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1 **Alkaline magmas in zones of continental convergence:**

2 **The Tezhsar volcano-intrusive ring complex, Armenia**

3

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24 **Abstract**

25 Alkaline igneous rocks are relatively rare in settings of tectonic convergence and little
26 is known about their petrogenesis in these settings. This study aims to contribute to a
27 better understanding of the formation of alkaline igneous rocks by an investigation of the
28 Tezhsar volcano-intrusive alkaline ring complex (TAC) in the Armenian Lesser Caucasus,
29 which is located between the converging Eurasian and Arabian plates. We present new
30 petrological, geochemical and Sr-Nd isotope data for the TAC to constrain magma genesis
31 and magma source characteristics. Moreover, we provide a new $^{40}\text{Ar}/^{39}\text{Ar}$ age of 41.0 ± 0.5
32 Ma on amphibole from a nepheline syenite that is integrated into the regional context of
33 ongoing regional convergence and widespread magmatism.

34 The TAC is spatially concentric and measures ~ 10 km in diameter representing the
35 relatively shallow plumbing system of a major stratovolcano juxtaposed by ring faulting
36 with its extrusive products. The plutonic units comprise syenites and nepheline syenites,
37 whereas the extrusive units are dominated by trachytic-phonolitic rocks. The
38 characteristic feature of the TAC is the development of pseudomorphs after leucite in all
39 types of the volcanic, subvolcanic and intrusive alkaline rocks.

40 Whole-rock major element data show a metaluminous (Alkalinity Index = 0-0.1),
41 alkalic and silica-undersaturated (Feldspathoid Silica-Saturation Index < 0) character of
42 the TAC. The general trace element enrichment and strong fractionation of REEs (La_N/Yb_N
43 up to 70) indicate a relatively enriched magma source and small degrees of partial melting.
44 All TAC rocks show a negative Nb-Ta anomalies typical of subduction zone settings. The
45 initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.704-0.705) and positive ϵNd values (+3 to +5) indicate an
46 isotopically depleted upper mantle and lack of significant crustal influence, which in turn
47 suggests the TAC magma has formed via differentiation from lithospheric mantle melts.

48 Regionally, the age of ~41 Ma places the TAC amid a Lesser Caucasian Eocene period
49 of dominantly calc-alkaline magmatism. The TAC's arc-like geochemical signatures are
50 interpreted to result from prior subduction of the Tethyan slab beneath the Eurasian
51 continental margin. The alkaline character, distinct from regional trends, is attributed to
52 Neotethyan slab rollback causing extension and inducing small degrees of decompression
53 melting of metasomatised lithospheric mantle.

54

55 **Keywords:** Alkaline igneous rocks, ring complex, Armenia, geochemistry, $^{40}\text{Ar}/^{39}\text{Ar}$
56 dating, pseudoleucite

57 **1. Introduction**

58 Studies of alkaline magmatism on the global scale have become a point of focus due
59 to the significant role of alkaline magmatic rocks for ore exploration, in particular
60 regarding prospecting for rare earth elements (REEs), niobium (Nb), tantalum (Ta) and
61 zirconium (Zr) (e.g. Chakhmouradian and Zaitsev 2012). Many alkaline igneous rocks are
62 found in rift-related intraplate settings (e.g. Gardar Province/Greenland, Upton et al.
63 2003; Kola Alkaline Province/Russia, Downes et al. 2005; East African Rift, Woolley
64 2001), but they also occur, albeit less frequently, in settings of plate convergence (Burke
65 and Khan, 2006; Hou et al. 2006). Plate convergence includes collisional events that cause
66 the welding of terranes into continental land and subsequent post-collisional episodes in
67 which convergence continues (Bonin et al. 1998). The occurrence of magmas with alkaline
68 affinities becomes more common only when the geodynamic context becomes entirely
69 intraplate in a post-orogenic episode (Bonin et al. 1998). In complex collisional and post-
70 collisional settings, the timing of specific types of magmatism depends on the geotectonic
71 geometries and the relative rates of crustal thickening and subsidiary subduction (Harris
72 et al. 1986). Importantly, convergent movement between colliding plates will continue for
73 30-50 Ma after the initial collision (Harris et al. 1986). On a global scale, deformed alkaline
74 rocks and carbonatites (DARCs) may be used as indicators of where ancient oceans have
75 opened and closed, and the presence of a variety of syenites, carbonatites and other
76 alkaline igneous rocks found in proximity to older DARCs indicate the recycling of
77 material from the underlying lithosphere based on the Wilson Cycle-type model (Burke
78 and Khan 2006). Thus, investigating alkaline magmatism in convergent settings, e.g. in
79 Tibet (Williams et al. 2004; Hou et al. 2006) and the Anatolian-Armenian-Iranian plateau
80 (Jackson et al. 1995; Neill et al. 2015), has become as important as studies of rift-related
81 settings to understand alkaline magma genesis.

82 The exact mechanisms responsible for magma generation in collisional tectonic
83 settings remain enigmatic. Models include slab break-off (Keskin 2003; van Hunen and
84 Allen 2011; Neill et al. 2015), large-scale delamination or thinning of the lithospheric
85 mantle (Innocenti et al. 1982; Pearce et al. 1990) and small-scale lithospheric detachment
86 driven by convection cells (Kaislaniemi et al. 2014; Neill et al. 2015). Moreover, the source
87 of magmas in compressional regimes and their chemical impact on the crust remains
88 disputed. Processes to generate primary magmas in collision zones may involve melting
89 of thickened lithosphere due to breakdown of hydrous phases at the continental suture
90 (Allen et al. 2013) and melting of deeply-subducted continental crust (Zhao et al. 2013).
91 To explain the alkaline character of the erupted or plutonic igneous rocks, several genetic
92 models and processes have been proposed:

- 93 1. Low degrees of partial melting of metasomatized upper mantle (Bodeving et al.
94 2017; Dawson 1987; Marks et al. 2008).
- 95 2. Melting of crustal sources, which could be located in the lower crust and mafic in
96 composition (Smith et al. 1988) or in the middle to upper crust and felsic in
97 composition (Downes 1987; Fitton 1987).
- 98 3. Fractional crystallization from alkali basalt parental magmas (DeLong et al. 1975;
99 Trumbull et al. 2003), with variable degrees of crustal assimilation (Fitton 1987;
100 Jung et al. 2007; Lan et al. 2011).
- 101 4. Fenitisation – a high temperature metasomatic alteration driven by alkali-rich
102 fluids incrementally expelled from alkaline or carbonatitic melts (Sindern and
103 Kramm 2000; Suikkanen and Rämö 2017).

104

105 Armenia, landlocked between the Black Sea and the Caspian Sea, forms part of the
106 Anatolian-Armenian-Iranian Plateau and is characterised by widespread Cenozoic

107 volcano-magmatic activity, starting in the Eocene at ~50 Ma and intermittently lasting
108 into the Holocene and historical times (Karakhanian et al. 2002; Moritz et al. 2016; Fig.
109 1a). Several studies focused on Quaternary volcanic cones on the Anatolian-Armenian-
110 Iranian plateau (Innocenti et al. 1982; Pearce et al. 1990; Keskin et al. 1998), including in
111 the Armenian segments of the Lesser Caucasus mountain range (Karapetian et al. 2001;
112 Karakhanian et al. 2002), and the Miocene/Pliocene magmatic evolution of the region
113 (Dilek et al. 2010; Neill et al. 2013; Kheirkhah et al. 2015). However, investigating the
114 much less studied Paleogene igneous rocks is important to gain a more complete
115 understanding of the long-term magmatic and geodynamic evolution in this setting of
116 continuing convergence and to improve our understanding of collision-driven continental
117 magmatism and mantle dynamics (Dilek et al. 2010; van Hunen and Allen 2011; Moritz et
118 al. 2016).

119 In this study, we use a range of petrological and geochemical methods to describe and
120 interpret the lithological variations of the Tezhsar volcano-intrusive alkaline ring
121 complex (or Tezhsar Alkaline Complex - TAC) in Armenia. We provide a new $^{40}\text{Ar}/^{39}\text{Ar}$
122 age and expand on previous petrological and geochemical studies (Abovyan et al. 1981;
123 Kogarko et al. 1995; Meliksetian 1971, 1989) with the aim to achieve a better
124 understanding of TAC petrogenesis and to integrate that into a model of alkaline magma
125 genesis within a setting of continuing plate convergence. We also highlight and discuss
126 the occurrence of cm-sized pseudoleucites in the TAC.

