

Carbon dioxide in geochemically heterogeneous melt inclusions from Mount Etna, Italy

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Key points:

- Melt inclusion geochemistry indicates that the melts supplying Mt. Etna are heterogeneous with respect to trace and volatile elements.
- Melts may be influenced by crustal carbonate assimilation, or by recycled plagioclase-rich cumulates in the mantle.
- Rapidly rising melts at Etna may become supersaturated in volatiles, causing a burst of shallow degassing, which may trigger eruptions.

Abstract

Mt. Etna is among the largest global volcanic outgassers with respect to carbon and sulfur, yet questions remain regarding the source of these volatiles and their systematics in the crust and mantle. The importance of heterogeneous mantle sources, mixing, crustal assimilation and disequilibrium degassing are investigated using melt inclusions erupted during the A.D. 1669 eruption of Mt. Etna, Italy. We find that the melt inclusion compositions define a mixing array between two geochemically distinct melts. One end-member melt is depleted in light rare Earth elements (LREE) and enriched in strontium (Sr), carbon and sulfur; the other is enriched in LREE and depleted in Sr, carbon and sulfur. We infer, through modeling, that the melts may either have been generated by melting a mantle source that includes a recycled oceanic crustal component; or they may have assimilated carbonate material in the crust. The resulting LREE-depleted, Sr-enriched melts were also alkali-rich, which enhanced the

33 solubility of carbon and sulfur. The LREE-depleted, Sr- and volatile-rich melt ascended
34 through the crust and likely became supersaturated with respect to CO₂ and sulfur. The melt
35 intruded into a LREE-enriched, relatively degassed magma body in the shallow crust, cooled
36 rapidly and vesiculated, likely triggering eruption. The melt inclusion array trapped by
37 growing olivines during this intrusion process records a snapshot of incomplete mixing
38 between the two melts. Mt. Etna is renowned for the large increases in CO₂ gas fluxes shortly
39 before and during eruption. The intrusion of supersaturated, CO₂-enhanced magmas into
40 shallow reservoirs may be a common process at Mt. Etna.

41

42 **1 Introduction**

43 Mt. Etna, Italy, is one of the most prolific volcanic outgassers [*Aiuppa et al.*, 2006; *Allard et*
44 *al.*, 1991; *Gerlach*, 1991; *Halmer et al.*, 2002], supplying almost 10% of the global volcanic
45 output of carbon dioxide (CO₂) annually [*Burton et al.*, 2013]. Explosive eruptions of Mt.
46 Etna over the past decade have been preceded by increases in the CO₂ gas flux from the
47 volcano, perhaps caused by the migration of CO₂-rich exsolved fluids ahead of the ascending
48 magma [*Aiuppa et al.*, 2006; *Aiuppa et al.*, 2007]. Melt inclusion studies have shown that
49 CO₂-rich fluids may segregate at deep levels and flush melts stored in shallow reservoirs
50 [*Andronico and Corsaro*, 2011; *Collins et al.*, 2009; *Métrich et al.*, 2004; *Spilliaert et al.*,
51 2006b]. The water (H₂O) and CO₂ content of melt inclusions has been used - assuming the
52 melts are vapor-saturated and have degassed in equilibrium - to estimate pressures of melt
53 inclusion entrapment of 150 to 400 MPa [*Corsaro et al.*, 2014; *Spilliaert et al.*, 2006a;
54 *Spilliaert et al.*, 2006b]. The large scatter in the CO₂ concentrations, which deviate greatly
55 from equilibrium closed system degassing paths (in common with many melt inclusion
56 volatile datasets) [*Métrich and Wallace*, 2008], has been ascribed to a wide range of
57 processes including gas fluxing, mixing and post-entrapment processes [*Bucholz et al.*, 2013;
58 *Gaetani et al.*, 2012; *Hartley et al.*, 2014; *Maclennan*, 2017; *Sides et al.*, 2014; *Wallace et al.*,
59 2015]. The origin of the carbon has been debated. Its isotopic composition, expressed as $\delta^{13}\text{C}$,
60 ranges from -4.5 to -1.0 per mil [*Allard et al.*, 1991; *Chiodini et al.*, 2010]. This isotopic
61 composition suggests either a heterogeneous and relatively heavy carbon reservoir in the
62 mantle, that was recycled during subduction [*Frezzotti et al.*, 2009], or a mixture between
63 MORB-like mantle carbon and a heavier crustal limestone component [*Chiodini et al.*, 2010;
64 *Marziano et al.*, 2008; *Mason et al.*, 2017; *Mollo et al.*, 2010]. The trace element
65 compositions of primitive melt inclusions suggest that the melts supplying Mt. Etna are
66 heterogeneous, implying not only different degrees of melting, but also a highly enriched

67 mantle source that was influenced by subduction fluids [*Correale et al.*, 2014; *Kamenetsky et*
68 *al.*, 2007; *Schiavi et al.*, 2015; *Viccaro and Cristofolini*, 2008].

69

70 In this study, the geochemistry of melt inclusions in tephra produced by the historic A.D.
71 1669 eruption are examined. This eruption was the largest of the past 500 years at Mt. Etna
72 [*Branca and Ferrara*, 2013; *Corsaro et al.*, 1996] and one that marked a significant change
73 in both the style of eruption and the composition of lavas [*Mulas et al.*, 2016]. A combination
74 of micro-analytical techniques are used to constrain the major, trace and volatile element
75 chemistry of melts trapped in olivine phenocrysts and to model processes that affect melt
76 batches and fractionate their chemistry. In particular, we seek to deconvolve the different
77 processes affecting the differentiation of the melt feeding the volcanic system at Mt. Etna,
78 how CO₂ and sulfur concentrations vary with trace element compositions and consequently
79 whether CO₂ is sourced from crustal carbonate or from the mantle. In doing so, the integrity
80 of the melt inclusions is tested along with the assumption of equilibrium degassing of melts
81 feeding Mt. Etna, Italy. These results have implications for the interpretation of pulses of CO₂
82 gas flux prior to eruptions [*Aiuppa et al.*, 2007].

83

84 **2 Geological Setting**

85 Mt. Etna (Sicily, Italy) is the largest active volcano in Europe and one of the most
86 persistently active volcanoes globally (**Figure 1**). It is situated at the intersection of several
87 major fault systems associated with the subduction of the African plate beneath the Eurasian
88 plate [*Doglioni et al.*, 2001; *Gvirtzman and Nur*, 1999], yet its lavas are geochemically
89 similar to ocean island basalts [*Montelli et al.*, 2006; *Schiano et al.*, 2001; *Schiavi et al.*,
90 2015; *Tanguy et al.*, 1997]. Melts originate in the asthenosphere [*Schiavi et al.*, 2015] and
91 interact with thick lithospheric mantle [*Corsaro et al.*, 2014; *Marty et al.*, 1994] and
92 carbonate- and cumulate-bearing crust [*Correale et al.*, 2014; *Corsaro et al.*, 2009]. Mt. Etna
93 rests upon a subvolcanic sedimentary basement made of marls and clays, limestones and
94 terrigenous sedimentary rocks (~ 2 km thick) that form the Maghrebian–Appennine Chain
95 [*Catalano et al.*, 2004]. These sediments overlie the Hyblean Plateau, a Mesozoic to Mid-
96 Pleistocene carbonate succession of limestone and dolomite [*Pedley and Grasso*, 1992],
97 which begins at a depth of ~5 km and has an average thickness of about 10 km and may
98 interact thermally with rising magmas [*Heap et al.*, 2013]. Despite the occurrence of variably
99 altered carbonate xenoliths, particularly in the lavas erupted in 1989 [*Michaud*, 1995], and

100 heavy carbon isotopes in volcanic gases that has been linked to carbonate assimilation
101 [*Chiodini et al.*, 2011; *Mason et al.*, 2017], petrological and geochemical evidence for direct
102 carbonate assimilation has been lacking.

103

104 Lavas erupted from Mongibello, the most recent (15 ka to present) volcanic edifice of the
105 Etnean succession, belong to a mildly alkaline series and have compositions that are variable
106 from trachybasalt to benmoreite [*Corsaro and Pompilio*, 2004] and references therein). Most
107 products are sodic (hawaiites) but, since the 1970s, there has been a shift towards a more
108 potassic affinity (K-trachybasalts), with varying degrees of K-enrichment. Petrological data
109 and geophysical evidence suggest that Mt. Etna's plumbing system is complex. A highly
110 porphyritic plagioclase-rich, K-trachybasalt is the most commonly-erupted magma during
111 both summit and flank eruptions, ascending from a shallow storage region (<5 km b.s.l.).
112 There is also infrequent eruption of nearly aphyric basaltic magma that may ascend directly
113 from a deeper region (10-12 km b.s.l) of the plumbing system. In the last 50 years this
114 magma has erupted in 1974 [*Bottari et al.*, 1975; *Corsaro et al.*, 2009; *Tanguy et al.*, 1997],
115 2001 [*Corsaro et al.*, 2007; *Métrich et al.*, 2004] and 2002-2003 [*Andronico et al.*, 2005;
116 *Spilliaert et al.*, 2006b]. Geophysical evidence suggests that magma reservoirs exist at 1-5
117 km and 10-15 km depth where there are cumulates and dyke structures, as indicated by
118 seismic high-velocity bodies [*Aloisi et al.*, 2002; *Hirn et al.*, 1991; *Patanè et al.*, 2006] and
119 recent petrological studies [*Corsaro et al.*, 2014]. There is also evidence, for some eruptions,
120 of deeper melt storage close to the Moho (e.g. from crystallization of pyroxene before
121 plagioclase in the 1974 lavas) [*Tanguy and Kieffer*, 1977].

122

123 Mt. Etna is an important global source of volcanic gases rich in sulfur and carbon, with
124 annual CO₂ fluxes of up to 6 x 10⁹ kg per year [*Burton et al.*, 2013]. Much of this carbon
125 outgassing flux occurs between eruptions [*Allard et al.*, 1991]. Previous melt inclusion
126 studies have shown the melts contain at least 0.3 wt.% sulfur at 140 MPa (from H₂O-CO₂
127 barometry) and magmas are fluxed with CO₂-rich magmatic vapor [*Allard et al.*, 2006;
128 *Collins et al.*, 2009; *Ferlito et al.*, 2008; *Spilliaert et al.*, 2006b]. The vapor may precede the
129 transport of magma to the surface on a timescale from days to weeks [*Aiuppa et al.*, 2007;
130 *Aiuppa et al.*, 2008].

131

132 The A.D. 1669 eruption, which began on 11th March and lasted for four months, was the

133 largest and most destructive in historical times, largely due to the relatively low elevation of
134 the vents (the main scoria cone, Monti Rossi, is at 800 m a.s.l.; **Figure 1**), the large volume
135 of lava erupted ($607 \pm 105 \times 10^6$ m) [Branca *et al.*, 2013] and the high average effusion rate
136 of 58 m/s. The lava flowed 17 km from the vent, impacting a densely-populated area and
137 partly destroying Catania (**Figure 1**) [Branca *et al.*, 2013]. Strombolian activity initially
138 produced a large, 1 km wide and 200 m high, scoria cone (**Figure 1**) and a thick, widespread
139 pyroclastic fall deposit along the lower south-east flank of the volcano [Mulas *et al.*, 2016].
140 The total tephra fall volume, including the Monti Rossi cone, is estimated to be 6.6×10^6 m
141 (about 3.2×10^6 m dense rock equivalent (DRE)) [Mulas *et al.*, 2016]. Later, the eruption
142 produced a wide ‘a’ flow-field [Branca and Vigliotti, 2015; Branca *et al.*, 2013].

143

144 Lavas erupted early in the A.D. 1669 eruption (denoted ‘SET1’ by [Corsaro *et al.*, 1996])
145 are more primitive than those erupted during the later stages of the eruption (‘SET2’).
146 Throughout the eruption the bulk rock mean MgO content decreases from a mean of 6.65
147 wt.% to 5.07 wt.% [Corsaro *et al.*, 1996]. This change in bulk composition has been
148 interpreted as evidence for fresh mafic magma intruding into a shallow reservoir
149 containing more evolved magma [Corsaro *et al.*, 1996]. However, a more recent study of
150 1669 lavas has shown that lavas erupted before 29 March 1669 (i.e. ‘SET1’) are
151 geochemically similar to lavas erupted after 29 March 1669 (i.e. ‘SET2’), and both are
152 similar to the Monti Rossi scoria compositions reported by [Mulas *et al.*, 2016]. The
153 significantly higher Al_2O_3 , SiO_2 and total alkalis of the ‘SET2’ reported by [Corsaro *et*
154 *al.*, 1996] are proposed to be due to plagioclase accumulation [Kahl *et al.*, 2017]. The
155 Monti Rossi cone, which we sample and analyze here, was formed rapidly, largely over
156 the first two days of the eruption: 11, 12 March 1669 [Mulas *et al.*, 2016] (equivalent to
157 the ‘SET1’ of [Corsaro *et al.*, 1996; Kahl *et al.*, 2017]).

158

159 A study of core to rim olivine compositions from the SET1 and SET2 lavas demonstrated
160 more complex syn- and pre-eruptive environments [Kahl *et al.*, 2017]. Olivine cores in the
161 ‘SET1’ lavas (which are similar to the Monti Rossi tephra; [Mulas *et al.*, 2016]) have a
162 composition of Fo_{75-78} , and are inferred to have formed in a partially degassed
163 environment together with clinopyroxene (Mg# 81–83), plagioclase (An_{66-75}) and Fe–Ti
164 oxides (Mt_{35-52}), at a temperature of ~ 1170 °C and pressures of < 1 kbar [Kahl *et al.*, 2017].
165 The olivine cores define a compositional plateau formed under relatively uniform

166 conditions, whereas the olivine rims (Fo₅₁₋₅₉) define a broad compositional range that may
167 form over a broad pressure range <1 kbar. The ‘SET2’ lavas, erupted later in the eruption
168 (not studied in the current work) contain olivines with similar composition cores, and
169 much less evolved rims (Fo₆₅₋₆₉). Three distinct magma reservoirs located in the volcano’s
170 shallow plumbing system and several events of magma recharge have been proposed,
171 based on studies of these olivines, in the 1.5 years leading up to the eruption, with the
172 SET1 and SET2 magmas being derived from a distinct, bifurcated feeding dyke system
173 [Kahl *et al.*, 2017].

174

175 The A.D. 1669 eruption marked a significant change in the geochemical and eruptive regime
176 of Mt. Etna [Clocchiatti *et al.*, 1988; Condomines *et al.*, 1995]. From A.D. 1600 to 1669,
177 volcanic activity was frequent, long-lasting and of high-volume effusive eruptions of
178 plagioclase-phyric lavas. In contrast, the period A.D. 1670-1750 was characterized by
179 sporadic and shorter eruptions with low effusion rates and more mafic lavas. This eruption
180 provides an opportunity to observe a large spectrum of geochemically diverse melts at a
181 critical point in Mt. Etna’s recent history and to understand how this melt heterogeneity maps
182 on to volatile systematics.

183

184 **3 Sampling and analytical techniques**

185 Glassy tephra was sampled from two localities (north-east: NEMR and south-west: SWMR)
186 at the base of the main scoria cone, Monti Rossi, in Nicolosi on the South-East flank of Mt.
187 Etna (**Figure 1**), from the MR1 unit of Mulas *et al.* [2016]. The scoria cone was erupted over
188 the first two days of the eruption [Corsaro *et al.*, 1996; Kahl *et al.*, 2017; Mulas *et al.*, 2016].
189 Melt inclusions with included oxide crystals were analyzed but showed no systematic trend in
190 major or trace element concentration with oxide-free MIs (**Supplementary Figure 1**),
191 suggesting they may be ‘pre-entrapment’ phases. Crystals were individually mounted in
192 CrystalBond and polished to expose melt inclusions before being re-mounted in Buehler
193 EpoThin resin and re-polished for analysis. The thirty-one melt inclusions analyzed in this
194 study are without cracks or shrinkage bubbles (**Figure 2**). We note that avoiding melt
195 inclusions with shrinkage bubbles may bias the dataset; it is possible we may miss an earlier
196 population of melt inclusions, for example (i.e. prior to any pre-eruptive mixing).

197

198 Trace elements, F, H₂O and CO₂ were analyzed by Secondary Ion Mass Spectrometry
199 (SIMS) using a Cameca ims-4f instrument at the NERC Ion Microprobe Facility at the

200 University of Edinburgh, UK. CO₂ analyses were performed first, with a high mass resolution
201 configuration, in order to enable good separation of C and Mg peaks. H₂O, F and trace
202 elements were then measured with a lower mass resolution configuration. Errors in CO₂ and
203 H₂O were assessed using repeat analyses of a suite of basaltic glass standards [*Pichavant et*
204 *al.*, 2009]. Precision for H₂O and CO₂ was 1%. Average accuracy, expressed as % recovery
205 of published compositions determined by FTIR, was 100.6%. NIST-610 was used as the
206 calibration standard for trace element analyses [*Jochum et al.*, 2011]. Accuracy was
207 monitored by analysis of international standards, NIST-610 and BCR-2G throughout
208 analytical sessions. The accuracy of published compositions, relative to NIST-610 and BCR-
209 2G standards [*Jochum et al.*, 2005; *Jochum et al.*, 2011] (given by |(100 – A)|, where A is
210 the % recovery (given by the unknown determination divided by the known values, expressed
211 as a %) (**Table S1**) was <16% for all trace elements and <5% for most trace elements (**Table**
212 **S1**). Precision was estimated as 1 standard deviation relative error and varied between 0.1%
213 (Ce) and 15.8% (Eu) using repeat analyses of BCR-2G [*Jochum et al.*, 2011]. Precision was
214 calculated for trace element ratios and volatile/trace ratios using repeat analyses of the same
215 standards. 1 percentage relative error (in parentheses) was calculated for La/Yb (0.5), Ce/Y
216 (2.9), CO/Nb (0.9) and HO/Ce (1.1).

217

218 Major elements, S and Cl were determined by electron probe microanalysis (EPMA) using a
219 Cameca SX100 instrument at the Department of Earth Sciences at the University of
220 Cambridge, UK. Full details of the analytical set-up for SIMS and EPMA and error analysis
221 are detailed in the **Supplementary Material Table 1**.

