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1 **Extreme isotopic variation documents extensional tectonics in arc magmas**
2 **from Methana, Greece.**

3

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18

19

20 **Key words:** subduction, Aegean Arc, crustal contamination, radiogenic isotopes,
21 extension

22

23 **Highlights:**

24 Volcanic products from Methana (Greece) show large isotopic variation

25 Isotopic signature and eruption style document tectonic regime

26 Greatest isotopic variation and explosive deposits during extension

27 Magma mixing responsible for isotopic arrays

28

29 **Abstract**

30 New Sr-Nd-Hf-Pb isotope data for volcanic rocks from the peninsula of Methana
31 (South Aegean Active Volcanic Arc, Greece) show a wide variation, and more
32 'enriched' isotopic signatures (e.g. elevated $^{87}\text{Sr}/^{86}\text{Sr}$ at 0.705-0.709) than those of
33 other active Aegean volcanic centres, all located on thinner crust. The data set is
34 best explained by polybaric AFC processes, with contaminants similar to country
35 rocks and xenoliths, showing moderately high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, and with isotopically
36 more evolved lower crust, similar to the pre-Alpine Ios basement. Pb isotope ratios
37 show some minor influence of assimilation of fluid-altered volcanic cumulates.
38 Intermediate lava domes with mafic enclaves were formed during periods of
39 compression, whereas an extensional period saw the deposition of explosive
40 products of bimodal composition, with the more felsic deposits showing the most
41 pronounced influence of crustal assimilation. The latter likely represent stalled
42 magmas from an earlier compressional period, which were remobilised and flushed
43 out by ascending mafic magmas during extension. Recognition of these
44 volcanological, geochemical and isotopic characteristics of deposits associated with

45 extensional tectonics in a modern arc will enable us to use these criteria to infer
46 paleo-tectonics from older volcanic deposits.

47

48 **1. Introduction**

49 The role of regional tectonics in the style of volcanism and the composition of the
50 erupted products at convergent plate margins has been increasingly recognised in
51 recent years (Defant, 1992; Elburg et al., 2004; Shinjo, 1999; Straub and Zellmer,
52 2012; Zellmer, 2009). The effects are most noticeable in complicated convergent
53 settings, such as near-collisional situations, where the arrival of small continental
54 fragments at the trench influences the stress regime of the arc as whole. The Aegean
55 arc is such a system, and for this study we concentrate on the volcanic peninsula of
56 Methana (Greece; Fig. 1). Methana is a nominally active volcano in the westernmost
57 part of the South Aegean Volcanic Arc, with a magmatic record extending from the
58 mid-Pliocene to 230 BC (Pe-Piper and Piper, 2013). It is a typical continental arc
59 volcano, consisting of mainly intermediate to felsic lava domes and minor explosive
60 magmatic deposits, emplaced upon a basement that consists of Mesozoic
61 limestones, with minor siliciclastic and *mélange*-type rocks (Dietrich and Gaitanakis,
62 1995). Since the reconnaissance-style analyses of Sr isotope ratios of the lavas that
63 were performed during the 1970's (Pe-Piper, 1975), it has been known that the
64 magmatic system of Methana has seen a greater influence of crustal materials than
65 the presently active Aegean volcanoes of Santorini and Nisyros, and this has been
66 confirmed by more recent data (e.g. Elburg et al., 2014; Woelki et al., 2018). The
67 style of magmatic activity on Methana, and the eruption rates, have been argued to
68 have been strongly influenced by regional tectonics (Pe-Piper and Piper, 2013). This
69 also affected the major and trace element geochemistry of the erupted products. For
70 instance, the most primitive magmas erupted during a period of strike-slip faulting

71 that provided crustal-scale pathways for magma transport to the surface (Pe-Piper
72 and Piper, 2013). In this scenario, the magmas erupted during this strike-slip event
73 would also be the least contaminated, as they would have had less opportunity to
74 interact with the country rocks. This idea, however, has not been tested with
75 systematic isotopic investigations, and the present paper will redress this omission.

76 The obtained whole rock major and trace element and Sr-Nd-Hf-Pb isotopic data for
77 the various igneous units, including their mafic enclaves, as well as country rocks
78 and xenoliths, will be used to assess the identity of potential assimilants, and the
79 processes that led to the wide range of geochemical and isotopic variation observed
80 in the volcanic products of Methana volcano. We will show that the wide geochemical
81 variation is dominantly a result of assimilation of a variety of crustal rocks, with the
82 most extensive range seen in the explosive deposits that surfaced during a period of
83 extensional tectonics.

84

85 **2. Geological setting**

86 The South Aegean Active Volcanic Arc is the present-day manifestation of the long-
87 lived convergence system between Africa and Europe, which has been active since
88 the Jurassic (Van Hinsbergen et al., 2005). Convergence between the two continents
89 has been accommodated by subduction, nappe stacking and periodic back-stepping
90 of the volcanic arc, which resulted in the present-day volcanic arc being located on
91 continental crust that originated from the East-African (Keay and Lister, 2002; Van
92 Hinsbergen et al., 2005) and 'Amazonian' (South American: Zlatkin et al., 2014)
93 cratons. Slab roll-back in a southward direction has been ongoing since the
94 Oligocene and was responsible for the formation of the Aegean Sea (Jolivet et al.,
95 2015).

96 The active South Aegean Volcanic Arc extends from the Saronic Gulf centres of
97 Methana and Aegina in the west, through Milos and Santorini to Yali-Nisyros in the
98 east (Fig. 1a). On the Greek mainland, west of the Saronic Gulf, the Crommyonia
99 volcanic centres were active around 4 and 2.5 Ma. The volcanic centre of Methana is
100 situated on the Pelagonian Unit (Pe-Piper and Piper, 2002) that forms the upper
101 nappe of the Internal Hellenides, of which the exposed rocks are dominated by
102 Mesozoic limestones, and which is thought to be underlain by the pre-Alpine
103 (perhaps even pre-Variscan) basement of the Cycladic Blueschist Unit, as exposed
104 on, for instance, Ios and Sikinos (Mizera and Behrmann, 2015). The area was
105 already part of a magmatic arc during the Miocene, and granitoids with ages between
106 11 and 17 Ma (Bolhar et al., 2010) are common on the Cycladic islands (e.g. Naxos)
107 and mainland Greece (e.g. Laurion). They are likely also present in the basement
108 underlying the present-day volcanic arc (e.g. Skarpelis and Kyriakopoulos, 1992).
109 The thickness of the crust under the Saronic Gulf has been estimated to be 30 km
110 based on the tomographic work of Karagianni et al. (2005), which is thicker than
111 underneath the other Aegean volcanic centres such as Santorini (20 km) and Nisyros
112 (25 km).

113 The tectonic evolution of the Saronic Gulf has been summarized most recently by
114 Pe-Piper and Piper (2013), who also presented absolute and relative ages for the
115 different volcanic units on the peninsula. They defined three main periods in the
116 tectonic evolution of Methana, whereby the first period (around 3.5 Ma) saw the
117 emplacement of volcanic domes along N-S faults (volcanic phase A; Fig. 1b). These
118 oldest volcanic deposits were partially eroded to yield the volcanoclastic 'apron'
119 assigned to Phase B. Volcanic phases C to E (early-middle Pleistocene, ca. 1.5-0.5
120 Ma) coincided with enhanced uplift and active NE-SW strike-slip faulting. Uplift
121 accelerated around 0.38 Ma, giving rise to steep normal faults, and associated

122 voluminous eruptions of volcanic phase F and G. Volcanic phase H, comprising the
123 most recent, historic activity, occurred during the waning stages of this regime.

124

125 **3. Analytical techniques**

126 A detailed description of the analytical techniques is given in supplementary material
127 S1, which also gives data on international standards.

128 All analyses were performed on agate-milled samples, with major elements being
129 determined by ICP-OES after Li-borate fusion-assisted dissolution, and trace
130 elements by ICP-MS after HF-HNO₃ dissolution in capped teflon vials. Reported Zr
131 concentrations are from ICP-OES analyses, as only the flux-assisted dissolution
132 procedure assures that all zircon is dissolved. Sr, Nd and Pb isotopic measurements
133 were performed, using a Thermo-Scientific Neptune at Ghent University, on the same
134 splits as those used for preparing the solutions for trace element analysis, after
135 isolation of the elements of interest. Hf isotopes were measured using a Thermo-
136 Scientific Neptune at the Vrije Universiteit Amsterdam on low- and high-pressure (for
137 zircon-bearing samples) dissolutions, after isolation of Hf from its matrix. During the
138 course of the analyses, international standards gave results within the uncertainty of
139 their accepted values (e.g. BHVO-2 (\pm 2SD): $^{87}\text{Sr}/^{86}\text{Sr} = 0.705020 \pm 0.000013$;
140 $^{143}\text{Nd}/^{144}\text{Nd} = 0.512975 \pm 0.000024$; $^{176}\text{Hf}/^{177}\text{Hf} = 0.283096 \pm 0.000018$; JB-2:
141 $^{206}\text{Pb}/^{204}\text{Pb} = 18.345 \pm 0.01$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.564 \pm 0.01$, $^{208}\text{Pb}/^{204}\text{Pb} = 38.287 \pm 0.02$)

142 Zircons were separated using heavy liquids and, after cathodoluminescence imaging,
143 analysed for their Hf isotope ratios by LA-MC-ICPMS (Nu Plasma combined with
144 NWR-213 ablation system) at the Department of Geosciences of the University of
145 Oslo, following the procedures described by Elburg et al. (2013). A few spots were
146 ablated for U-Pb dating with the same set-up to see whether a numerical age could

147 be determined with the set-up used. The results indicated that the age was < 5 Ma,
148 but no attempt at further quantification was made because of the lack of suitable
149 standards.

150

151 **4. Distribution and petrography of volcanic rocks**

152 We follow the newly established volcanic stratigraphy from Pe-Piper and Piper (2013)
153 for the description and interpretation of our data, ranging from the domes of Phase A
154 at the base (ca. 3.5 Ma) through to the historic eruption of Phase H at Mavri Petra.
155 Sample locations are given in Fig. 1b, and in supplementary material S2. Apart from
156 the igneous rocks, samples of country rocks and xenoliths were also obtained to
157 assess their role as crustal contaminants. Apart from Phase C, which also hosts
158 explosive deposits, all volcanic phases are dominated by effusive volcanic products.
159 In our description below, we first focus on the effusive deposits, and then on the
160 Phase C deposits.

161 The effusive deposits occur mainly in the shape of lava domes and flows. Mafic
162 enclaves are common (Fig. 2a,b), although their volume percentage, shapes and
163 sizes are variable. The groundmass of the lavas typically consists of very fine-
164 grained plagioclase, pyroxenes \pm hornblende. Most lavas are crystal-rich, with
165 plagioclase (showing polysynthetic twinning, oscillatory zoning and sieve-textured
166 zones) occurring as a common constituent. The lavas are generally hornblende- and
167 sometimes also biotite-bearing, but most deposits also contain lavas that are poor in
168 hydroxyl-bearing minerals. In many samples, the hornblende is partially to wholly
169 replaced by opacite (Fig. 3a), and in the hornblende-poor samples, some larger
170 aggregates can be recognised as pseudomorphs after hornblende or biotite, but they
171 are wholly replaced by hydroxyl-free minerals. Disequilibrium textures are common in

172 the hornblende-rich rocks: resorbed quartz crystals can be observed occasionally
173 mantled by small clinopyroxene crystals and occurring in the same sample as olivine
174 crystals, olivine crystals with Cr-spinel inclusions may be overgrown by hornblende or
175 clinopyroxene and biotite may be rimmed by hornblende or fine-grained pyroxene.
176 Orthopyroxene, clinopyroxene and Fe-Ti-oxides occur in most samples. Plagioclase,
177 hornblende or biotite commonly contain inclusions of apatite, and occasionally also
178 of zircon (Fig. 3d). Cathodoluminescence imaging shows that the zircons exhibit
179 oscillatory zoning (Fig. 3i, j), sometimes superimposed on sector zoning; no core-rim
180 structures were observed in any of the zircons.

181 Enclaves typically show mineralogical coherence with their host rock in terms of the
182 abundance of hydroxyl-bearing minerals. Their crystal size is variable, and smaller
183 enclaves typically contain crystals with higher aspect ratios but larger crystals, similar
184 to those seen in the host rock, also occur (Fig. 3e). Glass is more common in the
185 enclaves than in the host rocks, and many enclaves have a vesicular texture.

