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1 **Last Glacial Period Cryptotephra Deposits in an Eastern North**
2 **Atlantic Marine Sequence: Exploring Linkages to the Greenland Ice-**
3 **Cores**

4

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16 **Abstract**

17

18 The establishment of a tephra framework for the Greenland ice-cores spanning the last
19 glacial period, particularly between 25-45 ka b2k, provides strong potential for

20 precisely correlating other palaeoclimatic records to these key archives. Tephra-based
21 synchronisation allows the relative timing of past climatic changes recorded within

22 different depositional environments and potential causal mechanisms to be assessed.

23 Recent studies of North Atlantic marine records have demonstrated the potential of
24 tracing cryptotephra horizons in these sequences and the development of protocols

25 now allows a careful assessment of the isochronous nature of such horizons. Here we

26 report on tephrochronological investigations of a marine sequence retrieved from the
27 Goban Spur, Eastern North Atlantic, covering ~25-60 ka b2k. Density and magnetic
28 separation techniques and an assessment of potential transport and depositional
29 mechanisms have identified three previously unknown isochronous tephra horizons
30 along with deposits of the widespread North Atlantic Ash Zone II and Faroe Marine
31 Ash Zone III. Correlations between the new horizons and the Greenland ice-core
32 tephra framework are explored and despite no tie-lines being identified the key roles
33 that high-resolution climatostratigraphy and shard-specific trace element analysis can
34 play within the assessment of correlations is demonstrated. The previously unknown
35 horizons are new additions to the overall North Atlantic tephra framework for the last
36 glacial period and could be key horizons for future correlations.

37

38 Keywords: Tephrochronology; palaeoclimate synchronisation; volcanic ash;
39 isochrons; Iceland; major and trace element geochemistry

40

41 **1. Introduction**

42

43 The tracing of isochronous horizons of volcanic ash between different depositional
44 realms (tephrochronology) has considerable potential for the independent correlation
45 and synchronisation of disparate palaeoclimatic sequences and for assessing the
46 relative timing of past climatic events (Lowe, 2011). The potential of
47 tephrochronology to assess these relative timings is especially pertinent for the last
48 glacial period as there is evidence for several abrupt climatic changes preserved
49 within ice-cores from Greenland (e.g. GRIP Members, 1993; Johnsen et al., 2001;
50 NGRIP Members, 2004) and numerous North Atlantic marine cores (e.g. Bond et al.,

51 1993, 1997; Van Kreveland et al., 2000; Martrat et al., 2007; Hall et al., 2011; Zumaque
52 et al., 2012).

53

54 A large number of tephra horizons have been identified within multiple Greenland
55 ice-cores spanning the last glacial period (Abbott and Davies, 2012; Bourne et al.,
56 2013, 2015b; Davies et al., 2014). Bourne et al. (2015b) in particular increased the
57 number of horizons identified in the NGRIP, NEEM, GRIP and DYE-3 ice-cores and,
58 in combination with past studies, a framework of 99 geochemically characterised
59 tephra deposits has now been defined for the 25-45 ka b2k period. Developing a
60 framework of geochemically characterised horizons with strong stratigraphic and
61 chronological control is an essential first step towards the synchronisation of these
62 records to other palaeoclimatic sequences in a range of environments. A notable
63 feature of the ice-core framework is the dominance of deposits, closely spaced in
64 time, that have similar major element compositions relating to single sources, e.g. the
65 Icelandic Grímsvötn volcanic system. Subtle major element differences can be used to
66 discriminate between some deposits, but others have major element compositions
67 which are indistinguishable (e.g. Bourne et al., 2013).

68

69 This compositional similarity presents a challenge when attempting to correlate tephra
70 horizons from sequences with limited chronological and/or stratigraphic control. In
71 these instances it has been widely advocated that any available climatostratigraphic
72 evidence can be used alongside the compositional data to narrow down potential
73 correlatives (e.g. Newnham and Lowe, 1999; Newnham et al., 2004; Pearce et al.,
74 2008; Housley et al., 2012; MacLeod et al., 2015) and that trace element analysis of
75 the tephra deposits may provide a useful secondary compositional fingerprint for

76 testing and assessing the robustness of correlations (e.g. Allan et al., 2008; Abbott et
77 al., 2012, 2014; Albert et al., 2012; Lane et al., 2012; Bramham-Law et al., 2013;
78 Pearce et al., 2014; Bourne et al., 2015a).

79

80 Overall, there is an order of magnitude difference between the number of tephra
81 horizons identified in the Greenland ice-cores and North Atlantic marine sequences
82 between 25-60 ka b2k. Only a few marine records have been investigated for their
83 tephra content and there is a tendency to focus on visible horizons or on the coarse-
84 grained components ($>150\ \mu\text{m}$) (e.g. Lackschewitz and Wallrabe-Adams, 1997;
85 Wastegård and Rasmussen, 2014). As a result, only two ice-marine tie-lines have been
86 defined within the last glacial period. Firstly, the rhyolitic component of the
87 widespread North Atlantic Ash Zone (NAAZ) II ($55,380 \pm 1184\ \text{a b2k}$; Svensson et
88 al., 2008) has been traced within multiple ice and marine cores (e.g. Kvamme et al.,
89 1989; Grönvold et al., 1995; Lacasse et al., 1996; Zielinski et al., 1997; Haflidason et
90 al., 2000; Austin et al., 2004). Secondly, Faroe Marine Ash Zone (FMAZ) II, a visible
91 horizon identified in a number of marine cores from the Faroe Islands region
92 (Wastegård et al., 2006), was traced into the NGRIP ice-core by Davies et al. (2008)
93 (NGRIP 1848 m; $26,740 \pm 390\ \text{a b2k}$). A third ice-marine correlation was also
94 proposed between the NGRIP 2066.95 m horizon ($38,122 \pm 723\ \text{a b2k}$) and FMAZ
95 III, a thick and relatively scattered zone of glass shards traced between a number of
96 the Faroe Islands region cores (Wastegård et al., 2006; Davies et al., 2010). However,
97 Bourne et al. (2013) later highlighted the complexity of this period and identified a
98 series of closely spaced tephra horizons with similar glass compositions in the NGRIP
99 and NEEM ice-cores. Their compositions all fall within the broad compositional
100 envelope of FMAZ III and the marine deposit has been interpreted as resulting from

101 the amalgamation of primary tephra-fall from a number of volcanic events as a
102 consequence of low sedimentation rates at the marine core sites (Bourne et al., 2013;
103 Griggs et al., 2014). Therefore, the prior correlation between FMAZ III and a single
104 tephra layer in the ice-cores is no longer valid and should not be used as an ice-marine
105 tie-line. However, the tephra layers in the ice may still act as tie-lines if individual
106 homogenous horizons from those single events can be found in marine records. This
107 particular example highlights some of the complexities involved with defining
108 correlations between the records.

109

110 In recent years, there has been a shift towards the investigation of the cryptotephra
111 record preserved within marine sediments. Density and magnetic separation
112 techniques, previously applied to terrestrial sequences, have recently been
113 successfully used to extract fine-grained cryptotephra, preserved as discrete deposits
114 of glass shards, from a number of cores around the North Atlantic (e.g. Abbott et al.,
115 2011, 2013, 2014; Griggs et al., 2014; Davies et al., 2014). Magnetic separation
116 techniques are particularly important for the identification of basaltic cryptotephra in
117 North Atlantic marine records because of the dominance of basaltic tephra deposits
118 within the Greenland tephra framework (Abbott and Davies, 2012; Bourne et al.,
119 2013, 2015b). In addition to these methodological advances, Griggs et al. (2014)
120 outlined a protocol which uses a range of indicators to determine the potential
121 influence of transportation and depositional processes on the stratigraphic and
122 temporal integrity of marine tephra deposits. To date, these methods and approaches
123 have not been utilised to isolate cryptotephra in North Atlantic marine sequences
124 covering the 25-60 ka b2k period. The Greenland tephra framework in particular, now

125 demonstrates the potential for tephrochronological synchronisation if common
126 horizons can be identified.

127

128 Here we report on tephrochronological investigations of the 25-60 ka b2k period
129 within a marine core retrieved from the Goban Spur area in the eastern North Atlantic
130 (MD04-2820CQ). Potential correlations to the Greenland tephra framework are
131 explored with new high-resolution proxy data from MD04-2820CQ used to help
132 determine the stratigraphic position of the tephra horizons and trace element analysis
133 is utilised as a secondary compositional fingerprint.

134

135 **2. Materials and Methods**

136

137 *2.1 MD04-2820CQ*

138

139 MD04-2820CQ was retrieved from the Goban Spur area (49°05.29'N; 13°25.90'W;
140 Figure 1) and is a reoccupation of the OMEX-2K core site (see Hall and McCave,
141 1998a,b; Scourse et al., 2000; Haapaniemi et al., 2010). A Ca XRF record and a low-
142 resolution record of the percentage abundance of the polar foraminiferal species
143 *Neogloboquadrina pachyderma* (sinistral) (*Np(s)*) have been used to define a
144 preliminary stratigraphy for the sequence between MIS 3-2. A number of Dansgaard-
145 Oeschger events related to the Greenland Interstadial (GI) events in the Greenland
146 ice-cores are recognised within this record (Figure 2; Rasmussen et al., 2014).
147 Between 450-550 cm depth, high-resolution (up to 1 cm) records of *Np(s)* and ice
148 rafted debris (IRD) concentrations (150 µm-1 mm fraction) were generated to provide

149 a more detailed stratigraphy between DO-12 and DO-8 to help constrain the tephra
150 deposits within a climatic framework (Figure 6).

151

152 FIGURE 1

153

154 The tephra content of the core was initially investigated at a low-resolution (5 cm
155 contiguous samples) between 250-650 cm depth. Intervals with distinct peaks in glass
156 shard content above background levels were subsequently re-investigated at 1 cm
157 resolution to refine their stratigraphic position (Figure 2).

158

159 FIGURE 2

160

161 *2.2 Extraction of tephra-derived glass shards from marine sequences*

162

163 From the 5 and 1 cm samples, 0.5 g sub-samples of freeze-dried marine sediments
164 were immersed in 10% HCl overnight to remove carbonate material. Samples were
165 then wet sieved using 125 and 80 μm test sieves and 25 μm nylon mesh. The 25-80
166 μm fraction was then density separated using sodium polytungstate prepared to the
167 specific gravities of 2.3 and 2.5 g/cm^3 to split the material into the density fractions of
168 $<2.3 \text{ g}/\text{cm}^3$, to remove biogenic material, 2.3-2.5 g/cm^3 , to isolate rhyolitic material,
169 and $>2.5 \text{ g}/\text{cm}^3$ to isolate basaltic material (Turney, 1998). To further purify the >2.5
170 g/cm^3 fraction it was magnetically separated using a Frantz Isodynamic Magnetic
171 Separator. The methodology and conditions for magnetic separation are outlined in
172 Griggs et al. (2014) and allow the separation of non-magnetic quartz material from
173 any paramagnetic basaltic material. The $>125 \mu\text{m}$ and 80-125 μm grain-size fractions,

174 and the 2.3-2.5 g/cm³ and magnetic >2.5 g/cm³ density fractions, were mounted on
175 microscope slides in Canada Balsam for optical microscopy to quantify their glass
176 shard content.

177

178 *2.3 Geochemical analysis of individual glass shards*

179

180 Samples for geochemical analysis were prepared using the procedure outlined in
181 Section 2.2. The fraction of interest was then mounted in epoxy resin on a 28 × 48
182 mm frosted microscope slide to prepare thin sections of the glass shards. This was
183 achieved by grinding the material using decreasing grades of silicon carbide paper and
184 then polishing the surface using 9, 6 and 1 μm diamond suspension.

185

186 Major element compositions of individual shards were determined using electron-
187 probe micro-analysis (EPMA) at the Tephra Analytical Unit, University of Edinburgh,
188 using a Cameca SX100 with five wavelength dispersive spectrometers. The operating
189 conditions followed those outlined in Hayward (2012). Calibration was carried out
190 using pure metals, synthetic oxides and silicate standards and the secondary standards
191 of Cannetto Lami Lava, Lipari and BCR2g were analysed at regular intervals to
192 monitor for instrumental drift and assess the precision and accuracy of analysed
193 samples (see Table S18). For data comparison all analyses were normalised to an
194 anhydrous basis, i.e. 100 % total oxides, but all raw data analyses are provided in the
195 supplementary information (Tables S1-S17). Statistical comparisons between tephra
196 horizons have been made using the statistical distance test (D^2) of Perkins et al. (1995,
197 1998) and the similarity coefficient function (SC) of Borchardt et al. (1972).

198

199 Trace element compositions of single shards from one marine and one ice-core
200 horizon were analysed using laser ablation inductively coupled plasma mass
201 spectrometry (LA-ICP-MS) at Aberystwyth University. A Coherent GeoLas 193 nm
202 Excimer laser coupled with a Thermo Finnigan Element 2 high-resolution sector field
203 mass spectrometer was utilised (Pearce et al., 2011). Due to the small grain size of the
204 shards making up the ice-core horizon, a laser with a beam diameter of 10 μm and a
205 fluence of 10 J/cm^2 was pulsed at 5 Hz with a flash duration of ~ 10 ns. Despite the
206 larger grain size of shards in the marine horizon, a 10 μm laser beam diameter was
207 used for all analyses to limit any differential impact of fractionation effects. As a
208 potential correlation was being tested, the samples were analysed ‘side-by-side’ to
209 limit any potential influence of instrumental differences between analytical periods
210 (Pearce et al., 2014). Trace element concentrations were calculated using methods
211 outlined in Pearce et al. (2007), with ^{29}Si previously determined through EPMA used
212 as the internal standard and NIST 612 used as the calibration standard, taking
213 concentrations from Pearce et al. (1997). A correction factor was used to remove bias
214 in analyses caused by fractional effects (Pearce et al., 2011). Trace element
215 concentrations for individual shards are provided in Table S19 and analyses of the
216 secondary standards BCR2g and BHVO-2g are provided in Table S20.