222

223 Signal-to-noise ratios were calculated for all elements analyzed in order to assess the
224 contribution of natural variation and analytical error to the generation of sample variability.
225 The method described in [*Maclennan et al.*, 2003] was used:

226

$$\sigma_t^2 = \sigma_0^2 - \sigma_r^2$$

227

228 , where σ_t is the true variation of the sample set, σ_0 is the observed variation and σ_r is an
229 estimate of analytical error. The χ^2 distribution was used to assess the quality of σ_r , which
230 depends on the number of repeat analyses to estimate analytical precision, in order to test
231 whether signal-to-noise ratios are significant at a given confidence level. Signal-to-noise

232 ratios for all major and trace elements in glass are greater than the threshold for significant
233 variability at the 99% confidence interval. Signal-to-noise ratios are high for incompatible
234 and abundant elements. For example, Sr has a signal-to-noise ratio of $\sigma_t/\sigma_r = 11.5$, whereas
235 Nd, which is less abundant, has $\sigma_t/\sigma_r = 2.2$ and Nb, which is more incompatible has $\sigma_t/\sigma_r =$
236 4.8. Elements that were analyzed with low precision have low signal-to-noise ratios, such as
237 Gd ($\sigma_t/\sigma_r = 0.5$), and it is not possible to resolve natural variability through analytical noise.

238

239 **4 Results**

240 *4.1 Crystal assemblage*

241 The crystallinity of the tephra samples was estimated to lie in the range 10 to 25 vol.%
242 (consistent with the ‘porphyricity’ measured for the lava samples, which ranges from 21-30
243 vol% [Kahl *et al.*, 2017]), with olivine, plagioclase (which makes up 60-80 vol.% of the
244 crystals), augite and titanomagnetite. This crystal assemblage is consistent with other recent
245 studies of the 1669 eruption lava flows [Corsaro *et al.*, 1996; Kahl *et al.*, 2017]. Host core
246 olivine compositions fall within a narrow range, Fo₇₃₋₇₆ (see **Supplementary Material**)
247 overlapping the olivine compositions of the two dominant groups (Type IV and VII) of [Kahl
248 *et al.*, 2017]. Matrix glass magnesium numbers (Mg#) range from 37 to 42. The olivine cores
249 are in general too forsteritic to be in equilibrium with the carrier liquid using a K_d of ~0.30,

250 where K_d is equal to $\frac{\left(X_{Fe^{2+}}/X_{Mg}\right)_{ol}}{\left(X_{Fe^{2+}}/X_{Mg}\right)_{liq}}$ [Roeder and Emslie, 1970]

251 (**Supplementary Material Figure S6**).

252

253 *4.2 Melt inclusion major element composition*

254 Melt inclusion compositions may be modified by post-entrapment crystallization (PEC). The
255 extent of PEC was estimated using Petrolog3 in reverse fractional crystallisation mode, which
256 accounts for Fe-Mg diffusion between the host olivine and the melt inclusion [Danyushevsky
257 *and Plechov*, 2011b] and it was found that all inclusions experienced 5-10% PEC. This
258 affects the MgO and FeO of the melt inclusion and thus the Mg# is recalculated to 45-51
259 (shown in **Supplementary Table 5**). The Mg# was calculated for the matrix glass and melt
260 inclusions using only Fe assuming that FeO is 0.70 to 0.85 Fe [Metrich and Clocchiatti,
261 1989] (**Supplementary Table 5**). The major element compositions of the melt inclusions are
262 K-poor trachybasaltic, typical of pre-1970 lavas and similar to the plagioclase-rich and K-

263 poor products of the 1763 eruption [Corsaro *et al.*, 2009]. Major element oxide compositions
264 are within the field for post-1500 Etnean lavas [Corsaro *et al.*, 1996; Cristofolini and
265 Romano, 1982] and recent 21st century eruption melt inclusion analyses (**Figure 3**) [Collins
266 *et al.*, 2009; Métrich *et al.*, 2004; Schiavi *et al.*, 2015; Spilliaert *et al.*, 2006b] but far more
267 evolved than the olivine-hosted MI from the 4 kyr Fall Stratified eruption at Mt. Etna
268 (hereafter FS) [Kamenetsky *et al.*, 2007], considered one of the most primitive melts erupted
269 at Mt. Etna.

270

271 4.3 Melt inclusion trace element composition

272 The melt inclusions are relatively enriched in incompatible trace elements compared to N-
273 MORB. The trace element patterns normalised to primitive mantle for melt inclusions and
274 matrix glasses display greater enrichment in LREE and Nb than HREE (**Figure 4**).
275 Concentrations of Nb in the 1669 melt inclusions range from 50 to 140 ppm, La 60-140 ppm,
276 and Nd 50-100 ppm (**Figure 5a**), 2-3 times greater than the primitive FS MI measured by
277 [Kamenetsky *et al.*, 2007] (**Figure 5**, coloured circles), but within the range of recent
278 eruptions in 2001-2007 [Collins *et al.*, 2009; Schiavi *et al.*, 2015]. Ce/Y varies between 2 and
279 6 (**Figure 5b**) similar to the range in both the FS MI [Kamenetsky *et al.*, 2007] and 2001-
280 2006 melt inclusions [Schiavi *et al.*, 2015]. A.D. 1669 matrix glass compositions also lie
281 within this range (gray inverse triangles). The most enriched melt inclusions (with highest
282 LREE/HREE ratios) are also those with the highest absolute concentrations of LREE (**Figure**
283 **5a**). The full suite of crystals host compositionally-variable melts with Ce/Y ratios between 2
284 and 6 which is independent of the host olivine composition for both the A.D. 1669 MI and FS
285 (**Supplementary Figure 2**). It is worthy of note that the trace element diversity in the melt
286 inclusions far exceeds the diversity in whole rock compositions for the SET1 lavas, for which
287 Ce/Y only varies by ~ 3% and K₂O only from 1.3 to 1.6 wt% [Mulas *et al.*, 2016].

288

289 A correlation coefficient matrix reveals broad-scale correlation trends in the data
290 (**Supplementary Figure 3**). Ba, La, Nb, Ce, Pr, Nd and Zr show strong positive correlations
291 with each other ($r > 0.9$) but a weak negative correlation with HREE and Y ($r = -0.2$)
292 suggesting that the primary melts were generated from sources with variable LREE-
293 enrichment, or from variable degrees of fractional melting at a pressure where garnet is
294 present to fractionate HREE from LREE. Sr shows a weak negative correlation with the
295 LREE ($r = -0.4$; **Figure 5c**) and a positive correlation with HREE ($r = 0.3$) (**Supplementary**
296 **Figure 3**).

297

298 MI show varying degrees of Sr enrichment and depletion from the expected concentration
299 (Sr). Sr is determined using the relative compatibility of the neighboring REE in order of
300 compatibility, Ce and Nd, using $Sr^* = \left[\frac{[Ce]_{MI}}{[Ce]_{PM}} * \frac{[Nd]_{MI}}{[Nd]_{PM}} \right]^{1/2}$, where [Ce]
301 and [Nd] are the concentration of these elements in either MI or primitive mantle (PM)
302 [Sobolev and Nikogosian, 1994]. Sr/Sr* >1 suggests enrichment in Sr compared to the
303 expected concentration based on compatibility, and Sr/Sr* <1 suggests depletion in Sr. All FS
304 melts have Sr/Sr* >1 and Sr enrichment is greatest for the relatively LREE-depleted 1669
305 melts. Sr depletion scales with LREE-enrichment and increasing LREE/HREE ratios (**Figure**
306 **5c, Supplementary Figure 4**). Enrichment in fluid mobile elements, such as Ba, appears to
307 correlate with LREE-enrichment but not with Sr enrichment (**Supplementary Figure 3**).

308

309 4.4 Melt inclusion volatile systematics

310 H₂O concentrations in the 1669 melt inclusions exhibit a limited variability, with a range of
311 1.2-1.7 wt.% H₂O and a median of 1.4 wt.% (**Figure 6a**). Matrix glasses contain <0.6 wt.%
312 H₂O. The limited range and low values reflect either their entrapment pressure or their
313 diffusive equilibration during storage at low pressures (70-100 MPa) in the crust [Bucholz *et*
314 *al.*, 2013; Gaetani *et al.*, 2012]. As the H₂O concentrations may be re-set to low pressure
315 conditions by diffusive re-equilibration and be unrepresentative of their entrapment pressure.

316

317 CO₂ concentration in the melt inclusions varies from 40 to 1220 ppm; CO₂ concentrations in
318 matrix glasses are below detection (20 ppm; gray triangles, **Figure 6a**). Sulfur concentrations
319 in the melt inclusions vary between 80 and 1900 ppm (**Figure 6b**). Carbon and sulfur in melt
320 inclusions correlate well with one another ($r = 0.73$, **Figure: 6b, Supplementary Figure 3**).
321 Perhaps the most striking feature, however, of the covariance structure for the A.D. 1669
322 melt inclusion geochemistry is that CO₂ and sulfur both correlate negatively with
323 incompatible elements such as Nb, LREE, Ba and Zr (**Figure 6c**). For the A.D. 1669 data
324 alone, the correlation between CO₂ and Nb, for example, has an r value of -0.68 (CO₂ and e.g.
325 Ce, $r = -0.59$; Ba, $r = -0.51$; Zr, $r = -0.59$, **Supplementary Figure 3**). The most CO₂-rich and
326 S-rich melts are those with lowest Ce/Y and Ce/Y has negative correlation with CO₂ and S
327 with r values of -0.77 and -0.70 respectively. CO₂, however, correlates well with Sr and Sr/Sr
328 ($r = 0.63, 0.67$ respectively, **Figure 6d, Supplementary Figure 3**). Fluorine shows a high
329 degree of variability (0.14 - 0.24 wt.%) with no correlation with either host olivine Fo mol%

330 or degree of melt enrichment. Chlorine shows moderate variability (0.16 - 0.38 wt.%) with a
331 weak negative correlation with LREE enrichment ($r = -0.2$) and weak positive correlations
332 with HREE ($r = 0.5$) and host Fo content ($r = -0.4$).

333

334 **5 Discussion**

335 We have shown above that the 1669 melts, trapped in olivine, exhibit a linear mixing array of
336 compositions, with one end member enriched in LREE (and Zr, Nb), depleted (relative to
337 similarly compatible elements) in Sr and containing low concentrations of S and CO₂
338 (**Figures 5, 6; Supplementary Figures 3, 4**). The other end member melt is depleted in
339 LREE, and relatively enriched in Sr, CO₂ and S. Fractionation of pyroxene is not capable of
340 generating the range in, for example, Ce/Y observed in the melt inclusions (**Figure 5 a,b**);
341 the range in Ce/Y (and in other LREE/HREE trace element ratios) must instead be inherited
342 either from primary melts from the mantle or from modification of melts in the crust. Linear
343 correlations between S and CO₂ in melt inclusions are not expected to result from degassing
344 at Mt. Etna [*Spilliaert et al.*, 2006b], or elsewhere [*Métrich and Wallace*, 2008] owing to the
345 much lower solubility of CO₂ in silicate melts over sulfur [*Witham et al.*, 2012]. These trends
346 instead indicate an intrinsic relationship between trace element ratios and volatile systematics
347 generated by processes beyond simple fractional crystallization and degassing. We propose
348 that this array was generated by mixing the two liquids in a shallow magma reservoir prior to
349 eruption, where the mixing process was ‘captured’ by the entrapment of melt inclusions. We
350 discuss below why we believe that the LREE-depleted, Sr, C and S-rich end member may
351 have ascended rapidly from depth, supersaturated. First, however, we consider how the
352 relatively evolved 1669 end members of the mixing array may have been generated by
353 fractional crystallization of primitive melts beneath Mt. Etna (exemplified by the primitive
354 FS tephra melts [*Kamenetsky et al.*, 2007]), then we discuss the possible origin of the LREE-
355 depleted, Sr, C and S-rich end member in terms of mantle and crustal processes.

356

357 *5.1 Modelling fractional crystallization of two geochemically distinct melts*

358 The primitive melt observed as melt inclusions from the FS eruption [*Kamenetsky et al.*,
359 2007] was used as a starting composition to model fractional crystallization (using Petrolog3;
360 [*Danyushevsky and Plechov*, 2011a]) at NNO+1 [*Métrich and Clocchiatti*, 1996], 1100 °C
361 [*Kamenetsky and Clocchiatti*, 1996] and for two pressures: 100 MPa [*Kahl et al.*, 2017] and
362 400 MPa [*Kamenetsky et al.*, 2007], which might be suitable for FS melt fractionation. We
363 use examples of enriched and depleted (as indicated by Ce/Y) FS melt inclusions as a starting

364 point for the modeling because a) the FS melt inclusions are the most primitive to be
365 observed at Mt. Etna, at ~13 wt% MgO (other primitive whole rocks have < 9 wt% MgO;
366 [Corsaro and Métrich, 2016]) and b) the FS melt inclusions exhibit a similar range in Ce/Y to
367 the 1669 melt inclusions, which is independent of fractional crystallization and c) a full set of
368 compositional data (volatiles, major and trace elements) is available for the FS melt
369 inclusions. We recognize, however, that previous studies have identified that the FS tephra
370 has anomalously high CaO compared to other Mt. Etna magma compositions, as well as high
371 radiogenic Sr and Rb/Th, which has been ascribed to a high degree of melting of a mantle
372 source with considerable pyroxenite component [Corsaro and Métrich, 2016].

373
374 Fractional crystallization trends from Petrolog [Danyushevsky and Plechov, 2011a] at 100
375 and 400 MPa are marked onto **Figure 3** using the most depleted and enriched end member
376 FS melts as a starting point for each pressure. The melts erupted during the A.D. 1669 and
377 other recent eruptions have undergone fractionation of augite, as shown by the inflection
378 point on the liquid line of descent (LLD) at 9 wt.% MgO where CaO begins to be depleted in
379 the melt (**Figure 3**). Plagioclase crystallization begins at ~4 wt.% MgO, shown by depletion
380 in both Al₂O₃ and CaO together (**Figure 3**). The fractional crystallisation models, where the
381 order of crystallisation is: olivine→olivine+augite→olivine+augite+plagioclase, describes
382 well the Al₂O₃ and CaO contents of the melts, although cannot reproduce the observed K₂O
383 and Na₂O concentrations, which are higher than predicted from the models (**Figure 3 b,d**).
384 This may be a consequence of the relatively low alkali content of the FS melts compared to
385 other magma compositions from Mt. Etna, as identified previously [Corsaro and Métrich,
386 2016]. However, the models describe the evolution of the trace element concentrations well.
387 We find that 70% fractional crystallization at 1 kbar of the least LREE-enriched FS melt
388 (melts with the lowest Ce/Y; **Figure 5a**) [Kamenetsky et al., 2007] yields a melt with the
389 same LREE/HREE ratio as the least enriched melts in the A.D. 1669 melt inclusions (Ce/Y 2-
390 3), with a similar absolute concentration of trace elements (**Figure 5a**). In the same way, 70%
391 fractional crystallization of the most LREE-enriched FS melt (with Ce/Y 6) yields the
392 observed LREE absolute concentrations of the enriched melts (with Ce/Y 6) of the A.D. 1669
393 inclusion suite.

394
395 We propose that the array of evolved compositions in the A.D. 1669 melt inclusions requires
396 up to 70% fractionation of two primitive melt compositions that have similar end-member

397 trace element compositions to the FS melt but may be more alkali-rich. The LREE-depleted
398 and LREE-enriched melts mix (to produce the observed melt inclusion array) only after each
399 has undergone significant differentiation, thus yielding the observed high trace element
400 compositions and the array in LREE/HREE observed in the 1669 MI suite (Ce/Y: 2-6, Nb 50-
401 140, La 60-140) (**Figures 4, 5**). Mixing and fractionation was not concurrent because a) the
402 trace element array seen in the 1669 melt inclusions is associated with a limited range in the
403 MI major elements and is not systematic with the evolution of the olivine Fo mol.% and b)
404 melt inclusions within a single olivine crystal can have the full range of enrichment and
405 absolute trace element concentration observed in the entire dataset (**Supplementary Figure**
406 **2**). We have therefore established that the two end member melts that mixed to form the 1669
407 compositional array could feasibly have formed from the fractional crystallisation of liquids
408 similar to the two extreme compositions sampled by the melt inclusions in the primitive FS
409 tephra [*Kamenetsky et al.*, 2007]. But what then is the origin of the LREE, Sr and volatile
410 systematics of the two end member melts? Did these melts acquire their geochemical features
411 in the mantle or in the crust?

412

413 *5.2 Sr-enrichment in 1669 depleted melts*

414 Principal Component Analysis (PCA) of the 1669 melt inclusion trace element compositions
415 indicates that the first two principal components describe 50% of the variance in trace
416 element dataset (see **Supplementary Material**). The first principal component (PC1)
417 highlights an anomaly in the behaviour of Sr, caused by a process that is fractionating Sr
418 from other elements (**Supplementary Figure 5**). PC1 may be due to addition or removal of
419 plagioclase (Sr is compatible in plagioclase while all other REE are incompatible and become
420 enriched in the melt), or assimilation of Sr from some source or contaminant and this may
421 also affect the different PC1 scores of HREE compared to LREE. PC2 is positive for the
422 LREE and negative for the HREE (**Supplementary Figure 5**) and might therefore be related
423 to (1) the depth of melting and the presence of garnet in the melting region where HREE are
424 compatible, (2) the degree of mantle melting, which affects the degree of LREE enrichment,
425 or (3) the trace element composition of the mantle source. The process controlling PC2 is
426 responsible for the observed range in LREE/HREE of the end member melts. Sr, however,
427 does not behave like the LREE as expected (**Figure 4c, Supplementary Figure 3**). Sr has a
428 negative PC2 like the HREE, and this is likely to be due to the combined effect of the
429 strontium anomaly with non-orthogonal mantle and crustal processes (**Supplementary**
430 **Figure 5**). The PCA approach has not managed to clearly separate out the processes here.

431 The crucial difference between PC1 and PC2 is in the behaviour of the MREEs
432 (**Supplementary Figure 5**) and this is important for understanding the controlling processes.