186 Phase C is the only one to contain appreciable pyroclastic deposits in addition to lava
187 flows. There are minor pumice lapilli beds near Akri Pounda (Fig. 1b), originating
188 from a pyroclastic fall, consisting for 85-95% of juvenile, well-sorted, typically light
189 grey pumice fragments between 1 and 6 cm in size. Lithics are typically oxidised lava
190 blocks, similar to those found in the earlier Phase A and B deposits. The pumice is
191 rich in glass and its crystal cargo is dominated by plagioclase, orthopyroxene and Fe-
192 Ti-oxide; olivine (Fig. 3c), clinopyroxene, quartz and hydroxyl-bearing minerals are
193 rare. However, some intergrowths of plagioclase and orthopyroxene appear to be
194 pseudomorphs, likely after hornblende. Phase C lavas and pyroclastic density current
195 deposits are found near Akri Pounda and Agios Andreas, and consist of coarser and
196 more mafic material than the fallout deposits, which they overlie. Plagioclase and
197 clinopyroxene dominate the mineralogy, with olivine, sometimes as skeletal crystals,

198 as the third most abundant phase (Fig. 3f). These are the same minerals as those
199 found in the Phase C lava flows, particularly at Palaeo Kastro. Several samples from
200 the density current deposits contain quartz, mantled by clinopyroxene (Fig. 3b).
201 Anhydrous pseudomorphs after larger crystals of hornblende and biotite are scarce.

202 Within one of the Phase C lavas at Palaeo Kastro, a holocrystalline, phaneritic
203 igneous enclave (sample IM376) was found, contrasting in texture with the common
204 porphyritic enclaves. It consists of a more coarse-grained tonalitic part (plagioclase,
205 quartz, clinopyroxene pseudomorphs of hornblende; Fig. 3g), which is separated by a
206 quartz vein from a finer-grained dioritic part (plagioclase, clinopyroxene, partially
207 pseudomorphosed hornblende). The two parts were analysed separately.

208 Sampled country rocks comprise Mesozoic limestones and sandstones. Xenoliths
209 are uncommon within the volcanic deposits, and consist mainly of limestones and
210 calcareous sandstones, comparable to the country rocks.

211

212 **5. Geochemistry**

213 Our approach to sampling was not geared towards a representative selection
214 proportional to the volume of the eruptive products. We tested compositional
215 variability in a single volcanic phase by more dense sampling of Phase D, where we
216 collected 41 samples out of the total of 98 igneous samples. As sampling has been
217 carried out prior to the new volcanic stratigraphy of Pe-Piper and Piper (2013), we
218 failed to sample their Phase E, and Phase F is only represented by a single sample.
219 As we concentrate on the isotopic composition of the magmas, data from previous
220 studies (Dietrich et al., 1988; Francalanci et al., 2005; Pe-Piper, 1975), which do not
221 report complete Sr-Nd-Hf-Pb isotopic data, have not been used. All geochemical data
222 are given in Supplementary Materials S3-6.

223

224 *5.1. Major and trace elements*

225 Our analysed samples vary in silica content between 50 and 68 wt.%. The more
226 mafic samples (<57 wt.% SiO₂) are represented by the enclaves, the Phase C lavas
227 and pyroclastic flow deposits and a few samples from Phase B. Analyses with <54
228 wt.% SiO₂ comprise enclaves only. The densely sampled Phase D deposits span the
229 full range in silica content, from enclave DPM36 at 50.5 to host rock DPM42 at 60.1
230 wt.% SiO₂. MgO concentrations vary between 8 and 1 wt.% (Fig. 4a), with Mg#
231 (molar MgO/(MgO+FeO*)) ranging between 69 and 42. Scatter is pronounced in all
232 variation diagrams, making it hard to argue for curved or inflected differentiation
233 trends. TiO₂ concentrations show a rather monotonous decrease from 0.9 to 0.4
234 wt.% with increasing SiO₂ content (Fig. 4b), whereas K₂O continuously increases
235 from 0.9 to 2.7 wt.% (Fig. 4c), which corresponds to the medium-K trend of Gill
236 (1981). The two parts of the holocrystalline enclave IM376 stand out with respect to
237 their very low potassium content. Apart from a single low-Ca sample in Phase B, all
238 analyses show an aluminium saturation index (molar Al₂O₃/(Na₂O+K₂O+CaO)) of
239 less than 1. In terms of FeO*/MgO ratios, Methana defines a typical calc-alkaline
240 (Miyashiro, 1974) or low-Fe (Arculus, 2003) trend, and it classifies as being calcic in
241 the MALI classification of Frost et al. (2001).

242 For Methana as a whole, scatter is even more pronounced for trace elements when
243 compared to major elements, especially for the compatible elements such as Cr and
244 Ni: at an SiO₂ content around 54 wt.%, Cr varies between 400 and 20 ppm (Fig. 4d).
245 However, the basaltic andesites of Phase C are noticeably more homogeneous than
246 enclaves at the same silica content. Using MgO or Mg# on the x-axes gives some
247 reduction of scatter for the compatible (but not for the incompatible) trace elements,
248 but the Phase C products remain more homogeneous. Some of the Phase A

249 samples stand out in having elevated contents of some compatible elements (Cr 80,
250 Ni 50 ppm) at ca. 65 wt.% SiO₂. These samples also have significantly elevated Sr
251 contents (ca. 500 vs 300 ppm; Fig 4e). Other characteristics that stand out are high
252 Rb, Be and especially Cs, U and Pb (Fig. 4f) contents for the youngest (Phase H)
253 volcanics and enclaves, although K₂O (Fig. 4c) and Th are only marginally higher
254 than the main trend. Most trace elements display the expected compatible (Cr, Ni,
255 Sc, Co) or incompatible (Rb, Cs, Be, Ba, Nb, light rare earth elements (LREE))
256 behaviour with increasing SiO₂ contents, but Zr concentrations show an inflection at
257 60 wt.% SiO₂ (Fig. 4g), whereas Y (Fig. 4h) and the middle to heavy rare earth
258 elements generally decrease. Sr (Fig. 4e) and Eu show a scattered, marginally
259 decreasing trend with increasing SiO₂ content. Ratios of MREE/HREE such as Dy/Yb
260 are very scattered (Fig. 4i) but have a tendency to decrease with increasing SiO₂
261 content, apart from the data for Phase C, which show a clear increase in Dy/Yb ratios
262 (as well as Y contents).

263 Rare earth element patterns all show clear LREE over HREE enrichment (Fig. 5),
264 with typically a slightly concave-upward shape for the MREE-HREE patterns (apart
265 from phase C). All samples show a negative Eu anomaly, but this is more
266 pronounced for the more felsic samples. Primitive mantle-normalised trace element
267 diagrams (Fig. 6) show the expected hallmarks of subduction-related magmas, with
268 negative Nb-Ta and Ti anomalies, and a positive one for K and Pb. Nearly all
269 samples also have a negative Ba anomaly. The mafic-intermediate samples show a
270 positive Sr anomaly.

271

272 *5.2. Radiogenic isotope ratios*

273 In terms of radiogenic isotope ratios, most of the data form a broad concave trend
274 between $^{87}\text{Sr}/^{86}\text{Sr} = 0.7055$ at $^{143}\text{Nd}/^{144}\text{Nd} = 0.51266$ and $^{87}\text{Sr}/^{86}\text{Sr} = 0.7093$ at
275 $^{143}\text{Nd}/^{144}\text{Nd} = 0.51224$ (Fig. 7a), but the high-Sr samples from Phase A are displaced
276 towards lower $^{87}\text{Sr}/^{86}\text{Sr}$ (0.7050) relative to the main array, and the Phase H samples
277 appear to have high $^{143}\text{Nd}/^{144}\text{Nd}$ for their Sr isotope ratios. The holocrystalline
278 enclave IM376 is virtually indistinguishable from its host rock with regards to Sr and
279 Nd isotopic ratios. Local limestones have $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.707-0.708 (Fig. 7b), typically
280 with Nd contents too low to determine their Nd isotope signature. More siliciclastic
281 country rocks and xenoliths within some of the volcanic deposits extend the array to
282 slightly more 'crustal' values than the volcanics, with values for $^{87}\text{Sr}/^{86}\text{Sr} = 0.710$ at
283 $^{143}\text{Nd}/^{144}\text{Nd} = 0.51221$ (Fig. 7a).

284 Generally the values for $^{87}\text{Sr}/^{86}\text{Sr}$ (Fig. 7c) and $^{143}\text{Nd}/^{144}\text{Nd}$ become gradually more
285 'crustal' with increasing differentiation. The Phase C pumice, however, exhibits
286 abnormally high $^{87}\text{Sr}/^{86}\text{Sr}$ and low $^{143}\text{Nd}/^{144}\text{Nd}$ ratios when comparing its SiO_2 and
287 MgO content and its Mg#, to comparable samples from the other units. Even for
288 samples from a single eruptive phase, the correlation between Sr or Nd isotope ratios
289 and fractionation indices is poor. For the whole data set, the negative correlation
290 between Nb content and Nd isotopic composition (Fig. 7d) shows the highest
291 correlation coefficient ($r^2 = 0.41$) for an element (or elemental ratio) and a radiogenic
292 isotope ratio.

293 Our slightly more restricted set of Hf isotopic data shows a positive correlation with
294 Nd isotope ratios (Fig. 7e). There is some scatter, but there is no clear distinction
295 between the samples from different phases. Most volcanic samples fall towards the
296 high ϵHf side of the terrestrial array of Vervoort et al. (2011), especially at the higher
297 end ($\epsilon\text{Nd} > -2$) of the array. One of the calc-silicate xenoliths found in the Phase C
298 pumice airfall shows the clearest offset from the terrestrial array.

299 Pb isotope ratios show a poor correlation (Fig. 7f, g). Data for some volcanic phases
300 are better clustered than for others, but these are samples that were derived from a
301 restricted geographical area and the spatial distribution of the samples appears to be
302 the most important parameter with respect to the Pb isotope ratios. Both parts of
303 holocrystalline enclave IM376 (see inset in figs. 7f, g) have ratios of $^{207}\text{Pb}/^{204}\text{Pb}$
304 (15.55) and $^{208}\text{Pb}/^{204}\text{Pb}$ (38.3) that are significantly lower than those of the volcanic
305 samples (>15.67 and >38.7 respectively). The Phase C basaltic andesite sampled in
306 the vicinity of the xenolith, IM379, has the lowest Pb isotope ratios of all the volcanic
307 samples. Three samples from Phase A and B, also taken along the west coast of the
308 peninsula, bridge the isotopic gap between the phase C sample and the rest of the
309 Pb isotopic data array. Trends of Pb isotope ratios against $^{87}\text{Sr}/^{86}\text{Sr}$ or $^{143}\text{Nd}/^{144}\text{Nd}$
310 are scattered (Fig. 9b), but the Phase C pumice with the most crustal Sr and Nd
311 isotope ratios has the highest Pb isotope ratios. There are no obvious correlations
312 when Pb isotope ratios are plotted against differentiation indices, or ratios of trace
313 elements with contrasting aqueous mobility (e.g. Pb/Ce, Sr/Y or Th/U; not shown).

314

315 For five samples, 20 to 80 zircons per sample were analysed for their Hf isotope
316 ratios by LA-MC-ICPMS in order to assess their variability (e.g. Rojas-Agramonte et
317 al., 2017) and their similarity to the Hf isotope whole rock analyses (Fig. 7h). The
318 limited amount of material analysed with LA-MC-ICPMS and the correction for
319 interfering ions cause larger uncertainties on the measured ratio for each zircon spot
320 analysis compared to whole rock solution analyses, thereby giving a greater
321 uncertainty for the average Hf isotopic ratio for the zircons compared to the whole
322 rock analyses. However, the standard deviation of the laser ablation $^{176}\text{Hf}/^{177}\text{Hf}$
323 analyses for the zircon population from each sample can be compared to that for
324 zircon reference materials such as the Mud Tank or Temora-2 zircon (around 0.008%

325 during the course of the LA-MC-ICPMS analyses). The data for the five unknowns
326 show a somewhat larger standard deviation, between 0.009 and 0.013%, indicating
327 that the population is relatively homogeneous. Considering the uncertainties, the
328 average Hf isotopic composition for the population of zircons from each of the five
329 samples are very similar.

330 Taking the uncertainty of the LA-MC-ICPMS measurements into account, the Hf
331 isotope ratios of the zircons are similar to the ratio of the whole rock for the samples
332 with 60-65 wt.% SiO₂, but only in the case of the Phase A sample with 64 wt.% SiO₂
333 (DPM28) are the values of the zircons as well as the high- and low-pressure
334 dissolution of the whole rock equal within analytical uncertainty. For the other two
335 intermediate samples (IM29 and IM313 from Phase H and Phase D respectively), the
336 zircons have slightly lower Hf isotope values than the HP dissolution, which in turn is
337 lower than the LP dissolution. In the case of the zircons found in a Phase C basaltic-
338 andesite (IM36, with 55 wt.% SiO₂) the zircons' ¹⁷⁶Hf/¹⁷⁷Hf (0.282739 ± 38) is
339 markedly lower than for the host rock; this distinction is more marked for the low-
340 pressure (0.282896) than the high-pressure dissolution (0.282868) of the host rock,
341 indicating that the zircons have a more 'crustal' signature (lower ¹⁷⁶Hf/¹⁷⁷Hf) than their
342 host. The systematics are opposite for the phase D sample with 68 wt.% SiO₂
343 (DPM42), where the zircons have an average higher Hf isotope ratio than the host
344 rocks; also here, the HP dissolution of the host rock is closer to that of the zircons
345 than the LP dissolution.