217

218 **3. Results**

219

220 Of the 80 intervals investigated at low-resolution, 21 were selected for high-resolution
221 analysis resulting in the processing of 105 1 cm samples. Figure 2 integrates low-
222 resolution counts from intervals that were not reanalysed with the high-resolution
223 counts. These overall shard profiles were employed to select 17 samples for

224 geochemical analysis (Figure 2). Overall, the record contains a number of distinct
225 concentrations of brown glass shards and this type of shard is also present as a low
226 background. There is a more consistent background of rhyolitic shards throughout the
227 whole of the studied interval. Given the tephrostratigraphical record, the deposits are
228 grouped into five periods and used as a basis to present results below. To determine
229 the source of the glass shards, compositions are compared to glass and whole rock
230 analyses to allow material to be assigned to Icelandic rock suites and specific volcanic
231 systems.

232

233 *3.1 Period 1 - Post DO-3*

234

235 Between 275-279 cm a dispersed zone of shards with a low concentration of basaltic
236 shards and no discernible peak was identified. Geochemical characterisation shows
237 that the glass in this zone has a highly heterogeneous composition with shards of both
238 transitional alkali and tholeiitic composition present (Figure 3a). Similar
239 heterogeneity is observed in shards from both the less-than and greater-than 80 μm
240 grain-size fractions (Figure 3). This characterisation shows that the deposit is an
241 amalgamation of material from a number of volcanic eruptions from multiple volcanic
242 centres.

243

244 **FIGURE 3**

245

246 According to the stratigraphy for MD04-2820CQ, this zone of ash was deposited
247 during the stadial period following DO-3. In the NGRIP ice-core, FMAZ II was
248 deposited within Greenland Stadial (GS) 3 approximately 1000 years after the cooling

249 transition at the end of GI-3 (Davies et al., 2008). The composition of MD04-2820CQ
250 275-279 cm demonstrates that this deposit does not directly relate to the homogenous
251 transitional alkali basaltic FMAZ II horizon found within ice and marine sequences
252 (Figure 3b). Some shard analyses fall within the compositional envelopes of the
253 homogenous VZ 1x and the heterogeneous VZ 1 ash zones from cores on the
254 Reykjanes Ridge, but the greater heterogeneity of the 275-279 cm deposit suggests
255 they are unrelated (Figure 3b).

256

257 The compositional heterogeneity and lack of a distinct peak in the shard concentration
258 profile strongly suggests that this deposit represents a minor input of material,
259 potentially through iceberg rafting or secondary transportation processes such as
260 bottom currents, and cannot be regarded as isochronous.

261

262 *3.2 Period 2 – DO-5 to DO-3*

263

264 The highest glass shard concentration peak in the 25-80 μm fraction is observed
265 within period 2 at 342-343 cm (Figure 2). The maximum peak in the $>125 \mu\text{m}$ size
266 fraction is between 341-342 cm. Two narrow zones of ash below this high peak
267 between 355-360 cm and 370-375 cm depth were found in low-resolution counts, but
268 no distinct peaks in concentration were observed in the high-resolution counts.

269

270 Shards from the main peak and the two underlying ash zones have a basaltic
271 composition (Figure 4a). With the exception of a shard population $>80 \mu\text{m}$ in size in
272 the 373-374 cm sample, and a few outlying analyses that have affinities to the
273 Icelandic transitional alkali rock suite, these deposits have a tholeiitic composition

274 sourced from the Kverkfjöll volcanic system (Figure 4a). Although the analysed glass
275 shards are from four different depths, it is clear that the majority of shards from each
276 interval occupy the same compositional space on geochemical plots and hence are
277 related to one another. The relatively homogenous dominant population has SiO₂
278 concentrations between 48.5-51.0 % wt, CaO concentrations between 8.9-9.9 % wt and
279 FeO concentrations of ~15 % wt (Figure 4). Slight geochemical bimodality can be
280 observed, most notably within the TiO₂ concentrations and FeO/MgO ratios (Figure
281 4bi). This bimodality is present within the main shard peak at 342-343 cm and the
282 underlying zones of low shard concentration. However, the deposit at 373-374 cm has
283 proportionally more shards with high TiO₂ values than the other two deposits (Figure
284 4bi).

285

286 FIGURE 4

287

288 Determining potential correlatives, the isochronous nature and likely transport
289 mechanisms for these deposits is complex. Bourne et al. (2015b) identified a number
290 of tholeiitic basaltic tephra horizons with a Kverkfjöll source in the Greenland ice-
291 cores between GI-5.2 and GS-4. The composition of all 10 of these ice-core horizons
292 fall within the compositional field of the main population of the 342-343 cm and
293 underlying deposits (Figure 4b), hampering their correlation to individual ice-core
294 horizons. Some of these eruptives, however, have greater compositional
295 heterogeneity, such as GRIP 2064.35 m, NGRIP 1931.60 m and NGRIP 1950.50 m,
296 and cover the full compositional range observed in the marine deposit (Figure 4c).
297 The peak input of ash at 342-343 cm may represent a single primary tephra-fall event
298 related to one of these eruptions with the underlying deposits, between 355-360 and

299 370-375 cm, possibly representing downward movement of tephra within the
300 sediment column via bioturbation. This scenario seems unlikely, however, due to the
301 lack of a distinct background of basaltic shards between the deposits. An alternative
302 scenario is that the geochemical similarities are a consequence of the marine deposits
303 being composed of an amalgamation of glass shards from a number of eruptions.
304 Shards could be amalgamated during protracted input of material via primary fall and
305 post-depositional reworking, akin to the proposed depositional mechanism for FMAZ
306 III (see Section 1). This proposition is, however, not supported by the relatively
307 discrete nature of the peak input of ash to the site between 342-343 cm and the
308 underlying deposits, which implies that tephra delivery occurred as short-lived pulses
309 of material.

310

311 Delivery via repeated iceberg rafting events could create deposits of this nature. The
312 greater heterogeneity of the material at 373-374 cm depth, with a transitional alkali
313 composition similar to those of Katla eruptives in the Greenland tephra framework
314 between GI-5.2 and GS-4 (Figure 4ai), and an additional tholeiitic population from
315 Grímsvötn (Figure 4aii), may indicate that this material, with a slightly different
316 compositional signature, is derived from a prior iceberg rafting event. We cannot fully
317 test this proposition because an IRD record has currently not been established over
318 this period. However, the high concentration of coarse-grained shards ($>125\ \mu\text{m}$)
319 (Figure 2), in a relatively distal location to Iceland, supports iceberg rafting as the
320 transport process. Overall, this likelihood prevents the deposits in period 2 from being
321 useful regional isochrons but they could be used for local core correlations
322 (Brendryen et al., 2010).

323

324 *3.3 Period 3 – DO-9 to DO-8*

325

326 Period 3 is characterised by an approximately 20 cm thick zone of elevated basaltic
327 glass concentrations within which four small peaks in concentration can be observed.
328 Peaks at 456-457 cm, 460-461 cm, 464-465 cm and 472-473 cm depth are observed in
329 the 25-80 μm and $>125 \mu\text{m}$ grain size fractions and three can be clearly observed in
330 the 80-125 μm fraction. Each peak contains shards with affinities to either the
331 transitional alkali or tholeiitic rock suites of Iceland, with the material from each of
332 these rock suites displaying distinct heterogeneity (Figure 5a). Compositional
333 similarities between the deposits and the continuous nature of the ash deposition allow
334 the whole of the deposit between 455-475 cm to be interpreted as a single entity.

335

336 **FIGURE 5**

337

338 According to the MD04-2820CQ stratigraphy, this deposit spans the warming
339 transition related to DO-8 (Figure 2 and 6), akin to the FMAZ III deposit identified in
340 other North Atlantic marine records. Distinct similarities are evident between the
341 heterogeneous Grímsvötn-sourced material of FMAZ III characterised from a record
342 in the SE Norwegian Sea (Griggs et al., 2014) and the tholeiitic material present in
343 this ash zone (Figure 5). Homogenous Grímsvötn-sourced populations identified in
344 the Greenland tephra framework between GI-8c and GS-9 cannot be identified at any
345 depth in MD04-2820CQ (Figure 7a). The geochemical range of the tholeiitic material
346 in MD04-2820CQ encompasses that of glass in all the ice-core horizons (Figure 7a).
347 Despite the failure to correlate to an ice-core deposit, the MD04-2820CQ deposit can
348 be correlated to the marine FMAZ III due to the stratigraphic similarities and

349 geochemical affinity of the tholeiitic basaltic material. None of the Faroes Islands
350 region occurrences of FMAZ III contain a population of transitional alkali material as
351 observed in the MD04-2820CQ deposit (Figure 5; Wastegård et al., 2006; Griggs et
352 al., 2014). Two transitional alkali basaltic horizons from Katla were identified in early
353 GS-9 by Bourne et al. (2013, 2015b) and also fall within the range of the MD04-
354 2820CQ analyses, but the heterogeneity is far greater in the marine deposits and no
355 potential correlations can be suggested (Figure 7b).

356

357 FIGURE 6 AND 7

358

359 Griggs et al. (2014) interpreted FMAZ III in the Faroe Islands region as resulting from
360 the amalgamation of primary fall material from closely timed Grímsvötn eruptions.
361 Sediment accumulation rates are considered to be insufficient to allow the events to be
362 separated and secondary processes such as bioturbation and bottom currents may have
363 caused mixing of shards between depths. An ice-rafting transport and deposition
364 mechanism was ruled out by Griggs et al. (2014) due to a lack of a coeval IRD signal.
365 Within MD04-2820CQ, IRD concentrations are declining between 455-475 cm and
366 there is no direct co-variance with glass shard concentrations (Figure 6). This lack of
367 correlation could imply that the transport, deposition and post-deposition mechanisms
368 are common between the MD04-2820CQ and JM11-FI-19PC core sites. The
369 incorporation of transitional alkali material at the MD04-2820CQ site could result
370 from more southerly transport of material from these eruptions. This would also
371 account for the relative lack of transitional alkali eruptions in the Greenland tephra
372 framework during this interval. As highlighted earlier, the FMAZ III cannot be used
373 as a precise ice-marine tie-line (Bourne et al., 2013). However, the correlation of

374 MD04-2820CQ 455-475 cm to FMAZ III extends the geographical distribution of this
375 deposit and it can be used as a marine-marine tie-line.

376

377 A small peak in colourless shards occurs at 463-464 cm and major element analysis
378 shows that the glass has a rhyolitic composition and an affinity to the Icelandic
379 transitional alkali rock suite (Figure 8a). Two populations are apparent, one with
380 affinities to material from the rhyolitic component of NAAZ II and one with affinities
381 to a number of Katla-sourced rhyolitic horizons deposited during the last glacial-
382 interglacial transition and an underlying horizon in MD04-2820CQ at a depth of 497-
383 498 cm (Figure 8b and c). These compositional affinities and the low shard
384 concentration suggests that this material is not from a distinct volcanic event but may
385 relate to a background of reworked colourless shards in the sequence.

386

387 FIGURE 8

388

389 *3.4 Period 4 – DO-12 to DO-9*

390

391 During this period a series of three relatively discrete peaks (~1-3 cm) in brown glass
392 shards can be identified (Figure 2 and 6). The peaks in brown shards at 487-488 cm
393 and 524-525 cm depth are distinct across all grain-size fractions, whereas the peak at
394 511-512 cm is only evident within the 25-80 and >125 μm grain-size fractions. A
395 broad increase in colourless shards between 490-500 cm displays a double peak in
396 concentration within the 25-80 μm grain-size fraction at 493-494 cm and 497-498 cm.

397

398 *3.4.1 MD04-2820CQ 487-488 cm*

399

400 All shards in the 487-488 cm deposit are basaltic in composition with one dominant
401 and homogenous tholeiitic population (Figure 9). Some outliers with a transitional
402 alkali composition are also observed, but are primarily restricted to the >80 μm
403 fraction (Figure 9a). The main population is characterised by SiO_2 concentrations of
404 ~49.5 %wt, TiO_2 concentrations between 2.6-3.2 %wt, CaO concentrations between
405 10.1 and 10.9 %wt and FeO concentrations of ~13.8 %wt, showing affinities to the
406 Grímsvötn volcanic system (Figure 9).

407

408 FIGURE 9

409

410 A large number of Grímsvötn eruptives are found within the Greenland tephra
411 framework between 25-45 ka b2k with several showing compositional similarities to
412 the main population of MD04-2820CQ 487-488 cm (Bourne et al., 2015b).
413 Stratigraphic information from MD04-2820CQ is thus employed to provide a broad
414 constraint on the timing of this eruption relative to the main climato-stratigraphic
415 framework for the North Atlantic. Further discussion of this approach is provided in
416 Section 4. MD04-2820CQ 487-488 cm was deposited just prior to Heinrich event 4
417 (Figure 6), which is widely regarded to have occurred in GS-9 and between DO-9 and
418 DO-8 (Sanchez Goñi and Harrison, 2010). The high-resolution $Np(s)$ record for this
419 interval shows that MD04-2820CQ 487-488 cm falls within a cold period above two
420 distinct decreases in $Np(s)$ percentages, between 490-510 cm depth, and thought to be
421 related to warming over the DO-9 and DO-10 events (Figure 6iii). These events were
422 not apparent within the original low resolution $Np(s)$ record or the Ca XRF record
423 (Figure 2ii and 6iv). These stratigraphic constraints suggest deposition during the cold

424 period following DO-9, which is equivalent to GS-9 within the Greenland
425 stratigraphic framework (Rasmussen et al., 2014). The GS-9 interval has been fully
426 sampled in all the ice-cores that contribute to the Greenland tephra framework (see
427 Bourne et al., 2015b). In total, 10 Grímsvötn-sourced tephra horizons have been
428 identified in one or more of the Greenland cores (Figure 6b). Geochemical
429 comparisons show that no horizons provide a clear major element match to 487-488
430 cm. Therefore, a potential correlative to the marine horizon cannot be proposed
431 (Figure 10a).