433
434 The abundance of Sr in both the primitive FS melts and the 1669 LREE-depleted melts is
435 anomalous, as Sr is enriched with respect to its compatibility compared to other REE, i.e.
436 Sr/Sr* (**Figure 5; Supplementary Figure 4**). There is a strong negative correlation between
437 Sr/Sr* in the melt inclusions and LREE (La, Ce), Ba, Nb, Zr ($r = -0.82$ to -0.71); and a strong
438 positive correlation between Sr/Sr* and CaO, CO₂ and S ($r = 0.57$ to 0.67) (**Supplementary**
439 **Figure 3**). In the case of the FS melts, these correlations cannot be explained using olivine
440 fractional crystallization alone (or the post-entrapment crystallisation of olivine on the melt
441 inclusion walls) since this should affect elements with neighboring compatibility (Sr, Ce and
442 Nd) in a similar way. A number of processes that affect Sr enrichment in the FS primitive
443 melts and the more evolved 1669 melts are considered here.

444
445 Sr enrichment in melt inclusions may be caused by: (1) involvement of a Sr-rich mantle
446 source component either from pyroxenite [Correale *et al.*, 2012] or a ‘ghost plagioclase’
447 signature inherited from an eclogitic component in the mantle source [Sobolev *et al.*, 2000];
448 (2) plagioclase assimilation within the crust by primitive melts [Danyushevsky *et al.*, 2003],
449 in which LREE are highly incompatible; (3) accumulation of small fraction lower crustal
450 gabbroic melts [Annen *et al.*, 2005]; (4) assimilation of crustal carbonate over a range of
451 pressure and temperature [Carter and Dasgupta, 2015; Marziano *et al.*, 2008; Michaud,
452 1995]. The two potential sources of Sr, one from the mantle (eclogitic oceanic crust and/or a
453 pyroxenite source) and one from the crust (plagioclase, gabbroic cumulates or carbonates),
454 would have quite different implications for the volatiles, in particular the flux of volcanic
455 carbon, as (a) the solubility of volatiles in silicate melts is dependent on the major element
456 composition of the melt [Moore, 2008]; and (b) because some of these mechanisms involve
457 volatile-rich sources (e.g. crustal carbonate and/or recycled lithologies). We discuss each of
458 these mechanisms in turn.

459

460 5.2.1 Mantle source heterogeneity as the source of the Sr anomaly

461 Trace element and Sr isotope data for dyke-fed eruptions have revealed that mantle source
462 heterogeneities, and particularly the variable involvement of a clinopyroxenitic lithology,
463 have a strong influence over the degree of melting of the heterogeneous mantle and long-term
464 magmatic processes beneath Mt. Etna [Corsaro and Métrich, 2016]. The Sr anomaly in the

465 primitive melts could, therefore, be inherited from the mantle due to incorporation of (i)
466 small fractions of pyroxenite melt [*Correale et al.*, 2012; *Correale et al.*, 2014] or (ii) melts
467 of recycled lower oceanic crustal plagioclase-bearing cumulates in the melting region. In the
468 mantle melting region under Mt. Etna the restite of these recycled materials will be
469 plagioclase free (e.g. eclogite), with a low bulk partition coefficient for Sr. Melts derived
470 from recycled cumulates may therefore inherit the positive Sr/Sr anomaly of their sources
471 [*Sobolev et al.*, 2000].

472

473 We explore the possible mantle origins of compositional variation in the melt inclusion suite
474 by modelling incremental fractional melting of KLB-1 peridotite [*Davis et al.*, 2009;
475 *Jennings and Holland*, 2015] and KG1(8) pyroxenite [*Jennings et al.*, 2016; *Kogiso et al.*,
476 1998] at 1315 and 1500 °C after [*Jennings and Holland*, 2015] and [*Jennings et al.*, 2016]
477 respectively using pressure-temperature-melt fraction pathways for decompression melting
478 calculated assuming anhydrous and isentropic conditions according to [*Katz et al.*, 2003]
479 (further details are given in the **Supplementary Material**). Instantaneous 0.01 melt fractions
480 were generated by the model and accumulated to obtain the trace element composition of
481 melt fractions from 0 to 0.2. There are numerous solutions that can generate the FS melt end-
482 member LREE/HREE ratios using a combination of the degree of melting of both sources
483 and the degree of mixing between them (**Figure 7a**). A 10% pyroxenite, 90% peridotite
484 composition has been proposed previously for FS melts using mantle xenoliths [*Correale et*
485 *al.*, 2012], but our modeling suggests this solution is non-unique given the degrees of
486 freedom in a combination of melt fraction and proportions of mixing sources. A more
487 concrete result of the modeling is that there is no solution that gives a melt with both Sr
488 enrichment and LREE-depletion (**Figure 7**).

489

490 An eclogite melting signature (associated with melting of recycled gabbroic cumulates) was
491 proposed to explain the geochemistry of melt inclusions in olivines from Mauna Loa, Hawaii
492 [*Sobolev et al.*, 2000]. Sr-rich melts from Mauna Loa show depletion in incompatible
493 elements, including negative Nb and Zr anomalies [*Sobolev et al.*, 2000]. This distinctive
494 trace element signature may be inherited from plagioclase, as is commonly observed in
495 ophiolitic cumulates. It is proposed that gabbro may retain its chemical identity throughout
496 convective cycling in the mantle without mixing with other parts of the subducted oceanic
497 crustal sequence, yielding a ‘ghost plagioclase’ signature and Sr anomalies in the resulting
498 ocean island melts. Melting models for different mantle sources show that eclogite melts are

499 very small in volume and are readily lost in the bulk magma but even a small fraction of
500 eclogite-derived melts can have a significant effect on the REE chemistry. A mixture of 90%
501 peridotite melt and 10% eclogite-derived melt provide a possible explanation for the
502 observed REE and major element chemistry seen at Mauna Loa [*Sobolev et al.*, 2000]. The
503 same geochemical anomalies as observed in the Mauna Loa melt inclusions [*Sobolev et al.*,
504 2000] are observed in the Sr-rich, LREE-depleted FS and 1669 melts (**figure 5**), making
505 melting of recycled gabbroic cumulates in the mantle source region a plausible explanation
506 for the presence of such anomalies.

507

508 *5.2.2 Resorption of plagioclase as the source of the Sr anomaly*

509 Early-formed plagioclase crystals trapped in MI can react with the host olivine and melt at
510 high magmatic temperatures, resulting in a Sr-enriched melt composition [*Danyushevsky et*
511 *al.*, 2003; *Schiavi et al.*, 2015] (**Figure 7b**). Plagioclase assimilation by complete dissolution
512 was modeled using a plagioclase composition from a Mt. Etna eruption [*Viccaro et al.*, 2006]
513 that was similar in composition to the 1669 eruption [*Corsaro et al.*, 1996]. The blue line in
514 **Figure 7b** shows that up to 30% plagioclase dissolution is required to be mixed with the FS
515 depleted end-member to give a melt composition that, after fractional crystallization, will
516 have a high enough Sr concentration to match the LREE-depleted 1669 melts. However,
517 complete dissolution is not realistic and plagioclase reacts incongruently in the melt inclusion
518 according to plagioclase + melt + host olivine → spinel + olivine + melt [*Danyushevsky et al.*,
519 2003]. Overall, the vector describing the progressive assimilation of plagioclase is
520 inconsistent with the trends seen in the 1669 major and trace element data (vectors, **Figure 3**,
521 7).

522

523 *5.2.3 Lower crustal gabbro assimilation as the source of the Sr anomaly*

524 Localised re-melting of lower crustal gabbroic material is possible by fluid-rich,
525 metasomatised mantle melts with a more primitive bulk composition to the lower crust
526 [*Annen et al.*, 2005] (**Figure 7b**). Assimilation of gabbro was modeled for the Etnean AMLG
527 gabbro (enclosed in 2001 lavas), with the highest whole rock Sr [*Corsaro et al.*, 2014] (pink
528 box 1, **Figure 7b**). Melting of this gabbro (10%) was modeled using a batch melting equation
529 (see **Supplementary Material**, Equation 1) and mixed with the enriched end-member of the
530 FS melt to determine whether gabbroic assimilation could yield the positive Sr anomaly (and
531 LREE depletion) described by the 1669 melts (pink line, pink box 2 indicates 10% melted

532 gabbro composition, **Figure 7b**). Addition of gabbroic melts, even with 100% mixing, did
533 not give comparable Sr concentrations, primarily because the bulk solid-melt partition
534 coefficient for Sr is too high. Nor did the REE become fractionated enough to reduce the
535 LREE/HREE ratio and give a more depleted melt signature, comparable to the 1669 depleted
536 MI. Additionally, progressive assimilation of gabbro does not follow the major element oxide
537 trends seen in 1669 MI (**Figure 3**). We therefore reject re-melting of gabbro as a mechanism
538 to generate the observed Sr anomaly and LREE depletion observed in the FS and 1669 melt
539 inclusions.

540

541 *5.2.4 Magmatic assimilation of crustal carbonate and/or associated fluids*

542 A potential source of Sr is carbonate melt or fluid assimilation during transport and storage of
543 melts in the 40 km thick Etnean crust. The whole rock Sr isotope composition of the 1669
544 lavas ranges from 0.70330 to 0.70344 and are very similar to MORB [*Corsaro et al.*, 1996]).
545 This low radiogenic Sr isotopic composition does not preclude assimilation of Sr from
546 Cretaceous carbonates, however, which have Sr/Sr isotope of 0.707 and are significantly less
547 radiogenic than the continental crust (mean 0.716) [*Elderfield*, 1986].

548

549 Carbonate assimilation is modeled using a carbonate xenolith found in 1982 lava [*Corsaro et*
550 *al.*, 2014]. Addition of carbonate to the FS LREE-enriched end-member (green line, **Figure**
551 **7b**) yields a higher Sr concentration in the melt but reduces the LREE concentration, giving a
552 more depleted LREE/HREE, but Sr-enriched melt. Melt compositions generated by 40-50%
553 assimilation of carbonate into the enriched melt and up to 70% fractional crystallization are
554 very similar to the LREE-depleted and Sr-rich end-member melt of the 1669 eruption
555 (**Figure 7**). The carbonate assimilation here is the maximum possible since it is assumed here
556 that an enriched-FS end member melt is the parental melt, when in fact the depleted 1669
557 melt inclusions may have been sourced from a more depleted primitive melt. It is possible
558 that both parental melts have undergone some carbonate assimilation before mixing and by
559 different amounts, with the more depleted parental melt assimilating more carbonate so as to
560 result in a greater Sr anomaly than the enriched melt.

561

562 However, assimilation of these high percentages of carbonate material is unrealistic when we
563 consider their potential effect on major element oxides (**Figure 3**). Assimilation of carbonate
564 causes an increase in the CaO content of the melt (vectors: **Figure 3c**) and increased
565 clinopyroxene (cpx) nucleation and crystallization with compositional progression towards

566 Ca-Tschermak cpx [Mollo *et al.*, 2010]. This depletes the melt in MgO and SiO₂, consumes
567 olivine and plagioclase and crystallizes scapolite and spinel, thus changing the modal
568 proportions of phases in the system [Carter and Dasgupta, 2015; Marziano *et al.*, 2008;
569 Mollo *et al.*, 2010]. The model results in an enrichment of alkalis in the melt (**Figure 3b,d**) as
570 these are not compatible in cpx. The degree of assimilation, the resulting phase assemblage
571 and melt composition, and the CO₂ fluid release is PT dependent, with LP and HT conditions
572 having the greatest assimilation potential. Experiments show that at 0.5 GPa 21-48%
573 carbonate can be assimilated between 1100 °C and 1200 °C and the CO₂ fluid produced at 1
574 GPa between 1100 °C and 1175 °C increases from 0.09 to 0.28 g per gram of basaltic melt
575 [Carter and Dasgupta, 2015]. The CO₂-rich fluid phase causes dehydration of the melt and
576 increases the CO₂/H₂O ratio of the free fluid phase. The enhanced CO₂ fugacity in the fluid
577 phase and the increased melt CaO content may increase the solubility of CO₂ in the melt. The
578 composition of the C-O-H fluid affects the redox state of the carbonated system and
579 experiments by [Mollo *et al.*, 2010] show *f*O is lowered by two log units when a CO₂-rich C-
580 O-H fluid is present. However, fluid migration away from the reservoir may cause the
581 opposite effect.

582

583 The extent of carbonate assimilation is limited by the MgO content of the system [Carter and
584 Dasgupta, 2015]. Melts at Vesuvius are phonolitic in composition due to a reduction in MgO
585 and enrichment in alkalis, and show evidence for carbonate assimilation [Carter and
586 Dasgupta, 2015; Freda *et al.*, 2008]. Progressively more carbonate assimilation leads to
587 alkali-rich, MgO-poor and SiO₂-poor melts that are foiditic in composition, such as those
588 from the Colli Albani Volcanic District [Freda *et al.*, 2008; Gaeta *et al.*, 2009]. Oxygen
589 isotopes support carbonate assimilation by these magmas, as well as the presence of skarns
590 and the high CO₂ flux from Italian volcanic systems [Chiodini *et al.*, 2004]. For Mt. Etna it
591 has been estimated that 41-92% of magma (the experiments used a synthetic K-basalt) would
592 need to react with calcite to explain the observed emission rate of CO₂ [Carter and Dasgupta,
593 2015]. The 1669 melts, however, are not ultra-calcic and silica-poor as would be expected
594 from the percentage of carbonate required to yield the Sr anomaly (**Figure 7**). However, the
595 depleted 1669 melts do show a higher CaO content (**Figure 3c**) than the enriched melts.

596

597 5.3 The implications of melt heterogeneity for volatile systematics

598 The negative correlation between CO₂ and Nb ($r = -0.68$, **Figure 6c**, **Supplementary Figure**
599 **3**) contrasts with the positive correlation measured in vapor-undersaturated melt inclusions

600 from the Siqueiros fracture zone on the East Pacific Rise [Saal *et al.*, 2002] and calculated for
601 undegassed Mid-Atlantic Ridge basalts [Cartigny *et al.*, 2008]. Other CO₂-trace element
602 datasets in the literature either record significant variability in CO₂ with near-constant Nb
603 [Shaw *et al.*, 2010], or show no robust correlations between the two species [Dixon and
604 Clague, 2001; Helo *et al.*, 2011; Koleszar *et al.*, 2009; Workman *et al.*, 2006]. Melt
605 inclusions are usually partly degassed with respect to CO₂ and this lack of correlation
606 commonly reflects this. A negative correlation between CO₂ and incompatible trace elements
607 was observed in a melt inclusion suite from Skuggafjöll, Iceland [Neave *et al.*, 2014] and
608 could arise during olivine cooling, post-entrapment crystallization and the formation of a
609 shrinkage bubble . However, the low degree of PEC (5-10%; **Supplementary Table 5**)
610 observed in the 1669 melt inclusions and analysis of shrinkage-bubble-free MI means that the
611 full range in incompatible element concentrations is not reproducible with this mechanism.
612 Modeling of mid-ocean ridge volatile systematics has shown this negative correlation may
613 also arise during concurrent mixing and degassing at a range of pressures [Matthews *et al.*,
614 2017], although this mechanism cannot reproduce the CO₂-Sr-REE systematics we observe
615 for the 1669 melt inclusions.

616

617 We propose that the positive correlation between Sr and CO₂ ($r = 0.63$) and between Sr/*Sr (r
618 $= 0.67$) observed in the melt inclusion suite represents a mixing signature, as discussed
619 above. In order for two equilibrium melts, with different CO₂ concentrations, to mix at the
620 same pressure requires the solubility of CO₂ in the two melts to be different [Dixon, 1997;
621 Shishkina *et al.*, 2014]. The depleted and enriched melts observed in both the 1669 and FS
622 melt inclusion suites (one with low LREE and high Sr, the other with high LREE and low Sr)
623 have different major element oxide compositions, with up to 2 wt.% differences in CaO, KO,
624 NaO and AlO (**Figure 3**). These differences are sufficient to cause differences in CO₂
625 solubility. Melts that are rich in calcium (Ca) and alkalis (K and Na) stabilise higher
626 concentrations of CO₂ [Moore, 2008; Shishkina *et al.*, 2014]. Sulfur fluid-melt partitioning is
627 also reduced as the mole fraction of Ca and Al in the melt increases [Zajacz, 2015] leading to
628 the melt being able to dissolve more sulfur (in the absence of sulfide or sulfate saturation).
629 Differences in major element composition between the two end member melts may explain
630 the strong correlation between CO₂ and S ($r = 0.73$), and the negative correlations between
631 CO₂ and LREE ($r = -0.68$ to -0.59) and positive correlations between CO₂ and Sr ($r = 0.63$),
632 which are not consistent with degassing trends. A degassing trend would deplete CO₂ at

633 greater pressures than S, resulting in an array of shallow-trapped melts with low CO₂ and
634 variable sulfur. For a degassing trend alone, correlations between CO₂ and S and LREE and
635 Sr would not be expected. For CO₂ fluxing and degassing-induced crystallisation [*Cashman*
636 *and Blundy, 2000*], trends of increasing CO₂, decreasing S and increasing LREE would be
637 expected, which are not observed (**Figure 6**).

