prevailing direction when a volcano erupts. To account for this, we have included  
277 conservative estimates for ash fall, and large errors for those that are more uncertain (see Supplementary  
278 Table 11). For example, even for mid-ocean regions which are located on small islands (such as Vanuatu  
279 and Jan Mayen), we only estimate 85% of ash falling into the ocean, when it is likely to be higher.  
280 Further, by using Monte Carlo modelling, we incorporated the uncertainty in this value into the estimate.  
281 We use GVP data to investigate the number of each size of eruptive event from each region, deriving  
282 three scenarios ('low', 'medium' and 'high') of ash volume for each individual region in a similar  
283 manner to our estimate of total ash volume (Supplementary Table 12). From this we derive three  
284 estimates of ash volume for each of the regions. We use the results of the 'medium' scenario to inform  
285 further modelling. This is because it represents a middle point in possible ash volumes and is likely to  
286 be closest to the truth with respect to the magnitude of ash weathering. This process occurs when fresh

287 ash is weathered via surface runoff, with the content of the ash leached, to then enter the ocean in  
288 particulate or dissolved forms<sup>36,62</sup>. Evidence for the scale of this process may come from Montserrat,  
289 where Fe and Mn levels in rivers which drain fresh ash are enriched when compared to those which do  
290 not<sup>36</sup>. Further, large quantities of subaerially deposited ash may be resuspended and transported to  
291 the oceans, as was observed across Iceland in the aftermath of the Eyjafjallajökull eruption in  
292 2010<sup>63</sup>, and pumice rafting may act to transport ash further away from eruption locations<sup>64,65</sup>. Using  
293 this method does not allow us to indicate exactly how fast the depletion occurs, but evidence suggests  
294 there is no link between ash age and depletion factor (Supplementary Figure. 1), indicating that  
295 depletion occurs at an early stage of deposition and diagenesis.

296 Using the outputs from each simulation, we calculate results using equation 2 for calculation of the  
297 amount of Fe release:

$$298 \quad Fe \text{ release (mole)} = \left( \frac{V_{Ash} \times \rho_{Ash} \times Fe_{Ash} \times Fe_D}{55.845} \right) \times P_{ocean} \text{ (Eq. 2)}$$

299 Where  $V_{Ash}$  and  $\rho_{Ash}$  are the volume and density of ash, respectively,  $Fe_{Ash}$  is the average proportion of  
300 Fe in igneous rock as defined above, and  $Fe_D$  is the depletion of Fe as calculate using Equation 1.,  
301 55.845 is the atomic mass of Fe, used to convert from grams to moles, and  $P_{ocean}$  is the proportion of  
302 ash that settles into the ocean. As we use three scenarios for the ash volume estimation, we derive three  
303 ranges of total Fe and Mn supply, from which we extract the median to indicate a likely value for each  
304 scenario and set of models (Supplementary Table 13).

## 305 **References**

- 306 1. Global Volcanism Program, T. *Volcanoes of the World, v4.8.4*. (Smithsonian Institution, 2013).  
307 doi:doi.org/10.5479/si.GVP.VOTW4-2013.
- 308 2. Del Giorgio, P. A. & Duarte, C. M. Respiration in the open ocean. *Nature* **420**, 379–384 (2002).
- 309 3. Field, C. B., Behrenfeld, M. J., Randerson, J. T. & Falkowski, P. Primary production of the  
310 biosphere: Integrating terrestrial and oceanic components. *Science (80-. )*. **281**, 237–240 (1998).
- 311 4. Ciais, P. *et al.* Carbon and Other Biogeochemical Cycles. in *Climate Change The physical*  
312 *Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the*  
313 *intergovernmental Panel on Climate Change* (eds. Stocker, T. F. et al.) 465–570 (Cambridge  
314 University Press, 2013).
- 315 5. Tagliabue, A. *et al.* The integral role of iron in ocean biogeochemistry. *Nature* vol. 543 51–59