432

433 **FIGURE 10**

434

435 The transport mechanism for this deposit is unlikely to be iceberg rafting because of
436 the relatively homogenous geochemical signature of the material and a lack of co-
437 variance with IRD (Figure 6). Other potential mechanisms, sea-ice rafting and
438 primary airfall, would not impart a temporal delay and the deposit can be assumed to
439 be isochronous. The relative proportion of larger grains in the 80-125 μm and >125
440 μm fractions compared to other deposits, e.g. 524-525 cm, could be indicative of
441 transportation via sea-ice rafting. This deposit is considered to have strong
442 stratigraphic integrity as the peak in shard concentration is relatively discrete with
443 only a restricted downward tail in concentration, most likely due to post-depositional
444 bioturbation. Although not present in Greenland, if it was widely dispersed over the
445 North Atlantic, this volcanic deposit may be a useful isochron for linking this
446 sequence to other marine records.

447

448 *3.4.2 MD04-2820CQ 493-494 cm and 497-498 cm*

449

450 According to the stratigraphy for MD04-2820CQ, the slight increase in colourless
451 shards between 490-500 cm occurred during the short-lived cold period between DO-
452 10 and DO-9, based on an increase in $Np(s)$ percentages (Figure 2 and 6). Shards from
453 both peaks have a rhyolitic composition (Figure 8). The material from the larger peak
454 at 497-498 cm has affinities to the transitional alkali rock suite of Iceland and forms a
455 single homogenous population with SiO_2 concentrations between 70.5 and 71.5 %wt,
456 Al_2O_3 concentrations of ~13.5 %wt, K_2O concentrations of ~3.6 %wt and CaO
457 concentrations between 1.44 and 1.65 %wt (Figure 8). A source for these glass shards
458 could not be determined through comparisons to characterisations of proximal whole
459 rock rhyolites from Iceland, which may be due to the presence of other mineral phases
460 within whole rock analyses. However, compositional similarities to glass shards from
461 last glacial-interglacial transition rhyolitic tephra horizons sourced from the Katla
462 volcanic system (Figure 8b) strongly indicate that this is the volcanic source. Shards
463 in the overlying smaller peak at 493-494 cm fall into two populations, one with
464 affinities to the Katla material 4 cm below and one with strong overlap with shards
465 from 610-611 cm in the core from NAAZ II (Figure 8b and c). No rhyolitic horizons
466 have been isolated within the Greenland ice-core records between GI-9 and GI-11
467 (Bourne et al., 2015b).

468

469 The homogeneity of the 25 shards from the 497-498 cm peak and the predominance
470 of material in the 25-80 μm grain size fraction suggests that this represents primary
471 fall deposition. The upward tail in shard concentrations could be related to secondary
472 redistribution of material by bottom currents and the compositional bimodality in this
473 tail (493-494 cm sample) suggests reworking of the underlying Katla-sourced material

474 and NAAZ II input. Shards from NAAZ II (see Section 3.5) are present within
475 overlying sediments and are the likely primary constituent of the reworked
476 background of fine-grained rhyolitic material.

477

478 *3.4.3 MD04-2820 CQ 511-512 cm*

479

480 Brown shards from the peak at 511-512 cm are basaltic in composition with both
481 tholeiitic and transitional alkali material present. Distinct heterogeneity can be
482 observed in a number of components, e.g. Na₂O, K₂O, TiO₂ and FeO, and the
483 analyses cannot be grouped into clear populations (Figure 9). The glass peak is
484 directly associated with a peak in IRD, which combined with the geochemical
485 signature strongly suggests it is an ice-rafted deposit and cannot be assumed to be
486 isochronous.

487

488 *3.4.4 MD04-2820 CQ 524-525 cm and 529-530 cm*

489

490 The highest shard concentration in this period is found at 524-525 cm and exhibits a
491 broader rise in shard concentrations including a small shard peak 4 cm below the main
492 peak at 529-530 cm (Figure 2 and 6). The stratigraphy of MD04-2820CQ shows that
493 the tephra horizon falls on the decrease in $Np(s)$ percentage and increase in Ca content
494 of the sediment that has been related to warming at the onset of DO-11 (Figure 2 and
495 6). Shards from both the main peak and underlying peak have a tholeiitic basaltic
496 composition (Figure 9a). Shards from 524-525 cm form a homogenous population
497 characterised by distinctly high FeO concentrations between 14.5 and 16.7 %wt, low
498 CaO concentrations of ~9.25 %wt, TiO₂ concentrations of ~3.2 %wt and MgO

499 concentrations between 4.5 and 5.5 % wt (Figure 9). Comparison with proximal
500 deposits highlights similarities to the products of both the Kverkfjöll and Grímsvötn
501 volcanic systems (Figure 9b).

502

503 Four Grímsvötn-sourced deposits are found within the GS-12 climatic period and one
504 within GI-11 in the Greenland tephra framework (Bourne et al., 2015b). Statistical
505 comparisons show that none of these horizons are statistically different from 524-525
506 cm and all SC values exceed 0.95, due to the common source (Table 1). There is a
507 clear affinity between the main population of MD04-2820CQ 524-525 cm and NGRIP
508 2162.05 m with a low D^2 value and the highest similarity coefficient of 0.977; this
509 assessment is corroborated by major element biplot comparisons (Table 1; Figure 9b).
510 To test this affinity, the trace element composition of both horizons was determined.
511 Distinct differences can be observed in these characterisations, both in absolute
512 concentrations and trace element ratios (Figure 10c). These demonstrate that the two
513 horizons were not produced during the same volcanic event and cannot be correlated
514 between the archives. The differences in trace element composition could be due to a
515 number of factors, which will be discussed in Section 4.2.

516

517 TABLE 1

518

519 Assessing this deposit according to the protocol of Griggs et al. (2014) is problematic
520 as key indicators are contradictory. The homogenous composition of the deposit
521 suggests that this deposit was unlikely to be iceberg rafted, but it was deposited during
522 a period of increased IRD concentrations (Figure 6). It is possible that primary fall
523 deposition is superimposed on a period dominated by iceberg rafting. What is more,

524 iceberg rafting is typically thought to transport heterogeneous tephra deposits from an
525 amalgamation of tephra from a number of eruptions. Tracing this horizon in the same
526 stratigraphic position in another marine sequence would provide supporting evidence
527 for this interpretation.

528

529 Glass shards from the small peak at 529-530 cm were additionally geochemically
530 analysed to assess its relationship to the main overlying peak at 524-525 cm. All of
531 the shards have a tholeiitic basaltic composition (Figure 9a), with three distinct major
532 element populations present based on major oxides including FeO, CaO, MgO and
533 Al₂O₃ (Figure 8bii). Half of the shards from this deposit make up the main population
534 and indicate a source from either the Veidivötn-Bárdabunga or Reykjanes volcanic
535 systems (Figure 9b). One population is sourced from Grímsvötn or Kverkfjöll and has
536 compositional affinities to MD04-2820CQ 524-525 cm and the final population is
537 sourced from Grímsvötn and has affinities to MD04-2820CQ 487-488 cm (Figure 9b).
538 The only known tephra horizon in the Greenland ice-core framework between 25-45
539 ka b2k with a composition similar to the dominant population was deposited during
540 GS-5 and thus is not a correlative to this deposit. The similarity in geochemistry
541 between the sub-population and MD04-2820CQ 487-488 cm is likely to be
542 coincidental, with the Greenland tephra framework showing that Grímsvötn produced
543 many eruptives with similar compositions throughout this period (Bourne et al.,
544 2015b). The heterogeneity of this material could be linked to some iceberg rafting of
545 earlier events combined with downward reworking of material from the 524-525 cm
546 peak.

547

548 *3.5 Period 5 – DO-15 to DO-14*

549

550 The highest concentration of colourless shards was observed at 610-611 cm with
551 ~19,500 shards per 0.5 g dry weight sediment (dws) in the 25-80 μm fraction and
552 ~450 shards in the $>125 \mu\text{m}$ fraction in this cryptotephra (Figure 2b). A peak in shards
553 80-125 μm in diameter associated with this deposit occurs 1 cm above this depth
554 between 609-610 cm (Figure 2b). Within the proposed MD04-2820CQ stratigraphy,
555 the shard concentration peak falls on the cooling transition at the end of DO-15 as
556 shown by the rise in the *Np(s)* percentage (Figure 2b).

557

558 These colourless shards have a rhyolitic composition with affinities to the Icelandic
559 transitional alkali rock suite (Figure 8a) and are characterised by SiO_2 concentrations
560 of ~75.8 %wt, Al_2O_3 concentrations of ~11.7 %wt, FeO concentrations between 2.25
561 and 2.8 %wt and K_2O concentrations of ~4.2 %wt. Geochemical similarities are
562 highlighted between the MD04-2820CQ 610-611 cm deposit and other occurrences of
563 the rhyolitic component of NAAZ II (II-RHY-1) in North Atlantic marine sequences
564 and the GRIP ice-core (Figure 8c). There are some slight offsets between the MD04-
565 2820CQ characterisations and the older analyses, e.g. the MD04-2820CQ shards have
566 higher Na_2O and lower Al_2O_3 and SiO_2 concentrations, and these differences can be
567 attributed to the effect of sodium loss during the older analyses (Hunt and Hill, 2001;
568 Kuehn et al., 2011; Hayward, 2012). Therefore, these newer analyses represent a more
569 up-to-date characterisation of the II-RHY-1 component of NAAZ II and should be
570 utilised in future comparisons.

571

572 Identification of this horizon provides a direct ice-marine tie-line, a basal stratigraphic
573 constraint for the core, and a test of the proposed stratigraphy for MD04-2820CQ

574 because this horizon has been identified in the Greenland ice-cores and other marine
575 sequences on the cooling transition at the end of GI-15 (Grönvold et al., 1995; Austin
576 et al., 2004).

577

578 **4. Discussion**

579

580 *4.1 Tephrostratigraphy of MD04-2820CQ between ~25-60 ka b2k and implications* 581 *for the regional tephra framework*

582

583 This work represents one of the first studies to employ density and magnetic
584 separation techniques to isolate and identify cryptotephtras within North Atlantic
585 marine sediments between 25-60 ka b2k. Here, the identification of basaltic tephra
586 deposits has been improved when compared with previous studies, e.g. Abbott et al.
587 (2014), as magnetic separation of basaltic shards from the host sediment produced
588 purer samples for optical microscopy work and geochemical analysis preparation.

589

590 Overall, the tephrostratigraphy of MD04-2820CQ is complex and differing transport
591 and deposition processes have given rise to a range of contrasting deposits. For
592 example, the geochemical heterogeneity of the MD04-2820CQ 275-279 cm and 511-
593 512 cm deposits and to a certain extent the deposits between 340-380 cm depth
594 suggests they were deposited via iceberg rafting. Whilst three of the deposits, the
595 basaltic 487-488 cm and 524-525 cm and the rhyolitic 497-498 cm, have isochronous
596 characteristics and have the potential to act as tie-lines between records, however
597 none of these horizons were found to have correlatives within the current Greenland
598 tephra framework (Table 2; see section 4.2 for further discussion).

599

600 TABLE 2

601

602 Two of the deposits in MD04-2820CQ have been correlated to previously known
603 tephra horizons (Table 2). MD04-2820CQ 610-611 cm correlates to NAAZ II and
604 permits a direct link to the Greenland ice-cores and other marine sequences while
605 MD04-2820CQ 455-475 cm can be correlated to FMAZ III, a broad marine-marine
606 link around DO-8 to sequences in the Faroe Island region. The MD04-2820CQ 455-
607 475 cm deposit differs from FMAZ III occurrences in the Faroe Islands region as it
608 contains transitional alkali basaltic glass in addition to the tholeiitic basaltic glass
609 characteristic of the original deposit (Griggs et al., 2014). Further work on tracing the
610 FMAZ III at sites between the Goban Spur area and the Faroe Islands region may help
611 isolate the transportation and depositional processes controlling this contrast. At
612 present the MD04-2820CQ core site on the Goban Spur is the furthest south that
613 FMAZ III has been identified; this increase in geographical range of the deposit
614 suggests that it could be a key stratigraphic marker for the DO-8 event in widespread
615 marine records.

616

617 The identification of horizons that do not at present have correlatives in other
618 palaeoarchives adds three further volcanic events into the regional framework for the
619 25-60 ka b2k period (Table 2). Tracing these horizons within other sequences would
620 test our assertion that these are atmospherically-derived and potentially validate their
621 use as isochronous tie-lines. This is most relevant for the MD04-2820CQ 497-498 cm
622 deposit which has a broader shard count profile relative to the two basaltic deposits.
623 The timing of emplacement of the three deposits can be inferred from their

624 relationship to the high-resolution stratigraphy for MD04-2820CQ shown in Figure 6,
625 which can act as a guide for tracing these deposits in other records (Table 2).

626

627 The two basaltic deposits are thought to be sourced from the Grímsvötn and/or
628 Kverkfjöll volcanic systems, providing further support for the high productivity of
629 these systems during the last glacial period (cf. Bourne et al., 2015b). These results
630 also demonstrate that their eruptive products were transported south of Iceland, most
631 likely via direct atmospheric transport. Katla is thought to be the most likely source of
632 MD04-2820CQ 497-498 cm and a correlative could not be identified in the Greenland
633 ice-cores (Section 3.4.2; Bourne et al., 2015b). Indeed, no rhyolitic tephra horizons
634 from this source and very few Icelandic rhyolitic horizons are present throughout the
635 last glacial period in the Greenland ice-cores (Davies et al., 2014; Bourne et al.,
636 2015b). The identification of this Katla horizon within the cool interval between DO-
637 10 and DO-9 thus demonstrates that older rhyolitic eruptions from this source did
638 occur prior to the last glacial-interglacial transition (Lane et al., 2012).