127

128 **2. Geological history**

129 **2.1 Regional tectonic setting**

130 The TAC, located about 55 km north of Yerevan in the Lesser Caucasus, has formed in
131 the Eocene in a setting of general convergence between the Eurasian and Arabian plates

132 (Fig. 1a). This region was affected by two distinct collisional events and the emplacement
133 of the alkaline magmas of the TAC is crucial to the understanding of the tectono-magmatic
134 evolution of the region.

135 The TAC is located on basement of the South Armenian Block (SAB), which is a
136 microplate of Gondwanaland origin (Knipper and Khain 1980; Rolland 2017; Sosson et al.
137 2010). Proterozoic metamorphic basement of the SAB is exposed in the Tsakhkunyats
138 massif (Belov 1968; Aghamalyan 1998). Platform sedimentary cover of the SAB is
139 presented by folded Late Devonian to the Late Triassic sedimentary formations
140 (Arakelyan 1964; Aslanyan 1958). Ophiolites representing Jurassic oceanic crust were
141 obducted onto the northern margin of the SAB in the Late Cretaceous (90-84 Ma;
142 Rolland 2017). In the late Cretaceous to early Palaeogene (70-60 Ma), the SAB was
143 welded to the southern margin of Eurasia as a result of the closure of the northern branch
144 of the Neotethys and the termination of subduction (Rolland et al. 2009a, b; Moritz et al.
145 2016). The collision is marked by the Sevan-Akera suture zone, which is part of the
146 regional northern Neotethys suture (Hässig et al. 2013; Sosson et al. 2010). The closure
147 of the northern Neotethys branch caused a subduction jump towards the south and the
148 accretion of the SAB to the Eurasian margin resulted in formation of a Cretaceous-Eocene
149 flysch basin that overlies the ophiolites (Rolland 2017). At present, the Sevan-Akera
150 suture separates two tectonostratigraphic units, the Southern and Northern Tethyan
151 Provinces, which outline the continental provinces pre-dating the closure of the Tethys
152 Ocean (Fig. 1b; Adamia et al. 2011). The Sevan-Akera suture is located ~6 km northward
153 of the TAC. The second stage of accretion involving collision of the Arabian margin to the
154 SAB and the Tauride-Anatolian block caused the closure of the South Neotethys ocean
155 along the Bitlis-Zagros suture. This closure occurred in late Eocene to early Oligocene
156 times (40-25 Ma) based on geochronological and structural evidence (Agard et al. 2005;

157 Allen and Armstrong 2008; Rolland 2017). The convergence and collision between Arabia
158 and Eurasia induced regional compression and shortening in the overriding (SAB-
159 Eurasia) continental lithosphere (Agard et al. 2011), the formation of the Anatolian-
160 Armenian-Iranian orogenic plateau (Sheth et al. 2015) and lateral ejection of the
161 Anatolian and Iranian blocks, with the Armenian Highland (Lesser Caucasus and Eastern
162 Anatolia) in the centre (Phillip et al. 1989). Protracted Cenozoic magmatism lasted from
163 ~49 Ma to ~21 Ma and marked the final stages of the Neothethyan subduction, the main
164 Arabia-Eurasia collisions and subsequent post-collisional events, including emplacement
165 of the syn-collisional granite-leucogranite plutons of the Lesser Caucasus (Meliksetian
166 1989; Rezeau et al. 2017).

167 To explain the Palaeogene magmatism of the entire region, Dilek et al. (2010)
168 proposed the opening of an asthenospheric window beneath the arc mantle wedge and
169 the collision zone. The presence of adakites of Early Eocene age in the Pontides
170 interpreted as a result of slab window formation (Eyuboglu et al. 2011) supports this
171 hypothesis. Lordkipanidze et al. (1989) and Sahakyan et al. (2016) consider a subduction-
172 modified upper mantle source for Lower-Middle Eocene volcanism and an increase of
173 crustal input within the Late Eocene-Early Oligocene magmatic series of the Lesser
174 Caucasus.

175 Considering the age and location of the TAC ($^{40}\text{Ar}/^{39}\text{Ar}$ of 41.0 ± 0.5 Ma, this study;
176 36.3-37.5 Ma, K-Ar, Baghdasaryan and Ghukasyan 1985; 36-39 Ma, K-Ar, Meliksetian
177 1989), it formed in a plate convergence setting, in between two major collisional events
178 that occurred in region – first at the northern edge of the SAB in the Late Cretaceous to
179 Early Paleogene, and subsequently to the south of the SAB in the Late Eocene to Early
180 Oligocene. The TAC can thus be described as post-collisional relative to the initial
181 collisional event between the SAB and the Eurasian plate.

182

183 **2.2 Geological setting of the Tezhsar Alkaline Complex**

184 The TAC is located on the Pambak ridge at the northern edge of the SAB within the
185 Sevan-Shirak basin. To the south, the TAC is in contact with the Proterozoic metamorphic
186 basement of the SAB across the Marmarik Fault. Presence of abundant xenoliths from the
187 Tsakhkunyats basement, such as mica schists, confirms the affinity of the TAC to the SAB
188 continental terrane. To the north, the TAC borders the Margahovit intrusion comprising
189 porphyritic granosyenites. Country rocks exposed to the W-NW of the TAC comprise
190 Upper Cretaceous clastic and carbonate strata and Mid-to-Late Eocene extrusive igneous
191 rocks, which also outcrop to the E-SE. The Ulashik Fault cuts the TAC in SW-NE direction
192 with horizontal left-lateral displacement of intrusive and volcanic units reaching 700 m.

193 The TAC represents a ring complex that can be subdivided into several concentric
194 units of both volcanic and plutonic rocks. Such classical ring complexes are quite rare
195 (Johnson et al., 1999) and are of special interest considering their structural and
196 volcanological evolution as well as petrological aspects. According to Meliksetian (1971),
197 the TAC includes the following major units (Fig. 2):

- 198 1. Outer cone sheets characterized by inward-dipping contacts
- 199 2. Ring unit of volcanic alkaline rocks with a thickness up to 600 m characterised by
200 its concentric structure and inward-dipping contacts (Outer Volcanic Unit, OVU)
- 201 3. Central intrusive unit comprising syenites and nepheline syenites (Syenitic Unit,
202 SYU)
- 203 4. Ring dykes, circular bodies with sub-vertical contacts cutting both the volcanic and
204 central intrusive units
- 205 5. Resurgent volcanic unit, inside the central intrusive unit, formed by volcanic
206 breccias, dykes and subvolcanic rocks (Central Volcanic Unit, CVU).

207 For the purpose of the geochemical investigation in this study, we use a simplified
208 subdivision into Outer Volcanic Unit, Syenitic Unit and Central Volcanic Unit (Fig. 2).
209 Based on a structural analysis including bedding attitudes of units and relationships
210 between volcanic ring, cone sheets and central pluton, the presence of circular dykes and
211 remains of a volcanic centre, most researchers, namely Kotlyar (1958), Bagdasaryan
212 (1966) and Meliksetian (1971) concluded that the TAC formed via a caldera collapse and
213 the volcanic ring was emplaced through collapse along concentric faults. The
214 exceptionally large elliptical palaeocaldera structure of the TAC is $\sim 13.6 \times 11.5$ km in size
215 and has an area of ~ 131 km², comparable in dimensions to the Santorini caldera in the
216 Aegean Sea. Such a ring morphology provides a unique insight into the roots of an
217 alkaline volcano-plutonic complex.

218 Beyond the petrogenetic and structural significance of the TAC, there is also a
219 characteristic widespread development of pseudomorphs after leucite, which have been
220 studied in detail by B. Meliksetian (1970, 1971, 1979, 1989) and Yagi and Gupta (1978).
221 They feature in volcanic, subvolcanic and intrusive alkaline rocks and the largest crystals,
222 reaching up to 8 cm in size (Fig. 3) are found in porphyry tinguaitite dykes (Meliksetian
223 1978; Yagi and Gupta 1978). Their crystallographic habit is either icositetrahedral (in
224 volcanic rocks and dykes) or triakis octahedral (in intrusive syenites). In the Soviet
225 petrological literature according to Zavaricky (1934), pseudomorphism after leucite is
226 divided into two mineralogical and genetic types: "Pseudoleucites" referring to leucite
227 breakdown into nepheline and orthoclase, and "epileucites" describing pseudomorphism
228 after leucite composed of agglomerated orthoclase, muscovite, analcime, chlorite, calcite
229 and zeolites. In the Western petrological literature, usually both types are referred to as
230 pseudoleucites, and both types have been described in the TAC.

