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1 **Release of tephra-hosted iron during early diagenesis** 2 **fingerprinted by iron isotopes**

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12 **Abstract**

13 The micronutrient iron (Fe) plays a fundamental role controlling primary productivity in the upper
14 ocean, with volcanic eruptions and deposition of airborne volcanic material (termed tephra) a potential
15 source of Fe. Here, we investigate the geochemical and Fe isotopic ($\delta^{56}\text{Fe}$) composition of tephra layers,
16 sediments, and mixed tephra-sediment samples from the Integrated Ocean Drilling Program (IODP)
17 Hole 1396C, located offshore the volcanically active island of Montserrat in the Lesser Antilles,
18 Caribbean Sea. We find that buried tephtras, which have experienced diagenesis, exhibit lighter $\delta^{56}\text{Fe}$
19 (relative to standard IRMM-524a) compositions (down to $-0.26 \pm 0.04\%$, 2SD) than fresh tephra
20 deposited on Montserrat ($\delta^{56}\text{Fe} = 0.02 \pm 0.02\%$, 2SD). Such negative values suggest that isotopically
21 heavier Fe has been lost from the originally deposited material. Using multivariate statistical modelling
22 and mass balance constraints, we identify the outward Fe flux (with calculated $\delta^{56}\text{Fe}$ of $0.21 \pm 0.31\%$,
23 2SD, n=12) during non-reductive dissolution of tephra as the likely cause of the retention of these light
24 $\delta^{56}\text{Fe}$ compositions. Due to the widespread nature of tephra deposition, tephra diagenesis may provide
25 an important source of isotopically heavy dissolved Fe to the oceans. This process contrasts with more
26 commonly considered reductive dissolution processes, which provide a source of Fe enriched in light
27 isotopes to the oceans.

28 Introduction

29 As an essential micronutrient for phytoplankton photosynthesis, iron (Fe) availability is directly linked
30 to primary productivity and plankton community structure in modern high-latitude oceans (Falkowski
31 et al., 1998; Kolber et al., 1994; Martin and Fitzwater, 1988; Tagliabue et al., 2017). Because primary
32 productivity is one of the most important mechanisms determining air-sea CO₂ exchange, understanding
33 Fe biogeochemistry is key to understanding marine carbon cycling (Tagliabue et al., 2017).

34 Fe is supplied to the ocean via rivers, aeolian deposition, hydrothermal vents and remobilisation of
35 sediment-hosted Fe (Homoky et al., 2013; Johnson et al., 2020; König et al., 2021). In addition,
36 volcanism, and especially the eruptive dispersal of tephra, may provide an important episodic input of
37 Fe to the Earth's surface environment (Longman et al., 2022; Olgun et al., 2011). Explosive volcanism
38 results in the total eruption of ~1 km³ of tephra (or unconsolidated pyroclastic material including pore
39 space) every year (Pyle, 1995), and because most volcanoes are located islands or near continental
40 margins, as much as 45% of this tephra enters the ocean (Longman et al., 2022). Upon entering the
41 ocean, tephra reacts rapidly with seawater, releasing large quantities of macro- and micro-nutrients such
42 as Fe (Frogner et al., 2001; Jones and Gislason, 2008). A first estimate of the scale of this nutrient
43 supply indicates tephra may deliver between 50 – 500 Gmol yr⁻¹ of Fe to the oceans, with a median
44 value of 180 Gmol yr⁻¹ (Longman et al., 2022). The Fe delivery associated with tephra could therefore
45 alleviate nutrient deficiencies for phytoplankton in Fe-limited regions of the ocean (Achterberg et al.,
46 2013; Duggen et al., 2010; Moore et al., 2013; Olgun et al., 2013). Further, the release of other
47 micronutrients such as Mn during this process mean tephra may also supply other co-limiting nutrients
48 (Browning et al., 2021, 2014; Longman et al., 2020). The magnitude of this Fe source is also
49 highlighted by the observation that roughly 30% of Pacific sediment located close (within 1000km)
50 active arcs is comprised of tephra (Scudder et al., 2014, 2009). However, despite the potential
51 importance to oceanic Fe budgets, the supply of Fe from diagenesis of volcanic material within the
52 sediment is poorly constrained and not explicitly represented in ocean biogeochemical models of Fe
53 (König et al., 2021; Tagliabue et al., 2016).

54 One method for investigating the cycling of Fe in the ocean uses its isotopic composition, typically
55 presented as $\delta^{56}\text{Fe}$ relative to a measured standard. This composition can help trace the sources, sinks
56 and fluxes of Fe in the oceans and sediments (Conway and John, 2014; Homoky et al., 2013; Radic et
57 al., 2011), provided the external sources of dissolved (Fe in solution; dFe) and particulate (Fe associated
58 with particles $>0.2\mu\text{m}$; pFe) Fe to the oceans and the processes that fractionate Fe isotopes within the
59 ocean system are understood (Johnson et al., 2020).

60 Typically, sources of Fe to the ocean such as dust and Fe release from oxic sediment, have isotopic
61 signatures close to crustal values ($0.09 \pm 0.07\text{‰}$; Beard et al., 2003). However, these compositions may
62 be modified in parts of the ocean influenced by variable redox conditions (Johnson et al., 2020). For
63 example, in low-oxygen sedimentary environments, reductive dissolution of Fe (a product of
64 dissimilatory microbial reactions) leads to the release of negative $\delta^{56}\text{Fe}$ compositions to porewaters,
65 with values reaching as low as -3.3‰ (Homoky et al., 2009). Hydrothermal vent fluids typically have
66 $\delta^{56}\text{Fe}$ between -0.1 to -0.5‰ (Bennett et al., 2009; Johnson et al., 2020), but can be modified by the
67 precipitation of sulfides or oxides. These precipitation reactions occur when either of the species are
68 saturated in the fluids, with precipitates preferentially incorporating lighter (when sulfides form) and
69 heavier isotopes (when oxides form), thereby fractionating the Fe which remains in the fluid (Lough et
70 al., 2017).

71 In addition to these reductive dissolution pathways, heavy ($\delta^{56}\text{Fe} > 0\text{‰}$) lithogenic Fe signatures have
72 been observed in porewaters (Homoky et al., 2013; 2021) and seawater (Conway and John, 2014; Radic
73 et al., 2011) in some deep water locations. This has been attributed to non-reductive dissolution (NRD)
74 of lithogenic material in oxidising sediments, and indicates these oxic sediments may be an additional
75 source of dFe to the oceans (Abadie et al., 2017; Homoky et al., 2013; König et al., 2021). This process,
76 via the production of organomineral Fe colloids, may provide a mechanism by which lithogenic $\delta^{56}\text{Fe}$
77 compositions are added to the ocean interior from oxidising margins (Homoky et al., 2021). Notably,
78 the oxidative weathering of volcanoclastic material containing high organic carbon content ($>1\%$)
79 produces porewater with the highest concentration of Fe colloids with crustal isotope compositions
80 (Homoky et al., 2021).