- 316 (2017).
- 317 6. Jickells, T. D. *et al.* Global iron connections between desert dust, ocean biogeochemistry, and  
318 climate. *Science (80-. )*. **308**, 67–71 (2005).
- 319 7. Raven, J. A. Predictions of Mn and Fe use efficiencies of phototrophic growth as a function of  
320 light availability for growth and of C assimilation pathway. *New Phytol.* **116**, 1–18 (1990).
- 321 8. Wu, M. *et al.* Manganese and iron deficiency in Southern Ocean *Phaeocystis antarctica*  
322 populations revealed through taxon-specific protein indicators. *Nat. Commun.* **10**, (2019).
- 323 9. Peers, G. & Price, N. M. A role for manganese in superoxide dismutases and growth of iron-  
324 deficient diatoms. *Limnol. Oceanogr.* **49**, 1774–1783 (2004).
- 325 10. Robock, A. Volcanic eruptions and climate. *Rev. Geophys.* **38**, 191–219 (2000).
- 326 11. Ayrís, P. M. & Delmelle, P. The immediate environmental effects of tephra emission. *Bull.*  
327 *Volcanol.* **74**, 1905–1936 (2012).
- 328 12. Soreghan, G. S., Soreghan, M. J. & Heavens, N. G. Explosive volcanism as a key driver of the  
329 late Paleozoic ice age. *Geology* **47**, 600–604 (2019).
- 330 13. Lee, C.-T. A. *et al.* Volcanic ash as a driver of enhanced organic carbon burial in the Cretaceous.  
331 *Sci. Rep.* **8**, 4197 (2018).
- 332 14. Lee, C.-T. & Dee, S. Does volcanism cause warming or cooling? *Geology* **47**, 687–688 (2019).
- 333 15. Longman, J., Palmer, M. R., Gernon, T. M. & Manners, H. R. The role of tephra in enhancing  
334 organic carbon preservation in marine sediments. *Earth-Science Rev.* **192**, 480–490 (2019).
- 335 16. G. Perron, M. M., C. Proemse, B., Michal Strzelec, Melanie Gault-Ringold & R. Bowie, A.  
336 Atmospheric inputs of volcanic iron around Heard and McDonald Islands, Southern ocean.  
337 *Environ. Sci. Atmos.* (2021) doi:10.1039/D1EA00054C.
- 338 17. Jones, M. T. & Gislason, S. R. Rapid releases of metal salts and nutrients following the  
339 deposition of volcanic ash into aqueous environments. *Geochim. Cosmochim. Acta* **72**, 3661–  
340 3680 (2008).
- 341 18. Langmann, B., Zakšek, K., Hort, M. & Duggen, S. Volcanic ash as fertiliser for the surface  
342 ocean. *Atmos. Chem. Phys.* **10**, 3891–3899 (2010).
- 343 19. Achterberg, E. P. *et al.* Natural iron fertilization by the Eyjafjallajökull volcanic eruption.  
344 *Geophys. Res. Lett.* **40**, 921–926 (2013).
- 345 20. Olgun, N. *et al.* Surface ocean iron fertilization: The role of airborne volcanic ash from  
346 subduction zone and hot spot volcanoes and related iron fluxes into the Pacific Ocean. *Global*  
347 *Biogeochem. Cycles* **25**, n/a-n/a (2011).
- 348 21. Browning, T. J. *et al.* Strong responses of Southern Ocean phytoplankton communities to  
349 volcanic ash. *Geophys. Res. Lett.* **41**, 2851–2857 (2014).
- 350 22. Van Hulten, M. *et al.* Manganese in the west Atlantic Ocean in the context of the first global  
351 ocean circulation model of manganese. *Biogeosciences* **14**, 1123–1152 (2017).
- 352 23. Mahowald, N. M. *et al.* Aerosol trace metal leaching and impacts on marine microorganisms.  
353 *Nat. Commun.* **9**, (2018).
- 354 24. Tagliabue, A. *et al.* How well do global ocean biogeochemistry models simulate dissolved iron  
355 distributions? *Global Biogeochem. Cycles* **30**, 149–174 (2016).
- 356 25. Mahowald, N. M. *et al.* Atmospheric global dust cycle and iron inputs to the ocean. *Global*  
357 *Biogeochem. Cycles* **19**, (2005).