231

232 **3. Field observations**

233 Field campaigns in the TAC were carried out in 2008, 2012 and 2015 in order to
234 achieve two major aims: i) Help the completion of geological map (incl. GIS database) of
235 the complex; ii) sampling the various lithologies of the TAC for petrological and
236 geochemical investigations (Fig. 2). Sampling was focused on the three major units
237 generalised for the purposes of this study: The Outer Volcanic Unit (OVU), the inner
238 Syenitic Unit (SYU) and the Central Volcanic Unit (CVU) (Fig. 2), which have been
239 juxtaposed by ring faulting. In total, 46 samples were collected and analysed, and one of
240 those (sample 6-8-12 from the SYU) was used for $^{40}\text{Ar}/^{39}\text{Ar}$ age determination. Field
241 relations demonstrate that the syenitic magmas of the SYU intruded into the OVU (Fig.
242 3a). More localized and subordinate lithologies of the complex include syenitic pegmatites
243 (Fig. 3b) and pseudoleucite-bearing phonolites (Fig. 3c-f).

244

245 **4. Petrography**

246 The pioneering works of Meliksetian (1989) identified >50 different mineral species
247 in rocks of the TAC, including a variety of rare earth element (REE) and high field strength
248 element (HFSE) bearing phases. In our study, we focus on the major rock-forming
249 minerals in the three major rock units of the complex to provide a general overview of the
250 lithologies.

251 The volcanic rocks of the Outer Volcanic Unit (OVU) are typically porphyritic with an
252 aphanitic groundmass. Major minerals are plagioclase + clinopyroxene + amphibole +
253 biotite + alkali feldspar + Fe-Ti oxides ± nepheline, and apatite and titanite are present as
254 accessory phases. Plagioclase is euhedral to subhedral, weakly zoned and often shows
255 sieve textures (Fig. 4a). Euhedral clinopyroxene phenocrysts are up to 2 mm in size and
256 typically poikilitic. Volcanic breccias are observed occasionally, containing angular

257 fragments and xenoliths, the latter partly rich in quartz. Volumetrically small occurrences
258 of altered pseudoleucite phonolites are present, where we found pseudomorphed leucite
259 up to several cm in diameter. The deltoidal icositetrahedral crystal habit of the primary
260 leucite is well preserved, but leucite has been completely replaced by secondary minerals.
261 These are dominated by alkali feldspar and cancrinite-group minerals and comprise
262 minor amounts of analcime. Other phases found in the pseudoleucite are clinopyroxene,
263 biotite, apatite and calcite.

264 The volcanic rocks of the Central Volcanic Unit (CVU) are generally porphyritic with
265 a fine-grained matrix. They contain euhedral plagioclase + alkali feldspar + clinopyroxene
266 + amphibole + biotite + Fe-Ti oxides as major mineral phases. Some samples contain
267 amphibole glomerocrysts and clinopyroxene overgrowing biotite (Fig. 4b). Rare
268 pseudoleucite phonolites occur in this unit as well. The samples of the CVU are often
269 intensely altered.

270 The Syenitic Unit (SYU) comprises equigranular, phaneritic, medium to coarse-
271 grained syenites and nepheline syenites (Fig. 4c-h). Several samples show a trachytoidal
272 preferential alignment of feldspars. Major mineral phases are alkali feldspar + amphibole
273 + biotite + clinopyroxene + Fe-Ti oxides ± nepheline ± plagioclase. Garnet is rare but very
274 prominent in the coarse grained (pegmatitic) rock varieties, where euhedral to subhedral
275 brown garnet forms clusters with euhedral, black to dark green amphibole. Accessory
276 phases observed include zircon, titanite, fluorite, muscovite, apatite, calcite, sodalite and
277 cancrinite. Subhedral alkali feldspar is typically the most abundant phase, frequently
278 exhibiting significant alteration. Primary clinopyroxene commonly shows signs of
279 incipient alteration to green amphibole.

280

281 **5. Analytical methods**

282 Major and trace elements were analysed by standard X-ray fluorescence (XRF),
283 inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively
284 coupled plasma mass spectrometry (ICP-MS) methods. Detailed information about the
285 analytical methods used is provided in the supplementary material. Systematic
286 differences between analyses from different laboratories are not observed. If they exist,
287 they are likely to be small relative to the compositional effects of the magmatic processes
288 operating, and considered negligible for the overall interpretation of the dataset.

289 Strontium (Sr) and neodymium (Nd) isotope analyses were performed at the School
290 of Earth and Environment, University of Leeds. Conventional ion-exchange
291 chromatographic techniques were applied and samples were analyzed on a Thermo
292 Finnigan Triton multicollector mass spectrometer (see Halama et al. 2013 for details of
293 the analytical protocol). Information about reference materials analysed as well as
294 normalization and correction procedures applied is given in the supplementary material.

295 $^{40}\text{Ar}/^{39}\text{Ar}$ dating of amphibole from syenite sample 6-8-12 was performed using a CO_2
296 laser stepwise heating technique at the Institute of Earth and Environmental Science,
297 Universität Potsdam. The analytical protocol follows established procedures and a brief
298 summary about procedural aspects, standards used and corrections applied is provided
299 in the supplementary material. Calculation of ages and errors was performed following
300 Uto et al. (1997) using the total ^{40}K decay constant of $5.543 \times 10^{-10} \text{ a}^{-1}$.

301

302 **6. Results**

303 **6. 1. Rock classification and major element geochemistry**

304 The Total Alkali versus Silica (TAS) diagram was used to classify the volcanic rocks
305 from the OVU and CVU (Fig. 5a). For the intrusive rocks of the SYU, we used the
306 classification diagram of De La Roche et al. (1980; Fig. 5b). Whole rock geochemical

307 analyses are presented in Table 1. All volcanic rocks of the TAC are classified as alkaline
308 in the TAS diagram (Fig. 5a). Rocks of the OVU cover a wide compositional range from
309 basaltic trachyandesite to phonotephrite, tephriphonolite and phonolite. The
310 compositional range of the CVU rocks is more restricted, comprising trachyandesites and
311 trachytes. The plutonic rocks of the SYU are classified as nepheline syenites and syenites
312 based on the R1 and R2 parameters (Fig. 5b), which generally agrees with the
313 petrographic observations.

314 A further geochemical classification was carried out using various geochemical
315 indices (Table 1) that allow an evaluation of petrogenetic relationships (Shand 1947;
316 Frost et al. 2001; Frost and Frost 2008). The majority of the Tezhsar rocks are ferroan,
317 alkalic, metaluminous and silica-undersaturated. The Alkalinity Index (AI; AI = Al-(K+Na)
318 on a molecular basis) typically varies between 0 and 0.1, indicating that peralkaline rocks
319 (AI<0) are largely absent at the TAC. Values for the feldspathoid silica-saturation index
320 (FSSI; normative $Q-[Lc+2(Ne+Kp)]/100$, where Q = quartz, Lc = leucite, Ne = nepheline
321 and Kp = Kaliophilite) mostly range from -0.6 to 0. The negative FSSI values demonstrate
322 that the rocks are generally silica-undersaturated. Diagrams using the aluminium-
323 saturation index (ASI; molecular $Al/(Ca-1.67P+Na+K)$) and the modified alkali-lime index
324 (MALI; Na_2O+K_2O-CaO) classification demonstrate the predominantly metaluminous and
325 alkalic nature of the TAC rocks (Fig. 5c, d). Peraluminous compositions (ASI>1) are very
326 rare. Compared to the restricted compositions of SYU and CVU, the OVU shows the largest
327 variations in A/NK ratios.

328 Harker diagrams show a relatively smooth decrease of MgO, total FeO (FeO_T) and CaO
329 with increasing SiO₂ contents (Fig. 6a-c). MgO contents are below 3 wt% for OVU rocks
330 and SYU and CVU rocks have less than 1wt% MgO, demonstrating their highly evolved

331 character and suggesting substantial fractionation of mafic minerals prior to
332 crystallisation.

