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

Jack Longman^{a, b*}, Martin R. Palmer^b, Thomas M. Gernon^b, Hayley R. Manners^{b, c}, Morgan T. Jones^d

^a Marine Isotope Geochemistry, Institute for Chemistry and Biology of the Marine Environment (ICBM), University of Oldenburg, Carl von Ossietzky Str. 9-11, 26129 Oldenburg, Germany

^b School of Ocean and Earth Sciences, University of Southampton, Southampton, SO14 3ZH, United Kingdom

^c School of Geography, Earth and Environmental Sciences, University of Plymouth, Plymouth, PL4 8AA, United Kingdom

^d Centre for Earth Evolution and Dynamics (CEED), Department of Geosciences, University of Oslo, Sem Sælands vei 2A, 0371 Oslo, Norway

*Corresponding author; jack.longman@uni-oldenburg.de

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⁻¹, 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^{2,3}, largely
28 controlling carbon dioxide (CO₂) exchange between oceanic and atmospheric carbon pools. The
29 drawdown of atmospheric CO₂ 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 year⁴. The importance of micronutrients, and in particular iron (Fe), in controlling levels of primary
32 production has long been recognised^{5,6}, with Fe essential to many biological processes⁵. Manganese
33 (Mn) is also essential for phytoplankton photosynthesis⁷, with evidence it may act as a co-limiting
34 nutrient⁸, especially in parts of the ocean containing low levels of dissolved Fe⁹.

35 There are multiple ways through which volcanoes may affect the climate on a range of timescales from
36 hours to millions of years^{10,11}. Volcanism can induce global climatic cooling via radiative forcing from
37 sulfate injection¹², but also potentially by oceanic fertilisation associated with the input of nutrient-rich
38 ash^{13–16}. 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 seawater¹⁷, the impacts
40 of this process appear to be restricted to transient algal blooms observed directly after eruptions^{18,19}. In
41 these cases, discrete eruptions may briefly alleviate nutrient deficiencies by providing a source of
42 dissolved Fe^{11,18,20}. 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 deposition²¹.

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^{5,22,23}. Although ash
46 deposition has been invoked as a source of nutrients locally^{17,23}, it is not generally considered in models
47 of oceanic trace metal cycling^{22,24}. Olgun et al.²⁰ 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 10¹² g yr⁻¹ of ash is delivered to the
50 Pacific Ocean, releasing 0.003–0.075 Gmol yr⁻¹ 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⁻¹)²⁵.

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.²⁰). We combine this
58 approach with the most recently available constraints on global volcanism rates derived from the Global
59 Volcanism Program¹ 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 growth²⁶.

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 conditions²⁰. 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^{15,27}.

71 While experimental work suggests that basaltic ash releases higher absolute Fe concentrations during
72 dissolution than silicic ash²⁸, 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 samples²⁹, 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 alteration³⁰.

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 μm) particles (<1 – 4
80 %) than rhyolitic and silicic ash (30 – >50 %) due to their eruption characteristics³¹. 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 seawater¹¹.

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^{32–34}. 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 sediment³⁵.

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^{20,36}, 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^{23,37} (Table 1). Our simulations suggest a net flux of
111 between 90 – 500 Gmol Fe yr⁻¹ (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⁻¹) is higher than estimates of
114 global dissolved fluvial Fe flux (27 Gmol Fe yr⁻¹) and greater than the authigenic Fe flux (90 Gmol Fe
115 yr⁻¹) and that related to coastal erosion (140 Gmol Fe yr⁻¹; refs.^{6,38}). 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.^{23,39}). Hence, the available Fe from dust sources (calculated as 3 – 11 Gmol Fe yr⁻¹) 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⁻¹),
121 dust (5.6 Gmol Mn yr⁻¹) and hydrothermal activity (102 Gmol Mn yr⁻¹; ref.²²). Our simulations suggest
122 a likely net flux from ash diagenesis of 0.6 – 3.2 Gmol Mn yr⁻¹, (Fig. 3), with the median value from
123 the ‘medium’ scenario of 1.3 Gmol Mn yr⁻¹ comparable with both dissolved fluvial flux and atmospheric
124 deposition, but smaller than the hydrothermal Mn flux (Table 1) and particulate fluvial flux⁴⁰.