346

347 **6. Discussion**

348 *6.1. Mixing and assimilation*

349 Field and petrographic evidence (presence of enclaves, ubiquitous mineralogical
350 disequilibrium textures; Fig. 3b,c) shows that magma mingling and magma mixing
351 were important processes in the petrogenesis of the Methana lavas, and this is
352 supported by, for instance, the lack of inflection points on the Harker diagrams of
353 TiO_2 and Y (Fig. 4b,h). Magma mixing was likely accompanied by the selective
354 entrainment of certain minerals to explain excess scatter in the Harker variation
355 diagrams, as has also been mentioned by previous workers (Pe-Piper and Piper,
356 2013). Besides, the different phases may also have had different primary magmas,
357 as exemplified by the elevated Pb concentrations of the Phase H deposits. Ignoring
358 the complications of different primary magmas, fractionation and selective
359 entrainment of minerals for the moment, we will first assess the broad trends seen in
360 the radiogenic isotope data in order to identify end members and constrain the
361 processes that yielded these trends, refining the models proposed by Elburg et al.
362 (2014). Parameters for the simple mixing and Assimilation-Fractional Crystallisation
363 (AFC; DePaolo, 1981) models can be found in Table 1. For the AFC models, bulk
364 distribution coefficients were taken as 0.3 for Nd, 0.001 for Th and 1.7 for Sr except
365 for the high pressure (HP) AFC model, where it was 0.1. These values are based on
366 the general trends seen in the variation diagrams, and are in broad agreement with
367 the observed mineral assemblages (olivine, clinopyroxene, orthopyroxene,
368 plagioclase, hornblende).

369

370 *6.1.1. Exploring evolved end members*

371 The majority of the Sr and Nd isotopic data can be explained by simple mixing
372 between the two isotopically extreme samples from the Phase C deposits (Fig. 7a),
373 namely the basaltic andesites with relatively low Sr isotope ratios (0.7057) and high
374 Nd isotope ratios (0.51260), and the most isotopically evolved pumice ($^{87}\text{Sr}/^{86}\text{Sr} =$

375 0.7093, $^{143}\text{Nd}/^{144}\text{Nd} = 0.51224$). This yields a mixing line on which the majority of the
376 samples fall. The isotopically most primitive samples are similar to those analysed by
377 Woelki et al. (2018), and the reader is referred to this publication for an in-depth
378 discussion on the primary magma to the Methana volcanics.

379 Evidence for mixing of a geochemically and isotopically more evolved magma with
380 the basaltic andesites comes from petrographic data (Fig. 3b, c), as well as from the
381 observation that zircons with a much lower Hf isotope ratio than the whole rock were
382 found within mafic sample IM36 (Fig. 7h). The relative isotopic homogeneity of this
383 zircon population, combined with the petrographic observations of the elongated
384 euhedral shape of the zircons (Fig. 3d), the CL-imaging that shows magmatic
385 oscillatory zoning without any core-rim structure (Fig. 3i, j), and the maximum age of
386 5 Ma, shows that these zircons are unlikely to be xenocrysts derived from the country
387 rocks. Although a simple mixing line satisfactorily models most of the Methana
388 samples within Sr-Nd (and also Hf) isotopic space, scatter in diagrams of Sr-Nd-Hf
389 isotope ratios against an index of fractionation indicates that this cannot be the whole
390 story. For instance, the isotopically most evolved pumice samples of Phase C are not
391 the most evolved in terms of SiO_2 (Fig. 7c) or incompatible trace elements. We will
392 use Th as an index of fractionation (Fig. 8a), as Pe-Piper and Piper (2013) noticed a
393 correlation between the concentration of Th and the volume percentage of enclaves
394 in the deposits, and suggested that Th could trace the role of AFC (Assimilation +
395 Fractional Crystallisation) processes. In this model, the repeated input of less
396 fractionated magma (now represented by the enclaves) would provide the thermal
397 energy necessary for assimilation.

398 The first thing the $^{143}\text{Nd}/^{144}\text{Nd}$ versus Th diagram (Fig. 8a) shows is that the
399 interpretation of the Phase C products representing simple mixing between two end
400 members is not quite accurate, as the isotopically most primitive basaltic andesites

401 from Agios Andreas in the north (to which zircon-bearing sample IM36 belongs) have
402 a higher Th content than the basaltic andesites from Akri Pounda in the south , which
403 have slightly lower $^{143}\text{Nd}/^{144}\text{Nd}$. The latter seem to form a mixing line (curve i in Fig.
404 8a) with the Akri Pounda pumice samples, whereas the former lie on a mixing trend
405 (curve ii in Fig. 8a) with the Palaeo Kastro andesites at higher Th contents. The high-
406 Th end of the trend can be extended to the field for the Miocene granitoids, but these
407 are unlikely to be the material directly involved in the physical mixing process: The
408 zircons from those intrusives have present-day $^{176}\text{Hf}/^{177}\text{Hf}$ values dominantly between
409 0.2822 and 0.2826 (Bolhar et al., 2012), and are thus significantly less radiogenic
410 than the values for zircons from the Methana samples (0.28265-0.28285).

411

412 Phase D sample DPM42 has among the highest Th contents at intermediate
413 $^{143}\text{Nd}/^{144}\text{Nd}$; although Phase H sample IM29 has equally high Th contents, it isn't as
414 evolved in terms of SiO_2 content (62 vs 68 wt.%), and also has a higher $^{143}\text{Nd}/^{144}\text{Nd}$
415 ratio. Sample IM29 falls close to the isotopically less evolved Aegean Miocene
416 granitoids (from Samos and Kos; Altherr and Siebel, 2002) in this diagram, but it is
417 very different in its Sr content (330 vs 450-2000 ppm, not shown). Although a simple-
418 mixing curve between the most mafic (DPM36) and most felsic (DPM42) Phase D
419 samples could explain some of the observed variability in Methana, it does not
420 explain how DPM42 obtained its isotopic characteristics in the first place. Sample
421 DPM42 is also characterised by zircons that are isotopically more primitive (high
422 $^{176}\text{Hf}/^{177}\text{Hf}$ ratio) than the whole rock composition. This implies that crustal
423 contamination occurred after the onset of zircon crystallisation, which could argue for
424 the operation of AFC-type processes to explain the isotopic characteristics of the
425 evolved end members.

426

427 We modelled this AFC process by taking calc-silicate country rock IM26 (Upper
428 Jurassic calcareous sandstone) as the crustal end member and Phase D enclave
429 DPM36 as the more primitive melt. This yields a satisfactory fit (curve i in Fig. 8b) for
430 sample DPM42, but only with a high parameter R (rate of assimilation : fractionation)
431 of 0.8, and a remaining melt fraction of slightly less than 60 wt.%, meaning that more
432 than 30% of host rock would need to be assimilated. This high amount of assimilation
433 is mainly a reflection of the very low Th and Nd contents of this crustal end member.
434 If a pelitic, rather than calc-silicate, xenolith (IM362) is taken, the obtained AFC curve
435 is similar, but the amount of assimilated material is reduced to 13%. The curve can
436 be shifted upward (curve ii in Fig. 8b) to pass through sample IM29 by adjusting the
437 R parameter downward to ca. 0.4 (for IM26 as an assimilant) or 0.25 (for IM362).
438 With this lower rate of assimilation, the amount of melt remaining would be smaller;
439 this is contrary to what is observed for the SiO₂ content of Phase H sample IM29 (62
440 wt.%) versus Phase D sample DPM42 (68 wt.%). It is therefore more likely that
441 Phase H belongs to a different magmatic series, with inherently higher Th contents,
442 rather than being related to the Phase D deposits by a different rate of assimilation to
443 crystallisation (see further discussion in section 6.1.4).

444

445 Returning to the very 'crustal' Sr-Nd-Hf isotopic characteristics of the Phase C
446 pumices, it would be possible to explain these by a large degree of remelting of some
447 Miocene granitoid and mixing with small amounts of the basaltic andesitic melt.
448 However, this interpretation is not supported by the very moderate contents in the
449 rhyodacites of elements such as K, Rb and Ba (Fig. 8c), which are significantly
450 enriched in all the Miocene granitoids. As these are incompatible elements, AFC-type
451 processes would provide an even worse fit to the data than simple mixing.

452 The very crustal Sr-Nd-Hf isotopic characteristics of the Phase C pumice end
453 member are best explained by assimilation with material similar to that of the los
454 basement, with a $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of 0.5119 (Klaver et al., 2016). Depending on
455 whether the primitive end member is assumed to be enclave DPM36 (curve iii in Fig.
456 8b), or a hypothetical composition with a higher $^{143}\text{Nd}/^{144}\text{Nd}$ of 0.5127 (curve iv), the
457 pumice can be modelled by an R value of 0.8 or 0.4 respectively, and a total amount
458 of assimilation of 5 and 13%. This also fits the Sr isotope data (not shown) if the
459 assimilant has a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio around 0.74 and a Sr concentration of 100 ppm, which
460 has indeed been measured for the los basement (Buettner et al., 2005; Klaver et al.,
461 2016).

462

463 In conclusion, the isotopic and trace element data can be explained by the
464 assimilation of material similar to entrained xenoliths for the evolved but isotopically
465 less extreme end members of Phase D and H. However, this explanation does not
466 hold for the very 'crustal' isotopic signature of the Phase C pumice sample, for which
467 an isotopically more extreme contaminant similar to the los basement is needed. The
468 observed isotopic arrays are mainly a result of physical mixing between isotopically
469 primitive mafic magmas and the more evolved magmas that obtained their chemical
470 and isotopic characteristics as a result of AFC processes. However, when elemental
471 data are taken into account (e.g. Fig. 8a), it is obvious that variable primary magmas
472 may be involved as well, which will be explored further below in section 6.1.4.

473

474 *6.1.2. Pb isotopic constraints: los basement and localised fluid*

475 Arguments for the involvement of an assimilant similar to the los basement rocks can
476 also be made on the basis of the Pb isotopic signature. The majority of samples from

477 los are characterised by having high $^{208}\text{Pb}/^{204}\text{Pb}$ ratios relative to their $^{206}\text{Pb}/^{204}\text{Pb}$,
478 reflecting high time-integrated Th/U ratios (Klaver et al., 2016). The $^{208}\text{Pb}/^{204}\text{Pb}$ ratios
479 of the Methana samples (Fig. 7f, 9a) are higher than those of Santorini and Nisyros,
480 but lower than the field for Crommyonia (Soens, 2015). The Phase C pumice is again
481 an end member in the data set, with the highest $^{206,7,8}\text{Pb}/^{204}\text{Pb}$ ratios. However, one
482 of the Phase C samples, an andesite from Palaeo Kastro, which is the host to the
483 dioritic-tonalitic crystalline enclave, is significantly offset in Pb isotopic space towards
484 the low Pb isotopic ratios of this enclave. A slightly less pronounced offset is also
485 seen for two Phase A and one Phase B samples. The most obvious factor that these
486 samples have in common is that they were taken near the west coast of the
487 peninsula. However, there are also samples from the same area that do not display
488 this offset. In Pb-Nd isotopic space (Fig. 9b), these aberrant samples give the
489 impression that only the Pb isotopic signature was lowered to offset them from the
490 main array. The crystalline enclave itself would make a very inefficient contaminant,
491 as its Pb content (ca. 3 ppm) is lower than for any of the juvenile samples (> 5 ppm).
492 It appears more likely that some of the juvenile samples were affected by the same,
493 perhaps fluid-related, contaminant that affected the Pb isotopic composition of the
494 crystalline enclave. The isotopic signature of this Pb contaminant suggest a source
495 with only moderate time-integrated U+Th/Pb ratios, not dissimilar to Mid-Ocean
496 Ridge Basalt. The location of this source is as yet unclear, but it could potentially be
497 related to a mafic rock type such as the sliver of ophiolitic *mélange* exposed on the
498 NW side of the peninsula (Dietrich and Gaitanakis, 1995). The mode of
499 contamination could be by assimilation of fluid-altered volcanic cumulates, which
500 would be difficult to detect in other geochemical parameters.