333

334 **6.2. Trace element geochemistry**

335 Whole-rock trace element concentrations in the TAC are variable and show some
336 significant enrichment in Sr (up to ~5000 ppm), Ba (up to ~4000 ppm), Zr (up to ~1000
337 ppm) and Σ REE (up to ~1200 ppm), which is typical for alkaline igneous rocks
338 (Chakhmouradian and Zaitsev 2012). Incompatible trace elements such as Th and Zr
339 show pronounced enrichment with increasing silica, in particular evident for SYU and
340 CVU rocks (Fig. 6d, e). In contrast, Sr contents remain relatively constant for intermediate
341 rocks with <58 wt% SiO₂ and diminishing at higher silica contents (Fig. 6f). A chondrite-
342 normalised REE diagram (Fig. 7a) shows that both the volcanic and plutonic rocks of the
343 TAC are characterised by a strong fractionation between LREE and HREE with La_(N)/Yb_(N)
344 ratios predominantly around 10-40 but reaching values as high as 70. Absolute amounts
345 of LREE are generally higher in the SYU (~200-1000 x chondrite) compared to the OVU
346 and CVU (~40-500 x chondrite). Europium anomalies, defined as $Eu/Eu^* = \frac{Eu_N}{\sqrt{(Sm_N \times Gd_N)}}$, are
347 moderately negative in the volcanic units OVU (0.80 – 1.08) and CVU (0.68 - 0.91). The
348 majority of the SYU rocks have more pronounced negative Eu anomalies with Eu/Eu*
349 values between 0.44 and 0.97 (Fig. 7a). On primitive mantle-normalised trace element
350 diagrams (Fig. 7b-d), negative anomalies for Nb, Ta and Ti are the most prominent
351 features in all three units. In contrast, a strong relative enrichment of Th and U compared
352 to Rb and Ba is only significant in the SYU and CVU, but not discernible in the OVU.

353

354 **6.3 Sr and Nd isotopes**

355 Initial Sr and Nd isotope ratios of volcanic and plutonic rocks from the TAC,

356 recalculated to an age of 41 Ma, range from 0.7040 to 0.7052 and 0.51274 to 0.51283,
357 respectively (Table 1). 19 of 20 samples fall within the range 0.7040 to 0.7044 for the
358 initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. The Nd isotopic compositions correspond to positive ϵNd values
359 between +3.0 and +4.8 (Table 1).

360

361 **6.4 $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology**

362 One syenite sample (sample number 6-8-12) was dated by $^{40}\text{Ar}/^{39}\text{Ar}$ step heating. The
363 total gas age is 42.1 ± 0.5 Ma (Fig. 8; Table 2). We use the following criteria outlined by
364 Fleck et al. (1977) for defining a plateau age: (1) The plateau includes at least 50% of the
365 total ^{39}Ar released, (2) the ages of two contiguous steps in the plateau agree within 2s
366 error, excluding the J value error, (3) the plateau consists of three steps or more, and (4)
367 each degassing step contributing to the plateau contains >3% of the total ^{39}Ar released.
368 For the syenite sample 6-8-12, five plateau steps constituting 98.88% of the total ^{39}Ar
369 released can thus be used to define a plateau age of 41.0 ± 0.5 Ma (Fig. 8; Table 2). Using
370 the plateau steps only, a normal isochron age of 41.3 ± 2.5 Ma with a $^{40}\text{Ar}/^{36}\text{Ar}$ intercept
371 at 281 ± 58 is obtained. The corresponding inverse isochron yields an age of 41.2 ± 2.1 Ma
372 with $(^{40}\text{Ar}/^{36}\text{Ar})_i = 289 \pm 57$. The good agreement between the three ages underlines the
373 reliability of the age determination, with the plateau age of 41.0 ± 0.5 Ma representing the
374 most precise and hence preferred age.

375

376 **7. Discussion**

377 **7.1 Comparison with regional magmatic signatures**

378 The alkaline and highly evolved nature of the TAC rocks makes them distinct from
379 volcanic rocks outcropping in Armenia, which are typically transitional between alkaline
380 and subalkaline. This includes the trachybasaltic to trachyandesitic Pliocene-Quaternary

381 rocks from northern Armenia (Neill et al. 2013, 2015), as well as rocks from the large
382 polygenetic Aragats volcano (Connor et al., 2011) and from the Gegham, Vardenis and
383 Syunik Volcanic Highlands in South Armenia (Karapetian et al. 2001; Sugden et al.
384 submitted). A comparison with data for regionally related Miocene to Quaternary
385 Armenian igneous rocks from the Yerevan and Shirak regions (Neill et al. 2015) reveals a
386 general enrichment of the TAC rocks in almost all moderately to highly incompatible trace
387 elements (Fig. 7b-d). Key features, such as negative Nb-Ta and Ti anomalies and a relative
388 enrichment of LREE compared to HREE, are similar. Isotopically, the TAC rocks, which
389 plot on the Sr-Nd mantle array, overlap with plutonic rocks from the Meghri-Ordubad
390 pluton and with other Miocene to Quaternary volcanic rocks from Armenia (Fig. 9).
391 Quaternary volcanic rocks from Aragats (Lebedev et al. 2007; Connor et al. 2011) and the
392 Gegham Ridge (Lebedev et al. 2013) also overlap in their Sr-Nd isotopic compositions.
393 This comparison reveals that there is a broad Sr-Nd isotopic homogeneity across a large
394 area of the Armenian highlands from the Eocene to the Quaternary, indicating that similar
395 source regions are involved in magma genesis. Broadly contemporary (47-40 Ma) post-
396 collisional magmatic rocks from the Eastern Pontides (NE Turkey), which are
397 characterized by tholeiitic/calc-alkaline affinities enriched in LILE with pronounced
398 depletions in HFSE, also overlap in their isotopic composition (Aydınçakır & Şen 2013).
399 In contrast, extending the comparison to Eocene magmatic rocks in NW Iran reveals that
400 post-collisional granites and syenites from the Sanandaj-Sirjan Zone and granitoids from
401 the Urumieh-Dokhtar magmatic arc extend to significantly more radiogenic Sr-Nd isotope
402 compositions (Fig. 9).

403

404 **7.2. Magma differentiation and magma source geochemistry**

405 Both volcanic and plutonic rocks of the TAC are evolved and only a few samples are

406 of intermediate composition (Fig. 5a, b). The influence of mixing, fractional crystallization
407 and batch partial melting on the bulk geochemical composition of the rocks can be
408 evaluated using incompatible trace elements with different bulk solid/liquid partition
409 coefficients (Schiano et al. 2010). In the Rb/Nd vs. Rb diagram (Fig. 10a), the near-
410 horizontal trend for the majority of data points emphasizes the dominant role of fractional
411 crystallization, whereas mixing and differences in batch partial melting would yield
412 positive correlations (Schiano et al. 2010). This interpretation is supported by a curved
413 overall trend in the Rb vs. Rb/V diagram (Fig. 10b), which is consistent with fractional
414 crystallisation or mixing, but not with different degrees of partial melting (Schiano et al.
415 2010). Moreover, the coherent trend of the Rb/Ba vs. Ba diagram (Fig. 10c) reflects
416 feldspar fractionation and does not indicate any significant effects of hydrothermal
417 alteration. A major role of role of crustal contamination processes can also be excluded
418 based on the unradiogenic initial $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios that remain relatively constant
419 with increasing silica (Fig. 10d). Crustal contamination typically leads to an coupled
420 increase in $(^{87}\text{Sr}/^{86}\text{Sr})_i$ and SiO_2 , which is not observed for the TAC. The only sample with
421 an elevated $(^{87}\text{Sr}/^{86}\text{Sr})_i$ ratio (2-7-09) has a high Rb/Sr ratio of ~ 8 and might be affected
422 by a larger uncertainty in recalculation of the initial value and/or post-magmatic Rb or Sr
423 mobilization. There is also no indication of limestone assimilation, which would lead to a
424 significant enrichment in CaO (Fig. 6c).

425 Olivine is conspicuously absent in all TAC rocks, but the low MgO contents and the
426 highly evolved character point to preceding fractionation of mafic minerals (Fig. 6). The
427 decrease in $\text{CaO}/\text{Al}_2\text{O}_3$ coupled with increasing FeO_t/MgO ratios, Eu anomalies that
428 become more negative with increasing degree of differentiation, and decreasing Sr
429 contents and Dy/Yb ratios with increasing SiO_2 suggest a significant role of
430 amphibole/clinopyroxene and plagioclase fractionation whereas garnet fractionation

431 was insignificant (Fig. 11a-c). Typically, the OVU rocks are more primitive than both CVU
432 and SYU rocks. OVU rocks even retain Eu/Eu^* values close to 1, pointing to lack of
433 significant plagioclase fractionation (Fig. 11b).