- 358 26. Chase, Z., Hales, B., Cowles, T., Schwartz, R. & van Geen, A. Distribution and variability of  
359 iron input to Oregon coastal waters during the upwelling season. *J. Geophys. Res. C Ocean.* **110**,  
360 1–14 (2005).
- 361 27. Murray, N. A., McManus, J., Palmer, M. R., Haley, B. & Manners, H. Diagenesis in tephra-rich  
362 sediments from the Lesser Antilles Volcanic Arc: Pore fluid constraints. *Geochim. Cosmochim.*  
363 *Acta* **228**, 119–135 (2018).
- 364 28. Damby, D. E. *et al.* Assessment of the potential respiratory hazard of volcanic ash from future  
365 Icelandic eruptions: A study of archived basaltic to rhyolitic ash samples. *Environ. Heal. A Glob.*  
366 *Access Sci. Source* **16**, (2017).
- 367 29. Oelkers, E. H. & Gislason, S. R. The mechanism, rates and consequences of basaltic glass  
368 dissolution: I. An experimental study of the dissolution rates of basaltic glass as a function of  
369 aqueous Al, Si and oxalic acid concentration at 25°C and pH 3 and 11. *Geochim. Cosmochim.*  
370 **65**, 3671–3681 (2001).
- 371 30. Wada, K. Minerals formed and mineral formation from volcanic ash by weathering. *Chem. Geol.*  
372 **60**, 17–28 (1987).
- 373 31. Rose, W. I. & Durant, A. J. Fine ash content of explosive eruptions. *J. Volcanol. Geotherm. Res.*  
374 **186**, 32–39 (2009).
- 375 32. Toggweiler, J. R., Dixon, K. & Broecker, W. S. The Peru upwelling and the ventilation of the  
376 south Pacific thermocline. *J. Geophys. Res.* **96**, 20467 (1991).
- 377 33. Calvo, E., Pelejero, C., Pena, L. D., Cacho, I. & Logan, G. A. Eastern Equatorial Pacific  
378 productivity and related-CO<sub>2</sub> changes since the last glacial period. *Proc. Natl. Acad. Sci. U. S.*  
379 *A.* **108**, 5537–5541 (2011).
- 380 34. Sarmiento, J. L., Gruber, N., Brzezinski, M. A. & Dunne, J. P. High-latitude controls of  
381 thermocline nutrients and low latitude biological productivity. *Nature* **427**, 56–60 (2004).
- 382 35. Sawlan, J. J. & Murray, J. W. Trace metal remobilization in the interstitial waters of red clay  
383 and hemipelagic marine sediments. *Earth Planet. Sci. Lett.* **64**, 213–230 (1983).
- 384 36. Jones, M. T. *et al.* The weathering and element fluxes from active volcanoes to the oceans: A  
385 Montserrat case study. *Bull. Volcanol.* **73**, 207–222 (2011).
- 386 37. Raiswell, R. *et al.* Potentially bioavailable iron delivery by iceberg-hosted sediments and  
387 atmospheric dust to the polar oceans. *Biogeosciences* **13**, 3887–3900 (2016).
- 388 38. Poulton, S. W. & Raiswell, R. The low-temperature geochemical cycle of iron: From continental  
389 fluxes to marine sediment deposition. *Am. J. Sci.* **302**, 774–805 (2002).
- 390 39. Schroth, A. W., Crusius, J., Sholkovitz, E. R. & Bostick, B. C. Iron solubility driven by  
391 speciation in dust sources to the ocean. *Nat. Geosci.* **2**, 337–340 (2009).
- 392 40. Viers, J., Dupré, B. & Gaillardet, J. Chemical composition of suspended sediments in World  
393 Rivers: New insights from a new database. *Sci. Total Environ.* **407**, 853–868 (2009).
- 394 41. Paladio-Melasantos, M. L. *et al.* Tephra falls of the 1991 eruptions of Mount Pinatubo. in *Fire*  
395 *and mud; eruptions and lahars of Mount Pinatubo, Philippines, Philippine Institute of*  
396 *Volcanology and Seismology, Quezon City* (eds. Newhall, C. G. & Punongbayan, R. S.) 413–  
397 535 (University of Washington Press, 1996).
- 398 42. Longman, J., Palmer, M. R. & Gernon, T. M. Viability of greenhouse gas removal via artificial  
399 addition of volcanic ash to the ocean. *Anthropocene* **32**, (2020).
- 400 43. Elrod, V. A., Berelson, W. M., Coale, K. H. & Johnson, K. S. The flux of iron from continental  
401 shelf sediments: A missing source for global budgets. *Geophys. Res. Lett.* **31**, n/a-n/a (2004).