81 Here, we present Fe isotopic compositions from sediments, tephtras and mixed sediment-tephra layers
82 from offshore Montserrat in the Caribbean Sea to estimate the Fe isotopic composition of Fe lost during
83 tephra diagenesis. We combine these data with multivariate partitioning methods and calculations of
84 the depletion factors and mass balance calculations to estimate the isotopic composition of Fe supplied
85 to the ocean via dissolution of tephra during water column transport and early diagenesis.

86 Methods

87 Study Site, Sampling and Age Model

88 Integrated Ocean Drilling Program (IODP) Hole 1396C was drilled as part of Expedition 340 in August-
89 September 2012 (Le Friant et al., 2013). It is located ~30 km west of Montserrat at 16°30.5'N,
90 62°27.1'W (Fig. 1), and was drilled to a depth of 139.4 m below seafloor (mbsf). The core is carbonate-
91 dominated, with abundant tephra layers and a minor contribution from terrigenous sediments. Bulk
92 marine sediment and visually distinct discrete tephra layers were both sampled. For the samples from
93 the tephra layers, efforts were made to sample from the centre of the layer to attain a purely volcanic
94 signal. In addition to the IODP samples, we also studied fresh tephra from the 8th January 2010 eruption
95 of the Soufrière Hills volcano, Montserrat.

96 Elemental analysis

97 Freeze-dried and homogenized tephra (n=18) and sediment (n=44) samples were dissolved using a
98 mixed acid (HCl-HF-HNO₃) benchtop method. Solutions were diluted 1:5000 and analysed using a
99 Thermo X-Series at the University of Southampton following the protocol of Longman et al. (2022).
100 The certified reference material HISS-1 (sandy marine sediment), and procedural blanks were prepared
101 and analysed in the same manner. For this work, a full suite of major and trace elements was analysed.
102 Blank content was shown to be negligible for all elements, and recoveries for HISS-1 were within 10%
103 of expected values for most elements (see Supplementary Table 1). For Fe, 2 measurements of HISS-1
104 averaged 2950 ppm, with an expected value of 2460 (recovery 97%). Blanks for Fe were on average
105 0.66 ppm, or 0.02% of the standard material. Porewater analysis of Fe was completed using the method
106 of Murray et al. (2016). Briefly, pore waters were diluted to a 1:20 ratio using 1% distilled nitric acid

107 before analysis on a Leeman Labs Prodigy ICP-OES at Oregon State University. The fresh tephra was
108 analysed via X-Ray Fluorescence (Philips PW 2400) analysis at the University of Oldenburg. 600mg
109 of sample was mixed with 3600 mg of a 1:1 dilithiumtetraborate:lithiummetaborate mixture, pre-
110 oxidised at 500 °C with NH_4NO_3 and fused to form a glass bead. The in-house standard PS_S was
111 prepared and analysed in the same manner. Fe_2O_3 content in the measured standard was 4.91%, compared
112 to a long-term average of 4.76%.

113 Carbon analyses

114 Total organic carbon (TOC) measurements were made at Oregon State University following the method
115 of Goñi et al. (2003), as reported in Murray et al. (2016). Further details on methods, blanks and
116 reproducibility can be found in Murray et al. (2016).

117 Fe isotope analysis

118 A portion of the samples analysed for major and trace elements, and the fresh tephra sample, were
119 analysed for their Fe isotope composition ($n = 20$). Samples were homogenized using an agate pestle
120 and mortar prior to digestion of around 25mg of sample via a mixed acid ($\text{HNO}_3\text{-HClO}_4\text{-HF}$) closed-
121 vessel approach (Böning et al., 2004). Blanks and certified reference materials were dissolved in the
122 same manner as samples. Aliquots of the digested samples were then purified via column chemistry
123 (Böning et al., 2020; Dauphas et al., 2009). Samples were taken up in 6M HCl and Fe separation was
124 performed using 1.8 mL AG1X8 anion resin (100–200 mesh, Bio-Rad) loaded onto PP columns (Bio-
125 Rad). After separation, samples were treated with H_2O_2 to remove any organic compounds leached from
126 the columns, before drying. All purification was completed using ultra-clean acids in the clean
127 laboratory facilities of the ICBM, University of Oldenburg.

128 Purified samples were diluted (to 3% HNO_3 and 3.3 ppm Fe) and analysed using a Thermo-Scientific
129 Neptune *Plus* multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) at the
130 ICBM, Oldenburg. NIST 986 (National Institute of Standards and Technology, USA), a certified Ni
131 isotope standard, was quantitatively added to each sample and standard for mass bias correction (Oeser
132 et al., 2014). Signal intensity was ~15V for Fe and ~3V for Ni. Interference of ^{54}Cr on ^{54}Fe was

133 monitored and corrected using ^{52}Cr (Weyer and Schwieters, 2003). Analysis of each sample was
134 bracketed by a repeat standard (IRMM-524a), which is indistinguishable (within experimental
135 uncertainty) from the more widely used isotope standard IRMM-14 (González De Vega et al., 2020).
136 All results and comparisons to the literature are reported in delta notation relative to the mean of repeat
137 IRMM-524 values (n= 112):

$$138 \delta^{56}\text{Fe} (\text{‰}) = [({}^{56}\text{Fe}/{}^{54}\text{Fe}_{\text{sample}})/({}^{56}\text{Fe}/{}^{54}\text{Fe}_{\text{IRMM-524}})] * 10^3$$

139 The reference materials SDO-1 (Devonian shale, US Geological Survey), BHVO-2 (Hawaiian basalt,
140 US Geological Survey) and HISS-1 (marine sandy sediment, National Research Council of Canada)
141 were used to assess the accuracy of Fe separations and measurements. Measurements of SDO-1 ($\delta^{56}\text{Fe}$
142 = $0.027 \pm 0.017\text{‰}$, n=10, two digests, 2SD) were in good agreement with published values of $0.023 \pm$
143 0.028‰ (Schoenberg and Von Blanckenburg, 2005), and $0.026 \pm 0.045\text{‰}$ (Böning et al., 2020).
144 Measurements of BHVO-2 ($\delta^{56}\text{Fe} = 0.078 \pm 0.041\text{‰}$, n=3, 2SD) were within error of previously
145 published values of $0.121 \pm 0.049\text{‰}$ (Liu et al., 2014), and $0.100 \pm 0.060\text{‰}$ (Foden et al., 2018).
146 Procedural blanks were negligible (<0.1% of total Fe in the lowest concentration sample).