434 The pronounced depletions in HFSE (Nb, Ta, and Ti) in all TAC rocks emphasizes the
435 influence of subduction processes on the mantle source (Fig. 7). Similar negative HFSE
436 anomalies have been observed in alkaline rocks of the Longbaoshan Complex, North China
437 Craton (Lan et al. 2011) and carbonatites from east Tibet in the Himalayan collision zone
438 (Hou et al. 2006) and were attributed to subduction processes influencing the magma
439 source regions prior to continental collision. In addition, various trace element indicators
440 for source enrichment processes support the notion that the OVU and the CVU are
441 geochemically distinct (Fig. 11d-f). The OVU shows elevated Sm/Yb and Ba/La ratios, as
442 well as relatively low La/Sm and Th/Yb ratios compared to the CVU (Fig. 11d-f).
443 Collectively, these geochemical features of the OVU are interpreted as a signature of
444 moderate fluid enrichment via slab dehydration inherited from earlier subduction events.
445 Both CVU and OVU rocks share high Ba/Nb ratios, similar to arc volcanic rocks in general
446 (Fig. 12a). There is little overlap between the two groups as OVU rocks are additionally
447 characterized by, on average, higher La/Nb ratios and Ba/Nb ratios >100 , suggesting a
448 temporal evolution towards a decreasing subduction influence from the early OVU to the
449 late stage CVU. The more scattered trend towards lower Ba/Nb ratios in the syenites and
450 nepheline syenites is likely a result of progressive alkali feldspar fractionation and should
451 not be considered as the parental magma signature. The felsic plutonic rocks from the SYU
452 tend to exhibit a larger geochemical variability when compared with the volcanic rocks,
453 which is likely related to the fact that some show cumulate textures and may not
454 represent melt compositions. The CVU, in contrast, has compositions that are more tightly
455 clustered, with a faint indication of source enrichment from subducted sediments.

456 Mechanisms of enrichment of the mantle source can be distinguished using $[Hf/Sm]_N$ and
457 $[Ta/La]_N$ ratios (Fig. 12b), where TAC rocks are characterized by a subduction
458 metasomatism signature, clearly distinct from carbonatitic metasomatism.

459 Sr-Nd isotopic compositions are broadly overlapping with Eocene to Pliocene
460 magmas from the Meghri-Ordubad pluton and Pliocene to Quaternary volcanism in
461 central and northern Armenia, pointing to only minor spatial variations in the respective
462 mantle source regions (Fig. 10). The source of the TAC magmas is dominated by a depleted
463 mantle component and crustal contamination is essentially absent, as all of the possible
464 crustal contaminants would greatly enhance the radiogenic isotope signatures of the
465 magmas, which is not the case. Silica-undersaturated alkaline rocks commonly have
466 isotopic compositions that suggest a magma source in the mantle (Dunworth and Bell
467 2001; Kramm and Kogarko 1994). For instance, nepheline syenites from the Gardar
468 Province (Greenland) show Nd isotopic compositions typical for mantle-derived rocks
469 without any significant crustal assimilation (Halama et al. 2005; Marks et al. 2004).
470 Therefore, evolved silica-undersaturated rocks are interpreted as products of
471 differentiation from more primitive nephelinitic, basanitic or alkali basaltic magmas
472 derived from the upper mantle (Kramm and Kogarko 1994; Trumbull et al. 2003).
473 Basanitic volcanism is common to the south of TAC in the Syunik Volcanic Highland
474 (Sugden et al. submitted) near the Armenia-Azerbaijan-Iran border region.

475 The trace element evidence for a subduction modifications and the Sr-Nd isotopic
476 evidence for previous melt extraction suggest that the TAC magmas are predominantly
477 derived by low degrees of partial melting from a lithospheric mantle source which has
478 been affected by pre-Eocene subduction i.e., prior to post-collisional melt generation. This
479 magma generation model is also the preferred model for volcanism in East Anatolia
480 (Keskin 2003), and similar geochemical features in volcanic rocks from the Eastern

481 Pontides (Artvin Province) contemporary (47-40 Ma) to emplacement of the TAC were
482 also interpreted to be derived from a mantle source that had experienced metasomatism
483 by slab-derived fluids (Aydınçakır & Şen 2013). Post-collisional magmatic processes are
484 commonly affected by prior subduction processes and LILE-enriched mantle sources are
485 characteristic for these rocks (Bonin et al. 1998), typically resulting in calc-alkaline
486 magmatic suites (Harris et al. 1986). The TAC represents an unusual case insofar as the
487 post-collisional magmatic rocks are alkaline in character but also derive from a
488 subduction-modified mantle source.

489

490 **7.3. The age of the Tezhsar Alkaline Complex in a regional context**

491 The mid-Eocene age of 41.0 ± 0.5 Ma falls into a time of widespread magmatism in the
492 Lesser Caucasus region, which lasted from ~ 49 to ~ 38 Ma and comprised the
493 emplacement of alkaline and nepheline-bearing gabbros, monzonites and syenites as well
494 as gabbro-diorite-granodiorite-syenogranite complexes and granites (Ghukasyan et al.
495 2006; Melkonyan et al. 2008; Moritz et al. 2016). The magmatic activity was accompanied
496 by porphyry-type Cu-Mo mineralization that was dated at 44-40 Ma by Re-Os analyses of
497 molybdenite (Moritz et al. 2016). Slightly younger alkaline magmatism is represented by
498 the Bunduk alkaline complex (38-32 Ma) located ~ 15 km northeast of the TAC (Abovyan
499 et al., 1981; Meliksetian, 1989). This pluton intrudes the Middle-Late Eocene volcanic
500 suite of the Bazum ridge and the Bazum gabbro-granitoid intrusive complex, exhibiting
501 an elongate morphology, parallel to the segment of Pambak-Sevan fault.

502 Regionally, broadly contemporaneous magmatic activity is also recorded in the
503 Talysh mountain range (Azerbaijan/Iran) at around 41-38 Ma (Vincent et al. 2005), in the
504 Eastern Pontides (Turkey) at ~ 46 -40 Ma (Aydınçakır and Şen 2013) and in western
505 Georgia at ~ 47 -41 Ma (Lebedev et al. 2009). Further to the SE in the Zagros orogen, ~ 41

506 Ma old granites and syenites occur in the Piranshahr massif (Mazhari et al. 2009) and ~40
507 Ma granitoids in the Urumieh-Dokhtar arc (Kazemi et al. 2018). The peak of subduction-
508 related magmatism in Iran is also close to 40 Ma (Allen and Armstrong 2008), and a
509 magmatic flare-up lasting ~18 million years from 55 to 37 Ma has been postulated in the
510 Urumieh-Dokhtar belt and the Alborz Mountains in Iran (Verdel et al. 2011). Throughout
511 the Eocene, the plate convergence between the Arabian and Eurasian plates was
512 proceeding at rates of 2-3 cm/year (McQuarrie et al. 2003). Following the initiation of the
513 Arabia-Eurasia collision, arc magmatism declined in the Late Eocene (Allen and
514 Armstrong 2008). However, convergence was relatively rapid throughout Eocene-
515 Oligocene time, and only slowed since Early Miocene (Rosenbaum et al. 2002).

516 The age of the TAC falls within this period of extensive magmatism during
517 convergence between the Arabian and Eurasian plates, and its geochemical
518 characteristics demonstrate a subduction-related origin. This subduction signature is
519 inherited from prior northward subduction of the Neotethys ocean underneath the
520 Eurasian margin, leading to a preconditioning of the mantle (Verdel et al. 2011). Typical
521 calc-alkaline, subduction-related Eocene magmatism typical for active arc environments
522 is preserved in the oldest granitoids (49-44 Ma) of the Meghri-Ordubad pluton (Moritz et
523 al. 2016). The Lesser Caucasus experienced extension and crustal thinning at around 40
524 Ma causing decompression melting of the hydrated, subduction-influenced lithospheric
525 mantle (Verdel et al. 2011), which imparted its geochemical signature onto the TAC
526 magmas. Middle Eocene (ca. 49–40 Ma) extension, accompanied by magmatism, also
527 occurred in Iran (Ballato et al. 2011). The extension-related magmatism in an overall
528 setting of convergence (Rosenbaum et al. 2002) is caused by the rollback of the Neotethys
529 slab (Vincent et al. 2005; Verdel et al. 2011).