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 budgets²⁰. 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 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 Sea⁴¹.

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.³⁶, 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 supply⁶ (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.⁴²), which represent an
148 important source of Fe to the ocean system⁴³. 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 Fe^{2+} (and Mn^{2+}) to the overlying water column⁴⁴. These Fe- and Mn-
151 enriched waters may then be advected into the open ocean²⁶, as evidenced by the positive relationship
152 between dissolved Fe concentrations of ocean water and proximity to continental shelves⁴⁵. 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^{46,47}. This is supported by studies showing high Fe content
156 in some water masses affected by high volcanogenic sediment supply⁴⁸⁻⁵⁰. 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^{51,52}. This is supported by Fe
159 isotope evidence from the western Pacific Ocean^{53,54} and the Southern Ocean⁵⁵, 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⁻¹²⁴. 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 CaCO₃ 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/HClO₄ mix (at 130°C), followed by a HClO₄ digest (at 130°C) before a final HCl
181 dissolution. Digests were resuspended in 2% HNO₃ 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 values⁵⁶.

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.⁵⁷ 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 diagenesis⁵⁸, so variations in their concentrations in ash derived from a single
206 source largely reflect magmatic differentiation processes¹³. 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 diagenesis¹³ 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.⁵⁹) 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.¹). 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 km³ DRE), for each eruption we produce three possible scenarios; a low (e.g., 1 km³ for
238 VEI 5), medium (e.g., 5 km³ for VEI 5) and high (e.g., 10 km³ 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 km³ yr⁻¹, a 'medium' scenario of 1.07 km³ yr⁻¹ and a 'high' scenario of 1.81
243 km³ yr⁻¹ (Fig. 1e), all of which are broadly consistent with an earlier estimate of 1 km³ yr⁻¹ (ref.⁶⁰). 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 km³ yr⁻¹ (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 km³ yr⁻¹, 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 ± 1
264 wt.% Fe and 0.12 ± 0.02 wt.% Mn (Supplementary Table 9). To convert from volume to density we use
265 an average ash density of 1400 kg/m^3 , with a standard deviation of 133 kg/m^3 (ref.⁶¹). 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.²⁰). 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^{36,62}. 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 not³⁶. 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 2010⁶³, and pumice rafting may act to transport ash further away from eruption locations^{64,65}. 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 ρ_{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).

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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**

471 All correspondence and requests for materials should be directed to Jack Longman ([jack.longman@uni-](mailto:jack.longman@uni-oldenburg.de)
472 [oldenburg.de](mailto:jack.longman@uni-oldenburg.de)).

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.** ^a Estimates of Fe flux from ref.⁶. ^b 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.⁶⁶. ^c 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). ^d Estimates of Mn flux from ref.²².

Annual Fe Flux (Gmol yr⁻¹)	
Fluvial particulate total iron ^a	11192-17226
Fluvial dissolved iron ^a	27
Glacial sediments ^a	609
Atmospheric (i.e., aeolian) ^a	287
Hydrothermal ^a	251
Authigenic ^a	90
Early release from ash ^b	0.8-4.4
Diagenetic release from ash ^c	91-493
Annual Mn Flux (Gmol yr⁻¹)	
Dust ^d	5.6
Fluvial dissolved Mn ^d	0.3
Sediment ^d	3.4
Hydrothermal ^d	102.3
Early release from ash ^b	0.18-0.99
Diagenetic release from ash ^c	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.⁶⁷. (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 km³ 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 km³ yr⁻¹ for ‘low’, 1.07 km³ yr⁻¹ for ‘medium and 1.81 km³ yr⁻¹ 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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