147 Numerical analysis

148 Multivariate Partitioning

149 We used a series of multivariate techniques to determine the sediment provenance and the relative
150 contribution of each source to the sediment mixture deposited at Hole U1396C. First, we assessed the
151 relationships between element concentrations with r^2 matrices, x versus y element plots, and ternary
152 plots to identify trends, outliers, and simple covariation patterns (Supplementary Figures 1-5). Second,
153 we selected elements in the dataset that were predominantly affiliated with the aluminosilicate fraction
154 of the sediment and applied Q-mode Factor Analysis (QFA; Pisiias et al., 2013). To ensure the robustness
155 of the QFA results, we tested many combinations of elements, ran iterations with sample outliers
156 removed, and assessed the sensitivity of the results when an additional factor was added or subtracted.
157 Furthermore, we selected elements that were unique from those used in our tephra depletion model (Zr,
158 Ti; see below) to determine if an independent technique produced similar results. Guided by the x versus

159 y plots, ternary diagrams, and QFA results, elements and end-members were selected on the basis that
160 they could be statistically differentiated in the dataset. The element concentration data were then
161 modelled using constrained-least squares multiple linear regression (CLS; Pisiyas et al., 2013; Dunlea et
162 al., 2015; Dunlea and Murray, 2015).

163 In the CLS mixing models, thousands of combinations of possible end-members from published studies
164 or discrete layers measured in this study were tested to best fit the geochemical dataset in this study.
165 The CLS model aims to minimize the difference between the model and measured data. Our preferred
166 model was selected based on the strength of correlation coefficients of the CLS model and our
167 geological knowledge of which sediment sources would feasibly be found at Hole U1396C (see
168 Supplementary Tales. 5-9, Supplementary Text).

169 Tephra Fe depletion calculations

170 We used two approaches to calculate early diagenetic Fe depletion factors for samples that were tephra-
171 rich (>75% tephra contribution as estimated from the CLS model): Zr-normalisation after Lee et al.
172 (2018), and a multivariate CLS model. Zr-normalisation compares the Fe/Zr and Ti/Zr ratios of the
173 analysed ashes to a reference dataset of Caribbean volcanic rocks, derived from the GeoROC database
174 (c.f. Longman et al., 2021; Longman et al., 2022). Data were downloaded from <https://georoc.eu/>, with
175 all original publications and the specific search terms listed in the Supplementary Text. Here, Zr and
176 Zr/Ti are assumed to be immobile whereas Fe may be mobilised during early diagenesis (Lee et al.,
177 2018). The linear regression between the Fe/Zr and Ti/Zr of the igneous rock dataset is interpreted to
178 represent the unaltered protolith of the tephra analysed here (Supplementary Figure 1). Using this
179 relationship and the measured Ti/Zr of the tephra layers, an original Fe/Zr composition can be back-
180 calculated, and depletion factors (DF) estimated, using the following equation:

$$181 \quad DF_{Fe} = \frac{M_{Fe}^L}{M_{Fe}^O} = 1 - \frac{\left(\frac{C_{Fe}^{re}}{C_{Zr}^{re}}\right)}{\left(\frac{C_{Fe}^O}{C_{Zr}^O}\right)} \quad (\text{Eq. 1})$$

182 Where the left side of the equation is the Fe depletion factor, DF_{Fe} (in %), with M_{Fe}^O the original Fe
183 mass in the protolith and with M_{Fe}^L the mass of Fe lost from the protolith C_{Fe}^{re} and C_{Zr}^{re} are the mass
184 concentrations of Fe and Zr in analysed tephra, and C_{Fe}^O / C_{Zr}^O represents the Fe/Zr ratio of the protolith.
185 All masses are in wt%, with oxide content corrected where necessary.

186 A second approach, based on the end-member compositions and mass fractions from the CLS model
187 was also applied to the discrete tephra layer and bulk sediment samples. The mass fraction of each end-
188 member within each sample was multiplied by the concentration of Fe in that end-member. Summing
189 the contributions of Fe from each end-member provides an estimate of how much Fe is expected in each
190 sample if no Fe had been lost from the original tephra composition. As such, the total measured Fe in
191 the sample can be subtracted from the predicted Fe content to obtain a depleted fraction:

$$192 \quad f_{EM1} * [Fe]_{EM1} + f_{EM2} * [Fe]_{EM2} + f_{EM3} * [Fe]_{EM3} = \text{Total } [Fe]_{tephra} \text{ (Eq. 2)}$$

193 where f_{EM} = the fraction (0-1) of an end-member present in tephra. The difference between the predicted
194 total Fe concentration in tephra ($\text{Total } [Fe]_{tephra}$) and the independently measured Fe content in tephra
195 and sediment samples provides an estimate of the total Fe (wt. %) lost or gained during early diagenesis.

196 Results and Discussion

197 Sources of sediment in Hole U1396C

198 The multivariate statistical analyses identified three end-members defined from the major and trace
199 metal dataset in the aluminosilicate fraction (i.e., non-carbonate component) of sediment at Hole
200 U1396C. Because the Al and Ti concentrations are much higher than the concentrations of the other
201 trace elements, they have more influence on the outcome of the model. For example, the magnitude of
202 a small variation in Al can still be much larger than a relatively significant variation in Nb. To avoid
203 this bias toward higher concentration elements, we did not use Al and Ti in the CLS model and instead
204 relied on elements in the ppm range. The factor analysis suggests that three aluminosilicate components
205 can be distinguished with or without Al and Ti included. In our preferred model, the QFA uses a
206 combination of trace and rare earth elements (Co, Nb, Y, La, Ce, Eu, Yb, and Th) to explain 97% of the
207 data variability with three factors (Fig. 2). The first aluminosilicate factor identified in the QFA

208 explained 45% of the variability in the dataset and indicated a strong covariance (i.e., high VARIMAX
209 factor scores) among Nb, La, Ce, and Th throughout the samples (Fig. 2). The second factor explained
210 36% of the variability of the dataset and indicated a strong covariance among Y, Ce, Eu, and Yb. The
211 third factor explained 16% of the dataset and showed a covariance between Co and Eu.

212 After testing thousands of different combinations of end-members in the CLS model to find the best fit
213 for these element concentrations (Dunlea and Murray, 2015), QFA Factors 1-3 were interpreted to
214 represent a continental dust source and two andesitic tephra end-members, respectively. In the CLS
215 model, a continental dust end-member was chosen to approximate the composition of upper continental
216 crust (Rudnick and Gao, 2013). This interpretation is in accord with previous studies that show Saharan
217 dust forms a minor component of marine sediments in this area (Reid et al., 1996). The first andesitic
218 tephra with a more felsic composition used in the model was a discrete tephra layer measured in this
219 study (134.63 mbsf at Site U1396), but was also represented well by a subaerial tephra from Montserrat
220 (Sample 11.1.4C from Coussens et al., 2017). The second andesitic tephra end-member with a more
221 mafic composition than the other andesitic tephra layers is represented best by a tephra composition
222 from the Las Sierra volcanoes in Nicaragua (Schindlbeck et al., 2018), but the composition is also
223 similar to a subaerial tephra from Montserrat (Sample 9.2.1E from Coussens et al., 2017). Based on its
224 proximity, subaerial tephra from Montserrat was selected as the more likely for Site U1396C (Fig. 3).