530 The oldest rocks at TAC in the OVU show some geochemical characteristics
531 reminiscent of a dehydration fluid signature in arc magmatic rocks (high Ba/Nb, Ba/La
532 ratios; Figs. 7 and 11e, f). A clear arc signature, most evident in the pronounced negative
533 Nb-Ta anomalies, is present in all of the TAC rocks, similar to the Meghri-Ordubad pluton
534 at the Armenia-Iran border. However, the TAC rock compositions are distinct as they are
535 not calc-alkaline but alkaline (Fig. 5) with a pronounced enrichment in incompatible trace
536 elements (e.g. up to 5000 ppm Sr and typically 100-500 ppm Rb compared to <1000 ppm
537 Sr and 10-200 ppm Rb in rocks from Meghri). This geochemical character is not due to
538 long-lived differences in the mantle source compared to Meghri-Ordubad pluton since the
539 Sr-Nd isotopic characteristics are similar (Fig. 9). Instead, smaller degrees of melting
540 and/or a metasomatic enrichment episode(s) immediately prior to magma generation
541 have to be invoked. The very pronounced subduction signature in the TAC supports the
542 predominant melting of hydrated and HFSE-depleted lithospheric mantle, with
543 subordinate contributions from upwelling asthenospheric mantle (Verdel et al. 2011). The
544 occurrence of these alkaline rocks in a general setting of convergence is unusual, but can
545 be attributed to periods of localized extension in the Lesser Caucasus. The overall
546 convergence throughout Eocene and Oligocene is well established based on kinematic
547 data and modelling (Rosenbaum et al. 2002), but if the lithospheric structures allowed
548 ascent of mantle-derived magmas via localized faulting and/or rift tectonics alkaline
549 magmatism can develop even in collision zones (Harris et al. 1986). Development of an
550 extensional regime along this sector of Lesser Caucasus was previously suggested to
551 explain the alkaline character of Paleogene magmatic rocks, particularly those within
552 Armenia (Kogarko et al., 1995).

553

554 **7.4. Petrogenesis of pseudoleucite phonolites**

555 Based on optical microscopy and geochemical analyses including XRD, 6 types of
556 “epileucites” and 5 types of pseudoleucites were distinguished by their mineral
557 associations, host rocks and crystallographic habit (Meliksetian 1971, 1978). “Epileucites”
558 are considered to be a result of post-magmatic hydrothermal alterations, whereas
559 pseudoleucites are considered to be a result of disintegration of metastable K-Na leucite
560 into mixture of orthoclase and nepheline under subsolidus conditions ($T=600^{\circ}\text{C}$) in late
561 magmatic stage (Meliksetian 1978; Gittins et al. 1980). Yagi and Gupta (1978) mention
562 that the $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratio of 4.3 in pseudoleucites of porphyry tinguaitite dykes of TAC is the
563 highest among those studied worldwide highlighting the importance of resolving
564 complex’s evolutionary story to better understand the conditions of pseudoleucite
565 paragenesis.

566 The investigated leucite pseudomorphs occur in a phonolite (Fig. 3c-f). Relicts of
567 primary leucite are lacking, and they are generally rarely observed in leucite
568 pseudomorphs. The leucite pseudomorphs mainly consist of alkali feldspar but do not
569 contain nepheline, instead comprising abundant cancrinite (Fig. 13b-c). Different theories
570 about the genesis of leucite pseudomorphs were put forward (see Edgar, 1984, and
571 references therein), including (1) subsolidus breakdown of leucite to orthoclase and
572 nepheline, (2) reaction of leucite with a Na-rich liquid and (3) alkali ion exchange
573 reactions between leucites and Na-rich glass or fluid. We will briefly discuss these
574 theories in relation to the leucite pseudomorphs in the phonolite.

575 Subsolidus breakdown of common K-rich leucite would produce alkali feldspar and
576 kalsilite, hence a process to cause relative enrichment of Na is required to explain the
577 occurrence of Na-bearing phases in pseudoleucites. Leucite solid solutions with up to 40
578 wt.% $\text{NaAlSi}_2\text{O}_6$ were produced experimentally, and these experienced subsequent
579 breakdown into nepheline and alkali feldspar (Fudali 1963). However, natural leucite

580 does not contain excess amount of sodium to form this type of intergrowth on
581 decomposition (Viladkar 2010). The mineralogy of the leucite pseudomorph, comprising
582 abundant Na-bearing phases such as cancrinite and analcime (Fig. 13b-c), suggest that
583 they are derived from a Na-rich precursor phase. Hence, subsolidus breakdown of natural
584 K-rich leucite alone cannot explain their occurrence, but formation of a metastable Na-
585 rich leucite before breakdown might be possible (Taylor and MacKenzie 1975).

586 The pseudoleucite reaction is a reaction of leucite with a Na-rich magma to form alkali
587 feldspar and nepheline in the system $\text{NaAlSi}_3\text{O}_8 - \text{KAlSi}_3\text{O}_8 - \text{SiO}_2$ (Bowen and Ellestad 1937;
588 Edgar 1984). This reaction terminates the leucite stability field and leucite disappears by
589 reaction with the magma (Bowen and Ellestad 1937). The TAC leucite pseudomorphs,
590 however, are characterized by a well-preserved deltoidal icositetrahedral crystal habit,
591 reflecting the external shape of the precursor phase. It is difficult to envisage this reaction
592 to fully replace primary leucite without modifying the morphology of the leucites (Taylor
593 and MacKenzie 1975), which is so beautifully preserved (Fig. 3). Moreover, various minor
594 mineral phases that contain additional elements occur within the pseudomorphs. Some
595 of these (e.g. clinopyroxene, apatite) may be explained as primary magmatic inclusions,
596 but others (analcime, calcite) texturally appear as secondary phases (Fig. 13b-c). This
597 suggests that explaining the genesis of the leucite pseudomorphs based on the phase
598 relations in this petrogenetic system is an oversimplification (Edgar 1984).

599 Alkali ion exchange reactions between leucites and Na-rich glass or fluid was
600 proposed as mechanism to produce pseudomorphs after leucite that are similar in
601 composition to natural pseudoleucites (Taylor and MacKenzie 1975). Fluid-induced
602 reactions would facilitate the increase in Na content and formation of Na-dominated
603 phases, such as cancrinite and analcime in TAC. Cancrinite is assumed to replace
604 nepheline due to a reaction between nepheline and volatile-rich melts or fluids, a common

605 late magmatic– hydrothermal process (Martins et al. 2017). A reaction with fluids was
606 also used to explain pseudoleucite with intergrowth of alkali feldspar, sericite and
607 cancrinite from the Gardar Province, Greenland (Hesselbo 1986) and the replacement of
608 nepheline by analcime, cancrinite, sodalite and muscovite in pseudoleucite from India
609 (Viladkar 2010). Cancrinite is also an important constituent of the pseudoleucite
610 phenocrysts from Spotted Fawn Creek (Yukon Territory, Canada), where also garnet,
611 biotite, calcite, muscovite and plagioclase occur as inclusions within pseudoleucite
612 (Tempelman-Kluit 1969). Removal of K, addition of Na and water was attributed to the
613 entry of a fluid phase to permit the chemical exchange (Tempelman-Kluit 1969). The
614 presence of cancrinite in the TAC leucite pseudomorphs bears evidence for interaction
615 with a H₂O-CO₂-bearing fluid, possibly with minor amounts of S and Cl, as the general
616 formula for cancrinite is $(\text{Na,Ca,K})_{6-8}\text{Al}_{6-x}\text{Si}_{6+x}\text{O}_{24}(\text{CO}_3,\text{SO}_4,\text{Cl,OH})_{1-2}\cdot n\text{H}_2\text{O}$ with $x \ll 1$ and
617 $n = 1-5$ (Martins et al. 2017) illustrates. Given the scarcity of analcime in the TAC
618 pseudoleucites, a conversion of primary leucites into analcime via reaction with Na-rich
619 fluids as proposed for pseudoleucites from a phonolite dyke in Bohemia (Pivec et al. 2004)
620 seems unlikely. The texture of the TAC leucite pseudomorphs pseudoleucites has
621 resemblance to a “palisade texture”, in which orthoclase laths near the margins of the
622 pseudomorphs are oriented at right angles to the crystal boundaries (Tempelman-Kluit
623 1969). These textures can be interpreted to form by subsolidus reactions in response to
624 increasing fluid pressure when pervasive fluids come in contact with the leucite (Hesselbo
625 1986). All these lines of evidence point to a late/post-magmatic hydrothermal alteration
626 for the formation of the leucite pseudomorphs in the investigated phonolite, and they can
627 be referred to as “epileucites”. Complementary evidence for fluid-rich conditions during
628 the late to post-magmatic evolution of the TAC are the presence of pegmatites and the
629 widespread alteration in the CVU rocks.