639

640 *4.2 Testing correlations using stratigraphy and trace element analysis*

641

642 The stratigraphy of MD04-2820CQ and its likely relationship to the Greenland
643 climatic record was used throughout to assess the timing of the emplacement of the
644 tephra deposits. This climatostratigraphic approach was particularly crucial for
645 assessing potential correlatives for the MD04-2820CQ 487-488 cm and 524-525 cm
646 horizons and high-resolution records of $Np(s)$ and IRD were available for these
647 purposes.

648

649 The correlation of tephtras solely based on geochemical matches between horizons,
650 relies on every eruption having a unique geochemical signature. For the North
651 Atlantic region, however, the new Greenland tephra framework demonstrates that
652 multiple basaltic horizons with overlapping geochemical signatures were erupted
653 within relatively short time-intervals (Bourne et al., 2013, 2015b). Therefore, as is
654 required for many other tephrochronological studies, stratigraphic control was used
655 alongside the compositional data to guide the testing of correlations. This approach
656 does introduce an element of circularity if the tephra correlations are to be used as
657 climatically independent tools to test stratigraphic comparisons and the relative timing
658 of past climatic changes (see discussion in Matthews et al., 2015). However, in this
659 instance the approach is valid as the overall stratigraphy of MD04-2820CQ is
660 supported by distinct event markers such as Heinrich Event 4 and NAAZ II and there
661 is a strong relationship to the sequence of well-defined Greenland Interstadial events
662 recorded in the ice-cores. This relationship is especially apparent over the section
663 where high-resolution proxy data has been acquired. In addition, the stratigraphic
664 comparisons used to test correlations were broad and on a millennial-scale, and not
665 centennial or decadal-scale which is the potential magnitude of climatic phasing
666 between the environments.

667

668 The use of stratigraphy to guide correlations will be limited or problematic when
669 correlations are being assessed between the Greenland records and marine sequences
670 that have a less well-resolved stratigraphic framework, due to core location and/or
671 sedimentation rate differences. However, due to the high frequency of Icelandic
672 basaltic eruptions, particularly from Grímsvötn, some form of stratigraphic constraint
673 is essential for exploring potential tie-lines. We recommend that, when possible, high-

674 resolution stratigraphic information is gained over key intervals of interest to aid
675 correlation testing.
676
677 The potential correlation between MD04-2820CQ and NGRIP 2162.05 m was tested
678 using grain-specific trace element analysis, due to strong major element similarities
679 (Figure 10b). This analysis showed that the two horizons were not produced during
680 the same volcanic event (Figure 10c). The use of trace element analysis to test and
681 add robustness to correlations has been encouraged previously and its use is steadily
682 increasing within tephrochronological studies (see Section 1). Our work provides
683 further support for the use of this technique for testing correlations and for providing a
684 key insight into geochemical variability between Icelandic eruptions, specifically
685 those sourced from the Grímsvötn volcanic system. As basaltic magmas have
686 undergone relatively limited compositional evolution, intra-eruption variability in
687 trace elements from a single evolving system could be limited as significant fractional
688 crystallisation may not have occurred, this being the process which dominantly
689 controls trace element evolution (see Pearce et al., 2008). Therefore, it is of interest to
690 see clear trace element differences between two Grímsvötn-sourced eruptions with
691 highly similar major element compositions. In this instance, the differences could
692 result from magmatic evolution within a single, fractionating magma chamber
693 between eruptions or the eruptions tapped magma from different fissures within the
694 overall Grímsvötn system with similar major element but differing trace element
695 compositions. Trace element analysis of proximal deposits could provide an insight
696 into the intra-eruption variability of Grímsvötn basalts.

697

698 **5. Conclusions**

699

700 The potential for using density and magnetic separation techniques to identify tephra
701 deposits within North Atlantic marine sequences spanning ~25-60 ka b2k has been
702 clearly demonstrated. Applying these techniques to MD04-2820CQ has unearthed a
703 complex tephrostratigraphical record with differing transportation and depositional
704 processes operating at different times, but the identification of isochronous deposits
705 highlights the potential for using tephrochronology to link marine sequences. One of
706 the biggest challenges for establishing correlations is the high number of
707 compositionally similar eruptives preserved in the ice-cores within short time-
708 intervals. We have outlined how stratigraphic constraints can help reduce the number
709 of potential candidates and the need for high-resolution proxy data to constrain key
710 intervals. The use of stratigraphic constraints from proxy data could ultimately be
711 limited by the resolution of marine records. In addition, it has been shown that trace
712 element comparisons provide a secondary fingerprint that can test the robustness of
713 correlations suggested by major element geochemical similarities. Exploration of
714 further records in this region will help assess the isochronous nature of the key
715 deposits in MD04-2820CQ and represent a major step towards synchronisation of
716 regional marine archives using cryptotephra deposits.

717

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719

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733 improved fingerprinting and correlation techniques and uncertainty modelling: phase
734 II) – an INQUA INTAV-led project (International Focus Group on Tephrochronology
735 and Volcanism, project No. 1307s).

736 **Figures**

737

738 **Figure 1:** Location map of the MD04-2820CQ core site and other cores referred to
739 within the text.

740

741 **Figure 2:** (a) Climate and tephrostratigraphy of the last glacial period within the
742 MD04-2820CQ core. (i) XRF (ITRAX core scanning) Ca count rates (ii) percentage
743 abundance of *Neogloboquadrina pachyderma* (sinistral) (iii) tephrostratigraphy
744 incorporating 5 and 1 cm resolution shard counts. (b) Inset of climate and
745 tephrostratigraphy of colourless shards between 550-650 cm depth. This figure is an
746 expansion of the colourless shard counts that were truncated on Figure 2a. Red bars
747 denote depth intervals from which glass shards were extracted for geochemical
748 analysis.

749

750 **Figure 3:** Comparison of glass compositions from MD04-2820CQ 275-279 cm to that
751 from FMAZ II, VZ 1x and VZ 1 characterisations from Davies et al. (2008), Griggs et
752 al. (2014) and Lackschewitz and Wallrabe-Adams (1997). (a) Inset of total alkalis
753 versus silica plot. Division line to separate alkaline and sub-alkaline material from
754 MacDonald and Katsura (1964). Chemical classification and nomenclature after Le
755 Maitre et al. (1989). (b) (i) CaO vs FeO and (ii) K₂O vs TiO₂ biplot comparisons.
756 NGRIP data from Davies et al. (2008), JM11-19PC data from Griggs et al. (2014) and
757 VZ 1x and VZ 1 data from Lackschewitz and Wallrabe-Adams (1997). All plots on a
758 normalised anhydrous basis.

759

760 **Figure 4:** Compositional characterisation of MD04-2820CQ glass shard deposits
761 between 340-380 cm depth, comparisons to proximal Icelandic deposits and
762 comparisons with horizons with a Kverkfjöll volcanic source in the Greenland tephra
763 framework. (a) (i) inset of total alkalis versus silica plot. Division line to separate
764 alkaline and sub-alkaline material from MacDonald and Katsura (1964). Chemical
765 classification and nomenclature after Le Maitre et al. (1989). (ii and iii)
766 Compositional variation diagrams comparing analyses to deposits proximal to four
767 tholeiitic Icelandic volcanic systems. Compositional fields defined using glass and
768 whole rock analyses from Jakobsson et al. (2008) (Reykjanes), Höskuldsson et al.
769 (2006) and Óladóttir et al. (2011) (Kverkfjöll) and Jakobsson (1979), Haflidason et al.
770 (2000) and Óladóttir et al. (2011) (Grímsvötn and Veidivötn-Bardabunga). (b) (i)
771 Compositional variation diagram of glass between 340-380 cm depth in MD04-
772 2820CQ (ii) Compositional variation diagram of glass from ice-core horizons from
773 the framework of Bourne et al. (2015b). (c) Compositional variation diagram of glass
774 from MD04-2820CQ 342-343 cm and glass from three heterogeneous Kverkfjöll
775 eruptives identified between GI-5.2 and GS-4 in the Greenland tephra framework of
776 Bourne et al. (2015b). Ice-core horizons in bold are identified in multiple cores. All
777 plots on a normalised anhydrous basis.

778

779 **Figure 5:** Compositional characterisation of glass from MD04-2820CQ tephra
780 deposits between 455-475 cm depth and comparison to the glass characterised for
781 FMAZ III. (a) inset of total alkali vs. silica plot. Division line to separate alkaline and
782 sub-alkaline material from MacDonald and Katsura (1964). Chemical classification
783 and nomenclature after Le Maitre et al. (1989). (b) Compositional variation diagrams

784 for tholeiitic glass. FMAZ III data from JM11-19PC core outlined in Griggs et al.
785 (2014). All plots on a normalised anhydrous basis.

786

787 **Figure 6:** (a) High-resolution stratigraphy of the 450-550 cm interval within MD04-
788 2820CQ. (i) Stratigraphy of colourless glass shard concentrations. (ii) Stratigraphy of
789 brown glass shard concentrations. Red bars denote samples from which shards were
790 extracted for compositional analysis. (iii) High-resolution percentage abundance of
791 *Neogloboquadrina pachyderma* (sinistral). (iv) XRF (ITRAX core scanning) Ca count
792 rates. (v) High-resolution IRD counts. Light green bars highlight glass shard peaks
793 with homogenous compositions. (b) Greenland tephra framework between GI-8 and
794 GI-12 (Bourne et al., 2015b and references within) plotted on the NGRIP oxygen
795 isotope stratigraphy (NGRIP Members, 2004). Green lines denote horizons that can be
796 traced in multiple cores. Other horizons are only present in NGRIP (red), NEEM
797 (purple), GRIP (yellow) and DYE-3 (blue).

798

799 **Figure 7:** (a) Compositional comparisons of tholeiitic glass from MD04-2820CQ
800 Period 3 deposits and GI-8c and GS-9 tephtras in the Greenland tephra framework of
801 Bourne et al. (2013, 2015b). (b) Compositional comparisons of transitional alkali
802 glass from MD04-2820CQ Period 3 deposits and GS-9 tephtras in the Greenland
803 tephra framework. Ice-core data from Bourne et al. (2015b). Ice-core horizons in bold
804 can be traced in multiple cores and only data from the NGRIP occurrence have been
805 used for those horizons. All plots on a normalised anhydrous basis. The key for
806 analyses from MD04-2820CQ is the same as Figure 5.

807

808 **Figure 8:** (a) Inset of total alkali vs. silica plot focusing on rhyolitic material from the
809 MD04-2820CQ core. Normalised compositional fields for the Icelandic rock suites
810 derived from whole rock analyses in Jakobsson et al. (2008). Chemical classification
811 and nomenclature after Le Maitre et al. (1989). (b) Compositional variation diagrams
812 comparing low SiO₂ rhyolitic glass from MD04-2820CQ to geochemical fields for a
813 number of Katla-derived tephra horizons. Glass compositions from Lane et al. (2012)
814 (Vedde Ash and Dimna Ash), Matthews et al. (2011) (AF555; Abernethy Tephra
815 (MacLeod et al., 2015)) and Pilcher et al. (2005) (Suduroy). (c) Compositional
816 variation diagrams comparing high SiO₂ rhyolitic glass from MD04-2820CQ to fields
817 for marine and ice occurrences of the NAAZ II rhyolitic component. Glass data from
818 Austin et al. (2004) (MD95-2006), Wastegård et al. (2006) (ENAM93-20, ENAM33,
819 EW9302-2JPC), Brendryen et al. (2011) (SO82-05, MD99-2289) and Grönvold et al.
820 (1995). All plots on a normalised anhydrous basis.

821

822 **Figure 9:** Compositional characterisation of basaltic glass from deposits between 485
823 and 530 cm in MD04-2820CQ and comparisons with Icelandic proximal material. (a)
824 inset of inset of total alkali vs. silica plot. Division line to separate alkaline and sub-
825 alkaline material from MacDonald and Katsura (1964). Chemical classification and
826 nomenclature after Le Maitre et al. (1989). (b) Compositional variation diagrams
827 comparing analyses with material proximal to four tholeiitic Icelandic volcanic
828 systems. Compositional fields defined using glass and whole rock analyses from
829 Jakobsson et al. (2008) (Reykjanes), Höskuldsson et al. (2006) and Óladóttir et al.
830 (2011) (Kverkfjöll) and Jakobsson (1979), Haflidason et al. (2000) and Óladóttir et al.
831 (2011) (Grímsvötn and Veidivötn-Bardabunga). All plots on a normalised anhydrous
832 basis.

833

834 **Figure 10:** (a) Comparison of the main tholeiitic glass population of MD04-2820CQ
835 487-488 cm with glass compositional fields for GS-9 tephra horizons sourced from
836 Grímsvötn in the Greenland tephra framework of Bourne et al. (2015b). Horizons in
837 bold have been identified in multiple ice-cores. (b) Comparison of MD04-2820CQ
838 524-525 cm glass with characterisations of glass from tephra horizons in the
839 Greenland tephra framework of Bourne et al. (2015b). (c) Comparison of trace
840 element characterisations of individual shards from MD04-2820CQ 524-525 cm and
841 NGRIP 2162.05 m. All plots on a normalised anhydrous basis.

842

843 **Table 1:** Statistical comparisons of the main tholeiitic population of glass from
844 MD04-2820CQ 524-525 cm with glass from GI-11 and GS-12 tephra horizons within
845 the Greenland tephra framework. Some outliers were removed from the ice-core
846 characterisations. Critical value of 23.21 for statistical distance comparisons (10
847 degrees of freedom; 99 % confidence interval).

848

849 **Table 2:** Summary of tephra horizons in MD04-2820CQ with the potential to act as
850 widespread tie-lines to other palaeoclimatic sequences in the North Atlantic region.
851 The timing of events is based on the stratigraphy for the MD04-2820CQ record.