501

502 *6.1.3. High-Sr Phase A samples*

503 Some of the phase A host rocks, derived from two flows near the village of Loutsés,
504 have notably lower Sr isotopic ratios and higher Sr concentrations than the other
505 rocks, and fall outside of the main data trend in many diagrams (Fig. 7a, b). This
506 group of samples is also unusual in having high MgO, Cr and Ni contents (Fig. 4a, d)
507 for their SiO₂ contents of 65 wt.%, which is likely related to the presence of olivine
508 and clinopyroxene, overgrown by hornblende, observed in the samples.

509 One of the samples from this group (DPM28) was analysed for its Hf isotopic
510 characteristics by LP and HP whole rock dissolution as well as for the individual
511 zircon crystals, and gave no detectable differences between these analyses.
512 Therefore, the higher compatible element contents could reflect entrainment of
513 clinopyroxene and olivine cumulates, as these minerals would contribute negligibly to
514 the Hf budget. Further characteristics of these samples are moderately low Y
515 contents, similar to Phase D samples of the same silica content, but significantly
516 higher Dy/Yb ratios than most Phase D samples. Low Dy/Yb ratios are typical for
517 melts that underwent amphibole fractionation (Davidson et al., 2007), which has been
518 argued to have been an important process for the Methana lavas (Elburg et al.,
519 2014), whereas a low Y content in combination with high Dy/Yb ratios points towards
520 a role for garnet fractionation. Therefore, the high-Sr samples may document a
521 phase of fractionation at higher pressure during which plagioclase was not stable,
522 and hence Sr would have been an incompatible element. This can be modelled with
523 a primitive magma with Sr and Nd isotopic compositions as primitive as 0.7035 and
524 0.5129 respectively, and only 300 ppm Sr in this mafic magma, which increases to
525 the observed ca. 500 ppm during the high pressure phase of AFC, using an Ios-style
526 assimilant (Fig. 8d, Table 1). The slight increase of the ⁸⁷Sr/⁸⁶Sr ratio with decreasing
527 Sr concentrations within this group is likely related to a subsequent phase of
528 fractionation where plagioclase was crystallising. Alternatively, these samples could

529 have been derived from a different primary magma with higher Sr concentrations,
530 making crustal contamination less visible in the Sr isotope signature.

531

532 *6.1.4. Phase H*

533 Both the host rock and the enclaves of Phase G and Phase H are similar in their
534 silica and MgO content, and the differences in their trace element concentrations can
535 thus be illustrated by a normalised trace element diagram (Fig. 10) without the need
536 to correct for differences in degree of fractionation. Here the average of the Phase H
537 host rocks is normalised over the average of the Phase G host rocks, and the same
538 for the enclaves. This shows that the Phase H enclaves and host rocks both show
539 clear enrichments in certain elements compared to their Phase G equivalents, with
540 Cs >U >Pb = Be > Rb > Th >Sr > Ba = K. For the other elements, apparent
541 enrichments and depletions fall within the standard deviation of the corresponding
542 averages. Since the most incompatible elements are not those that are the most
543 enriched, smaller degrees of partial melting of an invariant source cannot be the main
544 cause for the distinctions between Phase G and H. Some of the enriched elements
545 are considered to be 'fluid mobile' (Cs, U, Pb), but other elements that show equal
546 enrichments, such as Be and to a lesser extent Th, are considered fluid immobile
547 (Ryan and Chauvel, 2014), whereas still other fluid-mobile elements such as Li do
548 not show significant enrichment. The lack of enrichment in the latter element could be
549 related to amphibole fractionation. However, the other discrepancies are more
550 difficult to explain if we would want to invoke a fluid component, for instance derived
551 from the subducted slab. The observed enrichments are broadly similar to those
552 seen in the (significantly more felsic) Crommyonia volcanics (Soens, 2015), which
553 appear to show the most pronounced imprint of assimilation of los-like material
554 based on their low Nd isotope ratios (Fig. 9b). Clearly, the Phase H volcanics have

555 significantly higher Nd isotopic ratios than the Crommyonia volcanics, but they do
556 trend towards the Crommyonia field in terms of Pb isotopic composition (Fig. 9a).
557 Remarkably, the Phase H *enclaves* are actually more similar to the Crommyonia
558 volcanics than the *host rocks* in terms of Pb isotopic composition. This could
559 potentially be related to two consecutive phases of assimilation, first with an Ios-like
560 contaminant followed by a contaminant more similar to xenolith IM362 for the host
561 rocks. However, we have not been able to find assimilants of which the whole rock
562 composition matches the pattern seen in Fig. 10 in our own data set, nor in the Ios
563 basement samples analysed by Klaver (2016) or among the Miocene granitoids
564 published by Altherr and Siebel (2002). Perhaps selective assimilation of a partial
565 melt of any of these rock types, with a specific residual phase such as rutile or
566 allanite, could explain the patterns. However, our lack of knowledge of either the
567 likely assimilant(s) or the processes involved does not permit more detailed
568 modelling.

569

570 *6.2. Geochemistry versus time and the relationship with tectonics*

571 The data presented here do not show any clear unidirectional progression with time
572 in the geochemistry of the magmas (Fig. 11), with the oldest and youngest deposits
573 (Phase A vs H) having similar and, for Methana, relatively high Nd isotope ratios
574 (epsilon Nd 0 to -2). Although the youngest volcanic phase (Phase H) appears quite
575 distinct in terms of its geochemical signature, as discussed above, it does not
576 represent the culmination of a progressive enrichment trend through time, as
577 samples from Phase G and phase D cannot be distinguished from each other in
578 terms of their incompatible trace element signature.

579 The changes in tectonic regime, documented by Pe-Piper and Piper (2013), mainly
580 appear to affect the Phase C deposits, interpreted to have erupted during the onset
581 of strike-slip faulting. These deposits also stand out from the others from a
582 volcanological point of view, with their higher content of explosive products (air fall
583 pumice and pyroclastic flow deposits). The air fall pumice deposits were erupted at
584 the start of Phase C, and contain samples with the most crustal Sr and Nd isotopic
585 signatures, even though they are not the most felsic ones (60-63 wt.% SiO₂). The
586 basaltic-andesitic lava flows and pyroclastic flow deposits are among the most mafic
587 (ca. 55 wt.% SiO₂) and isotopically most primitive on the island. They represent the
588 only eruptive phase during which mafic magmas formed their own deposits; other
589 mafic rocks are only found as enclaves within more evolved flows. This fits in with the
590 idea that the faulting taking place during phase C facilitated magma ascent and
591 eruption of these mafic magmas. During periods of compression, magmas stalled at
592 intermediate depths and suffered 'rheological death' as a result of hornblende
593 crystallisation. They could only erupt after being remobilised by a pulse of more mafic
594 magma, which we now find as enclaves within the intermediate-felsic deposits
595 (Elburg et al., 2014; Fig. 12).

596 The eruption of the isotopically most evolved magmas during this period of extension
597 is somewhat surprising, as it seems more logical that lavas would experience higher
598 degrees of crustal contamination as a result to hindered ascent during periods of
599 compression. The presence of olivine in some of the pumice samples, combined with
600 the fact that their pyroclastic fall deposits are directly overlain by pyroclastic density
601 current deposits containing juvenile basaltic-andesite clasts, of which some contain
602 quartz, suggests that the two contrasting magmas formed part of a single eruptive
603 phase. Contrasting with the case of mafic enclaves within a more felsic host rock, this
604 semi-simultaneous eruption of contrasting magmas could have been initiated by
605 felsic magma entering a magma chamber filled with mafic magma (Eichelberger et

606 al., 2000; Fig. 12). The pumice samples are also somewhat different from other
607 samples at similar SiO₂ contents and fall on the low-Sr, high-Y and high-Dy/Yb side
608 of the data set. Although higher Y contents can be associated with a dry fractionation
609 series (with pyroxene rather than amphibole as the main ferromagnesian phase), the
610 offset from the main array is too small to invoke a significant role for this process: a
611 typical hornblende-poor fractionation series such as seen on the island of Santorini
612 contains twice as much Y at 60-65 wt.% SiO₂ (Elburg et al., 2014) as the rather
613 modest 25 ppm seen in the Phase C pumice. The presence of pseudomorphs of
614 plagioclase and pyroxene, presumably after hornblende, supports the idea of
615 amphibole fractionation, but the higher Dy/Yb ratios of these deposits could possibly
616 indicate a minor role for garnet fractionation. Taken together, the trace element and
617 isotopic data may be explained by a prolonged period of AFC-type processes in a
618 magma chamber located at a deeper crustal level, with host rocks more similar to the
619 los basement than to the exposed Mesozoic country rocks and the entrained
620 xenoliths.

621 This idea of prolonged storage is supported by the age gap between the Phase A
622 (ca. 3.5 Ma) and Phase C deposits (ca. 1.4 Ma) (Pe-Piper and Piper, 2013): The
623 Phase C pumice deposits represent the first evidence of renewed magmatic activity,
624 and could represent magmas that were arrested in the deeper crust during the
625 waning stages of Phase A. During solidification, they had ample opportunity to ingest
626 the country rocks. The renewed magmatic activity during Phase C brought mafic
627 magma in contact with these solidified intrusions, which were remelted, and followed
628 the same pathway to the surface as the more mafic magmas, eventually erupting
629 coevally. Hence, it seems that during times of extension, we clearly see the effects of
630 mafic-felsic interaction at a deep crustal level, giving rise to explosive activity,
631 whereas during a compressional regime, effusive igneous activity only documents
632 the processes that are taking place at a shallow level in the crust (Fig. 12). Although

633 deeper assimilation also happens during compressional stages, the results thereof
634 never make it to the Earth's surface, but may be forming granitoids that only become
635 exposed after uplift and erosion.

636

637

638 **7. Conclusions**

639 The volcanic deposits of Methana peninsula show a wide variation in their
640 geochemical and isotopic characteristics and contain the most 'crustal' rock types of
641 the active South Aegean Volcanic Arc in terms of Sr-Nd-Hf composition, trending
642 towards the values for the extinct, more evolved centres of Crommyonia. In
643 combination with the high $^{207,8}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ isotopic compositions, the
644 data point towards an important role for assimilation of crustal rocks similar to those
645 of the Cycladic Basement of Ios, although these are nowhere exposed on Methana.
646 Assimilation of Mesozoic rocks, as exposed on Methana and entrained as xenoliths,
647 is likely to also have played a role. Assimilation thus took place at different crustal
648 levels, and some of the deeper stages of evolution may also have influenced the
649 crystallising mineral assemblages, with plagioclase-free fractionation resulting in high
650 Sr concentrations in some of the older samples. There is no temporal geochemical
651 trend in the volcanic deposits, although the youngest samples show unusual
652 enrichments of some elements, of which the source cannot be determined with
653 certainty.

654 The period of extension, during which the Phase C deposits erupted (Pe-Piper and
655 Piper, 2013), had an important effect on the igneous products, which were explosive,
656 rather than effusive, and contain isotopically more primitive mafic rocks as well as
657 pumice with the most 'crustal' isotopic signature. The latter likely obtained their

658 signature by stalling of the magma at deeper crustal levels during an earlier tectonic
659 compressional phase, where they assimilated Ios-type crust. They were remobilised
660 by mafic magmas during the extensional period, and followed the same path towards
661 higher crustal levels. Their emplacement took place explosively, forming deposits
662 that are more similar to those seen on the island of Santorini, of which the crust is in
663 a permanent state of extension (Feuillet, 2013), than to the typical lava domes of
664 Methana. However, the chemical and isotopic composition of the Methana pumice
665 deposits is very different from those of Santorini, as the Santorini magmas evolved
666 by predominantly shallow-level fractionation of pyroxene, rather than amphibole,
667 leading to Y enrichment in the more differentiated products. Moreover, even the most
668 evolved Santorini lavas typically have less crustal Sr-Nd-Hf isotopic compositions
669 than the most primitive Methana products. Both characteristics are likely related to
670 the thickness of the crust which is much thinner under Santorini (20 km) than under
671 Methana (30 km) (Karagianni et al., 2005).

672

673 The case of Methana clearly shows how the geochemical and isotopic characteristics
674 of a subduction-related volcano may vary in accordance with regional changes in
675 tectonic regime. The ability to recognise these characteristics and their relationship to
676 the tectonic conditions in a modern arc will enable us to use geochemical data of
677 igneous rocks from the earlier geological record to make inferences about their
678 palaeotectonic setting.