630

631 **8. Conclusions**

- 632 • A combination of small degrees of partial melting and pre-conditioning of the
633 mantle source by slab dehydration and subsequent metasomatic processes can
634 explain the alkaline, subduction-influenced geochemical character of the TAC.
- 635 • The Sr-Nd isotopic data demonstrate a mantle source with negligible crustal
636 influence. There is a broad isotopic overlap with Eocene to Quaternary magmatism
637 in other regions of Armenia, suggesting the regional presence of isotopically
638 similar mantle source regions.
- 639 • The emplacement of the syenitic units of the TAC was dated by $^{40}\text{Ar}/^{39}\text{Ar}$ at $41.0 \pm$
640 0.5 Ma. The emplacement of the TAC can thus be linked to a previously proposed
641 model of Eocene Neotethyan slab rollback driving decompression melting and
642 extension-related magmatism in Iran and Azerbaijan within a tectonic setting of
643 general convergence between the Arabian and Eurasian plates.
- 644 • The formation of leucite pseudomorphs is related to initial leucite crystallization
645 from an evolved, silica-undersaturated magma followed by subsolidus breakdown
646 and interaction with a late to post-magmatic fluid. The magmatic-hydrothermal
647 fluid percolating through the rocks caused alteration of nepheline into cancrinite
648 and amphibolitisation of clinopyroxenes. This fluid overprint may be responsible
649 for the plethora of REE-bearing phases described previously within the TAC and
650 hence be a crucial factor in the (re)distribution of rare elements in alkaline igneous
651 rocks.

652

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1161 **Figure captions**

1162

1163 **Figure 1** – (a) Geotectonic framework of the Caucasus region showing major
1164 tectonostratigraphic provinces, associated terranes and the location of Tezhsar Alkaline
1165 Complex (star) about 50 km north of Yerevan (modified after Adamia et al., 2011, and
1166 Rezeau et al., 2017). (b) Palaeogeographical reconstruction of the Eurasian-Arabian
1167 collision in the Ypresian (52Ma) just before formation of TAC (modified after Mederer et
1168 al., 2013). SAB – South Armenian Block, SAS – Sevan-Akera Suture, BZS – Bitlis-Zagros
1169 Suture, TAB –Tauride-Anatolian Block, NTP – Northern Tethyan Province, STP – Southern
1170 Tethyan Province.

1171

1172 **Figure 2** – Geological map of the Tezhsar Alkaline Complex. The inset show a simplified
1173 subdivision of the TAC which is used for the geochemical diagrams of this study.

1174

1175 **Figure 3** – Field relations (a, b) and hand specimen photographs (c, d) of the TAC. (a)
1176 Light coloured syenite intruding into dark grey volcanic rocks of the Outer Volcanic Unit.
1177 (b) Coarse-grained nepheline syenite pegmatite comprising dark patches of garnet and
1178 amphibole. (c) Phonolite handspecimen with idiomorphic leucite pseudomorphs
1179 reaching up to 2 cm in diameter. (d) Polished surface of a pseudoleucite phonolite. (e, f)
1180 Hand specimen of pseudoleucite megacrysts (up to ~8cm in diameter) as deltoidal
1181 icositetrahedra found in TAC phonolites. Samples are from old collections of B.
1182 Meliksetian and Z. Chibukhcyan.

1183

1184 **Figure 4** – Photomicrographs illustrating characteristic features of rocks from the TAC in
1185 plane polarized (PPL) and cross-polarized (XPL) light. (a) Plagioclase (Pl) phenocrysts in

1186 feldspathic matrix of a basaltic trachyandesite, OVU (XPL). (b) Biotite (Bt) surrounded by
1187 clinopyroxene (Cpx) with accessory apatite (Ap) in trachyte, CVU (PPL). (c)
1188 Clinopyroxene and titanite (Ttn) in nepheline syenite, SYU (PPL). (d) Amphibole (Amp) in
1189 syenite, SYU (PPL). (e) Sodalite (Sdl) and nepheline (Nph) in nepheline syenite, SYU (PPL).
1190 (f) Amphibolitization of clinopyroxene in syenite, SYU (PPL) (g) Garnet (Grt) in syenite
1191 with inclusions of alkali feldspar, SYU (PPL) (h) Garnet-amphibole cluster with alkali
1192 feldspar and nepheline in pegmatitic nepheline syenite, SYU (PPL).

1193
1194 **Figure 5** – (a) Total Alkali-Silica (TAS) classification diagram of the volcanic units (OVU
1195 and CVU) of the TAC. Alkaline-subalkaline division from Irvine & Baragar (1971). (b) R1-
1196 R2 classification diagram (from De La Roche et al., 1980) of the intrusive SYU unit of the
1197 TAC. (c) A/NK vs A/CNK diagram (after Shand, 1947) based on the molecular proportions
1198 of Al (A), Na (N), K (K) and Ca (C), showing that the rocks of the TAC can largely be
1199 classified as metaluminous. (d) Modified Alkali-Lime Index (MALI, after Frost and Frost,
1200 2008) plotted as a function of SiO₂ content for the TAC rocks that are generally alkalic in
1201 composition. Comparative data for Eocene magmatic rocks from the Talysh mountains,
1202 Azerbaijan (Vincent et al., 2005 – pink diamonds) and Pliocene-Quaternary volcanic rocks
1203 from central and northern Armenia (Neill et al., 2013, 2015 – orange field).

1204
1205 **Figure 6** – Harker diagrams of the TAC samples for selected major (a-c) and trace (d-f)
1206 elements. The limestone assimilation trend in (c) was calculated after Costa et al. (2013)
1207 using limestone composition WGZ-3 from Zhang et al. (2017). All symbols as in Fig. 5.

1208
1209 **Figure 7** – (a) Chondrite-normalised REE diagram highlighting more pronounced LREE
1210 fractionation and negative Eu anomalies within the SYU relative to the volcanic units of

1211 the TAC. Normalisation values from Boynton et al. (1984). (b-d) Mantle-normalised trace
1212 element diagrams of rocks from the TAC; (b) – OVU, (c) – SYU, (d) – CVU. Normalisation
1213 values after McDonough & Sun, 1995. Comparative data from Neill et al. (2015) for
1214 Pliocene-Quaternary volcanic rocks from central and northern Armenia.

1215

1216 **Figure 8** – $^{40}\text{Ar}/^{39}\text{Ar}$ age spectrum plot for the amphibole separate from syenite sample
1217 6-8-12.

1218

1219 **Figure 9** – Sr-Nd isotope diagram of the TAC data (red squares) in comparison to other
1220 Eocene-Quaternary igneous rocks in the Lesser Caucasus and adjacent regions. The
1221 mantle array is from Lebedev et al. (2007) after DePaolo & Wasserburg (1979). Data
1222 sources: (I) – Moritz et al. (2017); (II) – Aydınçakçır & Şen, (2013); (III) – Kazemi et al.
1223 (2018); (IV) – Mazhari et al. (2009); (V) – Connor et al. (2011); (VI) – Kheirkhah et al.
1224 (2009); (VII) – Neill et al. (2013; 2015) . Literature data were recalculated using the ^{87}Rb
1225 decay constant of $1.3972 \times 10^{-11} \text{ a}^{-1}$.

1226

1227 **Figure 10** – TAC samples plotted in various diagrams to evaluate effects of distinct
1228 magmatic processes. (a) Rb/Nd vs. Rb diagram (after Schiano et al. 2010) where
1229 horizontal trends reflect fractional crystallization and positive correlations can be caused
1230 by mixing or batch partial melting. (b) Rb vs. Rb/V diagram (after Schiano et al. 2010)
1231 where curved trends, as observed for the TAC rocks, reflect fractional crystallisation or
1232 mixing. (c) Rb/Ba vs. Ba diagram exhibiting a smooth trend indicative of feldspar
1233 fractionation. (d) Initial $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios of the TAC samples plotted against SiO_2
1234 content. All samples except one plot in a very narrow range of $(^{87}\text{Sr}/^{86}\text{Sr})_i$ ratios and there
1235 is no clear trend with increasing SiO_2 content. The sample with the elevated $(^{87}\text{Sr}/^{86}\text{Sr})_i$

1236 ratio (2-7-09) has a high Rb/Sr ratio of ~ 8 and might be affected by post-magmatic Rb
1237 and/or Sr mobilization and a larger uncertainty in recalculation.

1238

1239 **Figure 11** – Major and trace element indicators for fractionation and source enrichment
1240 processes. (a) $\text{CaO}/\text{Al}_2\text{O}_3$ vs FeO_t/MgO diagram showing fractionation trends for
1241 plagioclase, olivine and amphibole(am)/clinopyroxene(cpx) after Moritz et al. (2016). (b)
1242 Eu/Eu^* vs SiO_2 diagram depicting negative Eu anomalies in SYU and CVU samples,
1243 indicating plagioclase fractionation. (c) Dy/Yb vs SiO_2 diagram with fractionation trends
1244 for garnet and amphibole after Davidson et al. (2007). (d) La/Sm vs Sm/Yb diagram with
1245 approximate mineral stability thresholds of in mantle melt residues after Mamani et al.
1246 (2010). Note the distinct signatures for the two volcanic units of TAC. (e) Ba vs Nb/Y
1247 diagram displaying trends for fluid enrichment due to slab dehydration and mantle-
1248 derived melt enrichments after Kepehinskas et al. (1997). Slab fluid enrichment is
1249 prominent in the OVU rocks. (f) Th/Yb vs Ba/La diagram with trends for enrichment from
1250 subducted slab sediments and slab fluids from Woodhead et al. (2001). Elevated Ba/La
1251 ratios in OVU rocks suggest source enrichment via slab fluids.