852 *Only to be used as a marine-marine tie-point.

853

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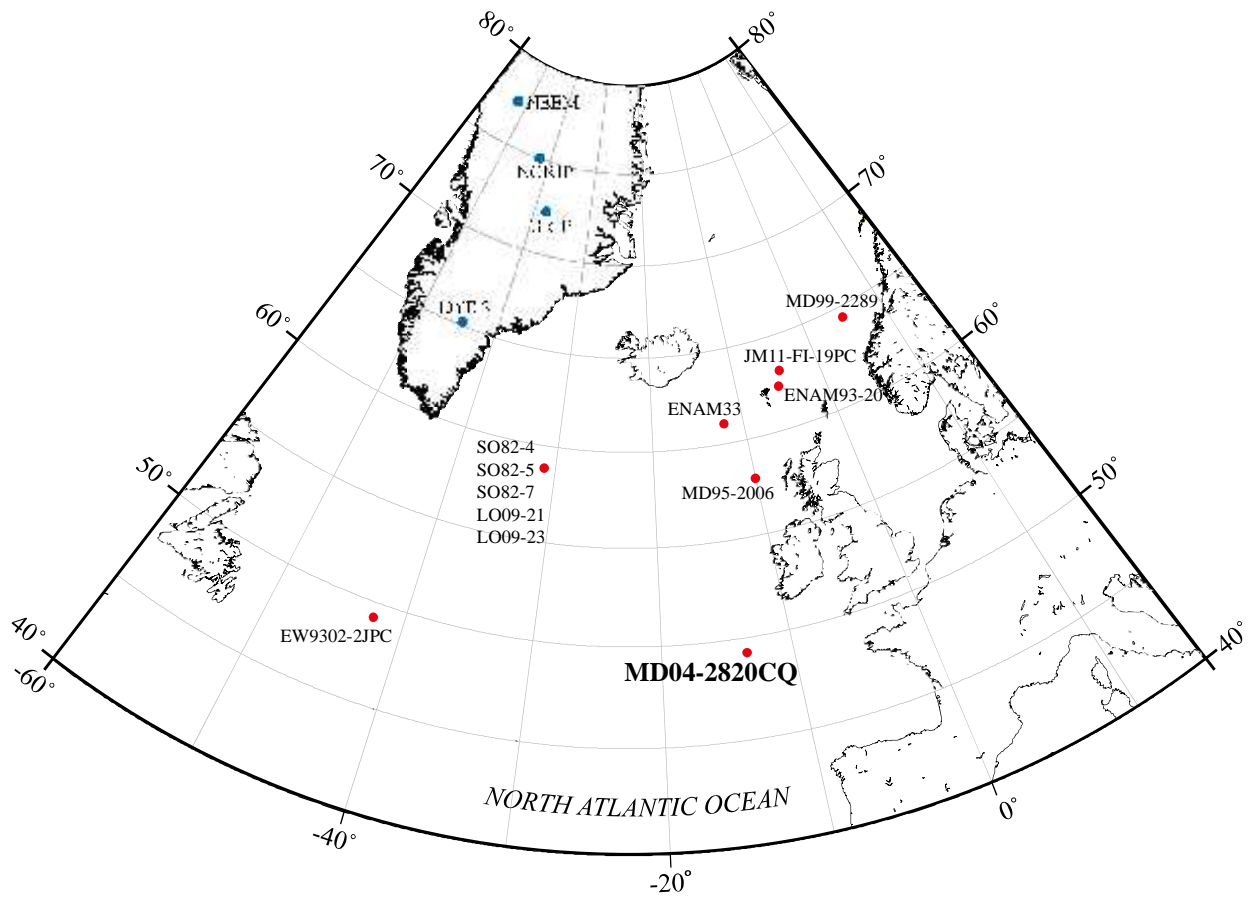
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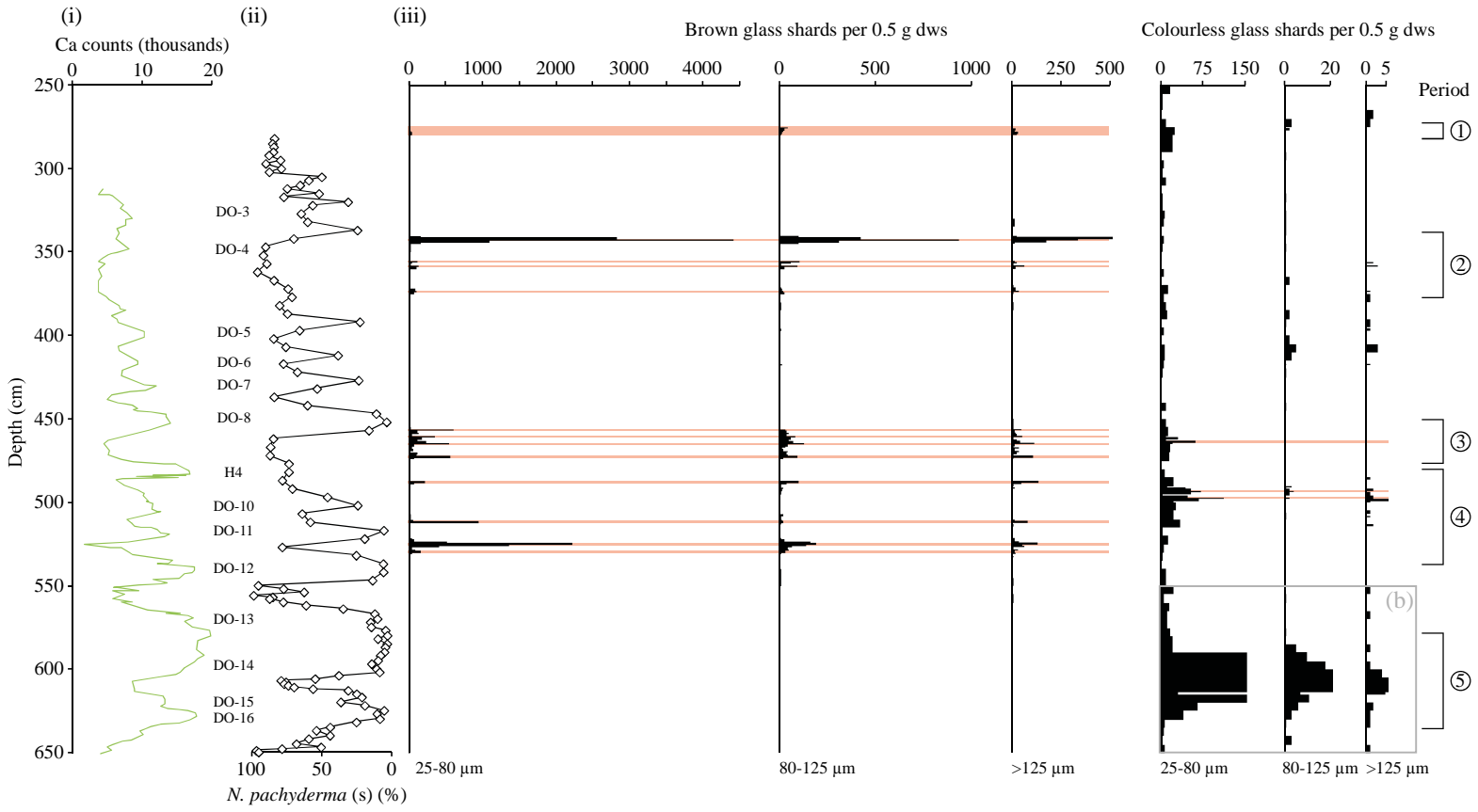
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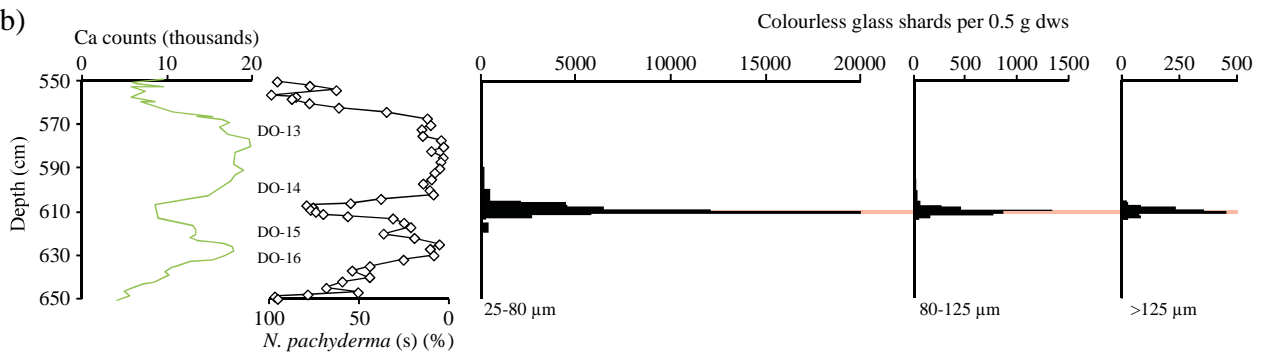
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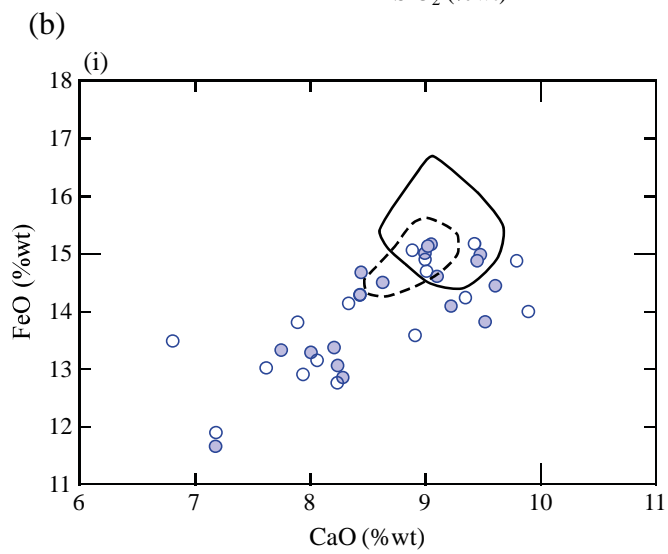
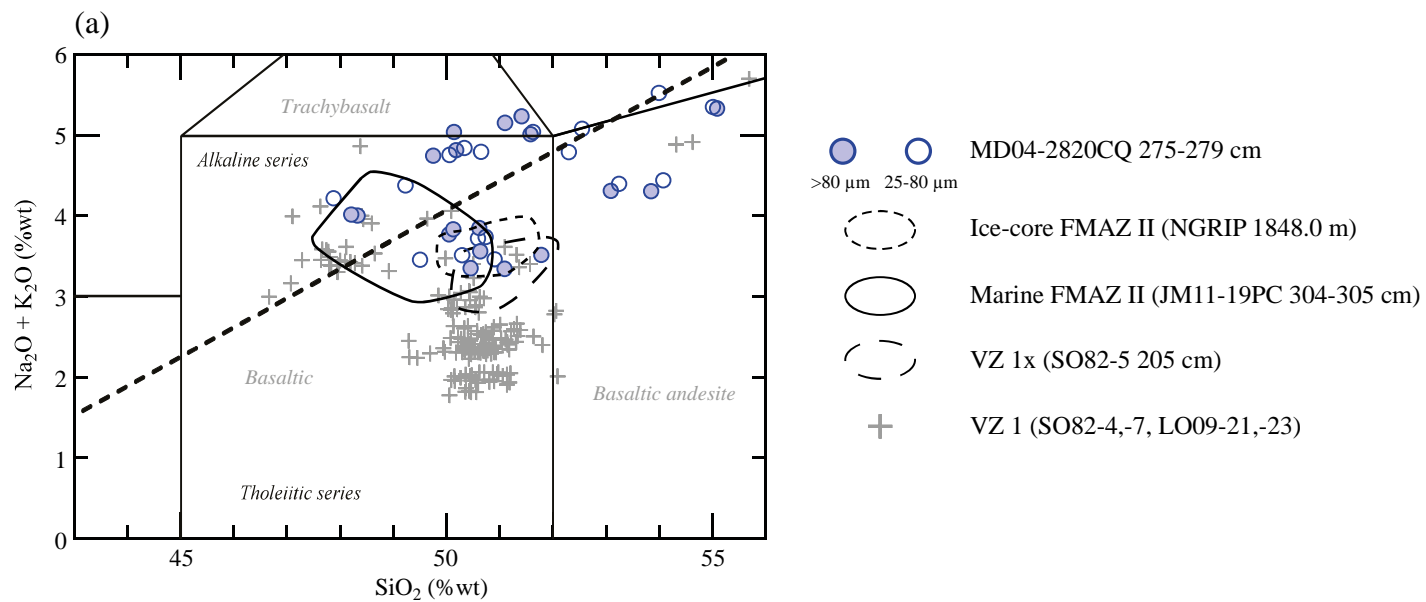