- 402 44. Aller, R. C. Sedimentary Diagenesis, Depositional Environments, and Benthic Fluxes. in  
403 *Treatise on Geochemistry: Second Edition* vol. 8 293–334 (Elsevier Inc., 2013).
- 404 45. Coale, K. H. *et al.* Southern Ocean Iron Enrichment Experiment: Carbon Cycling in High- and  
405 Low-Si Waters. *Science (80-. )*. **304**, 408–414 (2004).
- 406 46. Jeandel, C. & Oelkers, E. H. The influence of terrigenous particulate material dissolution on  
407 ocean chemistry and global element cycles. *Chem. Geol.* **395**, 50–66 (2015).
- 408 47. Jeandel, C. Overview of the mechanisms that could explain the ‘Boundary Exchange’ at the  
409 land–ocean contact. *Philos. Trans. R. Soc. A Math. Phys. Eng. Sci.* **374**, 20150287 (2016).
- 410 48. Lam, P. J. & Bishop, J. K. B. The continental margin is a key source of iron to the HNLC North  
411 Pacific Ocean. *Geophys. Res. Lett.* **35**, n/a-n/a (2008).
- 412 49. Nishioka, J. *et al.* Iron supply to the western subarctic Pacific: Importance of iron export from  
413 the Sea of Okhotsk. *J. Geophys. Res.* **112**, C10012 (2007).
- 414 50. Nishioka, J. *et al.* Intensive mixing along an island chain controls oceanic biogeochemical  
415 cycles. *Global Biogeochem. Cycles* **27**, 920–929 (2013).
- 416 51. Homoky, W. B. *et al.* Iron and manganese diagenesis in deep sea volcanogenic sediments and  
417 the origins of pore water colloids. *Geochim. Cosmochim. Acta* **75**, 5032–5048 (2011).
- 418 52. Homoky, W. B., John, S. G., Conway, T. M. & Mills, R. A. Distinct iron isotopic signatures and  
419 supply from marine sediment dissolution. *Nat. Commun.* **4**, 1–10 (2013).
- 420 53. Radic, A., Lacan, F. & Murray, J. W. Iron isotopes in the seawater of the equatorial Pacific  
421 Ocean: New constraints for the oceanic iron cycle. *Earth Planet. Sci. Lett.* **306**, 1–10 (2011).
- 422 54. Labatut, M. *et al.* Iron sources and dissolved-particulate interactions in the seawater of the  
423 Western Equatorial Pacific, iron isotope perspectives. *Global Biogeochem. Cycles* **28**, 1044–  
424 1065 (2014).
- 425 55. Abadie, C., Lacan, F., Radic, A., Pradoux, C. & Poitrasson, F. Iron isotopes reveal distinct  
426 dissolved iron sources and pathways in the intermediate versus deep Southern Ocean. *Proc. Natl.*  
427 *Acad. Sci. U. S. A.* **114**, 858–863 (2017).
- 428 56. Murray, N. A. *et al.* Data report: dissolved minor element compositions, sediment major and  
429 minor element concentrations, and reactive iron and manganese data from the Lesser Antilles  
430 volcanic arc region, IODP Expedition 340 Sites U1394, U1395, U1396, U1399, and U1400.  
431 **340**,.
- 432 57. Lee, C.-T. A. *et al.* Volcanic ash as a driver of enhanced organic carbon burial in the Cretaceous.  
433 *Sci. Rep.* **8**, 4197 (2018).
- 434 58. Brimhall, G. H. & Dietrich, W. E. Constitutive mass balance relations between chemical  
435 composition, volume, density, porosity, and strain in metasomatic hydrochemical systems:  
436 Results on weathering and pedogenesis. *Geochim. Cosmochim. Acta* **51**, 567–587 (1987).
- 437 59. Gernon, T. M., Hincks, T. K., Tyrrell, T., Rohling, E. J. & Palmer, M. R. Snowball Earth ocean  
438 chemistry driven by extensive ridge volcanism during Rodinia breakup. *Nat. Geosci.* **9**, 242–  
439 248 (2016).
- 440 60. Pyle, D. M. Mass and energy budgets of explosive volcanic eruptions. *Geophys. Res. Lett.* **22**,  
441 563–566 (1995).
- 442 61. Gudmundsson, M. T. *et al.* Ash generation and distribution from the April-May 2010 eruption  
443 of Eyjafjallajökull, Iceland. *Sci. Rep.* **2**, 572 (2012).
- 444 62. Aiuppa, A. *et al.* Major-ion bulk deposition around an active volcano (Mt. Etna, Italy). *Bull.*