679

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688

689

690 **Table captions:**

691

692 Table 1: Mixing end members for curves in Figures 7 and 8.

693

694

695 **Figure captions:**

696

697 Fig. 1a: Overview map of the Aegean area; b: Geological map of Methana after Pe-

698 Piper and Piper (2013) and Dietrich and Gaitanakis (1995) with samples indicated.

699 Sample pre-fix abbreviations: d=DPM; i=IM.

700

701 Fig. 2: Variable textures and sizes of enclaves in lavas from Phase D (a) and Phase

702 H (b).

703

704 Fig. 3: Thin section (a-g) and cathodoluminescence (h-i) images. PPL = plane

705 polarised light; XPL = crossed polars. a: host rock sample DPM28 from Unit A with

706 plagioclase and hornblende, which is almost completely replaced by opacite (PPL);

707 b: scoriaceous sample IM359 from the mafic deposits of Unit C, showing a rounded

708 quartz crystal rimmed by fine-grained pyroxenes (XPL); c: dacitic pumice sample

709 IM17b from Unit C, with a xenocryst of olivine, mantled by clinopyroxene and

710 hornblende (PPL); d: host rock sample IM29 from Phase H with euhedral zircon

711 enclosed in a large crystal of hornblende (PPL); e: enclave sample DPM35 from
712 Phase D, with a large hornblende crystal, now partially altered to opacite in a matrix
713 of smaller plagioclase and hornblende (PPL); f: sample IM36 from the mafic Agios
714 Andreas lavas of Phase C, showing the typical mineralogy of olivine, clinopyroxene
715 and plagioclase (XPL); g: holocrystalline enclave IM376 with plagioclase, quartz and
716 clinopyroxene (XPL); i and j: typical zircon crystals in samples IM29 (Phase H) and
717 IM313 (Phase D) respectively.

718

719 Fig. 4: Harker variation diagrams for igneous samples. Major element oxides in
720 weight percent and trace elements in ppm. Fields in K_2O diagram after Gill (1981).
721 Individual samples of which the isotopic characteristics are referred to in the text
722 have been indicated with their sample names.

723

724 Fig. 5: Normalised rare earth element diagrams for the different volcanic host rocks
725 and their enclaves. Normalising factors from Evensen et al. (1978).

726

727 Fig. 6: Normalised trace element diagrams. Normalising factors from Palme and
728 O'Neill (2014).

729

730 Figure 7: Bivariate diagrams relating to radiogenic isotope ratios. Fields shown are
731 for Santorini (S) and Nisyros (N) from the authors' data compilation. a: $^{143}Nd/^{144}Nd$
732 versus $^{87}Sr/^{86}Sr$ (note that limestones cannot be shown because Nd contents are too
733 low to determine their isotopic composition) with curve showing simple mixing for the

734 Phase C deposits (see Table 1 for end members); b: $^{87}\text{Sr}/^{86}\text{Sr}$ versus Sr
735 concentration; c: $^{87}\text{Sr}/^{86}\text{Sr}$ versus SiO_2 ; d: $^{143}\text{Nd}/^{144}\text{Nd}$ versus Nb; e: whole rock
736 epsilon Hf versus epsilon Nd, with the terrestrial array after Vervoort et al. (2011); f:
737 $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$, with inset to show the outlying holocrystalline enclave;
738 g: $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$, with inset to show the outlying holocrystalline
739 enclave; h: average LA-MC-ICPMS $^{176}\text{Hf}/^{177}\text{Hf}$ ratio of zircon versus whole rock
740 values, for both high-pressure (HP; dark colours) and low pressure (LP; light colours)
741 dissolutions. The grey field around the equal-Hf-isotope line shows the uncertainty of
742 the laser-ablation analyses. The 'add zircon' arrows indicate the way in which the
743 whole rock Hf isotopic signature changes by adding zircon.

744

745 Fig. 8: a: $^{143}\text{Nd}/^{144}\text{Nd}$ versus Th concentrations with curves showing simple mixing
746 models (see Table 1 for end members); b: as a, but with AFC models; c: $^{143}\text{Nd}/^{144}\text{Nd}$
747 versus K_2O concentration to show unsuitability of Miocene granitoids as mixing end
748 members; d: $^{87}\text{Sr}/^{86}\text{Sr}$ versus Sr concentration illustrating high pressure AFC model
749 for the high-Sr Phase A samples.

750

751 Figure 9: Isotope diagrams showing potential contamination by los basement and an
752 unknown unradiogenic Pb end member. a: $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$; b:
753 $^{143}\text{Nd}/^{144}\text{Nd}$ versus $^{208}\text{Pb}/^{204}\text{Pb}$.

754

755 Fig. 10: Trace element diagram, normalised over Phase G deposits, to show the
756 enrichments of Phase H, resembling those of Crommyonia samples from Soens
757 (2015).

758

759 Fig. 11: Epsilon Nd and Ce/Pb ratios of the various igneous units, arranged in
760 temporal order. No unidirectional temporal trend can be seen.

761

762 Fig.12: Cartoon illustrating the envisaged magmatic development during
763 compressional (left) and extensional (right) phases, after Eichelberger et al. (2000).

764

765

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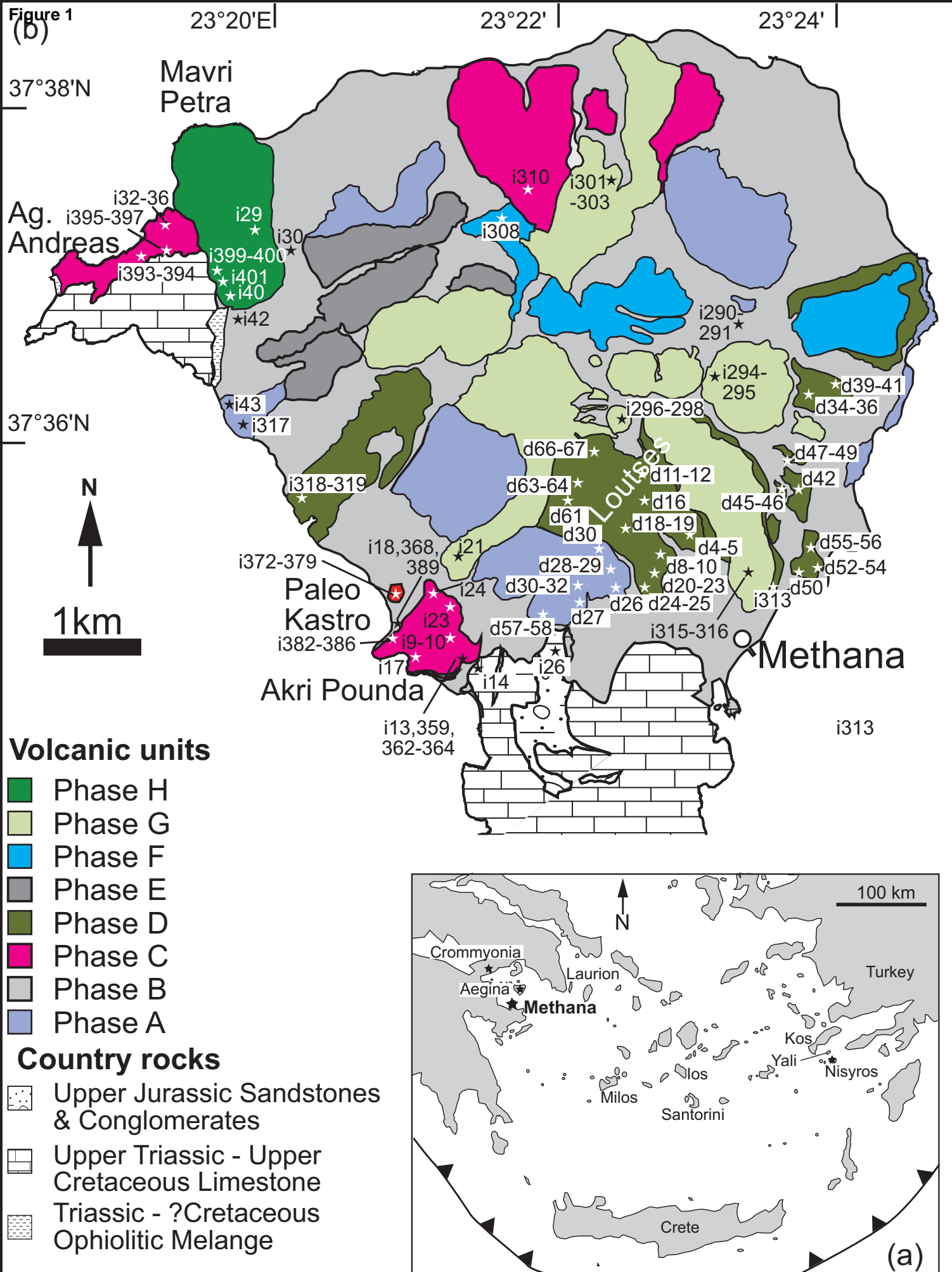


Fig. 1 Elburg et al.

Figure 2
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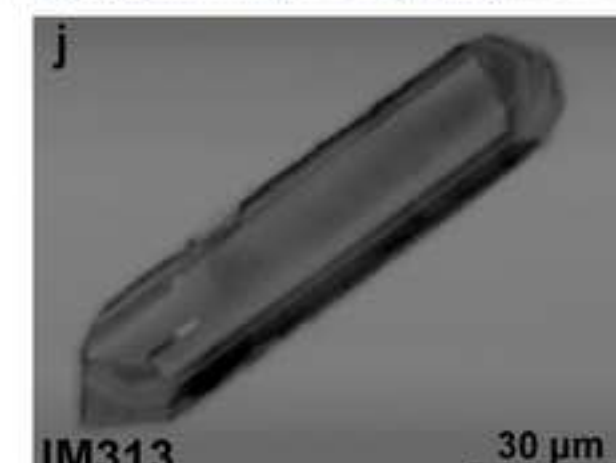
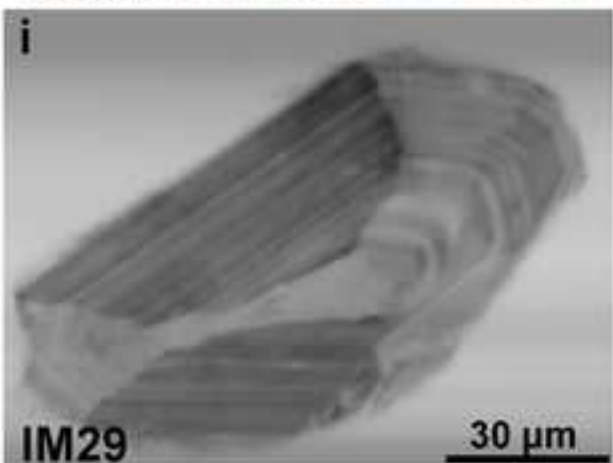
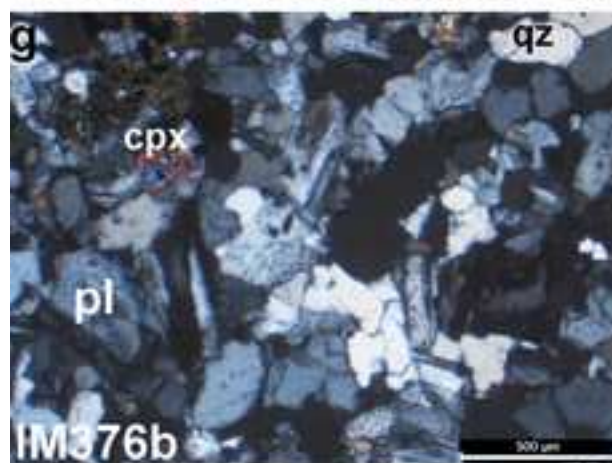
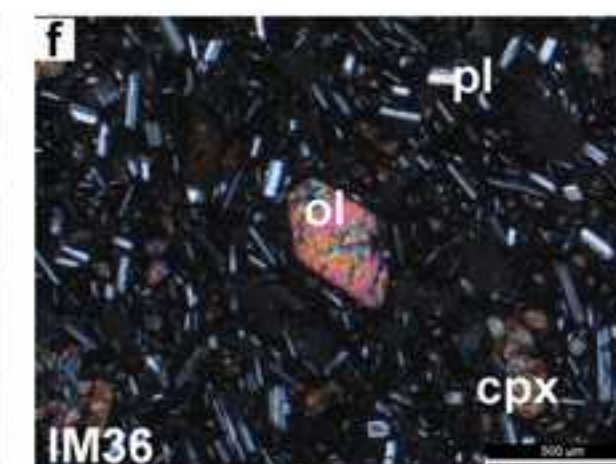
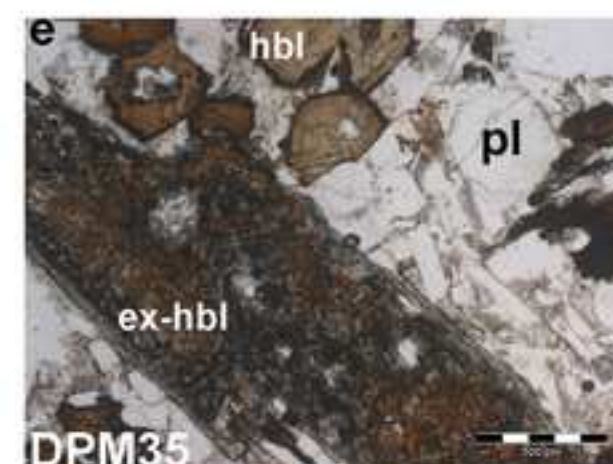
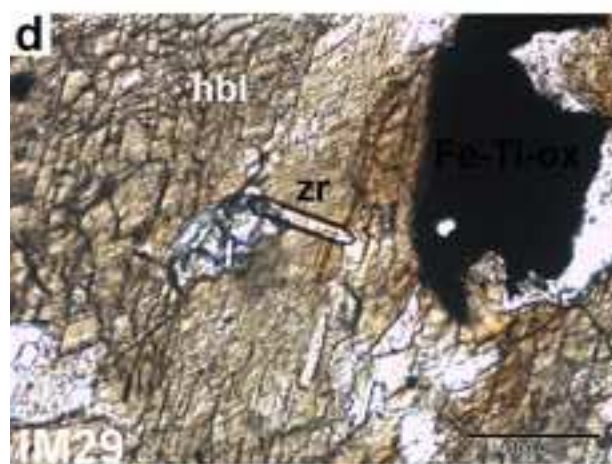
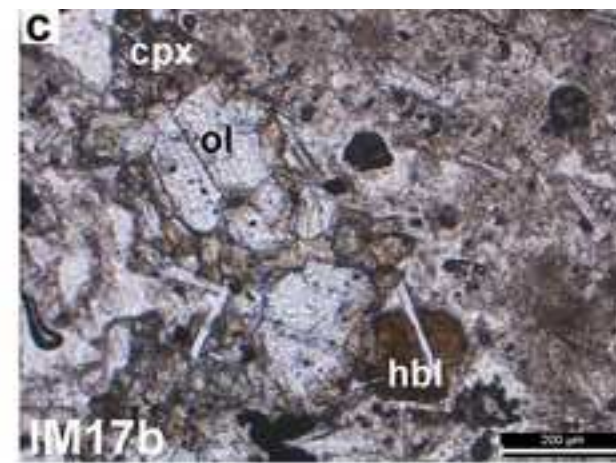
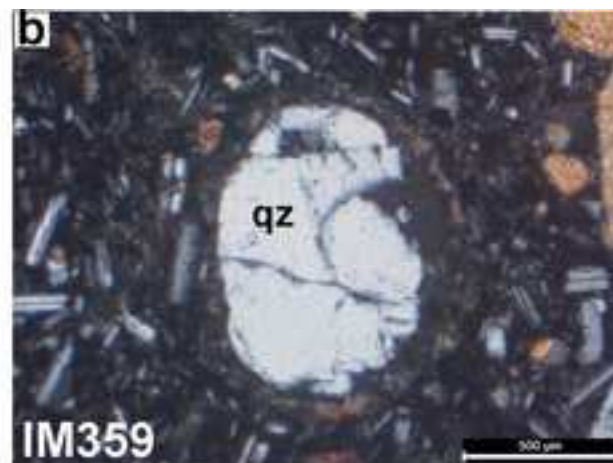
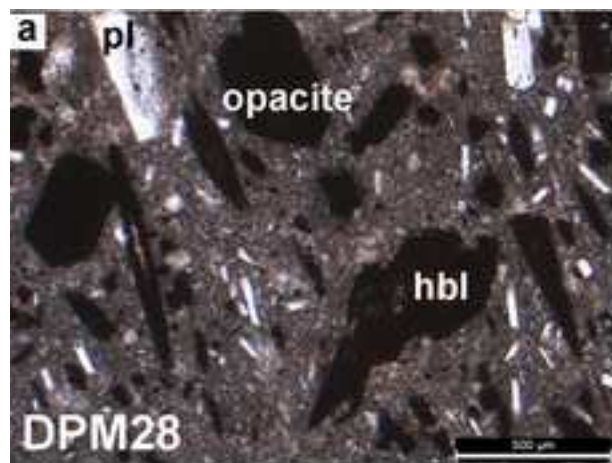