225 Previous work offshore Montserrat has indicated that sediments are a three-component mixture
226 (terrestrial, CaCO_3 and tephra) and that Cr depletion can be used as a proxy for tephra content (Peters
227 et al., 2000; Scudder et al., 2016). Our approach builds on this normative calculation, as it considers a
228 range of elements. Our findings support previous work that indicates much of the tephra in marine
229 sediments is not in discrete layers, but is in the 'dispersed' tephra component (Peters et al., 2000;
230 Scudder et al., 2009; 2014). That is, tephra that has undergone some form of mixing process (e.g.
231 bioturbation, transport in the water column) is not visible in sediment cores as discrete layers (Scudder
232 et al., 2009; 2016). As expected, with 'tephra layers' (identified as layers with $\text{CaCO}_3 < 10$ wt.%), the
233 tephra component is typically >85 wt.% (89 ± 13 wt.%, 1SD, $n=18$). However, in the bulk sediment
234 samples, the combined andesite tephra (i.e., the dispersed tephra component) contribution remains high

235 (29 ± 10 wt.%, 1 SD, n = 43), with a maximum of 55 wt.% (Fig. 3). An average of 29 wt.% is higher
236 than the previous upper estimate of dispersed tephra in this region's sediment (between 15 – 20 wt.%;
237 Peters et al., 2000), and confirms the importance of tephra deposition in Caribbean sediments.

238 Fe isotope systematics

239 The $\delta^{56}\text{Fe}$ values in tephra-rich samples from U1396C range from -0.26 to 0.01 ‰, with an average of
240 -0.12 ± 0.08 ‰ (1SD, n=19). 18 of 19 samples fall outside of the range of crustal rocks (0.09 ± 0.07 ‰,
241 as defined by Beard et al. 2003), and none have a $\delta^{56}\text{Fe}$ composition higher than these crustal rocks
242 (Fig. 4, Supplementary Table 2). Our measured Fe isotope value of terrestrial tephra on Montserrat
243 ($\delta^{56}\text{Fe} = -0.019 \pm 0.02$ ‰) is within the envelope of crustal rock compositions, and similar to previous
244 measurements of volcanics from the Lesser Antilles, which yielded a $\delta^{56}\text{Fe}$ value of 0.045 ± 0.039 ‰
245 (Foden et al., 2018). These measurements on the Lesser Antilles volcanics were completed on lava
246 samples from onshore outcrops, and so the comparability between the two values suggests little Fe
247 isotope fractionation occurs during the eruption of explosive volcanic products in the Lesser Antilles
248 arc. While airborne transport may alter Fe speciation (Maters et al., 2017) and total Fe content of the
249 tephra (Simonella et al., 2015), atmospheric processes do not significantly alter the Fe isotope
250 composition of the tephra.

251 Measurements of marine sediment and tephra samples from Hole U1396C, show considerable variation
252 from what may be considered a magmatic rock Fe isotope composition, with subaerial volcanic rock
253 isotope compositions typically between -0.054 and 0.1 ‰ (Foden et al., 2018; Johnson et al., 2020).
254 Thus, our data indicate that some process within the tephra-rich sediments leads more negative $\delta^{56}\text{Fe}$
255 values in the tephra recovered from marine sediments than observed in subaerial volcanic rocks. This
256 process may involve a diagenetic reaction, admixture of other sedimentary sources with distinct Fe
257 isotopic compositions, and/or interaction with Fe from seawater.

258 To investigate the possibility that the total isotopic composition ($\delta^{56}\text{Fe}_{\text{Total}}$) reflects the mixture of tephra
259 with terrigenous and carbonate contributions, we assume the isotopic composition is governed by the
260 mass-balance of these sources ($\delta^{56}\text{Fe}_{\text{ash}}$, $\delta^{56}\text{Fe}_{\text{terr}}$ and $\delta^{56}\text{Fe}_{\text{carb}}$, respectively; Eq. 3):

261
$$\delta^{56}Fe_{Total} = (\delta^{56}Fe_{Tephra} \times f_{Tephra}) + (\delta^{56}Fe_{terr} \times f_{terr}) + (\delta^{56}Fe_{carb} \times f_{carb}) \text{ (Eq. 3)}$$

262 Where f is the molar fraction of each component. However, as there is little evidence for any Fe-rich
263 carbonates such as siderite in the Caribbean Sea with only aragonite and Mg-rich carbonate reported
264 (Reid et al., 1996), this fraction is likely to contain low levels of Fe (Fe/Ca of below $30 \mu\text{mol mol}^{-1}$; see
265 Boyle, 1981). Any Fe associated with the biogenic carbonate will be present only in the form of Fe-Mn
266 diagenetic coatings (Boyle, 1981). As such, we consider the carbonate contribution to the isotopic
267 mixture to be negligible, and so simplify the equation as follows (Eq. 4):

268
$$\delta^{56}Fe_{Total} = (\delta^{56}Fe_{Tephra} \times f_{Tephra}) + (\delta^{56}Fe_{terr} \times f_{terr}) \text{ (Eq. 4)}$$

269 We can use our measured estimate of $\delta^{56}\text{Fe}$ for terrestrial tephra ($-0.019 \pm 0.023 \text{ ‰}$; $\delta^{56}\text{Fe}_{Tephra}$),
270 published estimates of the $\delta^{56}\text{Fe}$ of terrigenous material (c. $0.01 \pm 0.05 \text{ ‰}$; $\delta^{56}\text{Fe}_{Terr}$, Beard et al., 2003),
271 and the proportion estimates for tephra (combining the contribution of the two andesites) and
272 terrigenous material (f_{Ash} , f_{Terr}) from the CLS model to assess if a simple mixture may explain the
273 measured Fe composition in our samples. Using the values of $\delta^{56}\text{Fe}_{Tephra}$ and $\delta^{56}\text{Fe}_{Terr}$ and the error
274 defined above, the most negative $\delta^{56}\text{Fe}$ composition produced by these mixtures is -0.043‰
275 (significantly more positive than most of the samples measured from U1396C).