638

639 The major element parametrization of CO₂ solubility [*Shishkina et al., 2014*] (**Figure 8**)
640 yields equilibrium pressures of ~200 MPa for the high-CO₂ FS melt inclusions (rather than
641 400 MPa using *VolatileCalc*; [*Kamenetsky et al., 2007; Newman and Lowenstern, 2002*])
642 because these melts are rich in Ca and alkali elements, which enhances the solubility of CO₂.
643 The different solubilities for the depleted and enriched FS melts (red circles, low and high
644 Ce/Y; **Figure 8a**), caused by their different CaO and alkali contents, provides a mechanism
645 for CO₂-rich and CO₂-poor melts to mix at the same pressure, at ~200 MPa (**Figure 8b**),
646 rather than over the range 380-500 MPa as predicted by a solubility model that does not
647 include compositional dependence [*Kamenetsky et al., 2007*]. It is important to note,
648 however, that the FS melt inclusions contain shrinkage bubbles which may have sequestered
649 some CO₂ (there are three FS melt inclusions with CO₂ < 1000 ppm) [*Kamenetsky et al.,*
650 *2007*]; hence the actual trapping pressure was likely higher. For the 1669 melt inclusions
651 (orange triangles; **Figure 8**), those with the highest CO₂ (>500 ppm) are the most depleted in
652 their LREE contents (Ce/Y < 4), and are also richer in Ca and Mg but poorer in alkalis
653 (**Figure 3**) which yields a mean equilibration pressure of ~150 MPa (**Figure 8b**), although
654 there is considerable scatter [*Shishkina et al., 2014*]. However, the differences in major
655 element composition and CO₂ solubility for the 1669 melt inclusions cannot entirely
656 reconcile their saturation pressures (**Figure 8b**), with the more enriched melts (Ce/Y > 4)
657 exhibiting a large range (20-180 MPa) and a lower mean (70 MPa) equilibration pressure
658 than the depleted melts (with Ce/Y < 4; **Figure 8b**). If the melt inclusions were all entrapped
659 together, in one shallow storage region, one might expect them all to record similar
660 equilibration pressures, yet this is clearly not the case.

661

662 Another possibility to explain the observed range in ‘apparent’ pressures for the mixing array
663 (orange triangles, **Figure 8b**) is that the depleted end-member melt may be supersaturated
664 with respect to carbon and sulfur upon mixing. Supersaturation may develop when basalts
665 ascend from magma reservoirs to the surface faster than CO₂ can diffuse into bubbles, e.g. as
666 proposed for the Skuggafjöll melt in the Eastern Volcanic Zone of Iceland [*Neave et al.,*

667 2014], or in submarine basaltic glasses where CO₂ concentrations often exceed the
668 equilibrium concentrations predicted from solubility models [Dixon *et al.*, 1988; Helo *et al.*,
669 2011; Soule *et al.*, 2012]. Experiments were carried out to investigate the vesiculation of
670 basalts from Stromboli [Pichavant *et al.*, 2013]. Natural pumice and glass samples were used
671 to simulate melt ascent from 2-2.5 kbar to 0.25-0.5 kbar and it was found that, at a
672 decompression rate equivalent to an ascent rate of 0.25 to 1.5 m/s, CO₂ concentrations were
673 up to an order of magnitude higher than the solubility at the final pressure, corresponding to
674 supersaturation pressures of ~ 150 MPa. At low vesicularity and/or bubble number density,
675 CO₂ exsolution was limited by the rate of CO₂ diffusion through the melt, rather than the rate
676 of CO₂ transfer across melt/vesicle interfaces, resulting in disequilibrium degassing (similar
677 to rhyolite studies; [Mangan and Sisson, 2000]). The composition used by [Pichavant *et al.*,
678 2013] is slightly more hydrous (2.7 - 3.8 wt.%) than the 1669 Mt. Etna samples (1.4 wt.%),
679 but the CO₂ content is very similar (up to 1200 ppm). The ascent timescales for the melt to
680 become CO₂ supersaturated upon arrival into a shallow magma reservoir is on the order of
681 hours to days, depending on the vesicle number [Neave *et al.*, 2014], which is comparable to
682 the ascent times from reservoir depths estimated for Etnean eruptions of a few hours (from
683 seismicity during the explosive flank eruption in 2002 at Mt. Etna, [Patanè *et al.*, 2003]), or a
684 few days (from the A.D. 1669 contemporary records of vigorous seismic events preceding the
685 A.D 1669 eruption by 2 weeks and focused at the eventual site of the Monti Rossi cone
686 [Mulas *et al.*, 2016; Tanguy *et al.*, 1996] and references therein). Sulfur is strongly positively
687 correlated with CO₂ ($r = 0.73$) (**Supplementary Figure 3**), suggesting that the depleted melt
688 may also be supersaturated in sulfur upon mixing, consistent with the similar diffusivities of
689 CO₂ and S in basaltic melts [Baker *et al.*, 2005; Freda *et al.*, 2005].

690

691 **6 Implications and comparison with previous work**

692 Melt inclusions hosted by olivines erupted during the initial stages of the 1669 eruption of
693 Mt. Etna, Italy, preserve a record of melt mixing. Two relatively evolved basaltic melts (each
694 had undergone ~ 70% fractional crystallization) mixed to form an array of compositions with
695 one end member (perhaps slightly more primitive) depleted in LREE, enriched in Sr, Ca,
696 carbon and sulfur intruding a shallow storage region containing a melt relatively enriched in
697 LREE, and relatively depleted in Sr, carbon and sulfur. We propose that the LREE-depleted
698 melt, which was rich in Sr, may have been generated by either the incorporation of a melt
699 derived from a Sr-enriched recycled cumulate gabbro in the mantle, or by incorporation of
700 crustal carbonate. In either case, the modification in major element (Ca, Na and K, in

701 particular) composition of the melt caused the solubility of carbon and sulfur in the melt to
702 increase. Rapid rise of such depleted, volatile-rich melts may have cause the melt to become
703 supersaturated, such that upon arrival into the shallow plumbing system, where the melts
704 stalled and mixed with resident melts, a vigorous episode of degassing would have taken
705 place, both in response to rapid equilibration, but also in response to cooling upon mingling
706 with the stored melts. This cooling would have caused a burst of crystal growth, allowing
707 melt inclusions to be trapped which recorded the mingling and mixing of these two distinct
708 melts.

709

710 Magma mixing prior to and during the 1669 eruption of Mt. Etna is consistent with previous
711 work. Corsaro et al. [1996] identified two lava types based on their geochemistry: SET1 and
712 SET2. SET1 was erupted during 11-20 March 1669 and were more primitive than the later-
713 erupted SET2. The lava types were interpreted as having coexisted and interacted in the
714 magmatic storage system prior to eruption, with the lower density, volatile-rich SET1 magma
715 rising up through the SET2 magma. Kahl et al. [2017] deduced additional detail from study
716 of olivine core and rim compositions, combined with timescales from diffusion modeling.
717 SET1 magmas contained olivines with core compositions similar (Fo_{75-78}) to those we
718 analyse in this study (Fo_{74-75}) [Kahl et al., 2017]. The magma was invaded by a more evolved
719 melt 1-2 years prior to eruption, which gave rise to the lower forsterite rims, which continued
720 up to a few weeks or months prior to eruption [Kahl et al., 2017]. The intruding melts
721 ascending rapidly up to shallow levels in the system may have carried high fractions of
722 exsolved (and dissolved) volatiles.

723

724 Mixing between supersaturated melts (with their bulk CO_2 content enhanced by due to their
725 Ca- and alkali-rich composition) and stored, degassed melts shortly before eruption may
726 explain observations of enhanced CO_2 fluxes prior to eruptions at Mt. Etna [Aiuppa et al.,
727 2007; Aiuppa et al., 2008]. Mixing of magmas with markedly different compositions (mafic
728 injected into more evolved magmas) has been proposed as a means to trigger eruptions at
729 many stratovolcanoes [Venezky and Rutherford, 1997; Woods and Cardoso, 1997] but in the
730 case of 1669 and recent eruptions at Mt. Etna [Ferlito et al., 2010; Métrich et al., 2004;
731 Viccaro et al., 2006] both mixing magmas have a basaltic composition. The critical factors
732 controlling eruption triggering may be the differential volatile contents and solubility in the
733 melt due to differences in major element composition. Evidence is presented that indicates
734 that incompatible element-depleted melts may ascend rapidly through the mid- and upper

735 crust beneath Mt. Etna, developing supersaturation in the volatiles carbon dioxide and sulfur
736 and thereby suppressing their outgassing into a vapor phase. The arrival of these melts into
737 shallow magma storage areas may prompt rapid cooling and vesiculation, the conditions
738 necessary to trap melt inclusions (during rapid crystal growth) and to trigger eruptions
739 (through vesiculation and increase in overpressures). This process of intrusion of volatile-
740 charged, supersaturated melts may be a common process not only at Mt. Etna, but also at
741 many other basaltic volcanoes worldwide. This study further supports the growing assertion
742 that melt inclusion arrays of H₂O and CO₂ compositions only very rarely show degassing
743 pathways; more commonly the diffuse array of data reflects composition-dependent
744 solubility, disequilibrium (supersaturation in CO₂ over H₂O) and mixing.

745

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758

759 **References**

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1089

1090 **Figure captions**

1091

1092 **Figure 1:** Map of Mt. Etna with 1669 Monti Rossi scoria cone indicated. Lava flows from
1093 Monti Rossi cone to Catania are indicated in red from [Branca *et al.*, 2013] and sample sites
1094 at Monti Rossi cone are shown by black stars (SW and NE sides of cone). Map produced
1095 using *Geomapapp* (<http://www.geomapapp.org>) using the [Global Multi-Resolution](#)
1096 [Topography \(GMRT\) Synthesis](#) [Ryan *et al.*, 2009].

1097

1098 **Figure 2:** Photomicrographs of olivine crystals with melt inclusions (MI), oxide inclusions
1099 and matrix glass in samples: A: NEMR 67, B: SWMR 25, C: NEMR 141, D: NEMR 10. 500
1100 μ m scale bar marked.

1101

1102 **Figure 3:** Major element oxide (wt. %) compositions for A.D. 1669 MI and MG (this study)
1103 compared to (i) 3930 \pm 60 B.P. (4 kyear) Fall-Stratified basalts (FS) MI [Kamenetsky *et al.*,
1104 2007]; (ii) previous A.D. 1669 MI study [Clocchiatti and Metrich, 1984] (iii) A.D. 1669 WR
1105 lavas [Corsaro *et al.*, 1996]; (iv) 2002 MI [Spilliaert *et al.*, 2006b]; (v) 2001, 2002, 2006 MI
1106 [Schiavi *et al.*, 2015]. Symbols define different studies. The dashed line represents the
1107 modeled fractional crystallization path using the two end-member primitive FS melts at 1
1108 kbar (solid line) and 4 kbar (dashed line) with Petrolog3 software [Danyushevsky and
1109 Plechov, 2011b]. Color bar scales for Ce/Y, a measure of degree of LREE-enrichment.
1110 Vectors represent assimilation of contaminants (Carbonate - C, Plagioclase - P, Gabbro - G)

1111 by the two end-member FS melts, adapted from [Carter and Dasgupta, 2015; Mollo et al.,
1112 2010].

1113

1114 **Figure 4:** Trace element profile for this study of A.D. 1669 melt inclusions (MI: fine gray
1115 line), 1669 matrix glass (MG: black dashed lines) compared to (i) 3930±60 B.P. Fall
1116 Stratified (FS) eruption MI (blue line; [Kamenetsky et al., 2007]) and (ii) 2004, 2006, 2007
1117 eruption MI (coloured circles; [Collins et al., 2009]). All concentrations are normalised to
1118 primitive mantle [McDonough and Sun, 1995].

1119

1120 **Figure 5:** (a) Nd and La trace element concentrations (ppm) for A.D. 1669 MI (this study)
1121 compared to (i) 3930 ± 60 B.P. Fall-Stratified basalts (FS) MI [Kamenetsky et al., 2007]; (ii)
1122 2001-2006 MI [Schiavi et al., 2015]. Symbols as before. Solid black line represents modeled
1123 fractional crystallization (FC) path using two end-member primitive FS MI at 1 kbar and
1124 Petrolog3 software [Danyushevsky and Plechov, 2011a]. Color bars scale for Ce/Y, a
1125 measure of degree of LREE-enrichment: A.D. 1669 and FS: red-yellow, 2001-2006: gray-
1126 scale. (b) Ce against Y (ppm) for the same MI studies as (a) with gray lines of constant Ce/Y
1127 ratio and solid black lines as before. (c) La against Sr for 1669 MI showing negative
1128 correlation between Sr and LREE. (d) Sr against MgO showing breadth of Sr concentration in
1129 A.D. 1669 samples at a limited MgO wt.%. Solid black line as before.

1130

1131 **Figure 6:** (a) H₂O against CO₂ with closed (dotted lines) system degassing modeled from
1132 primitive FS melt compositions using SolEx [Witham et al., 2012]. Isobars marked (SolEx)
1133 for both FS conditions (solid black line) and 1669 conditions (solid gray line). Symbols as
1134 before for A.D. 1669 MI and MG (this study), 2002 MI [Spilliaert et al., 2006b] and FS
1135 [Kamenetsky et al., 2007] MI. (b) Positive correlation of CO₂ against sulfur in 1669 MI.
1136 Symbols and colour bar as before. (c) Negative correlation of CO₂ against Nb in 1669 MI and
1137 MG. Symbols and colour bar as before. FS MI do not follow the same correlation. (d)
1138 Positive correlation of CO₂ against Sr anomaly (Sr/Sr*). Sr* calculated from the relative
1139 compatibility of neighboring REE Ce and Nd, see text for details of calculation.

1140

1141 **Figure 7:** Model of possible mechanisms to account for Sr-rich, CO₂-rich depleted melts
1142 mixing with Sr-poor, CO₂-poor enriched melts in the shallow crust. MI symbols for 1669, FS
1143 and 2001, 2002, 2006 same as before. Fractional crystallization (FC) of FS-melt modeled by
1144 Petrolog3 software [Danyushevsky and Plechov, 2011a] indicated by vertical arrows. (a)

1145 Model of mantle melting: (i) KG1(8) pyroxenite melting at $F=0.01$ accumulated fractions
1146 (turquoise), ticks mark degree of melting. (ii) KLB-1 peridotite melting at $F=0.01$
1147 accumulated fractions (dark blue line), ticks mark degree of melting. (b) Models of
1148 contaminant assimilation: (i) plagioclase (blue line) assimilation: ticks mark fraction of
1149 contaminant mixed into depleted and enriched FS-melts and blue arrows signify 70% FC of
1150 the end-member melts after 30% contamination by plagioclase; (ii) 10% gabbro melt (pink
1151 line) assimilation: ticks mark fraction of contaminant mixed into enriched FS-melts. Pink box
1152 1 is the whole rock (WR) composition of the AMLG gabbro [Corsaro *et al.*, 2014] and box 2
1153 is the composition of the 10% batch melt from this gabbro (iii) carbonate (green line)
1154 assimilation, ticks mark fraction of contaminant mixed into LREE-enriched and LREE-
1155 depleted FS-melt. Green box is the composition of Etnean carbonate xenolith contaminant.
1156 The green arrows signify 70% FC of the LREE-enriched melt after 0% carbonate assimilation
1157 (i), and 50% carbonate assimilation (ii).

1158

1159 **Figure 8:** a) Melt inclusion CO_2 concentrations plotted against Ce/Y for both 1669 melts
1160 (orange triangles) and FS melts (red circles); b) Saturation pressures calculated using major
1161 element parameterization [Shishkina *et al.*, 2014], which takes into the account the variable
1162 CaO and alkali contents of the end member melts, plotted against Ce/Y.