Figure 4

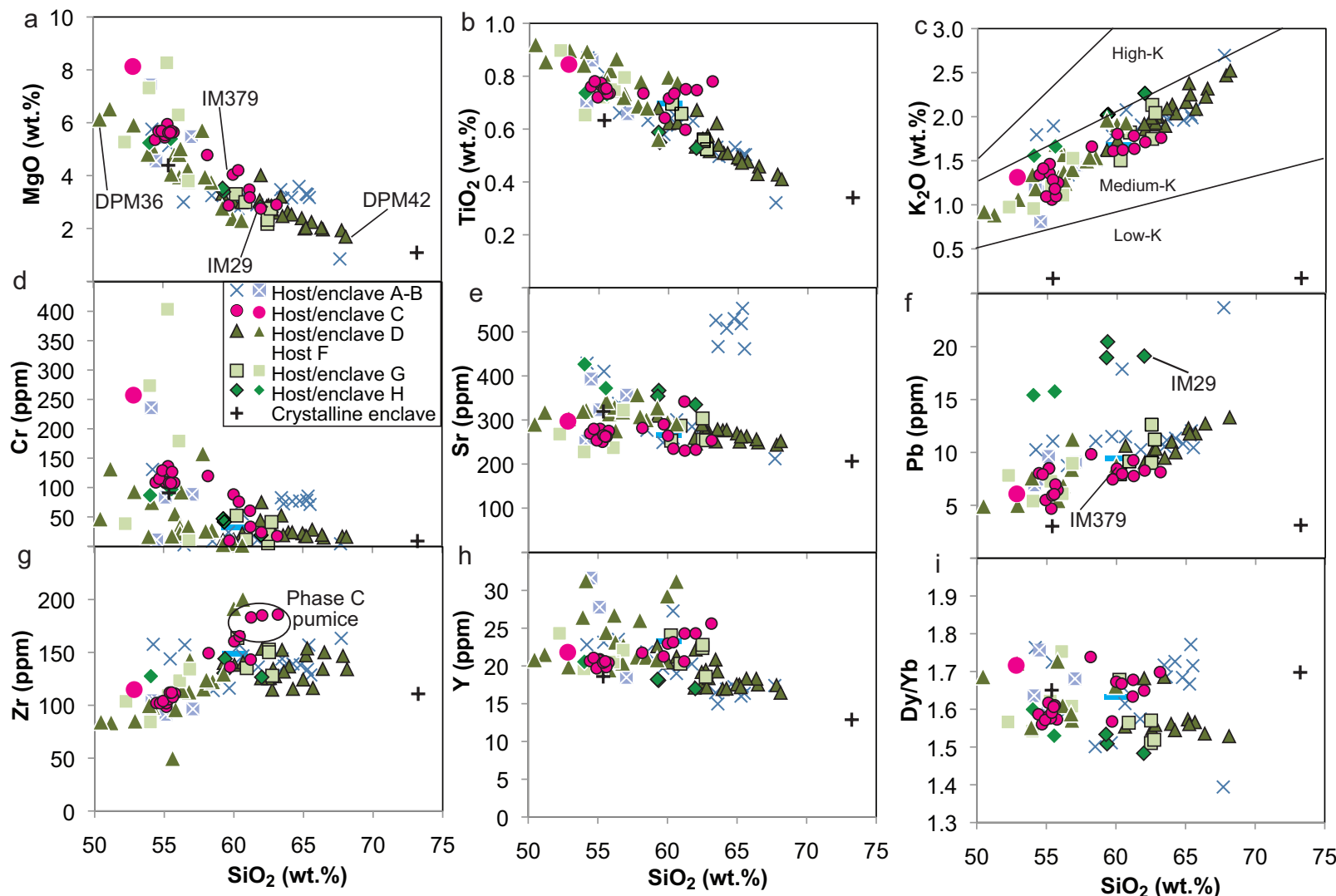


Fig. 4 Eburg et al.