276 One of the key diagenetic processes which acts on tephra in marine sediment is dissolution and leaching
277 (Jones and Gislason, 2008; Longman et al., 2019). Here, we focus on those 12 samples containing >75
278 wt.% ash (the closest representatives of ‘pure’ tephra samples within our sample suite) to test whether
279 diagenesis favours the loss of heavy Fe isotopes and the retention of isotopically light ($\delta^{56}\text{Fe}$ lower than
280 -0.1‰) Fe in the sediment. In this mass balance calculation, we assume that the measured $\delta^{56}\text{Fe}$
281 ($\delta^{56}\text{Fe}_{Measured}$) is the result of the modification of the original tephra, with the Fe lost through early
282 diagenesis represented by the proportion f_{Lost} . In this scenario, the $\delta^{56}\text{Fe}_{Measured}$ comprises the following
283 mass balance (Eq. 5):

284
$$\delta^{56}Fe_{Measured} = (\delta^{56}Fe_{Tephra} \times f_{Tephra}) - (\delta^{56}Fe_{Lost} \times f_{Lost}) \text{ (Eq. 5)}$$

285 The calculated $\delta^{56}Fe_{Lost}$ values, are considered representative of the isotopic composition of the Fe lost
286 during early diagenesis, and f_{Lost} is the proportion of Fe present in the protolith lost. f_{Lost} can be estimated
287 using depletion factor (DF_{Fe}) calculations (see Methods and Materials), which estimate how much of
288 the original Fe has been lost (using a Zr depletion model as detailed in Lee et al. (2018), and as second
289 CLS-based model, using outputs from the multivariate partitioning). Therefore, f_{Tephra} is calculated by
290 subtracting f_{Lost} from 1. By rearranging equation 5, and using these independent DF_{Fe} estimates as f_{Lost} ,
291 we can solve for $\delta^{56}Fe_{Lost}$ as follows:

$$292 \quad \delta^{56}Fe_{Lost} = (\delta^{56}Fe_{ash} \times f_{Tephra}) - (\delta^{56}Fe_{Measured}) / f_{Lost} \text{ (Eq. 6)}$$

293 As we use two methods to estimate DF_{Fe} , we derive two estimates for $\delta^{56}Fe_{Lost}$ (see Fig. 5), but they are
294 in good agreement (Supplementary Figure 2), with significant correlation between the two ($r^2=0.65$, p-
295 value 0.02, n=12), indicating both approaches yield similar outputs, although the ranges vary (CLS
296 Model -3 – 54%, Zr normalisation model -12 – 80%). Both approaches suggest generally positive values
297 for $\delta^{56}Fe_{Lost}$ relative to the original isotopic composition of the tephra. A single sample appears to have
298 gained Fe through diagenesis, potentially through reprecipitation of Fe-bearing phases, reflected in the
299 negative model result (Fig. 5). The results derived from Zr-normalisation show slightly higher mean
300 values for $\delta^{56}Fe_{Lost}$ ($0.36 \pm 0.28\%$, 1SD, n=12) within uncertainty of the mean value derived from our
301 CLS modelling approach ($0.21 \pm 0.15\%$, 1SD, n=12). These positive values for $\delta^{56}Fe$ are similar to
302 measurements of Fe supplied to porewater and seawater via non-reductive dissolution (NRD), as
303 inferred in oxidizing pore water $\delta^{56}Fe$ from tephra-rich sediments near the Crozet Islands ($0.16 \pm$
304 0.05% ; Homoky et al., 2009), the Cape Margin (0.22% ; Homoky et al., 2013), South Western Atlantic
305 ($\delta^{56}Fe = 0.07 \pm 0.07\%$; Homoky et al., 2021) and New Guinea Coastal waters ($0.37 \pm 0.15\%$; Radic et
306 al., 2011). It is assumed NRD does not truly represent a chemical reaction, rather a physical breakdown
307 of particles into smaller fractions, a process which should not lead to isotopic fractionation. However,
308 the binding of these small particles to ligands is known to fractionate the Fe, with shifts of between +0.2
309 to +0.5% observed experimentally (Dideriksen et al., 2008; Morgan et al., 2010) and in the natural
310 environment (Ilina et al., 2013). Therefore, it is likely the isotopic fractionation observed here is
311 representative of first the NRD breakdown of tephra particles, followed by a range of secondary

312 chemical reactions involving strong Fe-binding ligands, which fractionates the Fe. Such a process has
313 been invoked to explain the positive $\delta^{56}\text{Fe}$ values observed in North Atlantic surface waters (between
314 +0.3 to +0.7‰, despite the primary Fe source being dust (which typically has $\delta^{56}\text{Fe}$ values close to 0‰;
315 Conway and John, 2014).

316 NRD of lithogenic particles occurs either during transport through the water column or at the sediment-
317 seawater interface, and may occur in both oxic or dysoxic water column and/or pore water (Homoky et
318 al., 2021, 2013; Radic et al., 2011). Thus, the rapid consumption of pore water oxygen observed in
319 sediments offshore Montserrat (Hembury et al., 2012) does not preclude the occurrence of NRD. NRD
320 results in a net release of isotopically heavy dissolved Fe (dFe with $\delta^{56}\text{Fe} > 0\text{‰}$) to bottom water
321 (Abadie et al., 2017; Labatut et al., 2014) or to seawater during transport through the water column
322 (Labatut et al., 2014). Previous studies have shown that NRD may only result in small benthic Fe fluxes
323 in some settings (Homoky et al., 2013), but fluxes out of the sediment may be enhanced in locations of
324 high lithogenic (e.g. dust, riverine particles) deposition and/or sediment re-suspension (Klar et al., 2018;
325 Labatut et al., 2014; Lam et al., 2020).

326 The regular and large-scale input of tephra from volcanoes in Central America (e.g. Schindlbeck et al.,
327 2016), and the Lesser Antilles (Coussens et al., 2017; Palmer et al., 2016) provides a significant source
328 of volcanic material for the Caribbean Sea. In a similar manner to western Africa, where input of
329 lithogenic material via riverine input leads to a large supply of Fe from NRD (Klar et al., 2018), our
330 data suggest the deposition of tephra in the Caribbean may act as a source of Fe, via NRD. Indeed,
331 tephra is known to rapidly release Fe via interactions with seawater (Jones and Gislason, 2008), and
332 during early diagenesis (Longman et al., 2022, 2019). This release from tephra is inferred from the
333 relatively high Fe content in pore waters from U1396C (typical values between 10 – 50 μmol ; Fig. 2),
334 and dissolution of tephra is also reflected in the volcanogenic Sr isotope composition of the pore waters
335 (Fig. 4; Murray et al., 2018).

336 Further evidence for release of dFe from tephra in the marine sediments comes from data from the
337 Crozet Islands (Homoky et al., 2009). Here, the signal of NRD (and likely ligand binding) was identified
338 in the Fe released to the pore water (with isotopic compositions between -0.01 and 0.12‰), and was