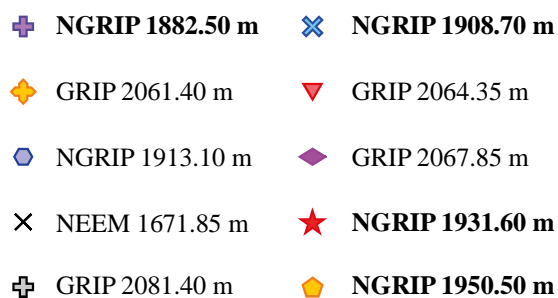
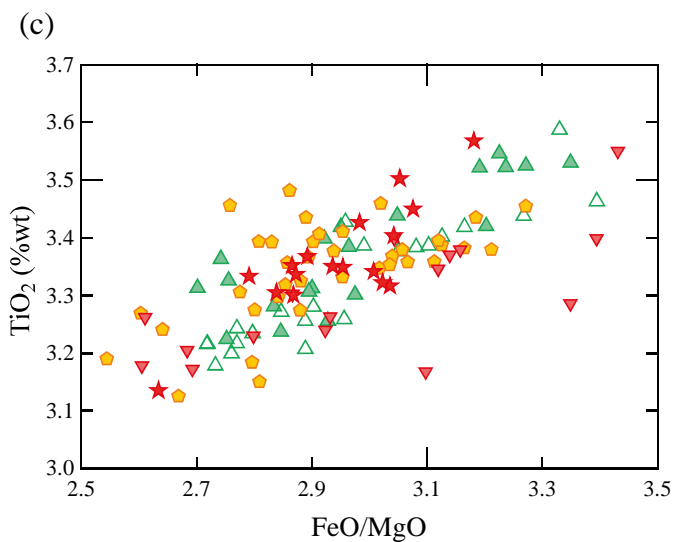
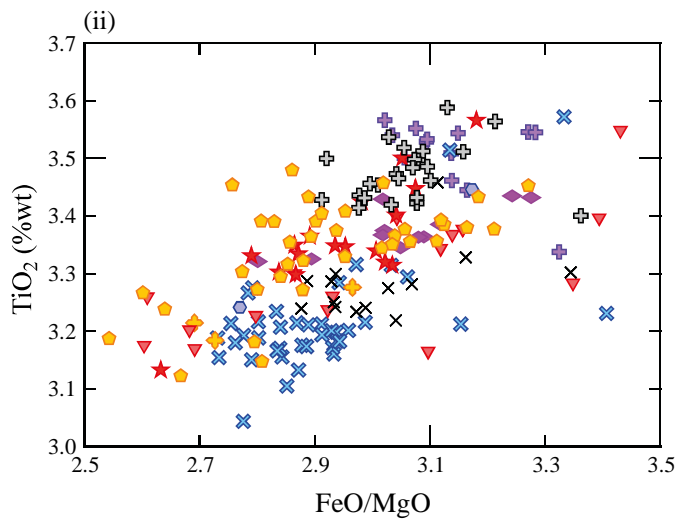
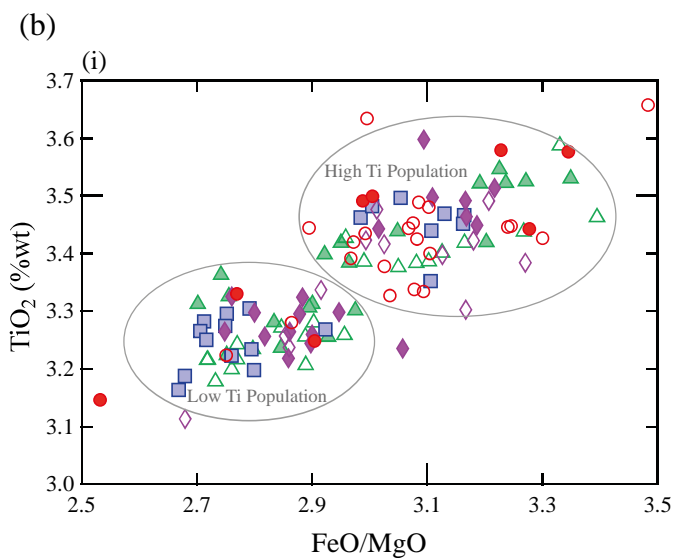
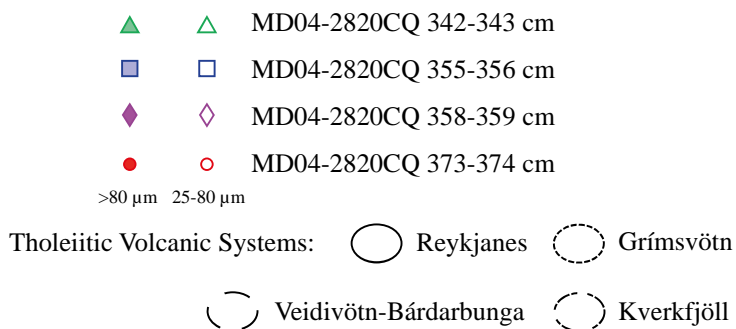
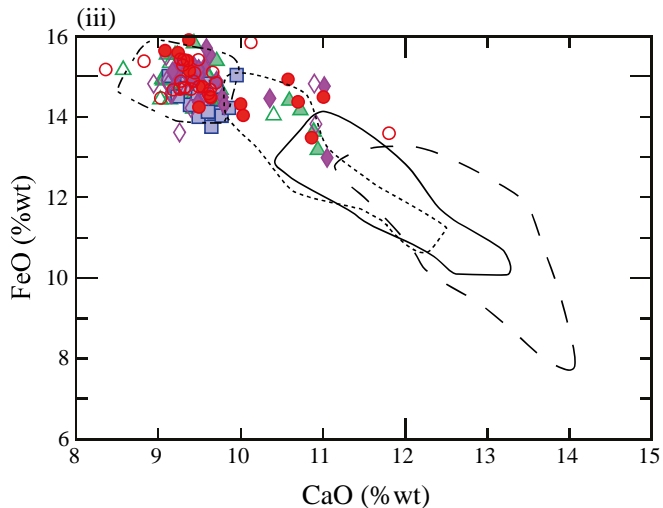
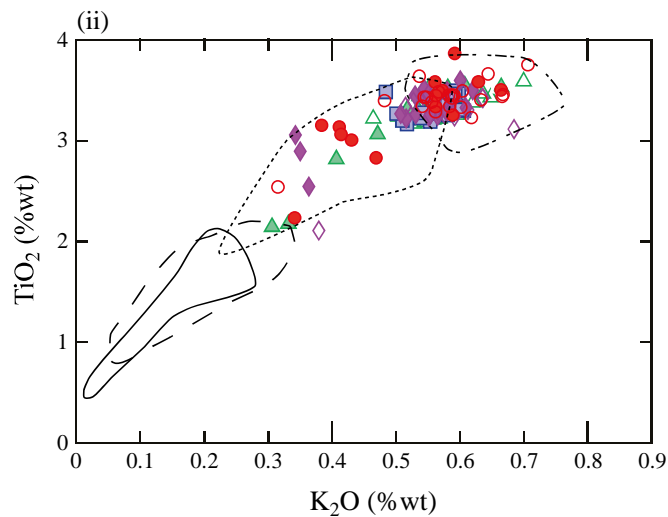
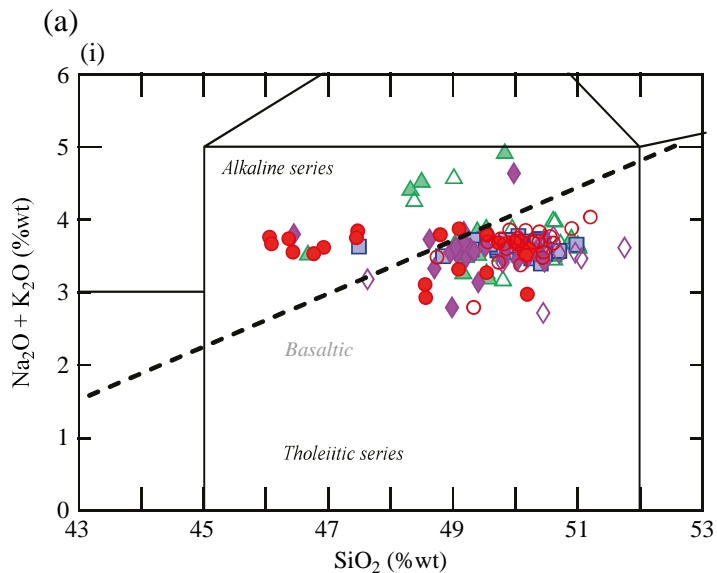
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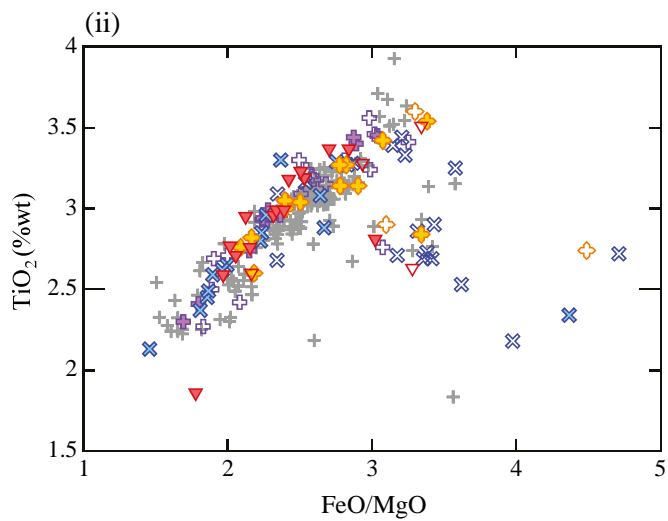
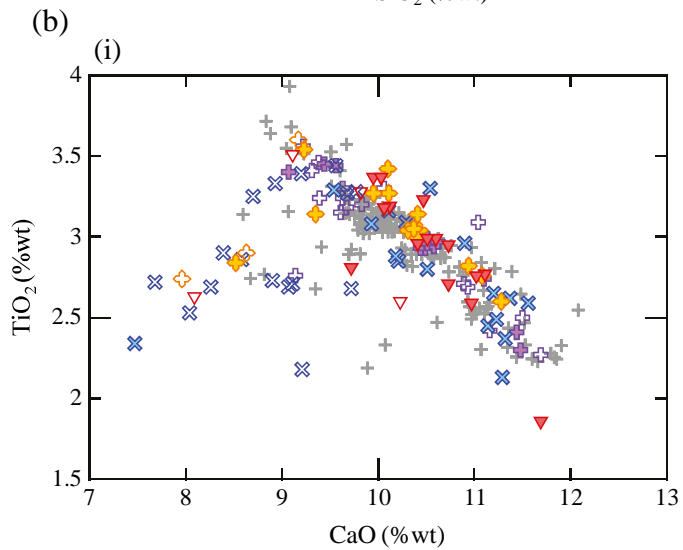
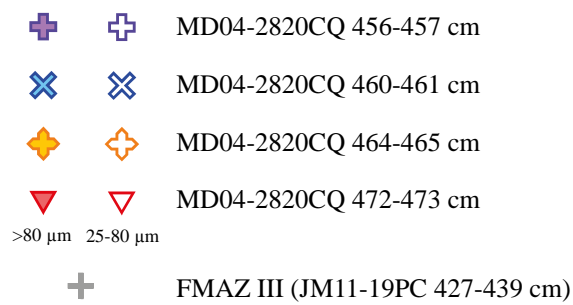
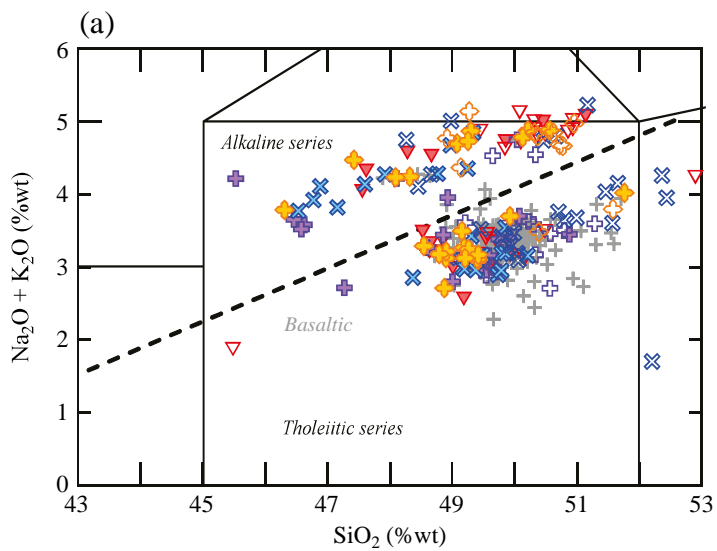


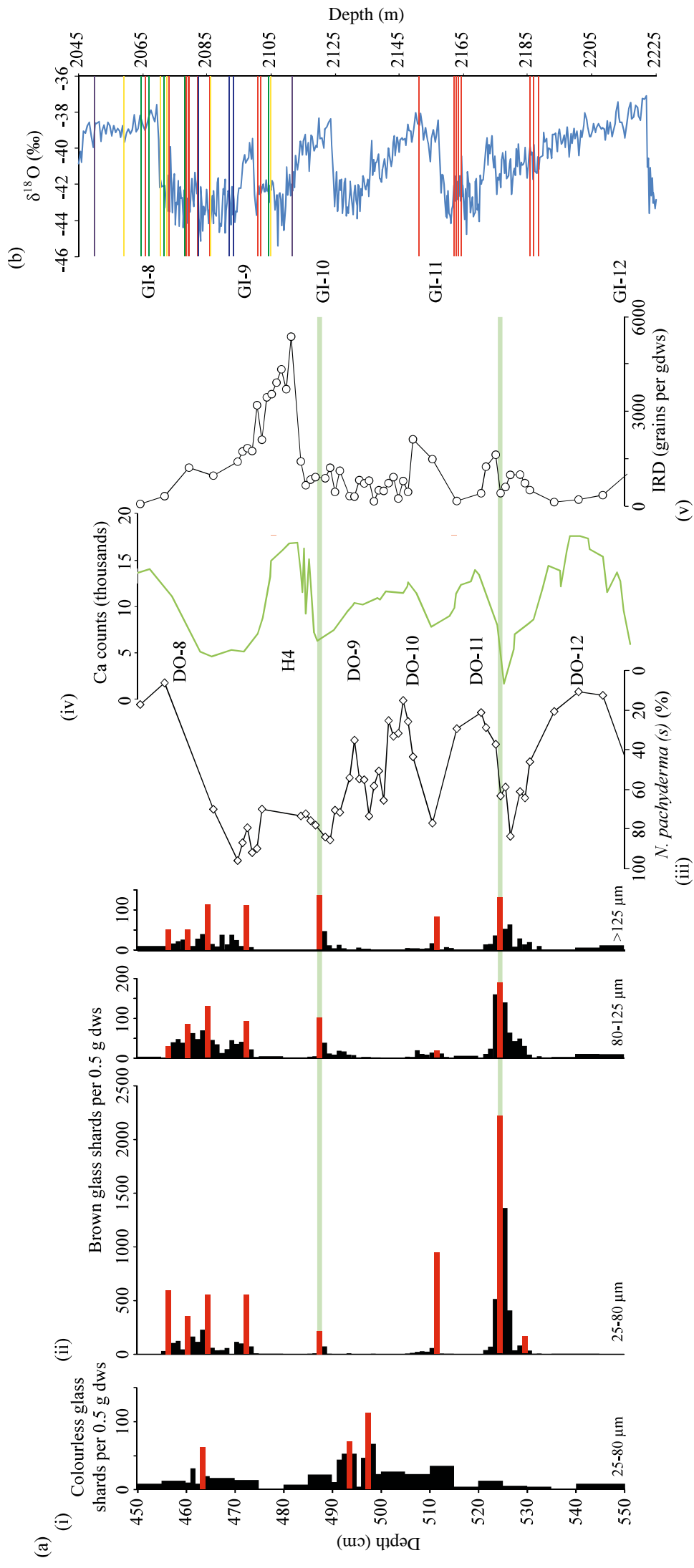
(b)