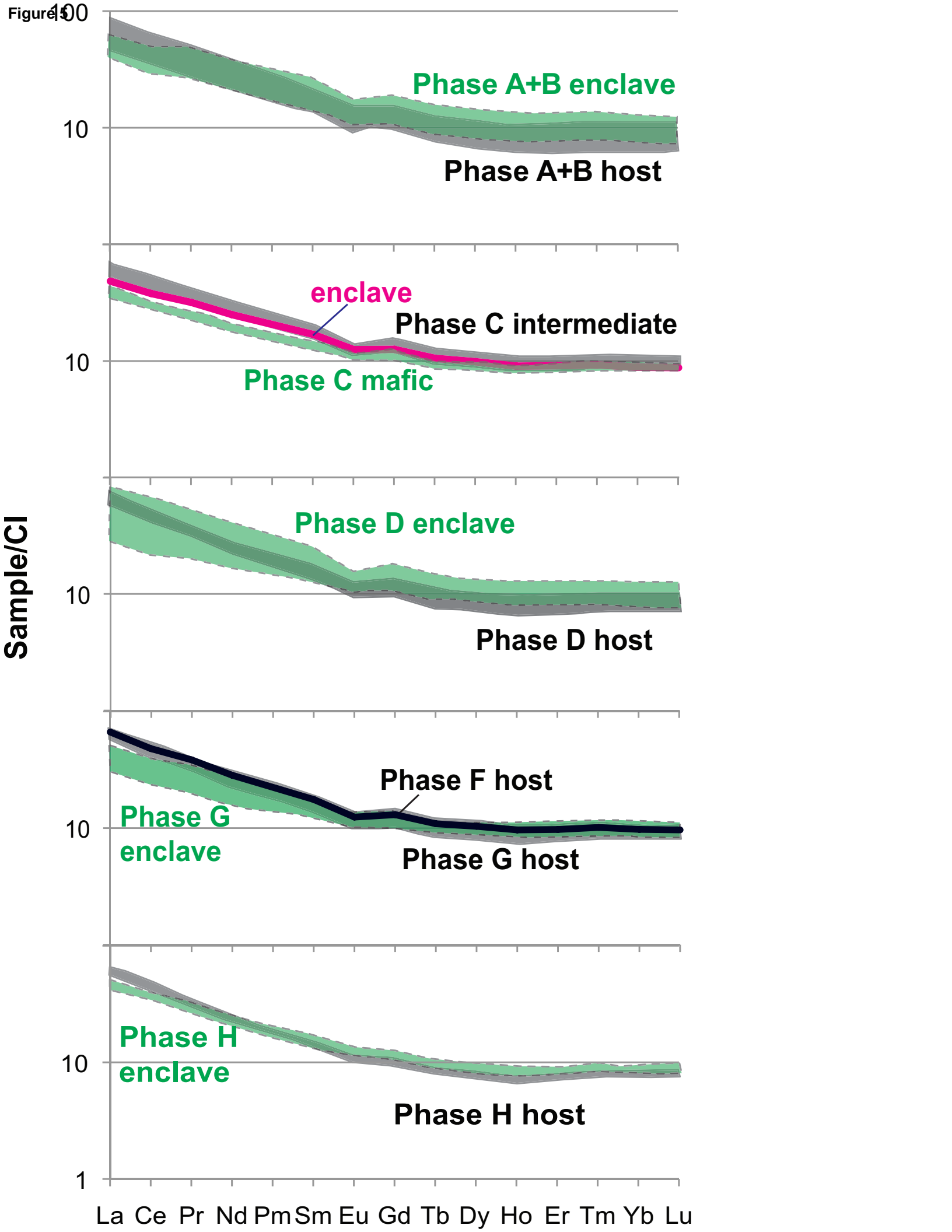


Figure 6

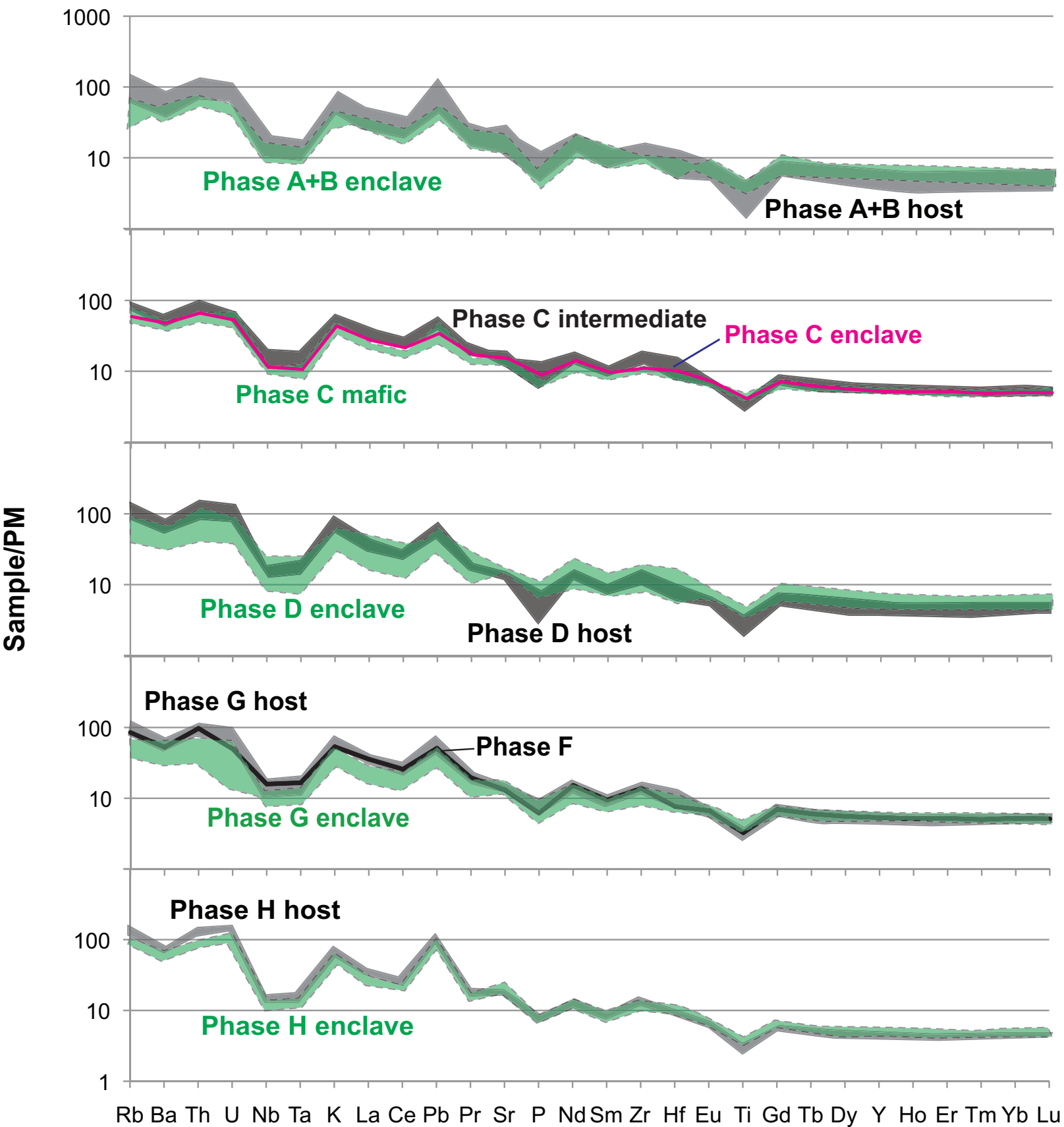


Figure 7

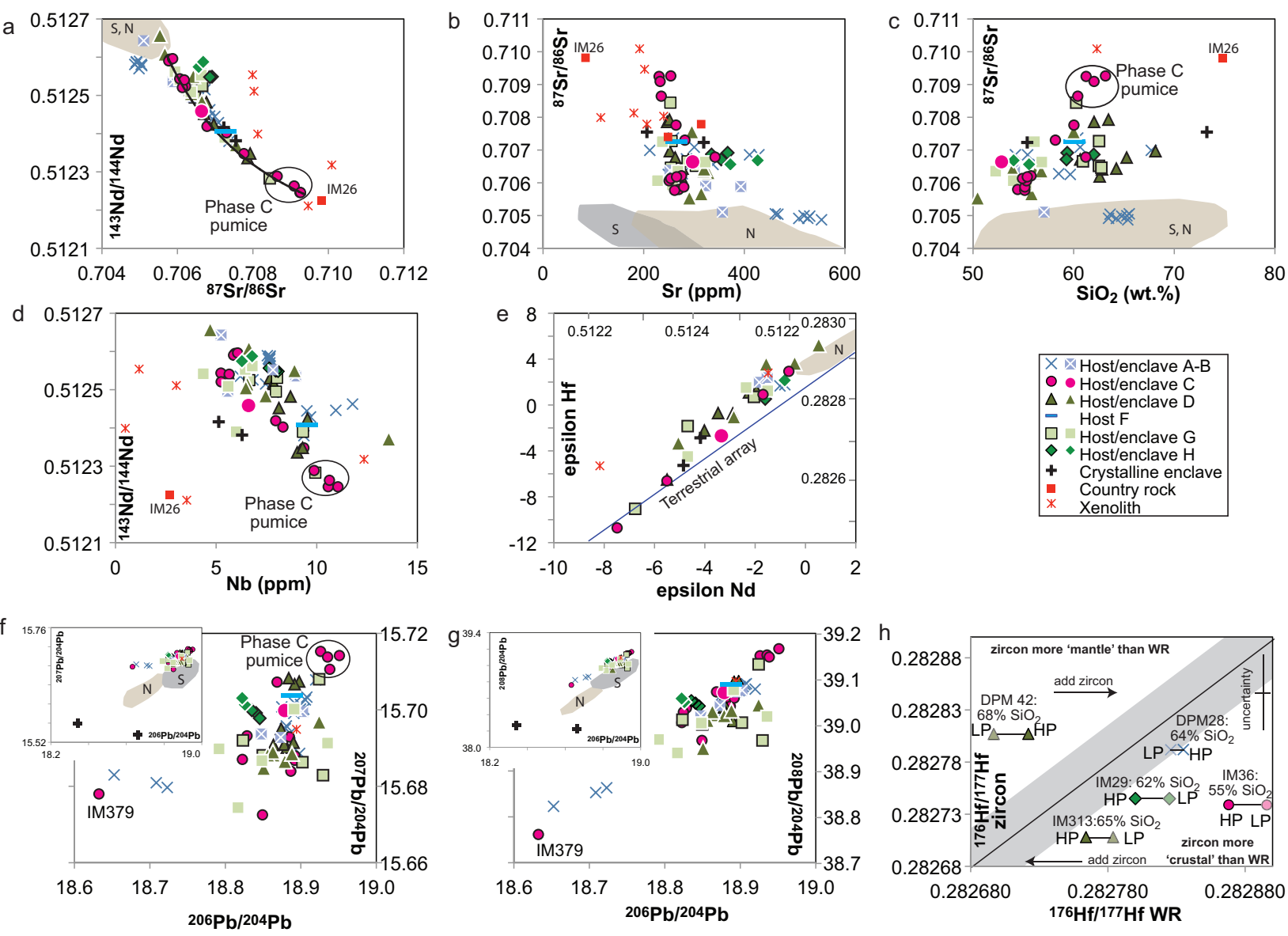


Figure 8

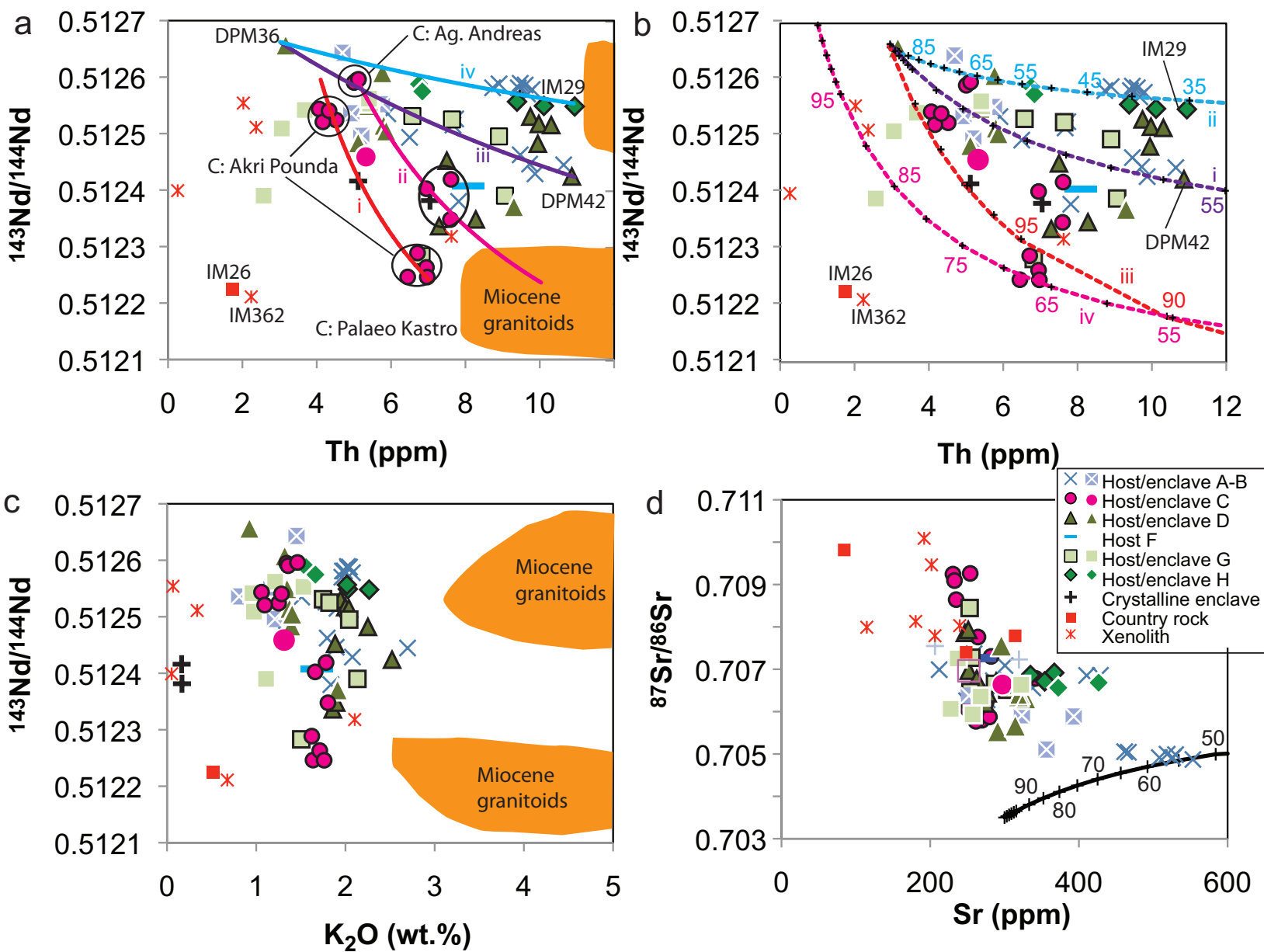


Fig. 8 Elburg et al.

Figure9

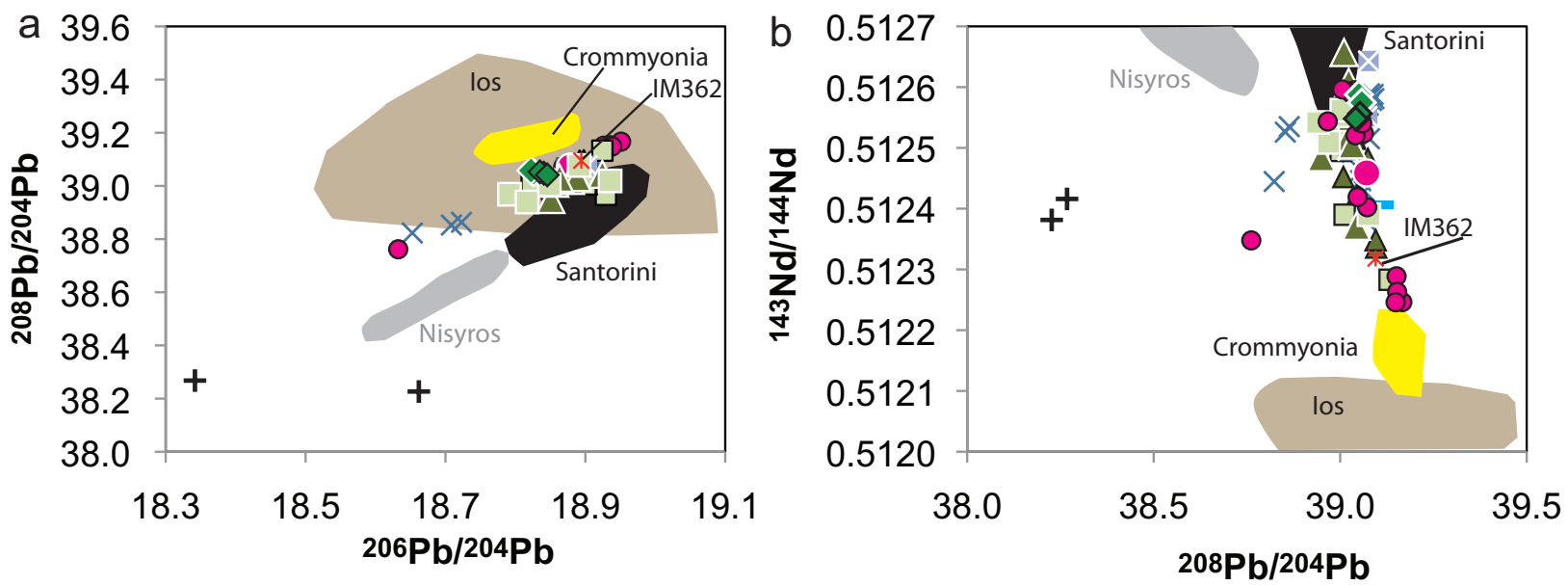


Fig. 9 Elburg et al.