339 linked to high concentrations of colloidal Fe (Fe associated with particles between 1 – 1000 nm in size;
340 cFe) (Homoky et al., 2011, 2009). Previous analysis of pore waters in the Caribbean has indicated that
341 there is very little cFe relative to Crozet in fresh tephra layers collected from Montserrat previously. At
342 Montserrat, $<0.01 \mu\text{mol cm}^{-2} \text{yr}^{-1}$ of cFe is supplied to porewaters, whilst at Crozet cFe supply is
343 calculated to be $>1 \mu\text{mol cm}^{-2} \text{yr}^{-1}$ (Homoky et al., 2011). However, this absence of porewater Fe
344 colloids in fresh tephra was shown to result from the undersaturation of Fe-bearing smectite clays
345 (Homoky et al., 2011) and a lack of organic carbon to complex Fe nanominerals (Homoky et al., 2021).
346 We argue therefore that the source of cFe to the seawater is release from dissolving volcanic tephra
347 during transport through the water column and at the sediment-water interface. This conclusion is
348 supported by the systematic offset between calculated $\delta^{56}\text{Fe}_{\text{Lost}}$ at Montserrat and the signature of Crozet
349 pore waters of around 0.2 to 0.3‰. Evidence for the impact of NRD on regional Fe budgets may be
350 identified in $\delta^{56}\text{Fe}$ compositions of western North Atlantic seawater. Measurements of seawater down
351 to 4200 metres depth offshore Bermuda yielded $\delta^{56}\text{Fe}$ values between 0.2 to 0.74‰ (Conway and John,
352 2014; John and Adkins, 2012), which are within the range of our calculated $\delta^{56}\text{Fe}_{\text{Lost}}$ values (Fig. 5). As
353 discussed above, these Fe isotope compositions have been attributed to a mixture of dust fractionation
354 and organic ligand-mediated processes (Conway and John, 2014; John and Adkins, 2012; König et al.,
355 2021). We also propose that input of dFe from tephra-rich sediment alteration may play a role in these
356 isotopically heavy $\delta^{56}\text{Fe}$ values in the Bermudan samples by advection of extensive benthic nepheloid
357 layers from the Caribbean and Gulf of Mexico (Feely, 1975; McCave, 1986), but analysis of Caribbean
358 Sea seawater would be required to test this hypothesis.

359 Conclusions

360 We measured the major and trace element concentration and Fe isotopic composition of tephra and
361 sediment layers from the Caribbean Sea. The bulk sediment is dominated by biogenic carbonate, but
362 using a multivariate partitioning approach, we determined that aluminosilicate material in the sediment
363 is a mixture of three primary sources, two linked to tephra deposition and one linked to terrestrial input.
364 Overall, dispersed tephra comprises 29% of all sediment analyzed in this study. Fe isotope analyses
365 indicate that tephra within the sediment, which has undergone water column transport and subsequent

366 diagenesis, has $\delta^{56}\text{Fe}$ values that are isotopically lighter than its source material, with $\delta^{56}\text{Fe}$ values as
367 low as -0.26‰. This is considerably lighter than measured $\delta^{56}\text{Fe}$ from fresh tephra (which we show to
368 be close to 0 ‰). Modelling of these Fe isotope data using multivariate partitioning suggests that the
369 negative $\delta^{56}\text{Fe}$ values of sediment hosted tephra layers results from the loss of heavy Fe isotopes during
370 tephra dissolution and diagenesis. This Fe loss most likely occurs as the result of non-reductive
371 dissolution of the tephra. We suggest the release of this tephra-hosted Fe may play a considerable role
372 in marine biogeochemical cycles such as the supply of nutrients for phytoplankton metabolism. Further,
373 the deposition of volcanic material may have an impact on the mean Fe isotope composition of seawater
374 in the vicinity of volcanoes.

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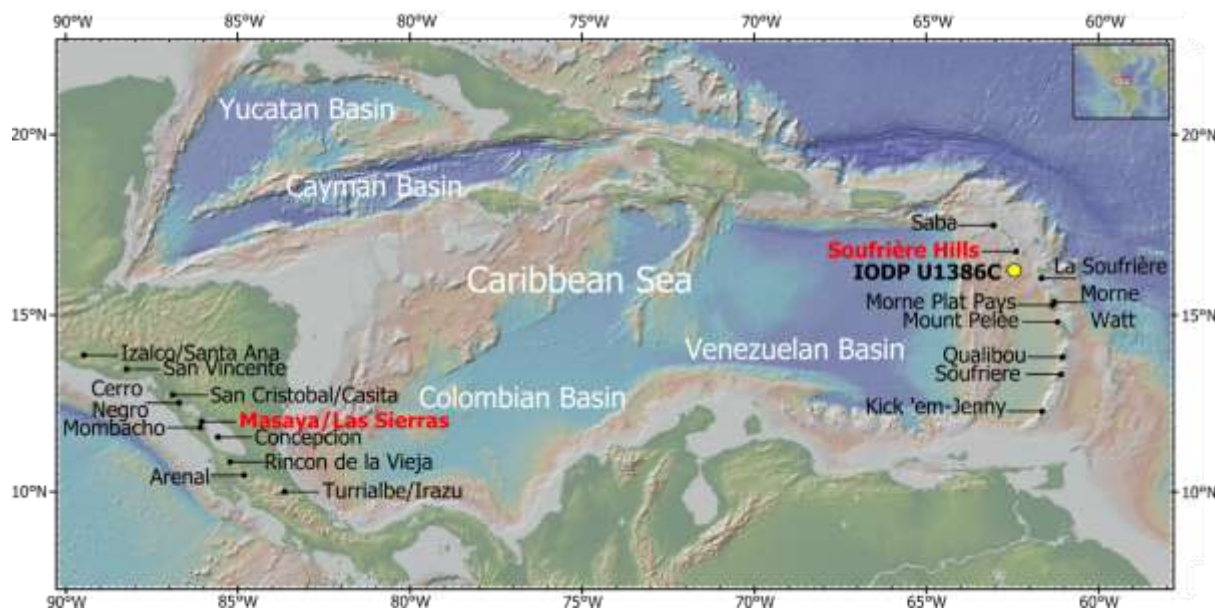
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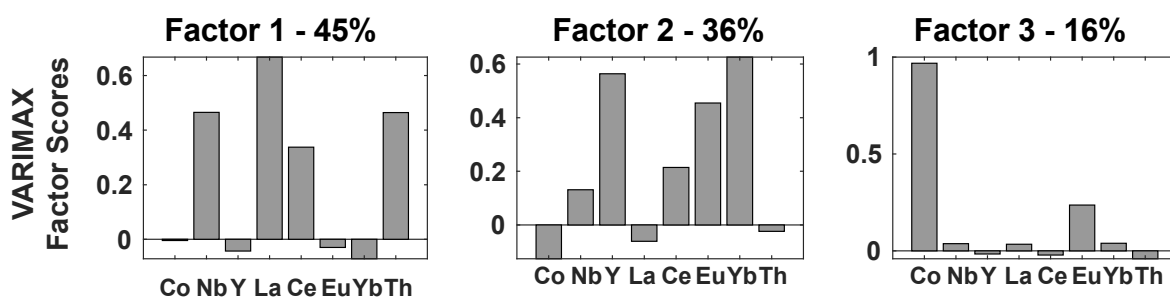
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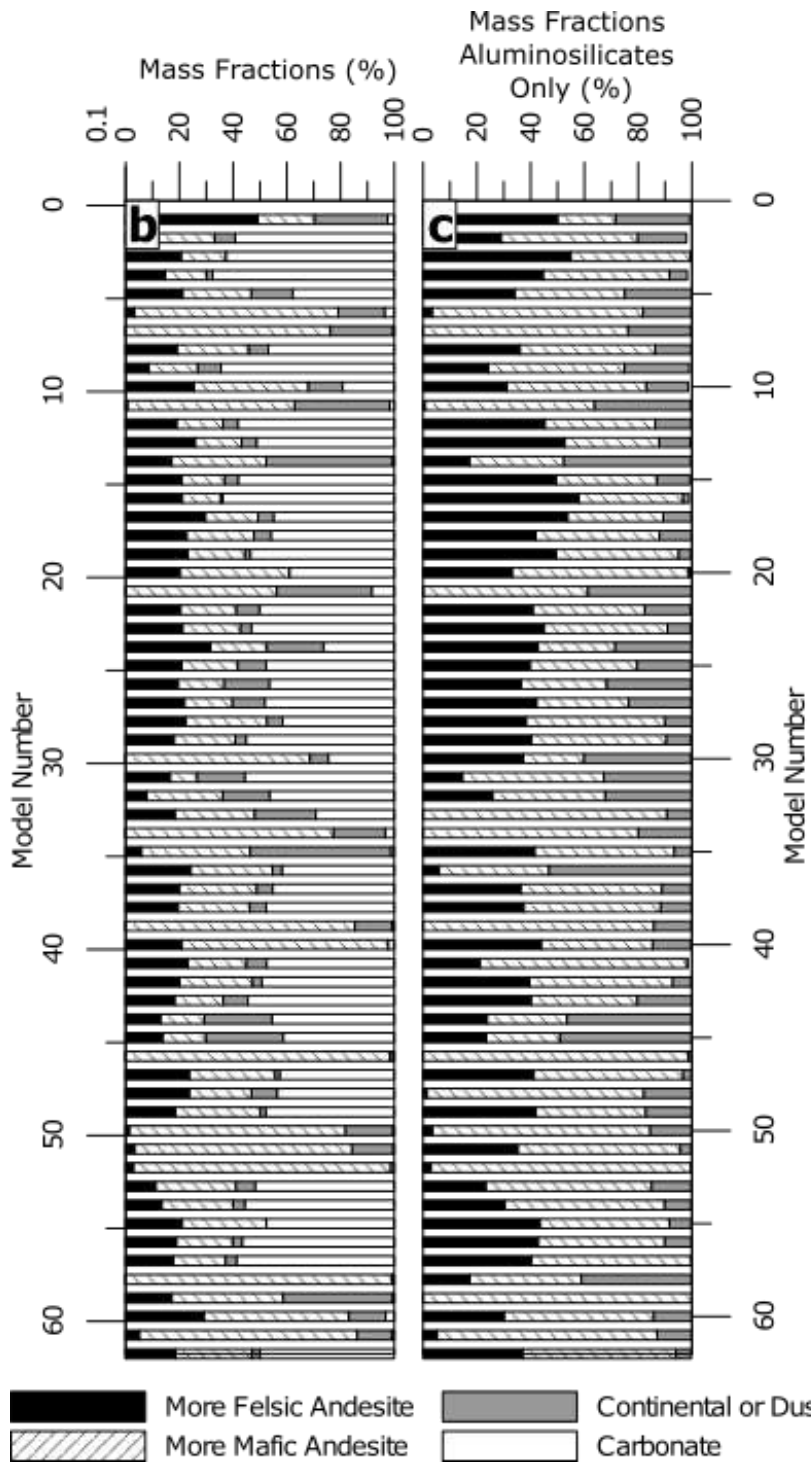
610 **Figures**