Mt Etna

Valle del Bove

Ionian Sea

Mt Rossi

★ ■ Nicolosi

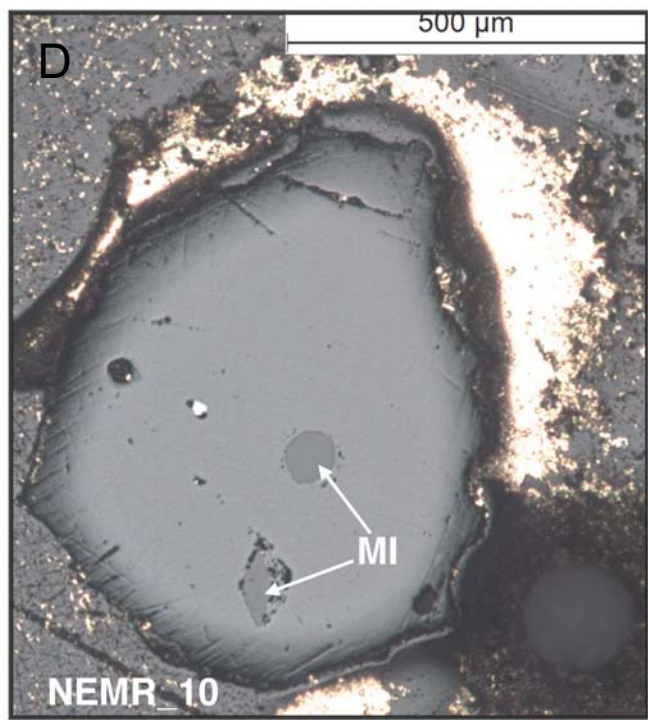
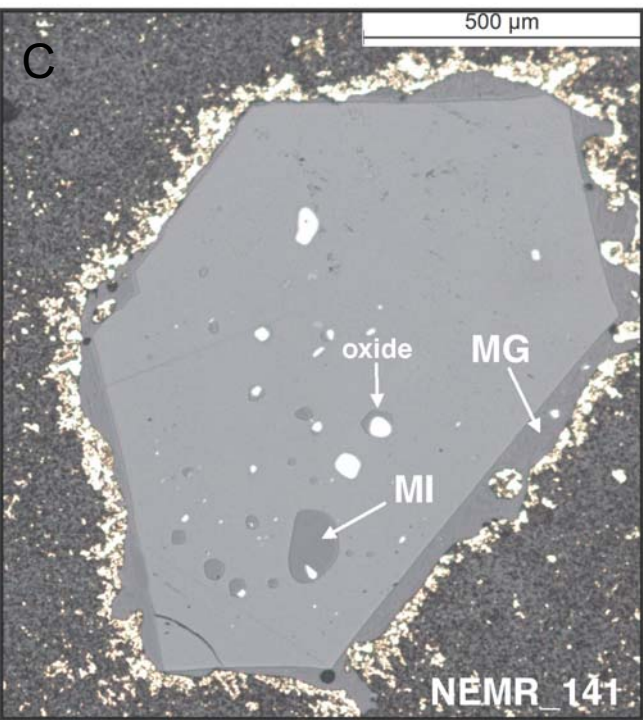
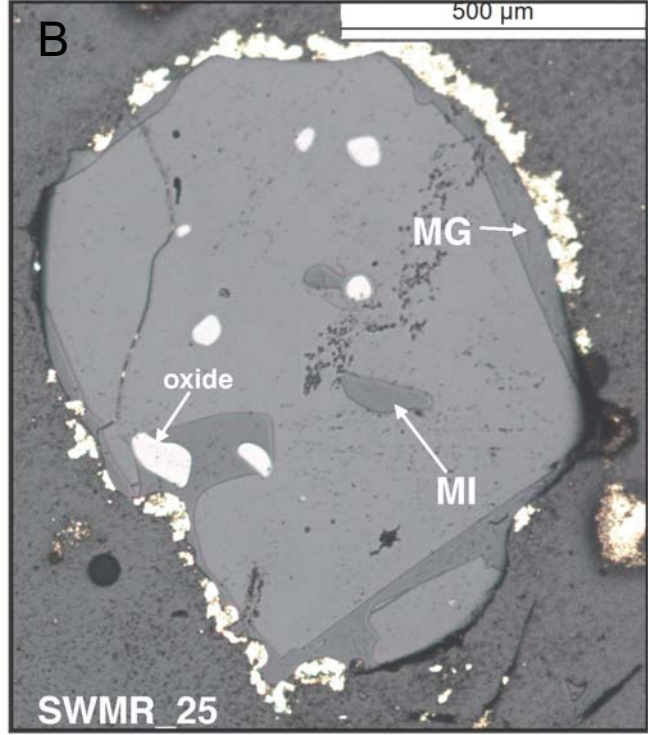
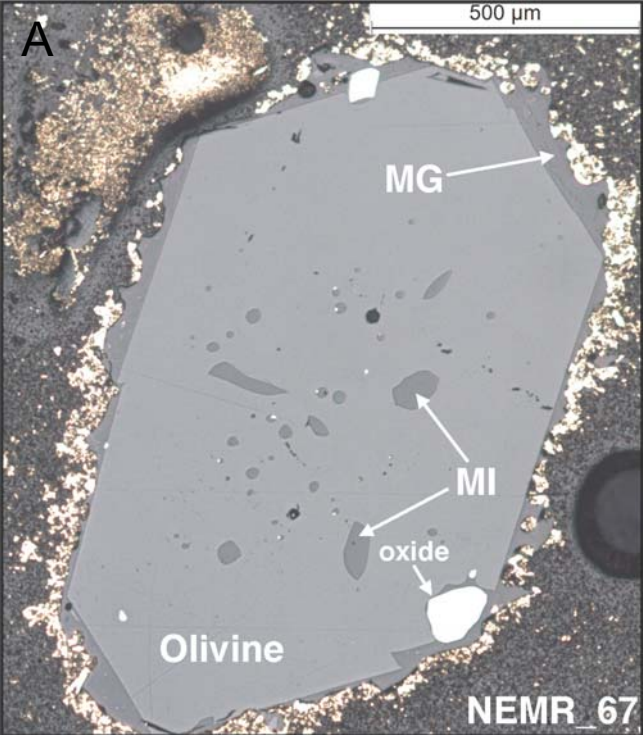
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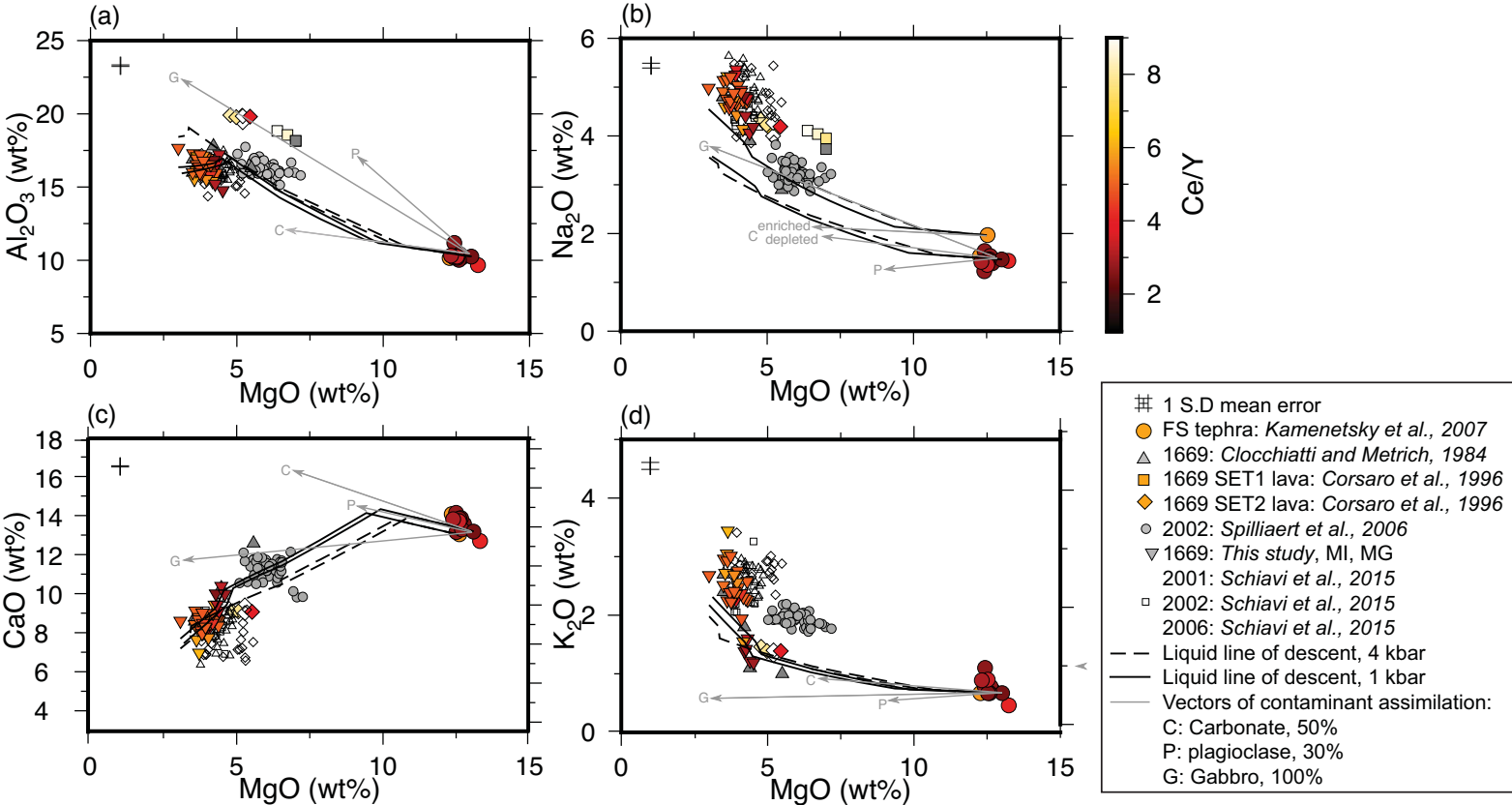
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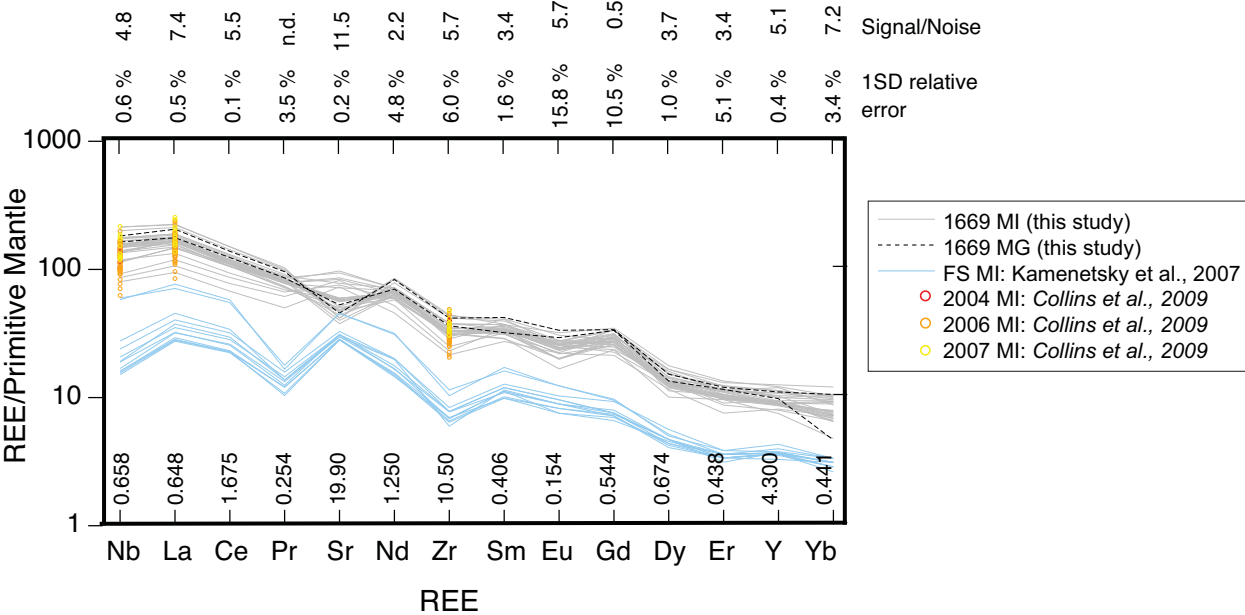


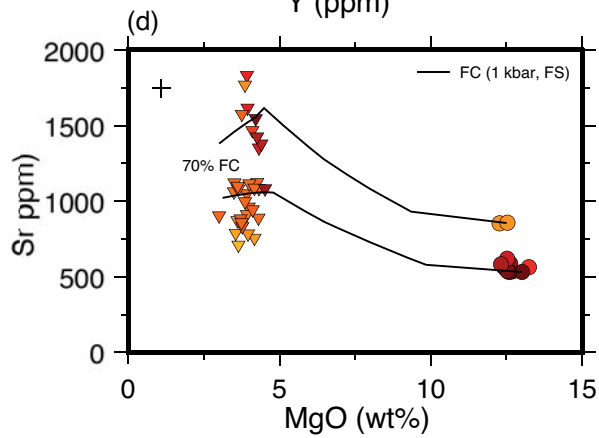
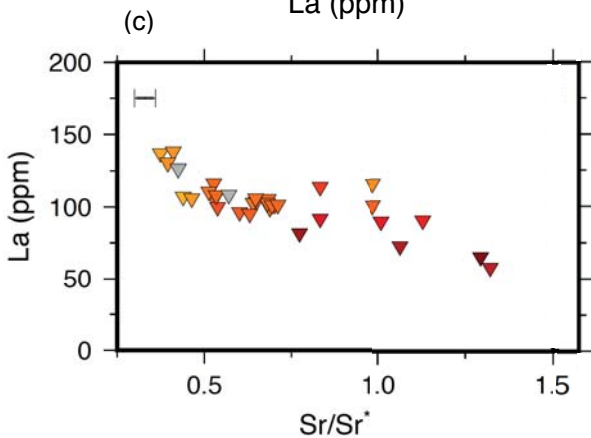
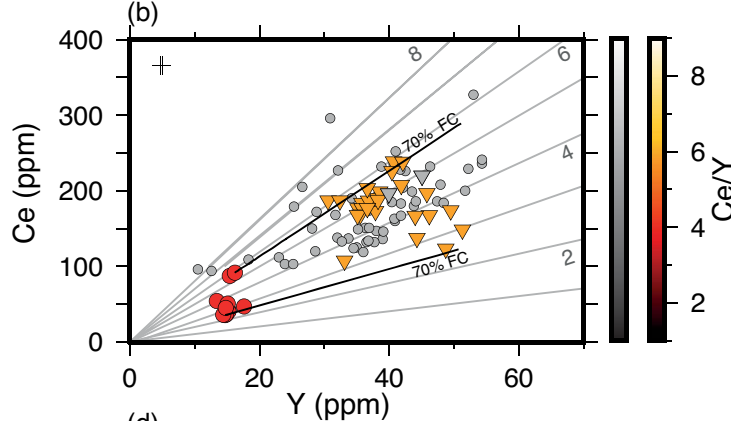
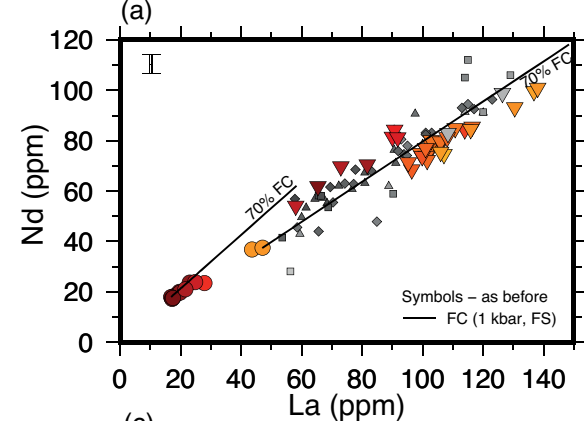
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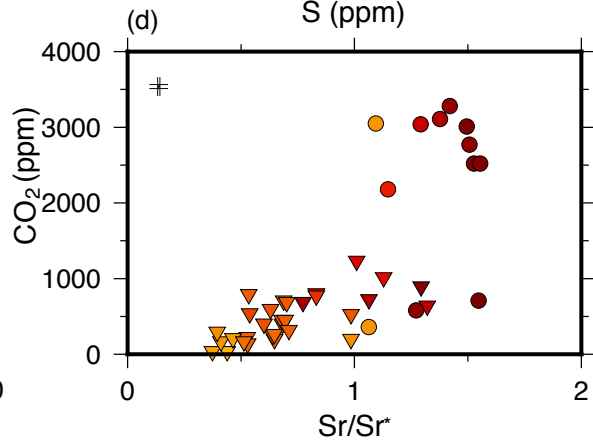
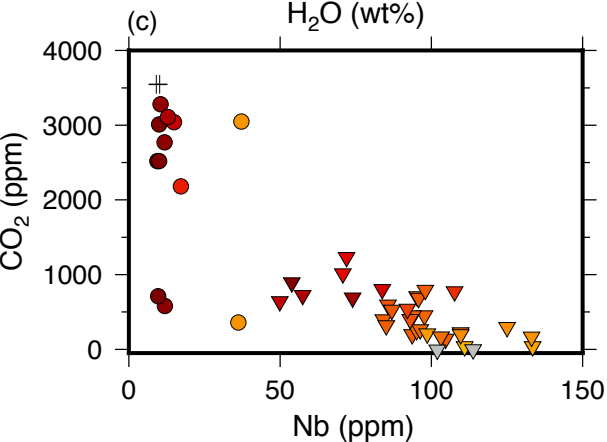
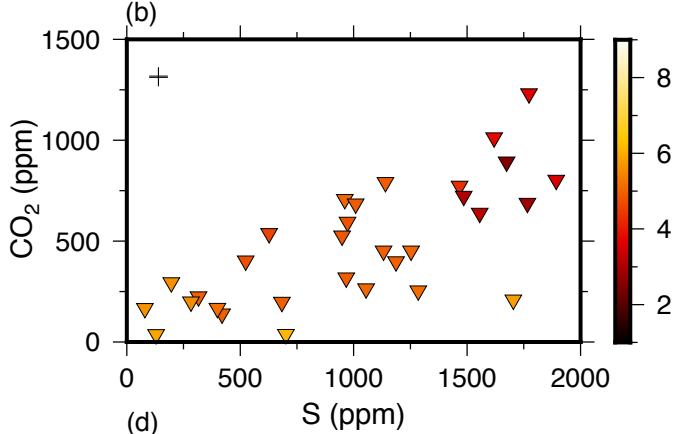
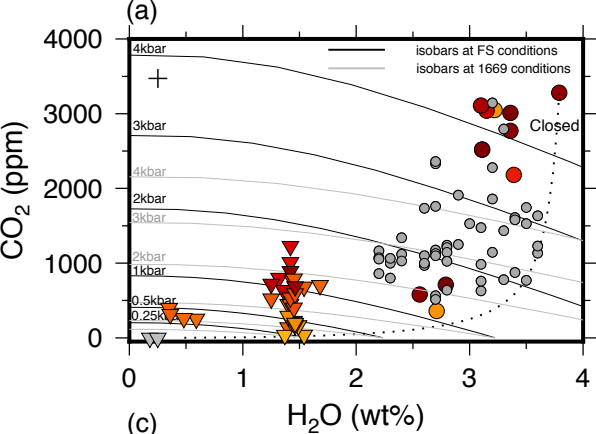
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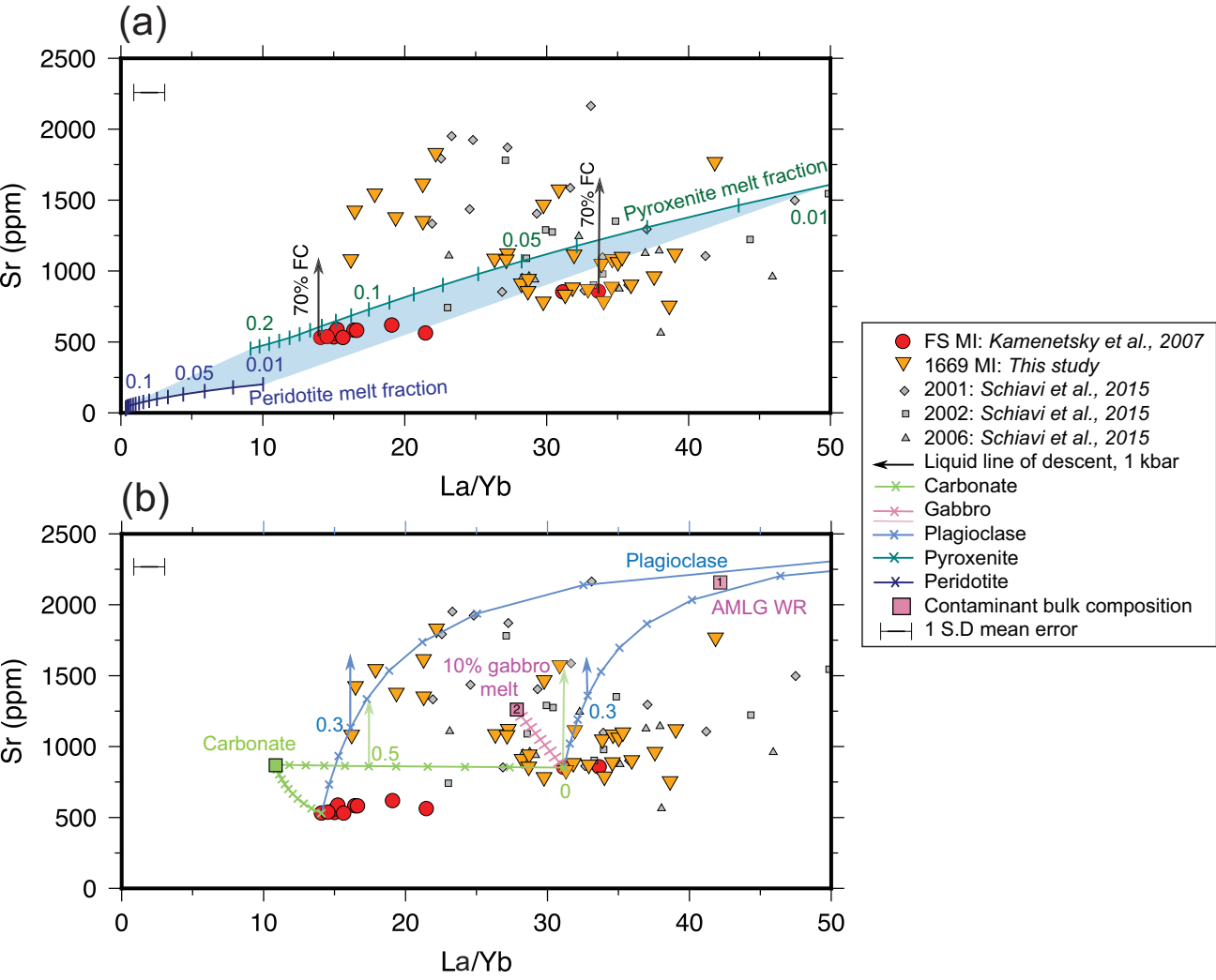