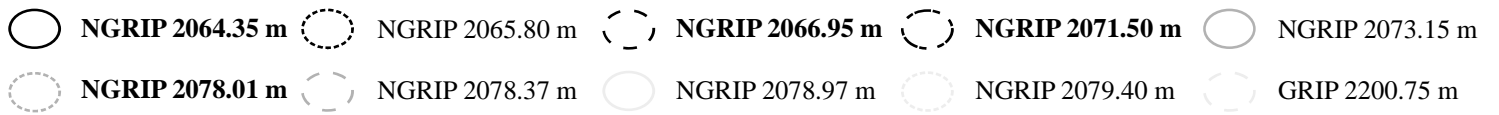
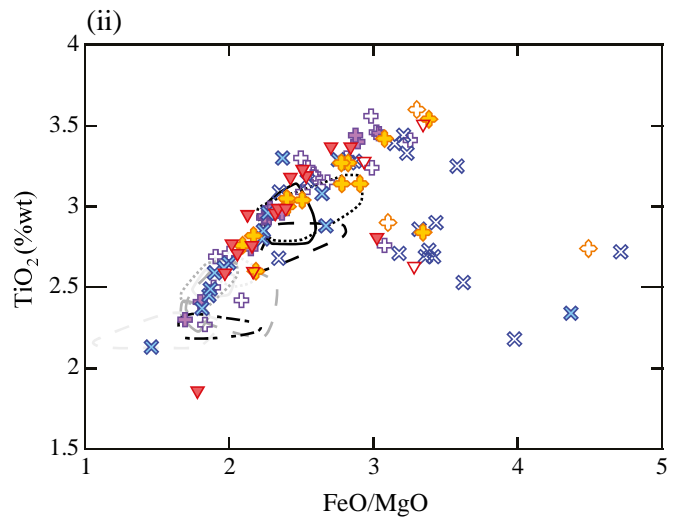
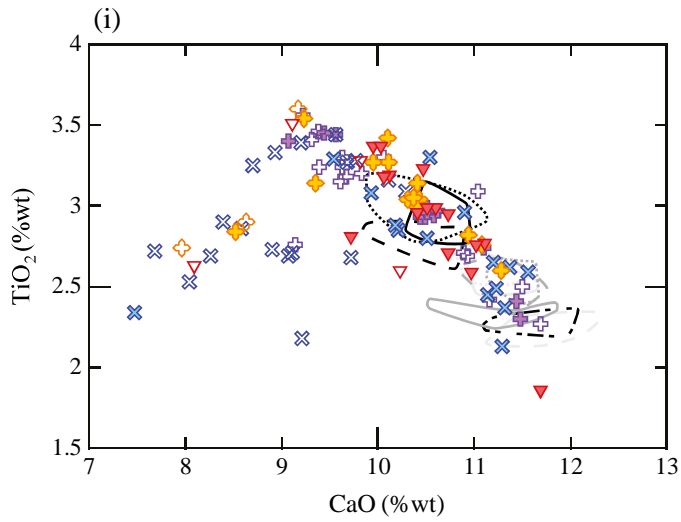




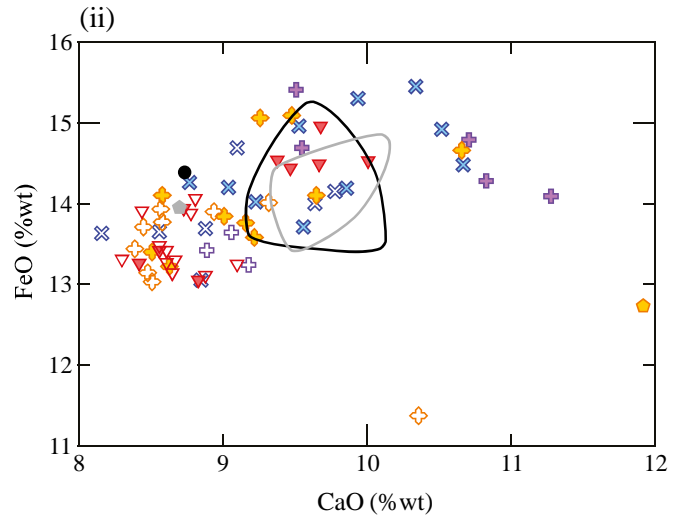
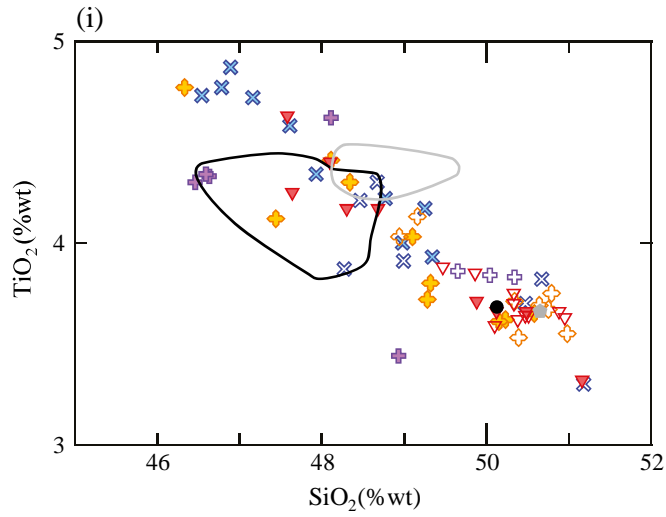


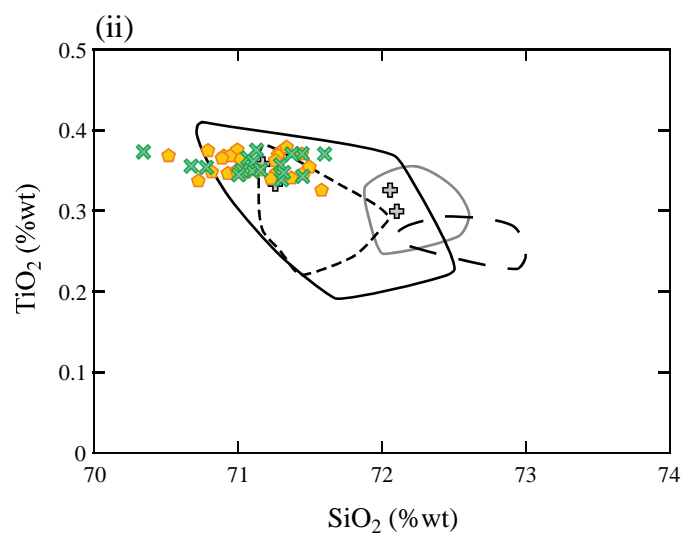
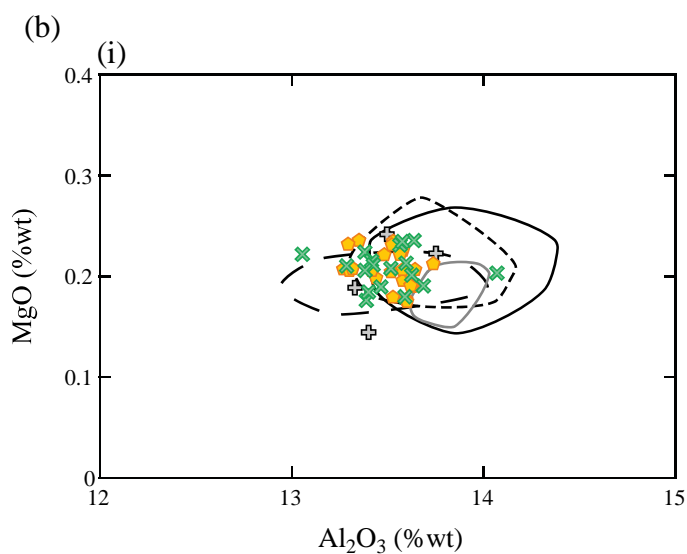
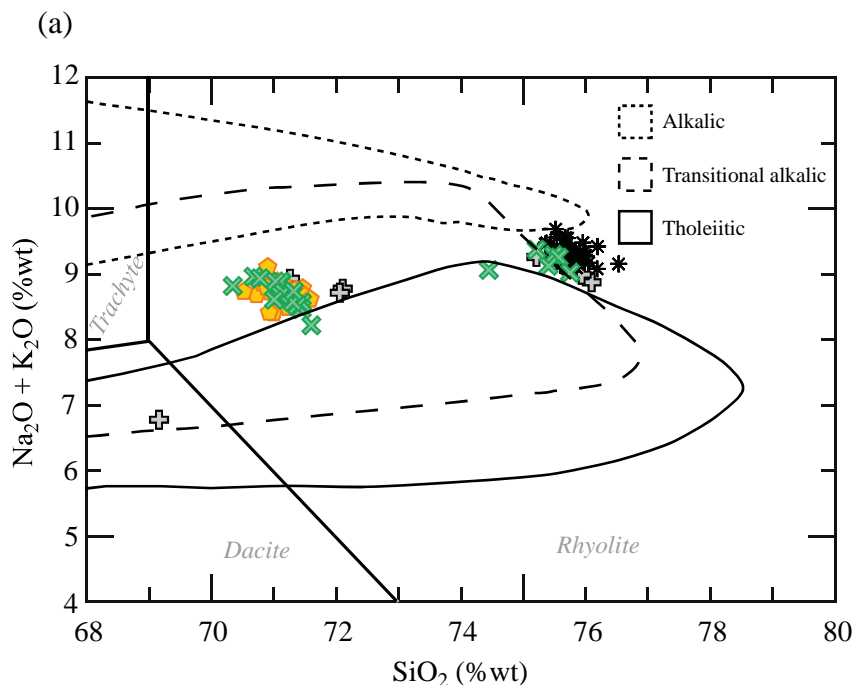


(a)

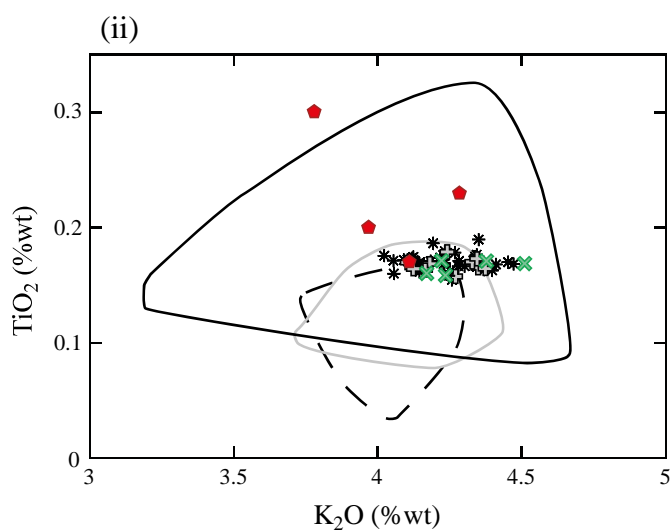
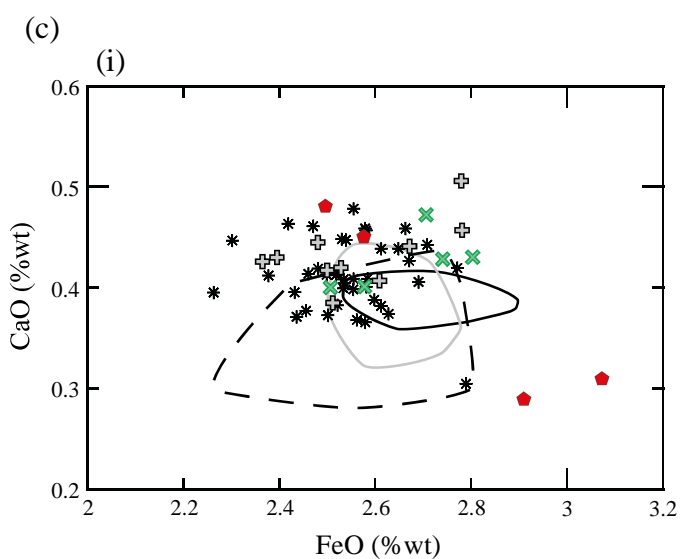


(b)