611
 612 Figure 1: Map indicating location of Hole U1396C (yellow circle) within the Caribbean Sea area. Also
 613 shown are the locations of the primary recently active volcanoes in the region. The location of Las
 614 Sierras, and Soufrière Hills volcanoes, used in the modelling here, are indicated by bold red text. Map
 615 created in ArcMap 10.3, Environmental Systems Resource Institute, ArcMap 10.3 ESRI, Redlands,
 616 California, <http://desktop.arcgis.com/en/arcmap/>.



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 618 Figure 2: The VARIMAX factor scores from the Q-mode factor analysis. Elements affiliated with the
 619 aluminosilicate fraction produced three factors that explain 97% of the variability of the dataset (45%,
 620 36%, and 16%, respectively).



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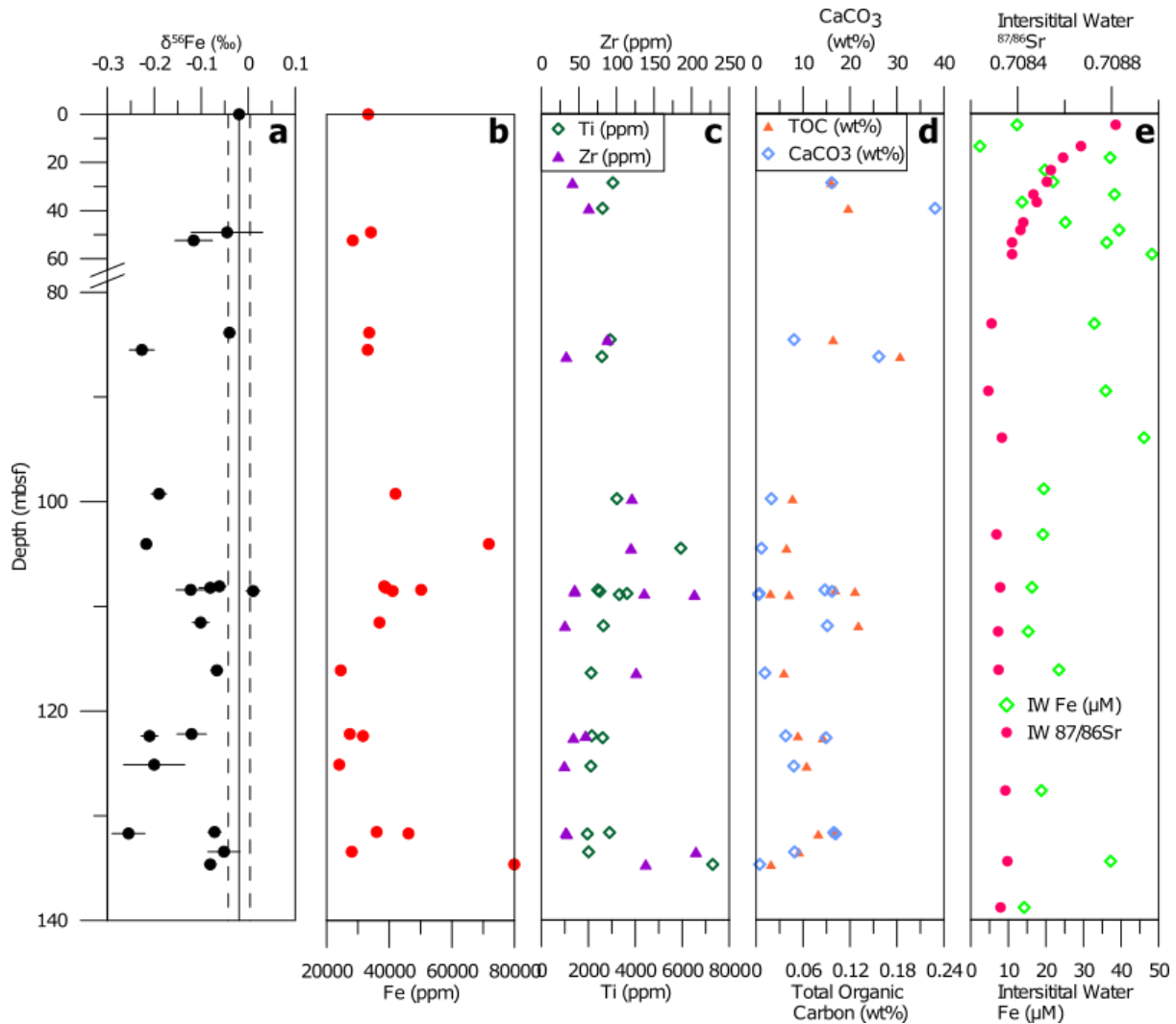
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Figure 3: a) The results of the CLS model. Modelled end-member mass fractions in each discrete layer or bulk sediment sample plotted with the same scale as panel a. Black and hashed white indicate the mass fractions of the more felsic and more mafic andesites, respectively. Grey represents contributions from an upper continental crust or dust source. The remaining white area represents the carbonate