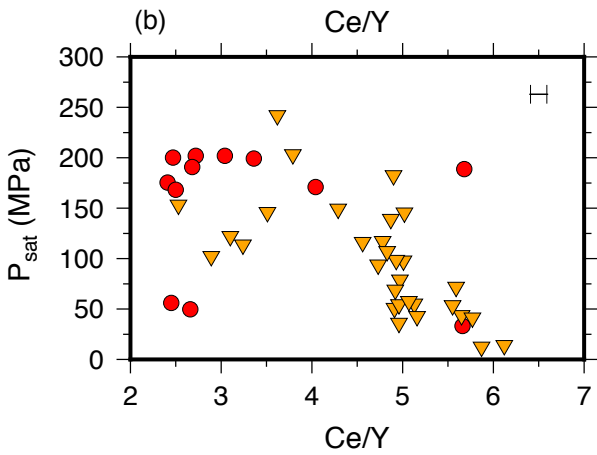
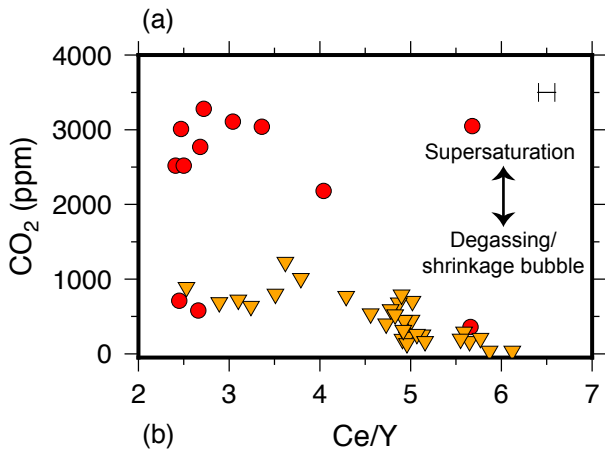












Supporting Information for “Carbon dioxide in geochemically heterogeneous melt inclusions from Mount Etna, Italy”

L. C. Salem,¹ M. Edmonds¹, R. A. Corsaro,² and J. MacLennan¹

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Introduction The following supplementary material supplies detailed methodological and analytical details in addition to those provided in the main manuscript text. Equations and methods used to model mantle melting are described in Sections S1, Analytical Techniques and conditions are described in Section S2 and S3. The Principle Component Analysis methodology is described in section S4. Data tables and supplementary figures are also included that support the manuscript and are referenced in the main text.

Melting equations and models S1 A batch melting equation [Winter, 2010] was used to model melting of the ALMG Etna gabbro [Corsaro *et al.*, 2014]. Let C_o be the trace element concentration of the original rock before melting, C_m be the trace element concentration of the melt, D_i be the bulk partition coefficient of element ‘i’ and F be the wt% fraction of melt produced

$$C_m = \frac{C_o}{D_i(1 - F) + F}, \quad (1)$$

Incremental fractional melting of KLB-1 peridotite [Davis *et al.*, 2009; Jennings and Holland, 2015] and KG1(8) pyroxenite [Kogiso *et al.*, 1998; Jennings *et al.*, 2016] at T_p 1315 °C and 1500 °C were modeled using the methods outlined in Jennings and Holland [2015] and Jennings *et al.* [2016] respectively. These models use P-T-F (pressure-temperature-melt fraction) pathways for decompression melting calculated assuming anhydrous and isentropic conditions according to the method of Katz *et al.* [2003]. The differential equation (provided by Katz *et al.* 2003, originally McKenzie 1984) for dF/dP is numerically integrated using a fourth-order RungeKutta scheme. For peridotite melting, the solidus, liquidus and melt productivity parametrization of Katz *et al.* [2003] were used, along with

the thermal properties of *Shorttle et al.* [2014]. For pyroxenite melting, the new solidus, liquidus and melt productivity parametrization of *Jennings et al.* [2016] for the KG1(8) composition was used. The parameters used are listed in Table A1 of *Jennings et al.* [2016] and the new thermodynamic model for calculating phase relations during mantle melting from 0.001 to 60 kbar and from 800 °C to liquidus temperatures in the system NCFMASOCr is outlined in *Jennings and Holland* [2015]. The trace elemental partition coefficients and bulk peridotite and pyroxenite compositions of *Stracke and Bourdon* [2009] were used in conjunction with the phase relations calculated by *Jennings et al.* [2016] and *Jennings and Holland* [2015] in order to compute the full trace element composition of the melt at each 0.01 fractional melt increment. Instantaneous 0.01 melt fractions were generated by the model and then accumulated to obtain the composition of melt fractions from 0 to 0.2.

Analytical Method: Secondary Ion Mass Spectrometry (SIMS) S2

All SIMS analyses were performed on a Cameca ims-4f instrument at the NERC Ion Microprobe Facility at the University of Edinburgh, UK in one analytical session in October 2013. Carbon (C) was measured separately from other volatiles and trace elements in the first round of analysis. When measuring C, the SIMS is configured with a high mass resolving power in order to ensure good separation of ¹²C and ²⁴Mg²⁺ peaks. Other volatiles and trace elements were subsequently measured in a second round of analyses. SIMS measurements of C were the first measurements made on the samples. Samples were then C-coated and analyzed by EPMA after SIMS to prevent the risk of contamination from the C-coat. Measurements were made using a primary O⁻ ion beam with an accelerating voltage of 15 kV, a beam current of 5 nA, a secondary accelerating voltage of

4500 V minus a 50 V offset, to resolve the tail of the C-peak from the Mg²⁺ peak, and a 25 μm image field. The ion beam was rastered over an area of approximately 20 μm^2 for 180 seconds as a pre-sputter prior to analysis to remove surface contamination. The raster was then switched off and a 15 μm beam centered in the middle of the rastered area was used to make measurements. The following isotopes were measured for 15 cycles, with counting times in seconds in parentheses: ¹²C(5), ²⁴Mg²⁺(10), ²⁸Si²⁺(2) and ³⁰Si(2). Only counts from the final 8 cycles, when count rates reach an asymptote and the effects of surface contamination are minimal, were retained to calculate C concentrations. A background correction was performed by subtracting the number of C counts measured using the CO₂-free standard BIR-1G [Jochum *et al.*, 2005]. C concentrations were calculated using a calibration curve constructed with a suite of basaltic glass standards (17-2, S5-14, S4-13, S2-3) of CO₂ content 0-3000 ppm [Pichavant *et al.*, 2009]. Accuracy expressed as % recovery of published compositions determined by Fourier-transform infrared spectroscopy (FTIR), was 100.6%. Precision was estimated as 1SD (σ) = 0.7% using 3 repeat analyses of each standard.

Water (H₂O), fluorine (F) and trace elements were measured as part of the same analysis set-up after C analyses had been completed. Measurements were made using a primary O⁻ ion beam with an accelerating voltage of 15 kV, a beam current of 5 nA, a secondary accelerating voltage of 4500 V minus a 75 V offset and a 25 μm image field. The ion beam was rastered over the same area as the C analysis but for 120 seconds. Analyses were made with a spot size of approximately 25 μm x 25 μm cantered in the pit made during the preceding C analysis. The following isotopes were measured for 10 cycles, with counting times in seconds in parentheses: ¹H(5), ¹⁹F(5), ³⁰Si(2), ³⁵Cl(5), ⁴⁷Ti(3), ⁸⁴Sr(3), ⁸⁸Sr(3), ⁸⁹Y(3),

⁹⁰Zr(3), ⁹³Nb(3), atomic mass 130.5(3), ¹³⁸Ba(3), ¹³⁹La(3), ¹⁴⁰Ce(3), ¹⁴¹Pr(5), ¹⁴³Nd(5), ¹⁴⁹Sm(8), ¹⁵¹Eu(10), ¹³⁸BaO+¹⁵⁴Gd(5), ¹⁴⁰CeO+¹⁵⁶Gd(4), ¹⁵⁷Gd(8), ¹⁵⁹Tb(5), ¹⁶¹Dy(5), ¹⁶⁵Ho(5), ¹⁶⁷Er(8), ¹⁶⁹Tm(8), ¹⁷¹Yb(10) and ¹⁷⁵Lu(10). Peak positions were verified before each analysis, and mass 130.5 was measured to determine the electron multiplier backgrounds in each cycle, which were always sufficiently close to zero to be ignored. The overlap of BaO on Eu was monitored using the mass 154 peak (¹³⁸BaO+¹⁵⁴Gd(5)) and the overlap of the light REE, Gd and Tb oxides, on the heavy REE by use of mass 156 (¹⁴⁰CeO+¹⁵⁶Gd(4)). Only the first 5 or 6 cycles of each 10 cycles of analyses were used due to mass drift. H₂O concentrations were calculated using a calibration curve constructed with 17-2, S2-3 and S5-14 glass standards with H₂O contents of 4.82, 3.15 and 3.46 wt.% respectively *Pichavant et al.* [2009]. Accuracy expressed as % recovery of published compositions determined by Fourier-transform infrared spectroscopy (FTIR), was 100.6%. Precision was estimated as 1SD = 1.1% using 3 repeat analyses of 17-2 and S2-3. Drift was monitored using repeat analyses of 17-2 and S2-3 at the start, middle and end of each day. 2-7% drift in calculated H₂O concentrations was observed on three days of H₂O data collection and a linear correction was made. F concentrations were calculated using a calibration curve constructed with the international standards NIST-610 and BCR-2G [*Jochum et al.*, 2005, 2011]. Accuracy was monitored by analysis of international standards NIST-610 and BCR-2G throughout analytical sessions. Average accuracy expressed as % recovery of published compositions determined by FTIR, was > 70% for all trace elements. Precision was estimated as 1σ relative error and varied between 0.1% (Ce) and 15.8% (Eu) using repeat analyses of BCR-2G [*Jochum et al.*, 2011]. Precision was calculated for trace element ratios and volatile/trace ratios using repeat

analyses of the same standards. 1 σ percentage relative error is in parentheses: La/Yb (0.5), Ce/Y (2.9), CO₂/Nb (0.9) and H₂O/Ce (1.1). Concentrations were calculated by normalizing ³⁰Si to Si determined subsequently by EMPA at the University of Cambridge. The following international standards were measured at the start of each day to monitor the calibration and drift: BCR-2G, BIR-1G and NIST-610 (Jochum et al., 2005, 2006). The trace element content of 17-2 and S2-3 was also monitored throughout each day to check for drift, though none was observed. Absolute element concentrations were calculated using JCIION-6 software, where corrections were also made for oxide interferences of light REEs on the heavy REEs and BaO on Eu. The magnitude of oxide correction relates to the offset voltage at which the data are processed. Minor sample charging variations were checked (and corrected for) by use of the CeO/Ce ratio (based on the corrected mass ¹⁵⁶CeO/¹⁴⁰Ce ratio).

Analytical Method: Electron probe microanalysis (EPMA) S3 Major element compositions of macrocrysts, matrix glasses and melt inclusions were determined using a Cameca SX100 instrument at the University of Cambridge, UK. Glass analyses were performed with a spot size of 5 μ m, an operating potential of 15 kV and a beam current of 6 nA. Olivine analyses were performed with a spot size of 1 μ m, an operating potential of 15 kV and a beam current of 20 nA. Counting times were as follows for glass: Mg(80), Si(20), Fe(40), Ca(40), Al(80), Na(10), Ti(60), K(10), Mn(90), Cr(80), P(60), Cl(90), S(120), F(120), and for olivine: Mg(20), Si(20), Fe(20), Ca(60), Al(90), Ni(60), Ti(60), Mn(40), Cr(40), P(90). Calibration standards were as follows: jadeite for Na, periclase for Mg, Si glass for Si, K-feldspar for K, rutile for Ti, fayalite for Fe, corundum for Al, apatite for P, and pure metals for Cr, Mn and Ni. Data reduction was performed using

the inbuilt CamecaX-Phi PeakSight software for glass analyses and PAP corrections for mineral analyses. Most analyses returned totals of 98.5-101.5 wt.%. Samples with totals outside this range or with inappropriate stoichiometry were discarded. MgO content of the St. Johns Island Olivine standard was determined with a precision of 0.1(1SD) wt.% (n=13).

Principal Component Analysis (PCA) S4 [*Albar`ede, 1996; McKenzie and O'Nions, 1998*] is a method to extract uncorrelated variables from sets of data, to allow the main trends to be isolated. PCA analysis of the 1669 melt inclusion trace element compositions indicates that the first two principal components (PC1 principal component 1 with standard deviation 2.738 and PC2 principal component 2 with standard deviation 2.642) describe 50% of the variance in trace element dataset. Plotting PC1 and PC2 across the element array (Supplementary Figure S5) shows that PC1, which involves all trace elements behaving similarly (PC1) except Sr (PC1), highlights an anomaly in the behaviour of Sr. There is some variability in PC1 for the HREE with more compatible elements 0. If the process that is fractionating Sr from other elements results in its depletion in the melt, PC1 may be due to fractional crystallization of plagioclase; Sr is compatible in plagioclase while all other REE are incompatible and become enriched in the melt. However, if Sr is being enriched in the melt, PC1 may be due to assimilation of Sr from some source or contaminant, and this process may also affect the different PC1 scores of HREE compared to LREE. PC2 is positive for the LREE and negative for the HREE (Supplementary Figure S5) and this pattern of vectors could result from a variable primary melt composition (i.e. a melting signature). PC2 might be related to (1) the depth of melting and the presence of garnet in the melting region where HREE are compatible, (2) the

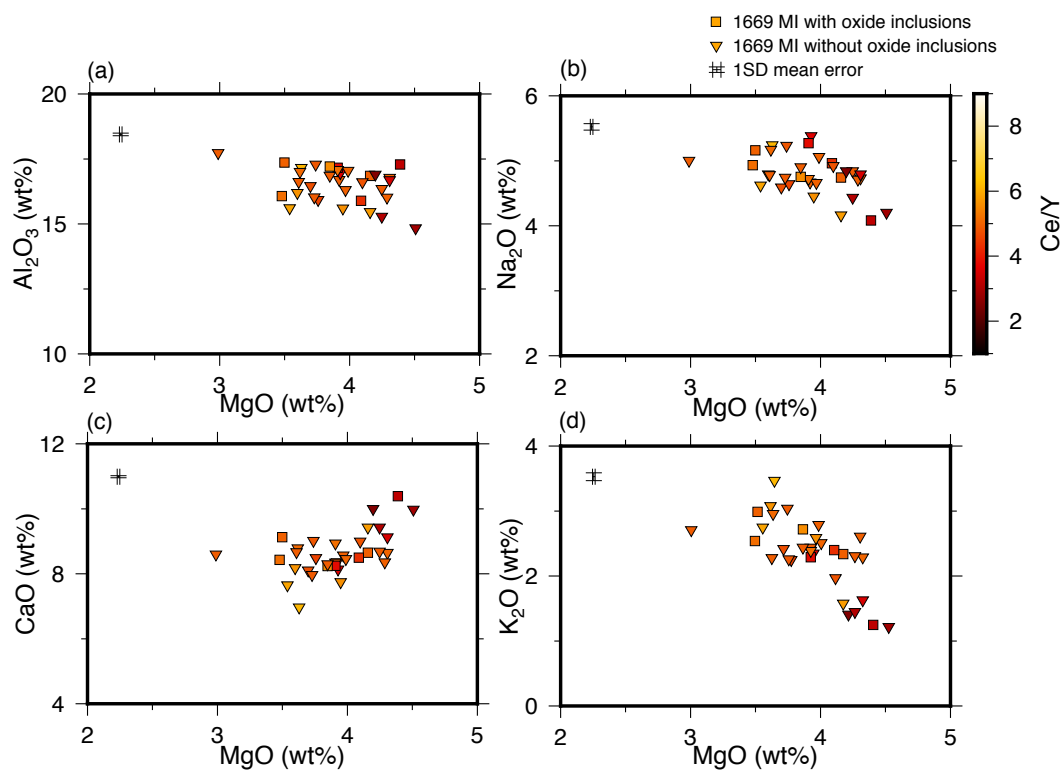


Figure S1. Major element oxide (wt.%) compositions for A.D. 1669 MI (this study) with daughter oxide inclusions (squares) and without trapped oxide inclusions (triangles). Color bar scales are for Ce/Y, a measure of degree of LREE-enrichment.