Figure 10

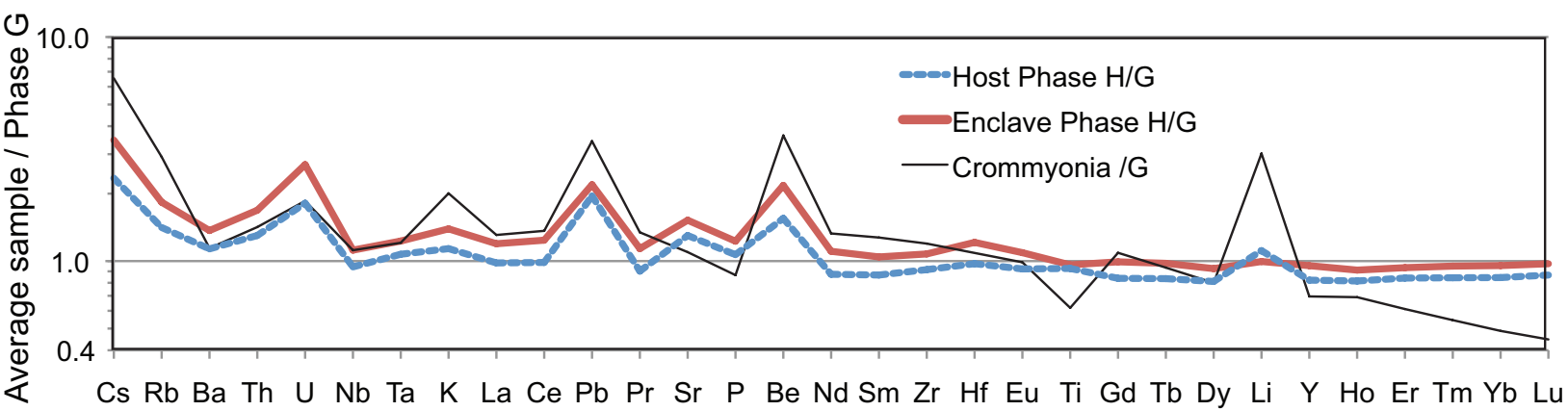


Fig. 10 Elburg et al.

Figure 11

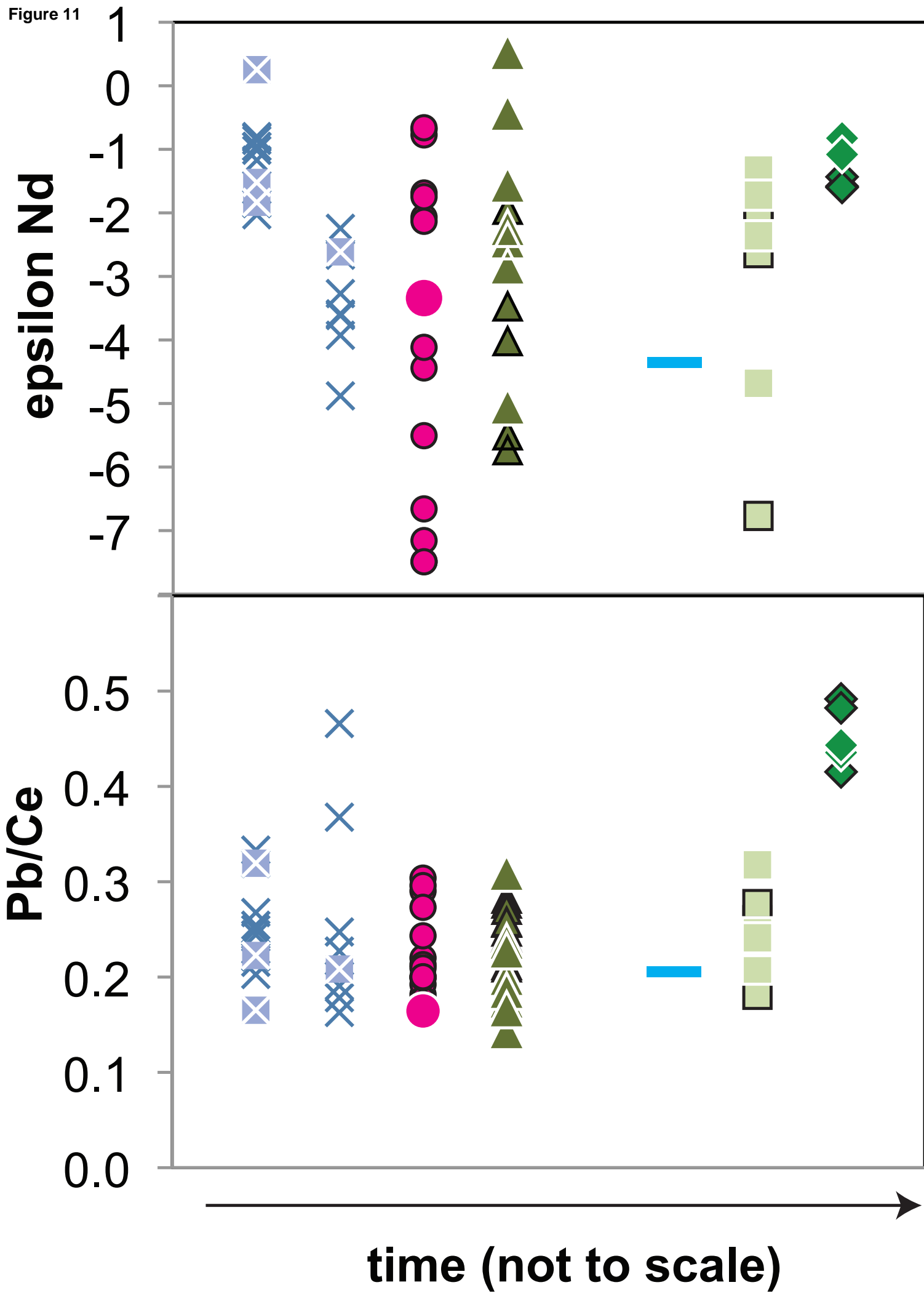


Figure 12

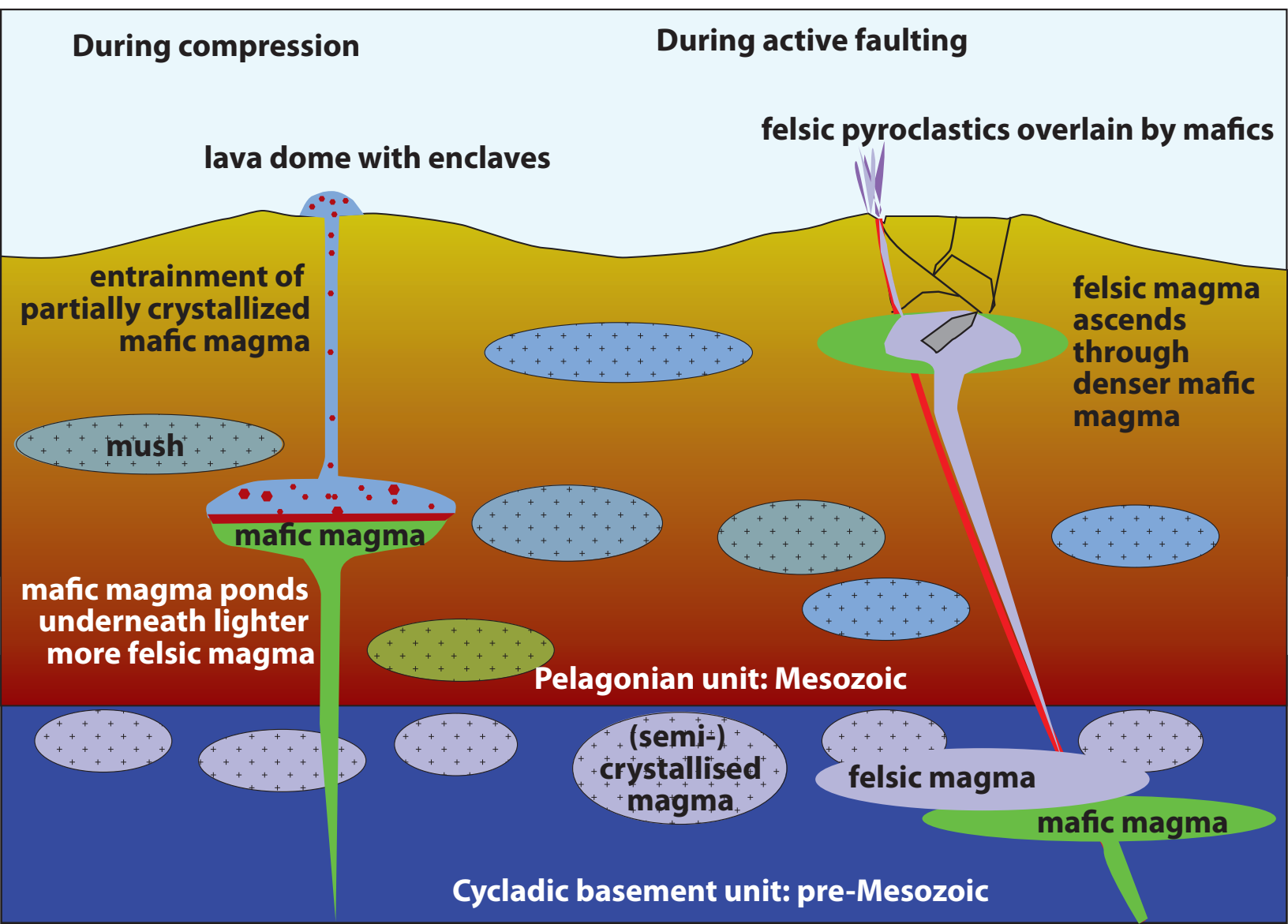


Table 1

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Table 1: Mixing end members for curves in Figures 7 and 8.

| | Curve | $^{143}\text{Nd}/^{144}\text{Nd}$ | Nd (ppm) | Th | $^{87}\text{Sr}/^{86}\text{Sr}$ | Sr (ppm) | R |
|----------------|-------------|-----------------------------------|----------|----|---------------------------------|----------|-----|
| Phase C mixing | Fig. 7a | | | | | | |
| primitive | | 0.51265 | 12 | | 0.7055 | 300 | |
| evolved | | 0.51224 | 22 | | 0.7093 | 250 | |
| | Fig. 8a i | | | | | | |
| primitive | | 0.5126 | 12 | 4 | | | |
| evolved | | 0.5122 | 22 | 7 | | | |
| | Fig. 8a ii | | | | | | |
| primitive | | 0.5126 | 12 | 5 | | | |
| evolved | | 0.5122 | 22 | 10 | | | |
| Phase D mixing | Fig. 8a iii | | | | | | |
| primitive | | 0.51266 | 12 | 3 | | | |
| evolved | | 0.51242 | 17 | 11 | | | |
| Phase D mixing | Fig. 8a iv | | | | | | |
| primitive | | 0.51266 | 12 | 3 | | | |
| evolved | | 0.51255 | 16 | 11 | | | |
| Phase D AFC | Fig. 8b i | | | | | | |
| primitive | | 0.51266 | 12 | 3 | | | |
| assimilant | | 0.51222 | 6 | 2 | | | 0.8 |
| Phase H AFC | Fig. 8b ii | | | | | | |
| primitive | | 0.51266 | 12 | 3 | | | |
| assimilant | | 0.51222 | 6 | 2 | | | 0.4 |
| Phase C AFC | Fig. 8b iii | | | | | | |
| primitive | | 0.51266 | 12 | 3 | | | |
| assimilant | | 0.5119 | 48 | 15 | | | 0.8 |
| Phase C AFC | Fig. 8b iv | | | | | | |
| primitive 2 | | 0.5127 | 9 | 1 | 0.7055 | 350 | 0.4 |
| assimilant | | 0.5119 | 48 | 15 | 0.743 | 100 | |
| Methana HP AFC | | | | | | | |
| primitive | Fig. 8d | 0.5129 | 9 | | 0.7035 | 300 | 0.3 |
| assimilant | | 0.5122 | 30 | | 0.725 | 100 | |

Bulk distribution coefficients were taken as 0.3 for Nd, 0.001 for Th and 1.7 for Sr except for the high pressure (HP) model, where it was 0.1. R = ratio assimilation / fractionation (for AFC models).