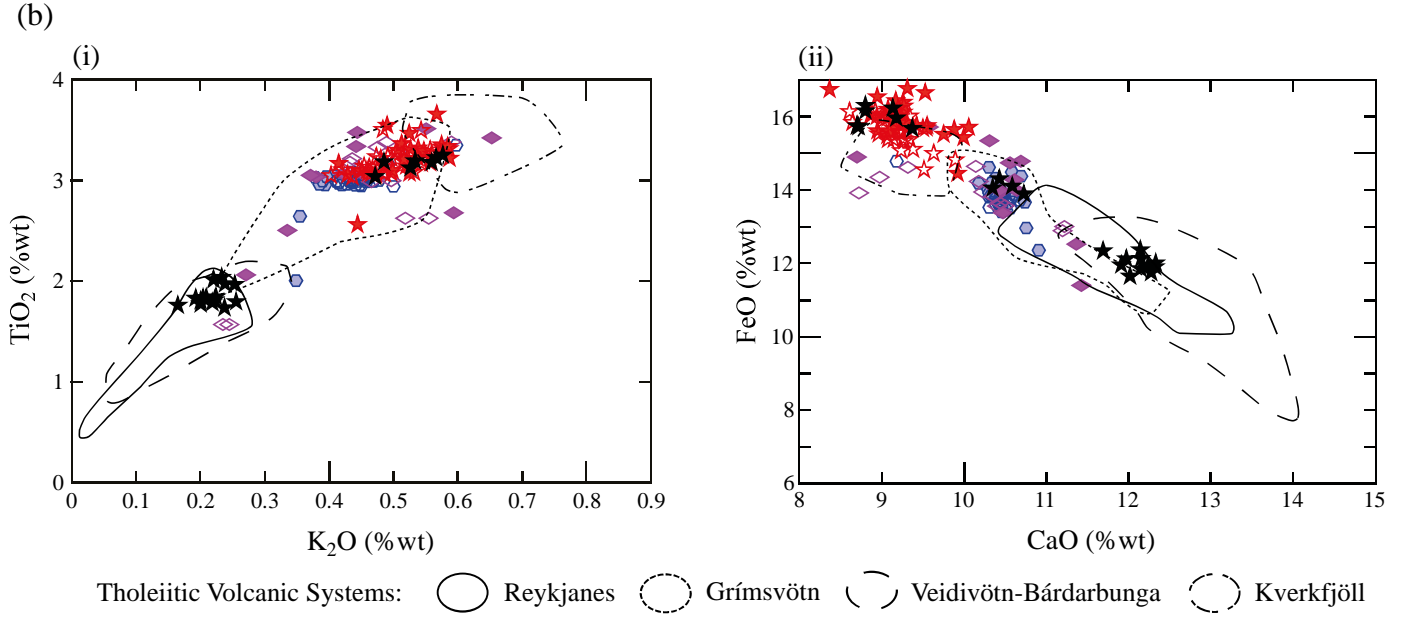
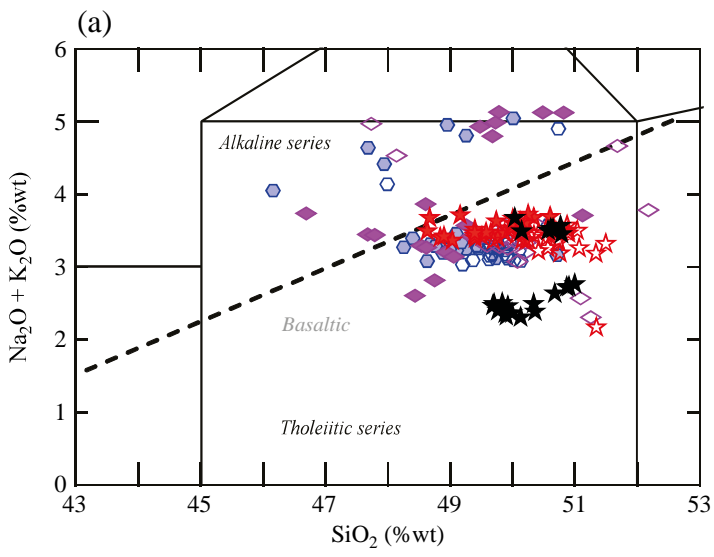




○ Vedde Ash ○ Dimna Ash ○ AF555 Tephra ○ Suduroy Tephra



II-RHY-1: ○ SO82-05, MD99-2289 ○ MD95-2006 ○ ENAM93-20, ENAM33, EW 9302-2JPC ◆ GRIP



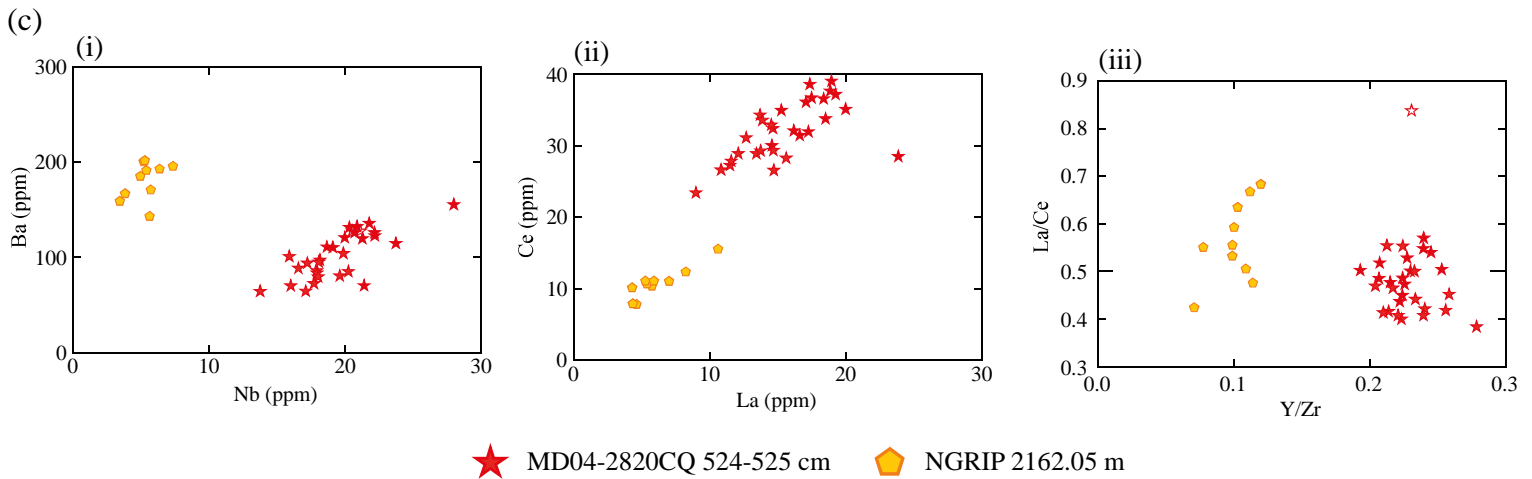
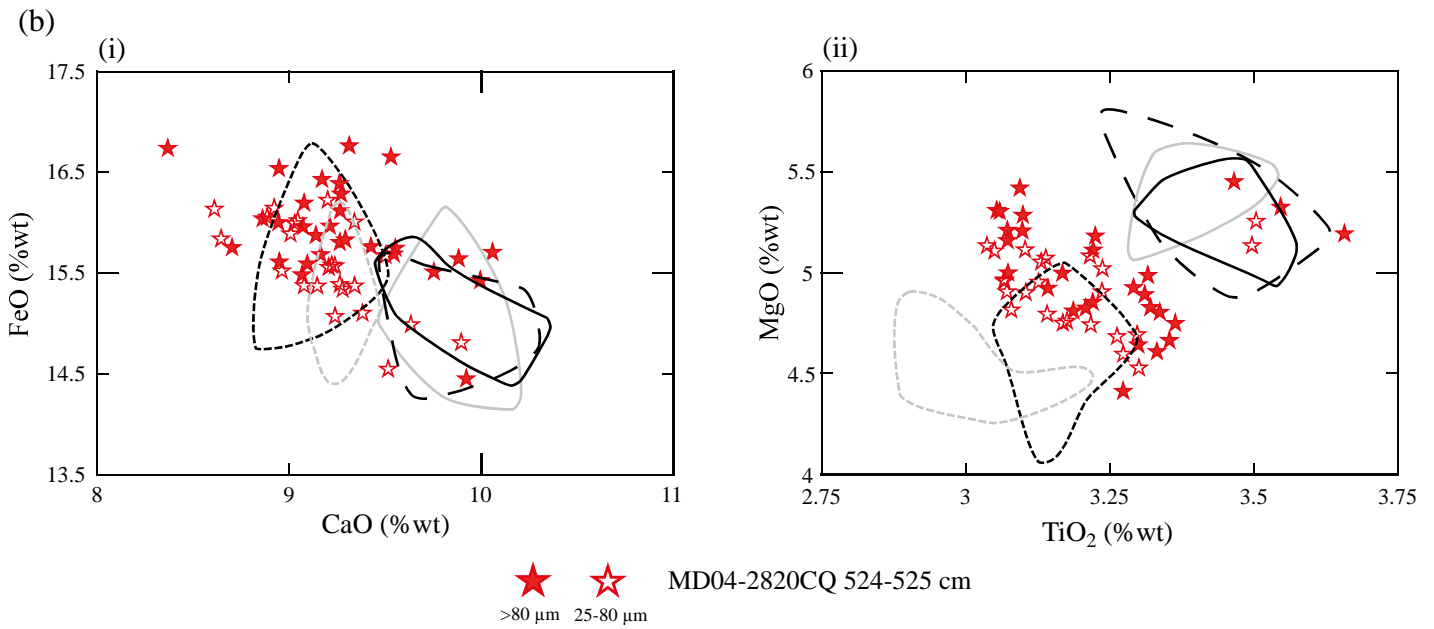
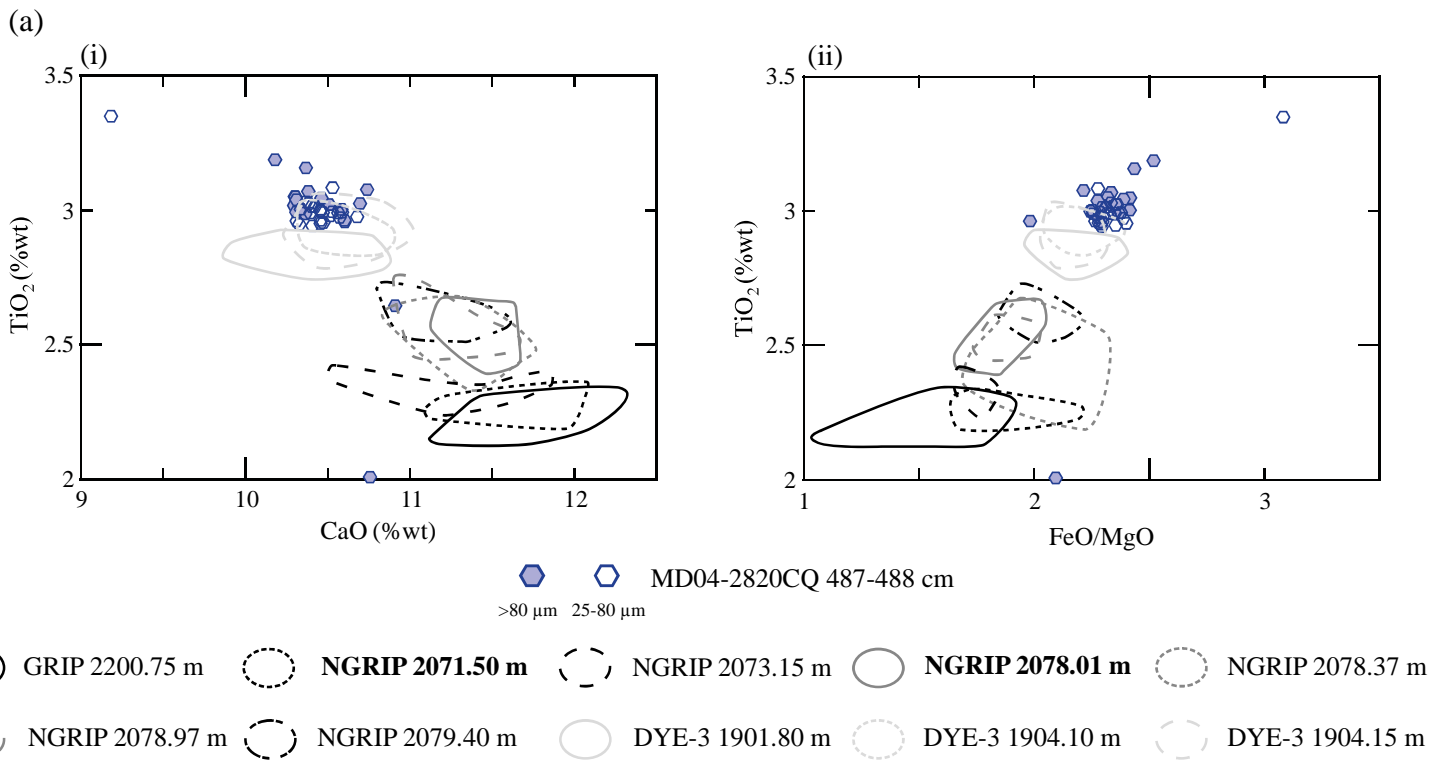


Table 1:

Ice core horizon	D²	SC
NGRIP 2150.90 m	10.042	0.959
NGRIP 2162.05 m	1.740	0.977
NGRIP 2162.60 m	8.349	0.959
NGRIP 2163.35 m	9.709	0.953
NGRIP 2164.10 m	8.239	0.952

Table 2:

Depth Interval	Timing	Composition	Potential Source	Correlations
456-473 cm	DO-8 warming	Heterogenous Tholeiitic Basaltic	Grímsvötn, Iceland	FMAZ III*
487-488 cm	Between DO-10 and DO-9	Tholeiitic Basaltic	Grímsvötn, Iceland	New horizon
497-498 cm	DO-11	Transitional alkali Rhyolitic	Katla, Iceland	New horizon
524-525 cm	DO-11 warming	Tholeiitic Basaltic	Grímsvötn, Iceland	New horizon
610-611 cm	DO-15 cooling	Transitional alkali Rhyolitic	Tindfjallajökull, Iceland	NAAZ II