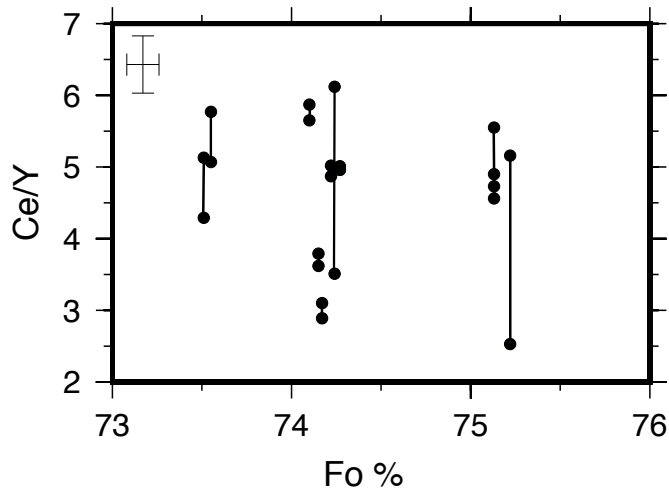


Figure S2. Host Fo composition against Ce/Y as a measure of LREE-enrichment for A.D. 1669 MI (this study). The black vertical lines join analyses of MI in the same olivine host crystal. The range of Ce/Y for each line indicates a lack of correlation between LREE-enrichment and Fo content.

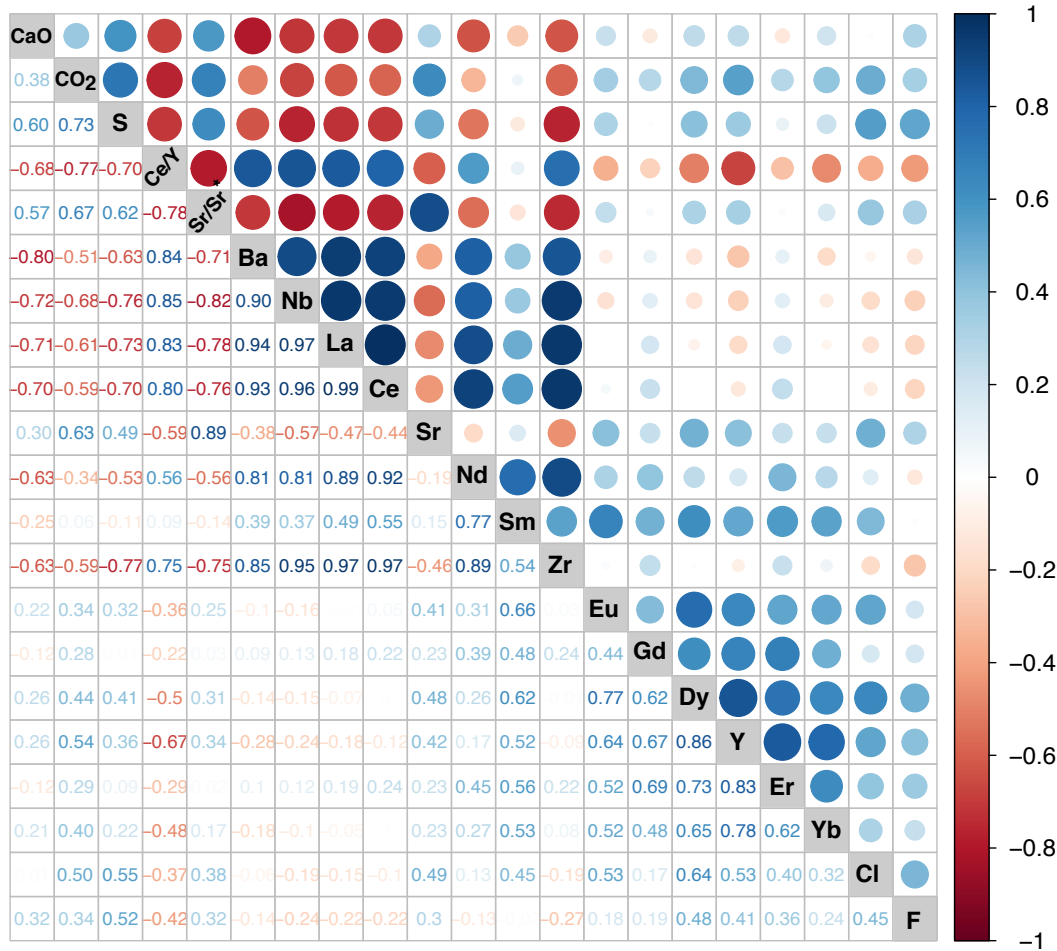


Figure S3. Cross-Correlation matrix generated by the corrplot package in R showing positive and negative correlation between species measured in MI. Blue symbols denote positive correlation and red, negative, the size of the symbol denotes the strength of the correlation. Larger symbols denote a stronger correlation. In the upper-right of the plot large dark symbols show strong correlations and small pale symbols, weak correlation. In the lower-left of the plot regression values (r) are shown and colored by the same scale.

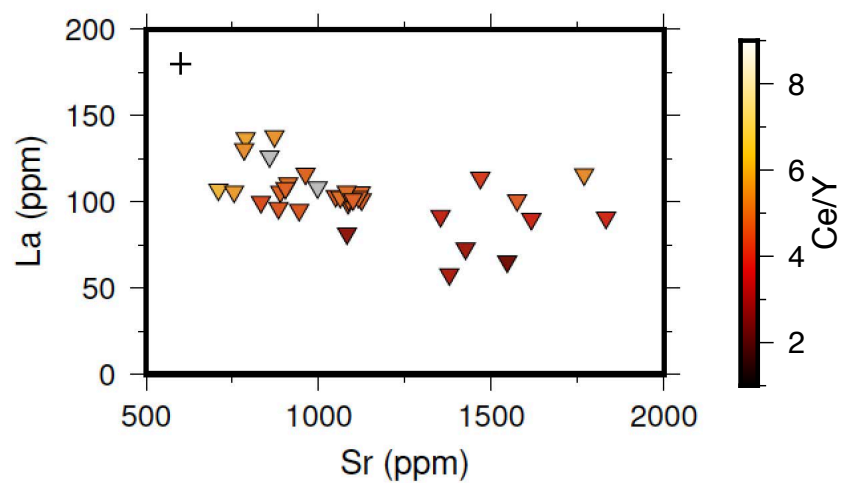


Figure S4. Negative correlation of La against Sr (ppm). Symbols and color bar as before.

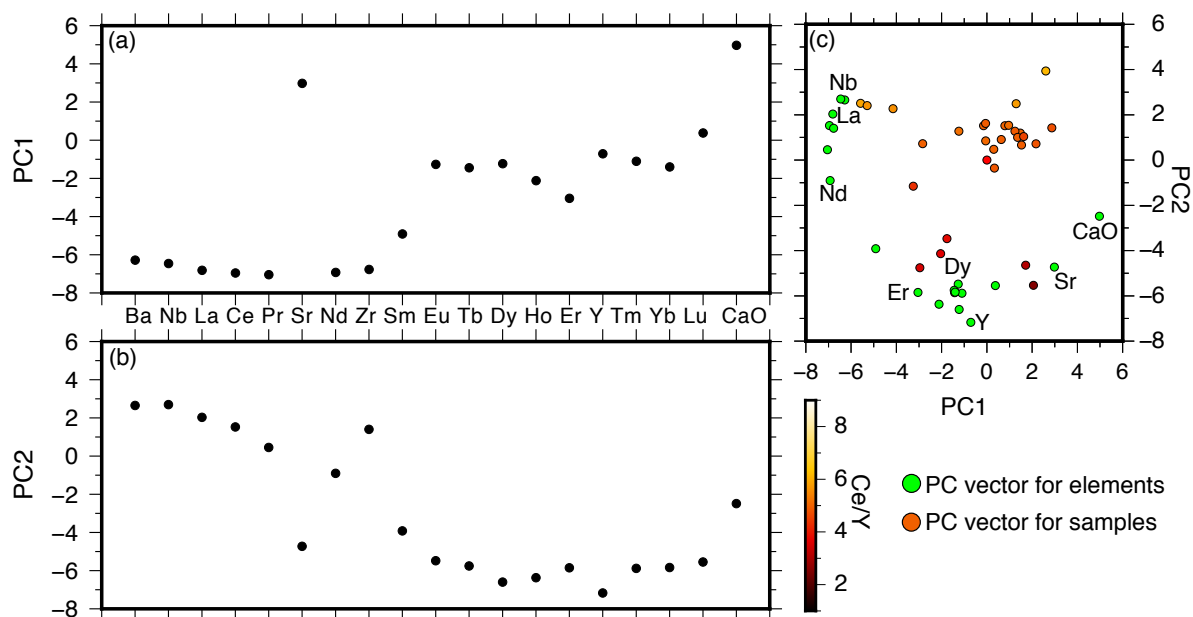


Figure S5. Principle Component Analysis of PC1 (a) and PC2 (b) for each element analyzed. (c) PC1 plotted against PC2 vectors for each MI analyzed, colored for degree of LREE/HREE enrichment (same as before). Vectors of PC1 and PC2 from (a) and (b) are also plotted and labeled by element (green circles).

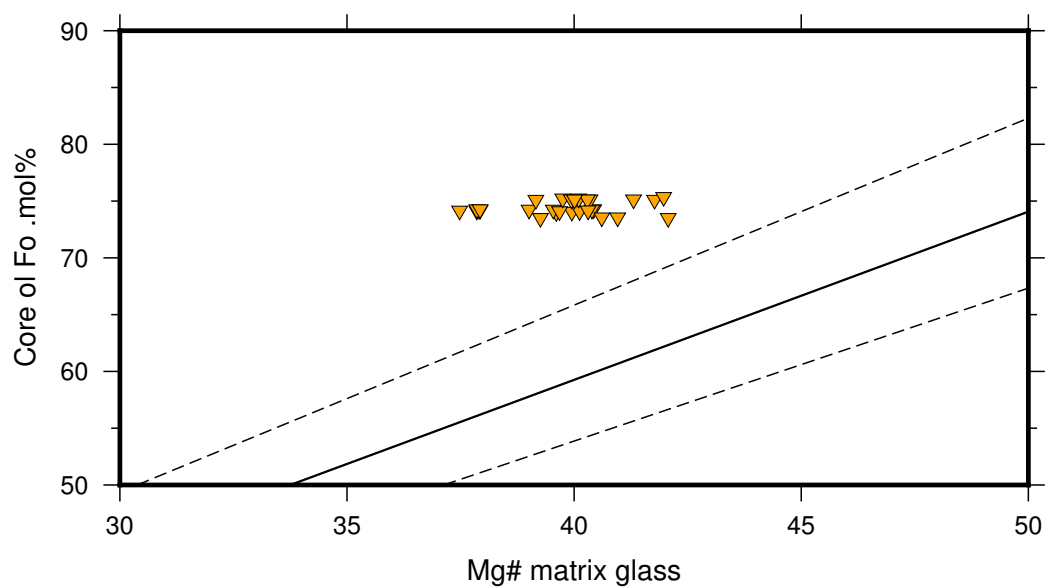


Figure S6. Rhodes plot of host olivine core Fo content against Mg# of the corresponding matrix glass for 1669 olivine crystals. Solid line represents $K_D = 0.3$, dashed lines $\pm 10\%$

Table S1. Summary of estimated accuracy and precision for all elements measured by EPMA and SIMS. Precision is expressed as 1σ percentage relative error (%P) and was calculated using ^arepeat analysis of basaltic glass standards by EPMA, ^brepeat analyses of standards NIST-610 and BCR-2G for trace elements [Jochum *et al.*, 2005, 2011], ^brepeat analyses of 17-2, S2-3 and S5-14 glass standards for H₂O [Pichavant *et al.*, 2009], and ^brepeat analyses of 17-2, S5-14, S4-13, S2-3 glass standards for CO₂ [Pichavant *et al.*, 2009]. ^cAccuracy is expressed as % recovery (A%) with respect to NIST-610 and BCR-2G standards [Jochum *et al.*, 2005] for trace elements and a range of standards with compositions given by Shishkina *et al.* [2010] and Pichavant *et al.* [2009] for CO₂ and H₂O.

Technique	EPMA	SIMS	SIMS
Element	%P ^a (MI)	%P ^b (MI)	%A ^c (MI)
SiO ₂	0.3		
TiO ₂	1.6		
Al ₂ O ₃	0.9		
FeO _t	1.2		
MnO	7.6		
MgO	0.7		
CaO	0.4		
Na ₂ O	2.9		
K ₂ O	4.8		
Cr ₂ O ₃	55.8		
P ₂ O ₅	3.6		
NiO	33.9		
S	1.0		
Cl	3.2		
F	33.2		
H ₂ O		1.1	100.6
CO ₂		0.7	100.6
Sr		0.2	102.6
Y		0.4	108.9
Zr		1.6	115.6
Nb		0.6	106.3
Ba		0.1	105.6
La		0.5	100.9
Ce		0.1	101.2
Pr		2.5	104.9
Nd		4.8	99.0
Sm		6.0	98.0
Eu		15.8	98.5
Gd		10.5	102.6
Tb		3.5	103.0
Dy		1.0	102.0
Ho		9.3	102.5
Er		5.1	99.6
Tm		15.3	104.7
Yb		3.4	102.4
Lu		6.3	102.8

Table S2. Melt inclusions major, trace and volatile element data acquired by EPMA and SIMS with calculated trace element and volatile ratios, Sr/Sr* and host olivine Fo mol.% for NEMR melt inclusions

MI Name	NEMR	10a	10b	26a	67a	67b	67c	76a	76b	80a	113a	113b	114a	126a	126b	140a	140b
SiO ₂ wt. %	48.36	50.22	48.45	50.33	49.59	50.58	49.59	46.8	51.89	49.8	49.68	50.3	49.47	45.72	50.03	49.75	
TiO ₂	1.93	2.09	1.65	2.05	2.03	2.12	1.4	1.82	1.8	1.81	1.98	1.92	1.91	1.49	1.59	1.71	
Al ₂ O ₃	15.54	16.13	17.29	16.24	16.98	15.95	15.82	16	17.09	16.71	16.28	16.7	16.94	15.39	16.89	17.09	
FeO _T	9.74	10.35	10.98	10.55	10.9	11	11.74	11.02	9.97	10.56	10.42	10.81	11.43	11.57	10.98	10.98	
MnO	0.19	0.17	0.21	0.32	0.24	0.17	0.3	0.26	0.24	0.16	0.3	0.14	0.23	0.33	0.23	0.12	
MgO	3.55	3.61	3.51	3.98	4	4.3	4.1	3.49	3.64	4.32	4.26	3.92	3.63	4.17	3.94	3.92	
CaO	7.66	8.19	9.14	8.58	8.47	8.37	8.51	8.44	6.98	8.66	8.7	8.36	8.8	9.44	8.15	8.26	
Na ₂ O	4.6	4.77	5.14	4.64	5.04	4.69	4.94	4.91	5.22	4.71	4.82	4.67	5.15	4.14	5.36	5.25	
K ₂ O	2.72	3.05	2.96	2.76	2.48	2.58	2.37	2.51	3.44	2.26	2.28	2.41	2.93	1.55	2.26	2.26	
P ₂ O ₅	1.14	1.1	0.89	0.9	0.86	0.91	0.95	0.77	0.95	0.83	0.71	0.82	0.89	0.49	0.77	0.66	
H ₂ O	1.54	1.49	0.35	1.45	1.4	1.4	1.44	0.59	1.37	1.68	1.54	1.46	0.48	1.43	1.42	1.42	
Cl	0.23	0.23	0.23	0.23	0.25	0.23	0.38	0.23	0.25	0.22	0.2	0.24	0.23	0.29	0.33	0.37	
Host Fo	74.1	74.1	74	74.3	74.3	74.3	73.5	73.5	74.2	74.2	74.2	74.2	73.6	73.6	74.2	74.2	
S ppm	129	80	1187	316	1253	420	1467	1285	701	961	1009	684	1055	1704	1773	1619	
CO ₂	37.3	166	397.4	223.7	450.6	139.2	771	253.7	37.9	705.4	683.4	197.3	263.7	208.4	1228	1010.3	
Ba	1053	1076.4	930.3	931.1	909.9	873.1	1025.6	912.1	977.4	822	857.3	851.9	911.2	841.7	853.5	796	
Nb	133.5	133.1	84.2	109.7	97.7	104.7	107.7	95.2	111	95.3	95.8	93.7	96.3	98.6	90.8	70.8	
La	136.8	138	105.5	116.4	102.8	105.9	113.9	102.8	107.1	99.2	101.4	103.4	105.9	106	90	90.8	
Ce	238.6	238.1	185	207.5	182.7	190	196.6	183.6	186.9	176.6	179.4	179.6	186.7	186.9	167.4	166.7	
Sr	788.5	871.9	962.1	962.1	1115.6	889.1	1468.4	1062.7	709.7	1085.2	1124.2	1049.5	1081	755.2	1615.8	1832.3	
Nd	99.5	100.9	77.8	85.5	78.3	79.2	84.4	80.1	74.6	75.1	76.5	77.9	79.6	75.5	81.5	84.3	
Sm	15.7	14.4	12.4	14.2	13	12.7	13.8	12.9	11.1	12.4	12.9	12.8	12.6	13.5	14.2	15.9	
Zr	429.7	440.1	308.5	376.3	326.8	349.6	344.1	323.3	315.4	326.8	329.3	332.3	335.4	327.3	285.1	303.4	
Eu	3.8	3.5	4	3.6	3.4	3.2	3.8	3.4	2.4	2.9	2.9	4	3.6	3.7	4	4.5	
Gd	16.1	17.4	13.3	14.7	14.3	13.1	15.2	15	12.2	14.1	13.5	14	12.2	11.6	17.5	14.6	
Dy	8.7	9.2	8.4	9.3	8	8.1	10.6	8.5	6.4	8.1	7.7	8.2	9	8.2	9.7	10.2	
Y	40.7	42.1	37.2	41.9	36.4	38.3	45.8	35.8	30.6	35.2	36.8	36.6	36.8	32.4	46.2	44	
Er	5.2	4.8	4.6	4.8	4.2	4.7	5.1	4.1	4	4.4	4.2	4.1	4.4	3.6	5.1	4.6	
Yb	4	4.2	2.7	3.1	3.2	3.1	3.8	2.9	2	3.1	3.7	3.1	3.9	2.7	4.2	4.1	
F	1751	1875	2060	1686	2085	1720	2480	1977	1565	1813	1809	1825	1932	1620	1812	1731	
Ce/Y	5.9	5.7	5	5	5	5	4.3	5.1	6.1	5	4.9	4.9	5.1	5.8	3.6	3.8	
La/Yb	34	32.9	39	37.6	31.9	34.6	29.8	35	53.5	34.6	27.2	33.9	27.2	38.6	21.3	22.2	
CO ₂ /Nb	0.3	1.2	4.7	2	4.6	1.3	7.2	2.7	0.3	7.4	7.1	2.1	2.7	2.1	17.1	14.3	
H ₂ O/Ce	64.5	62.6	18.9	69.9	76.6	73.7	73.2	32.1	73.3	95.1	85.8	81.3	25.7	76.5	84.8	85.2	
Sr/Sr*	0.4	0.4	0.7	0.5	0.7	0.5	0.8	0.6	0.4	0.7	0.7	0.6	0.6	0.5	1	1.1	