626 fraction of bulk sediment. b) The CLS modelled mass fractions of only the aluminosilicate fraction of
 627 the samples (excluding the carbonate fraction).

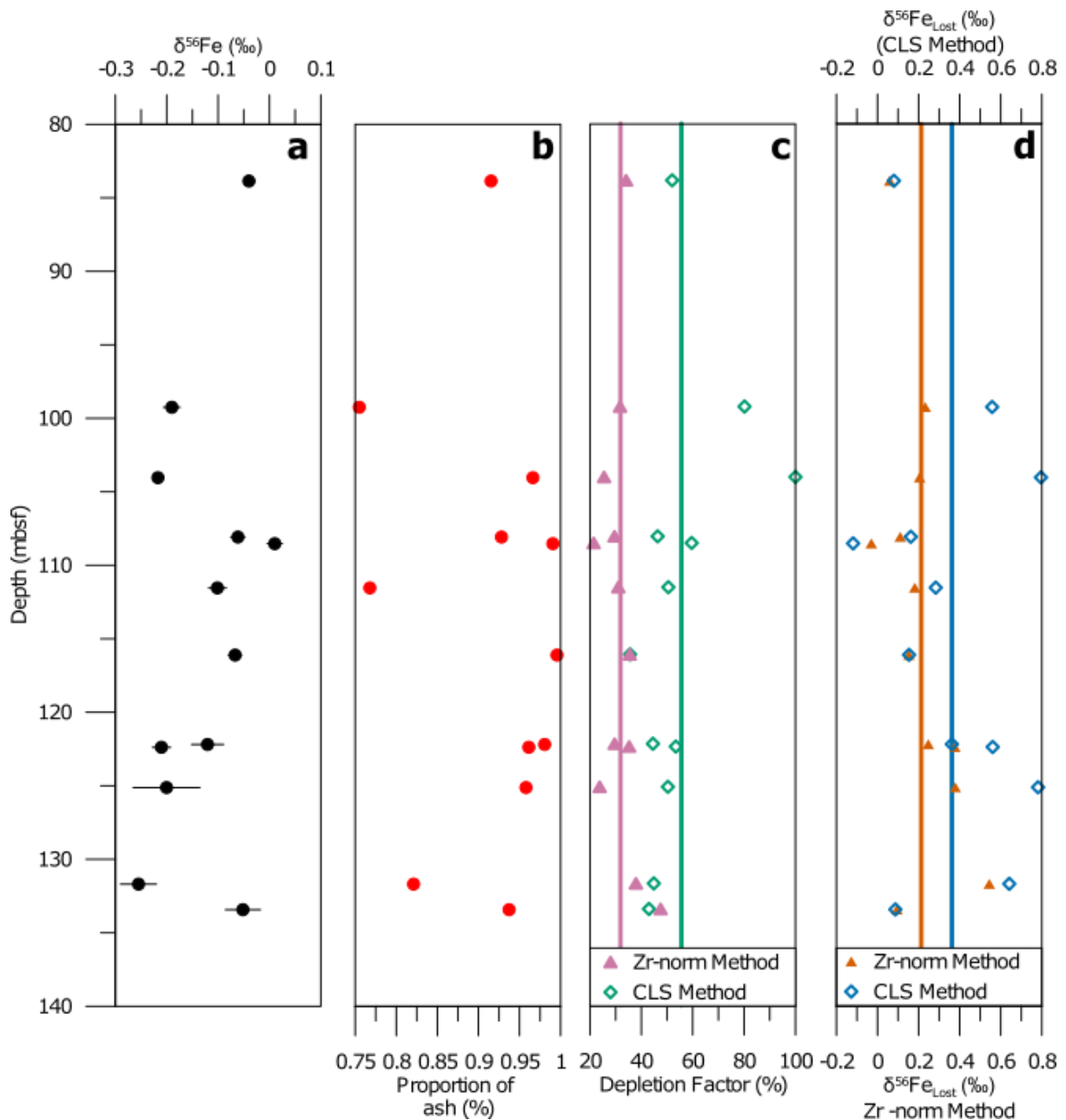
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630 Figure 4: Geochemical parameters from U1396C. (a) Fe isotope composition of analysed samples, with
 631 error bars indicating measurement error (2SD). The measured value of terrestrially emplaced ash from
 632 Montserrat indicated with a black line, with measurement error indicated by dashed lines. (b) Fe content
 633 of samples analysed for isotopic composition. (c) Ti and Zr content for the same samples. (d) calcium
 634 carbonate and organic carbon (total carbon) content for the same samples. (e) Interstitial water Fe
 635 content and Sr isotope composition (from Murray et al., 2018).

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639 Figure 5: Parameters used in the mass balance modelling of the lost Fe fraction ($\delta^{56}\text{Fe}_{\text{Lost}}$), or the isotopic
 640 composition of Fe flux from samples with >75% tephra. (a) Bulk $\delta^{56}\text{Fe}$ measurements for the samples
 641 with high enough ash content to be modelled (>75%). (b) The proportion of ash in each sample, as
 642 calculated from the multivariate modelling. (c) Fe depletion factor (DF) calculations, DF Method 1
 643 from Lee et al. (2018) and DF Method 2 from our multivariate partitioning. Individual models are
 644 indicated with coloured symbols, and the mean of each method is highlighted with a coloured line (d)

645 The calculated $\delta^{56}\text{Fe}_{\text{Lost}}$ for each of the samples, with the calculations made using the depletion factors
646 displayed in panel c. Again, the mean of the outputs is highlighted with a coloured line.