- 445 *Volcanol.* **68**, 255–265 (2006).
- 446 63. Thorsteinsson, T., Jóhannsson, T., Stohl, A. & Kristiansen, N. I. High levels of particulate matter  
447 in Iceland due to direct ash emissions by the Eyjafjallajökull eruption and resuspension of  
448 deposited ash. *J. Geophys. Res. Solid Earth* **117**, 0–05 (2012).
- 449 64. Jutzeler, M. *et al.* On the fate of pumice rafts formed during the 2012 Havre submarine eruption.  
450 *Nat. Commun.* **5**, 1–10 (2014).
- 451 65. Rossi, E., Bagheri, G., Beckett, F. & Bonadonna, C. The fate of volcanic ash: premature or  
452 delayed sedimentation? *Nat. Commun.* **2021 121** **12**, 1–9 (2021).
- 453 66. Jones, M. T. *et al.* Riverine particulate material dissolution as a significant flux of strontium to  
454 the oceans. *Earth Planet. Sci. Lett.* **355–356**, 51–59 (2012).
- 455 67. Wessel, P. & Smith, W. H. F. A global, self-consistent, hierarchical, high-resolution shoreline  
456 database. *J. Geophys. Res. B Solid Earth* **101**, 8741–8743 (1996).
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## 463 **Author contributions**

464 J.L., M.R.P and T.M.G. designed the study, interpreted the data and wrote the manuscript, with input  
465 from M.T.J. J.L. collated data and performed the modelling. H.R.M. performed ICP-MS analysis on  
466 sediment and ash samples and acquired the data. M.T.J. provided data from ash dissolution experiments  
467 and contributed to their interpretation.

## 468 **Competing interests**

469 The authors declare no competing interests.

## 470 **Materials and Correspondence**

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## 473 **Data Availability**

474 Authors can confirm that all relevant data are included in the paper and/or its supplementary information  
475 files. Supplementary Data 1 and 2, along with Supplementary Table 12, may be found at  
476 10.6084/m9.figshare.19107644.

## 477 **Tables**

478 **Table 1: Global Fe and Mn fluxes comparing previously published estimates of sources and the**  
479 **new estimates presented here.** <sup>a</sup> Estimates of Fe flux from ref.<sup>6</sup>. <sup>b</sup> Value of diagenetic Fe and Mn fluxes  
480 developed using our new estimates of global ash production and oceanic deposition and estimates of  
481 element release during 6-month experiment from ref.<sup>66</sup>. <sup>c</sup> Estimates of diagenetic Fe and Mn flux from  
482 this study, with the range representing the ‘small’ and ‘large’ ash deposition scenarios (see Methods  
483 and Supplementary Table 13). <sup>d</sup> Estimates of Mn flux from ref.<sup>22</sup>.