Table S3. Melt inclusions major, trace and volatile element data acquired by EPMA and SIMS with calculated trace element and volatile ratios, Sr/Sr* and host olivine Fo mol.% for NEMR and SWMR melt inclusions and matrix glasses

MI Name	141a	141b	SWMR		6a	6b	6c	41a	46a	46b	50a	50b	50c	50d	57a	67a	109a	NEMR	140 MG	SWMR	46 MG
SiO ₂ wt. %	49.67	48.51	45.33	46.65	47.98	48.32	48.99	50.36	50.73	47.91	48.26	51.3	49.6	48.81	47.45	50.81	51.13				
TiO ₂	2.06	1.89	1.85	1.8	2.41	1.63	1.52	2.19	1.85	1.51	1.69	1.79	2.1	1.86	1.87	2.27	2.23				
Al ₂ O ₃	16.78	16.62	14.77	15.21	15.53	17.22	16.83	17.01	17.14	16.39	15.86	17.66	17.22	16.54	16.55	15.96	16.79				
FeO _T	10.62	11.93	12.46	11.77	10.05	11.41	11.46	9.96	9.9	9.8	9.87	9.72	11.03	10.83	10.84	11.07	10.61				
MnO	0.19	0.29	0.29	0.19	0.25	0.25	0.23	0.2	0.18	0.19	0.21	0.15	0.25	0.2	0.25	0.24	0.22				
MgO	4.17	4.32	4.52	4.26	3.96	4.4	4.21	3.92	3.86	3.71	3.77	3	3.75	4.11	3.62	3.74	3.86				
CaO	8.66	9.14	9.99	9.44	7.76	10.4	10.01	8.95	8.25	8.12	8.5	8.61	9.03	9.01	8.68	7.98	8.31				
Na ₂ O	4.72	4.77	4.18	4.41	4.43	4.06	4.82	4.7	4.73	4.57	4.62	4.98	5.21	4.9	4.76	4.72	4.88				
K ₂ O	2.31	1.6	1.19	1.42	2.56	1.22	1.38	2.36	2.69	2.39	2.22	2.68	2.23	1.94	2.25	3.01	2.41				
P ₂ O ₅	0.83	0.88	0.53	0.47	0.69	0.27	0.33	0.67	0.61	0.63	0.59	0.61	0.46	0.49	0.49	1.1	0.57				
H ₂ O	1.42	1.32	1.46	1.25	1.4	1.36	1.42	1.46	1.46	1.46	1.42	1.45	1.25	1.46	0.36	0.18	0.25				
Cl	0.21	0.31	0.24	0.24	0.26	0.24	0.3	0.19	0.22	0.19	0.16	0.22	0.19	0.21	0.17	0.23	0.19				
Host Fo	74.2	74.2	74.2	74.2	75.1	75.4	75.2	75.2	75.1	75.1	75.1	75.1	75.2	75.1	75.1	74.2	75.2				
S ppm	1132	1893	1766	1485	196	1556	1674	399	283	524	627	1140	949	973	967	70	150				
CO ₂	450.3	800.5	686.5	721.2	293.4	637.4	890.6	167.1	198.6	401.1	537	789.3	524.7	592.8	317.5	0	0				
Ba	880.2	709.1	582.7	587	1035	489.8	551.4	883.2	932.5	823.3	818.2	934.2	863.7	798.4	828.4	951.5	876.1				
Nb	93.9	83.8	74	57.5	125	49.9	53.9	103.2	109.7	93	92.1	98	87	85.7	85.1	113.8	102				
La	101.2	91.8	81.7	73	130.4	58	65.4	110.7	115.9	96.4	99.9	108.1	101	95.3	101.5	126.4	108.4				
Ce	176.9	173.7	148.3	137.3	225.8	107.2	123.1	198.7	203.3	168.2	172.9	187.8	177	167.7	176.5	219.7	196.2				
Sr	1087.4	1353	1082.3	1425.8	784.4	1378.7	1546	911.9	1768.8	883.7	832.6	903.6	1574.6	943.6	1099.8	857.9	997				
Nd	73.9	81.2	70.5	69.7	93.2	54.1	61.8	84.9	84.5	68.5	73.8	81.3	77	71.3	72.2	98.9	83				
Sm	12.2	14.3	13	12.3	15.2	10.5	13.2	14.3	13.2	11.1	11.9	13	13.2	12.6	12.9	16.2	12.3				
Zr	324.6	296.5	303.9	249	415.6	214.4	230	368.4	378.6	312.1	327.8	348.5	323.2	305.9	305.4	414.7	361.1				
Eu	2.9	4.7	4	3.7	4.1	3.2	3.8	3.8	3.9	3	3.3	3.8	3.5	3.7	3.5	4.9	4.3				
Gd	14.7	17.9	17.2	12.8	13.9	11	15.8	14	16.3	14.1	15.6	14.2	13.8	15.1	15.2	17.4	17.2				
Dy	7.6	11.3	10.6	8.2	8.5	7.4	9.9	8.6	8.5	7.9	7.2	7.9	8.6	8.5	8.2	9.7	8.6				
Y	35.9	49.5	51.3	44.3	40.4	33.1	48.7	38.5	36.6	35.5	37.9	38.3	36.6	35.1	35.8	45.1	39.9				
Er	4.1	5.6	5.4	4.7	4.9	3.1	4.7	3.8	4.4	4.1	4.4	4.2	4.6	4	4.3	5	4.8				
Yb	3.8	4.3	5	4.4	4.4	3	3.7	3.9	2.8	3	3.2	3	3.3	3.3	2.9	4.4	1.9				
F	1831	2017	2068	1764	1645	1961	2021	1412	1513	1681	1573	1687	1729	1592	1936	1786	1553				
Ce/Y	4.9	3.5	2.9	3.1	5.6	3.2	2.5	5.2	5.6	4.7	4.6	4.9	4.8	4.8	4.9	4.9	4.9				
La/Yb	26.3	21.3	16.2	16.5	29.8	19.4	17.9	28.2	41.9	31.8	31.3	35.9	30.9	28.7	35.3	28.7	55.7				
CO ₂ /Nb	4.8	9.6	9.3	12.6	2.3	12.8	16.5	1.6	1.8	4.3	5.8	8.1	6	6.9	3.7	0	0				
H ₂ O/Ce	80.3	76	98.4	91	62	126.8	115.4	73.5	71.8	86.2	82.1	77.2	70.6	87	20.4	8.2	12.7				
Sr/Sr*	0.7	0.8	0.8	1.1	0.4	1.3	1.3	0.5	1	0.6	0.5	0.5	1	0.6	0.7	0.4	0.6				

Table S4. Host olivine major and minor element data acquired by EPMA with calculated Fo mol.% for olivine compositions at the core of each crystal and adjacent to each analysed MI

MI Name	Location	NEMR	10a	10b	26a	67a	67b	67c	76a	76b	80a	113a	113b	114a	126a	126b	140a	140b	
SiO ₂ wt.%	adj ol	38.05	38.36	38.37	38.48	38.56	38.52	38.23	38.45	38.52	38.79	38.69	38.54	38.67	38.33	38.51	38.41		
TiO ₂	adj ol	0	0.02	0.03	0.04	0.04	0.01	0.04	0.04	0.03	0.03	0.04	0.03	0.03	0.05	0.02	0.03	0.04	
Al ₂ O ₃	adj ol	0.03	0.01	0.03	0.02	0.03	0.01	0.04	0.04	0.02	0.04	0.04	0.03	0.03	0.04	0.04	0.02	0.02	
FeO _T	adj ol	23.38	23.44	23.4	23.77	23.16	23.76	24.12	23.71	23.97	22.68	23.55	23.46	23.52	24.36	23.47	23.54		
MnO	adj ol	0.43	0.45	0.44	0.49	0.46	0.43	0.52	0.4	0.45	0.46	0.47	0.45	0.4	0.49	0.39	0.4		
MgO	adj ol	37.69	38.13	38.07	37.87	38.26	38.02	37.35	37.55	37.78	38.15	38.08	38.06	38.26	37.49	37.92	38.17		
CaO	adj ol	0.31	0.33	0.3	0.36	0.3	0.35	0.34	0.31	0.3	0.35	0.35	0.32	0.3	0.3	0.33	0.34		
Cr ₂ O ₃	adj ol	0	0.03	0	0	0.01	0.02	0	0	0	0.02	0	0	0	0	0	0		
P ₂ O ₅	adj ol	0.02	0.02	0.05	0	0.01	0.02	0	0.05	0.02	0.01	0.08	0.01	0.02	0	0	0.02	0.01	
NiO	adj ol	0.03	0.04	0.06	0.04	0.05	0.04	0.02	0.04	0.03	0	0.04	0.02	0.07	0.04	0.07	0.02	0.02	
Fo mol.%	adj ol	74.2	74.4	74.4	38.49	74	74	73.4	73.8	73.7	75	74.2	74.3	74.4	38.41	38.41	38.59	38.59	
SiO ₂ wt.%	core	38.46	38.46	38.46	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.01	0.01	
TiO ₂	core	0.02	0.02	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	
Al ₂ O ₃	core	0.03	0.03	0.03	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	
FeO _T	core	23.79	23.79	23.94	23.31	23.31	23.31	24.29	24.29	23.74	24.17	24.17	23.97	24.35	24.35	23.85	23.85		
MnO	core	0.44	0.44	0.46	0.51	0.51	0.51	0.5	0.5	0.46	0.45	0.45	0.46	0.42	0.42	0.43	0.43		
MgO	core	37.54	37.54	37.57	38.07	38.07	38.07	37.37	37.37	37.59	37.48	37.48	37.86	37.52	37.52	37.96	37.96		
CaO	core	0.31	0.31	0.3	0.35	0.35	0.35	0.35	0.35	0.34	0.33	0.33	0.32	0.3	0.3	0.32	0.32		
Cr ₂ O ₃	core	0.01	0.01	0	0.01	0.01	0.01	0	0	0.04	0	0	0	0	0	0	0		
P ₂ O ₅	core	0.03	0.03	0	0	0	0	0	0.04	0.01	0.04	0.03	0	0.03	0	0	0.04	0.04	
NiO	core	0.07	0.07	0.02	0.04	0.04	0.04	0.06	0.06	0.05	0.03	0.03	0.06	0.01	0.01	0.01	0.03	0.03	
Fo mol.%	core	73.8	73.8	73.7	74.4	74.4	74.4	73.3	73.3	73.8	73.4	73.4	73.8	73.3	73.3	73.3	73.9	73.9	
MI Name	Location	141a	141b	141c	SWMR		6a	6b	25a	41a	46a	46b	50a	50b	50c	50d	57a	67a	109a
SiO ₂ wt.%	adj ol	38.44	38.5	38.37	37.83	37.74	38.11	37.85	38.02	38.17	38.19	38	38.03	37.98	37.97	38.02	38.02	37.32	
TiO ₂	adj ol	0.02	0	0.04	0.03	0.02	0.03	0.01	0.03	0.03	0.03	0.03	0.03	0.03	0.02	0.02	0.06	0	
Al ₂ O ₃	adj ol	0.05	0.04	0.05	0.03	0.03	0.02	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	
FeO _T	adj ol	22.93	24.15	23.82	23.55	23.53	22.5	22.42	22.56	22.49	22.48	22.66	22.51	22.59	22.71	22.09	22.46		
MnO	adj ol	0.42	0.45	0.45	0.44	0.43	0.46	0.44	0.39	0.43	0.42	0.42	0.43	0.42	0.46	0.43	0.45		
MgO	adj ol	38.49	37.84	37.93	37.81	38.14	38.45	38.65	38.08	38.28	38.3	38.4	37.97	38.4	38.29	38.02	38.53		
CaO	adj ol	0.32	0.3	0.31	0.33	0.33	0.29	0.3	0.35	0.31	0.33	0.33	0.31	0.33	0.31	0.3	0.32	0.28	
Cr ₂ O ₃	adj ol	0	0	0.01	0.01	0.03	0	0	0	0.02	0	0.02	0	0.03	0	0.02	0.02	0	
P ₂ O ₅	adj ol	0.03	0.01	0.02	0.02	0.02	0.02	0.02	0	0.02	0	0	0	0	0	0.01	0.01	0.01	
NiO	adj ol	0.07	0.04	0.05	0.09	0.06	0.06	0.04	0.05	0.07	0.06	0.06	0.06	0.06	0.06	0.04	0.05	0.06	0.02
Fo mol.%	adj ol	74.9	73.6	74	74.1	74.3	75.3	75.4	75.1	75.2	75.2	75.1	75.1	75.1	75.2	75.2	75.4	75.4	
SiO ₂ wt.%	core	38.4	n.d.	38.4	37.68	37.73	38.04	38.12	38.12	38.12	38.12	38.12	38.12	38.12	38.12	38.12	38.12	38.12	
TiO ₂	core	0.01	n.d.	0.01	0.02	0.02	0.02	0	0.02	0.02	0.01	0	0.01	0.01	0.01	0.01	0.02	0.01	
Al ₂ O ₃	core	0.02	n.d.	0.02	0.02	0.02	0.04	0.01	0.02	0.02	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	
FeO _T	core	23.84	n.d.	23.84	23.53	23.53	22.72	22.44	22.33	22.33	22.51	22.51	22.51	22.51	22.51	22.51	22.51	22.92	
MnO	core	0.48	n.d.	0.48	0.46	0.46	0.39	0.48	0.43	0.43	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.5	
MgO	core	37.9	n.d.	37.9	37.79	37.79	38.1	38.28	38.35	38.35	38.28	38.28	38.28	38.28	38.28	38.4	38.32	38.22	
CaO	core	0.3	n.d.	0.3	0.37	0.37	0.35	0.28	0.32	0.32	0.32	0.32	0.32	0.32	0.32	0.25	0.31	0.31	
Cr ₂ O ₃	core	0.01	n.d.	0.01	0	0	0	0.02	0	0.01	0.01	0	0.01	0.01	0	0	0.03	0	
P ₂ O ₅	core	0.04	n.d.	0.04	0.03	0	0.05	0.01	0.01	0.01	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0	
NiO	core	0.02	n.d.	0.02	0.04	0.04	0.04	0.03	0.04	0.04	0.04	0.04	0.05	0.05	0.05	0.05	0.05	0.05	
Fo mol.%	core	73.9	n.d.	73.9	74.1	74.1	74.9	75.3	75.4	75.4	75.2	75.2	75.2	75.2	75.2	75.4	74.9	74.8	

Table S5. Melt inclusion (MI) Mg# before and after PEC correction, Matrix glass (MG)Mg# and host olivine Fo% = $100 * (\text{MgO}/X_{\text{MgO}} / (\text{MgO}/X_{\text{MgO}} + \text{FeO}/X_{\text{FeO}}))$

Sample name	Mg# MI before PEC	Mg# MI after PEC	Fo% host olivine	Mg# MG
NEMR 114a	41.8	46.3	74.0	n.d
NEMR 26a	38.8	45.6	74.0	40.4
NEMR 140a	41.6	45.8	74.2	40.1
NEMR 140b	41.4	45.7	74.2	40.1
NEMR 113a	44.8	46.8	74.2	n.d.
NEMR 113b	44.8	46.8	74.2	n.d.
NEMR 67a	42.8	47.1	74.4	37.9
NEMR 67b	42.1	46.2	74.3	37.9
NEMR 67c	43.7	46.8	74.3	37.9
NEMR 141a	43.7	46.7	74.2	37.9
NEMR 141b	41.8	47.0	74.2	37.9
NEMR 141c	42.0	45.0	74.2	37.9
NEMR 10a	42.0	46.1	74.1	37.5
NEMR 10b	40.8	46.0	74.1	37.5
NEMR 76a	40.9	45.8	73.5	n.d.
NEMR 76b	38.5	45.2	73.5	39.8
NEMR 126a	38.6	45.1	73.5	40.4
NEMR 126b	41.7	46.6	73.5	40.4
NEMR 80 mg	n.d.	n.d.	73.8	37.9
NEMR 28 mg	n.d.	n.d.	74.1	39.7
SWMR 25a	43.8	47.3	75.1	41.5
SWMR 109a	39.8	47.2	75.1	39.3
SWMR 41a	43.3	48.9	75.3	39.9
SWMR 46a	42.1	48.12	75.2	41.9
SWMR 46b	43.8	47.8	75.2	41.9
SWMR 50a	43.6	47.2	75.1	40.2
SWMR 50b	42.9	47.2	75.1	40.2
SWMR 50c	43.0	47.5	75.1	40.2
SWMR 50d	37.9	47.0	75.1	40.2
SWMR 67a	42.9	51.3	75.1	40.3
SWMR 6a	41.8	47.5	74.2	n.d.
SWMR 6b	41.7	47.2	74.2	n.d.
SWMR 57a	40.2	47.1	75.2	41.3
SWMR 74 mg	n.d.	n.d.	75.0	39.9