<b>Annual Fe Flux (Gmol yr<sup>-1</sup>)</b>	
Fluvial particulate total iron <sup>a</sup>	11192-17226
Fluvial dissolved iron <sup>a</sup>	27
Glacial sediments <sup>a</sup>	609
Atmospheric (i.e., aeolian) <sup>a</sup>	287
Hydrothermal <sup>a</sup>	251
Authigenic <sup>a</sup>	90
Early release from ash <sup>b</sup>	0.8-4.4
Diagenetic release from ash <sup>c</sup>	91-493
<b>Annual Mn Flux (Gmol yr<sup>-1</sup>)</b>	
Dust <sup>d</sup>	5.6
Fluvial dissolved Mn <sup>d</sup>	0.3
Sediment <sup>d</sup>	3.4
Hydrothermal <sup>d</sup>	102.3
Early release from ash <sup>b</sup>	0.18-0.99
Diagenetic release from ash <sup>c</sup>	0.39-2.19

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## 488 **Figures**

489 **Figure 1: Global map indicating volcanic provinces used in this study, and compilation of data**  
490 **from the Global Volcanism Program (GVP).** (a) source regions used to construct unaltered protolith  
491 compositions, indicated by numbers and coloured shading: I) Aleutian Island arc, II) Central American  
492 volcanic arc, III) Lesser Antilles island arc, IV) Iceland, V) Azores, VI) Kerguelen, VII) Sunda arc,  
493 VIII) Kyushu-Ryukyu arc, IX) Izu-Bonin arc, X) Kamchatka-Kurile arc, XI) Taupo volcanic zone. Map  
494 was created using the vector shorelines of ref.<sup>67</sup>. (b) percentage of eruption events occurring at each type  
495 of volcanic location, denoted by colour and symbols for fully continental (star), intermediate locations  
496 on plate boundaries (upward-pointing triangle), oceanic (square) and unknown (downward-pointing  
497 triangle). (c) proportion of each rock type as a percentage of all eruptive events since 1960. Rock types  
498 are foidite (f), basalt (b), trachybasalt (tb), trachyte (t), phonolite (p), andesite (a), rhyolite (r), dacite (d)  
499 and trachyandesite (ta). (d) proportion of each rock type as a percentage of all ash deposited via  
500 eruptions since 1960, with rock types labelled as in panel c. (e) erupted ash volume (in km<sup>3</sup> DRE) of  
501 each year since 1960, using GVP data representing the three ash volume scenarios (see Methods); ‘low’  
502 (pink line), ‘medium’ (blue line) and ‘high’ (green line). The horizontal lines indicate the average values  
503 for each of the scenarios; 0.47 km<sup>3</sup> yr<sup>-1</sup> for ‘low’, 1.07 km<sup>3</sup> yr<sup>-1</sup> for ‘medium and 1.81 km<sup>3</sup> yr<sup>-1</sup> for ‘high’.

504 **Figure 2: Depletion factors for each volcanic province for both manganese and iron.** Box plots  
505 detailing the distribution of depletion factor data from each volcanic province are presented for  
506 manganese (a) and iron (b), indicating likely levels of depletion/adsorption in each locality. Colour of  
507 the boxes indicates the ocean region of each province, either Atlantic (green), Indian (pink), North and  
508 West Pacific (blue) or East Pacific (orange). Boxes are defined between the first and third quartile (the  
509 interquartile range, IQR), with minimum and maximum whiskers representative of 1.5 times the IQR,  
510 and suspected outliers (>1.5 times the IQR) indicated by black circles.

511 **Figure 3: Monte Carlo simulations of likely Iron and Manganese supply to the oceans annually,**  
512 **representative of the ‘medium’ ash volume scenario.** Presented are simulations for iron (a) and  
513 manganese (b). For both panels the amount of ash supplied annually is presented along the x-axis, with  
514 the total annual supply of the element on the y-axis. These Monte Carlo simulations are indicated by

515 circles, with their colour indicating the depletion factor used in the simulation. A summary of the data  
516 is presented as a box plot on the right of each panel, developed in the same manner as those shown in  
517 Fig. 2.

518 **Figure 4: Plots of Fe/Zr and Mn/Zr versus Ti/Zr for the Aleutian arc.** Presented here are data for  
519 (a) Fe and (b) Mn. In blue are GeoRoc-derived protolith compositions, from which the linear  
520 relationships indicated the lower right of each panels are defined. Red circles indicate measured altered  
521 ash deposit analyses, plotted against the expected trend for unaltered material. The dashed lines indicate  
522 the percentage depletion. Similar graphs for all other active volcanic regions can be found in  
523 Supplementary Figures 4-7.

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