1252

1253 **Figure 12** – Trace element ratio diagrams of TAC rocks. (a) Ba/Nb vs La/Nb. Alkali
1254 feldspar fractionation trend highlighted as a result of Ba depletion. Field boundaries after
1255 Jahn et al. (1999). (b) $(\text{Ta}/\text{La})_N$ vs $(\text{Hf}/\text{Sm})_N$. Influence of subduction metasomatism is
1256 suggested by strongly decreasing $(\text{Ta}/\text{La})_N$ ratios. Field boundaries after La Flèche et al.
1257 (1998). Comparative data for Eocene magmatic rocks from the Talysh mountains,
1258 Azerbaijan (Vincent et al., 2005 – pink diamonds) and Pliocene-Quaternary volcanic rocks
1259 from central and northern Armenia (Neill et al., 2013, 2015 – orange field).

1260

1261 **Figure 13** – Pseudoleucite from the OVU of the Tezhsar Complex. (a) Scanned thin section
1262 image of a single pseudoleucite crystal. (b,c) Back-scattered electron images of (b) the
1263 boundary between matrix and pseudoleucite and (c) the interior of the pseudoleucite.
1264 Note the presence of cancrinite (Ccn) and analcime (Anl), other mineral abbreviations as
1265 in Figure 4.
1266

Figure 1

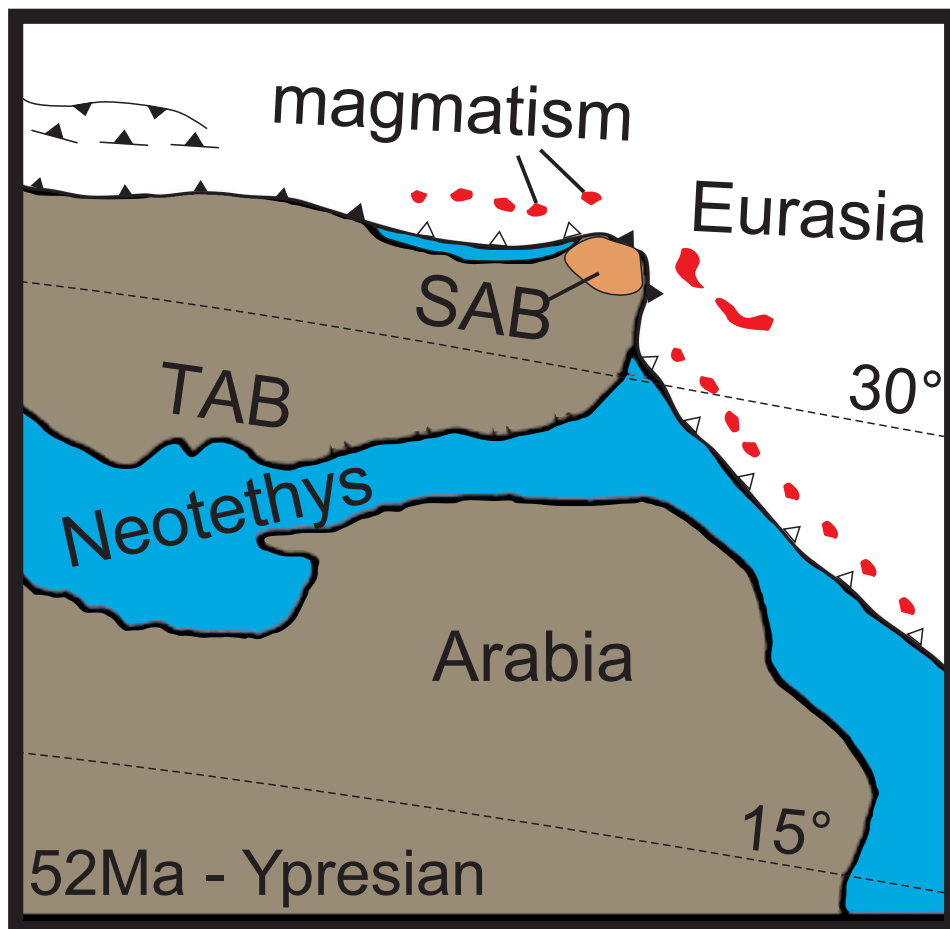
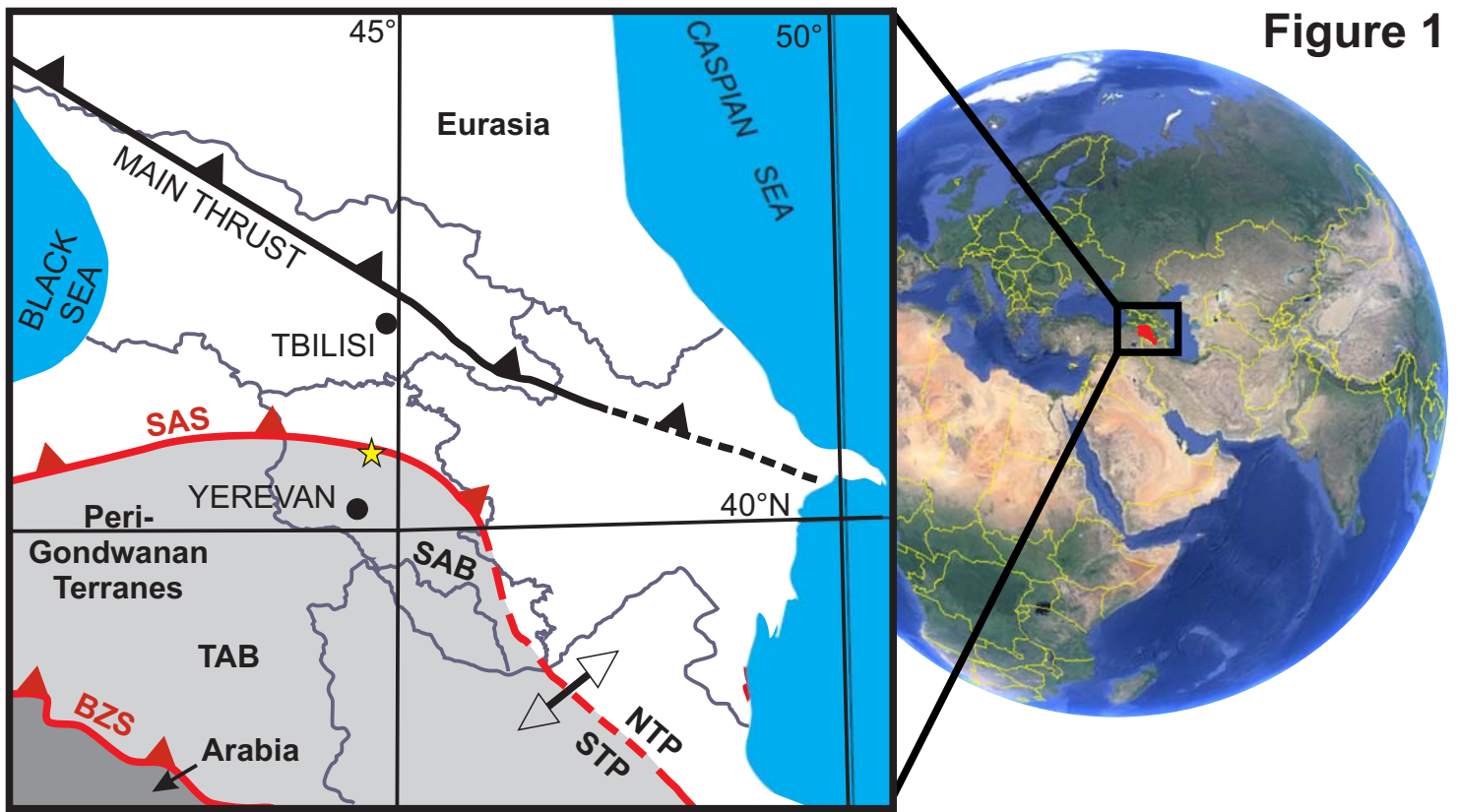


Figure 2

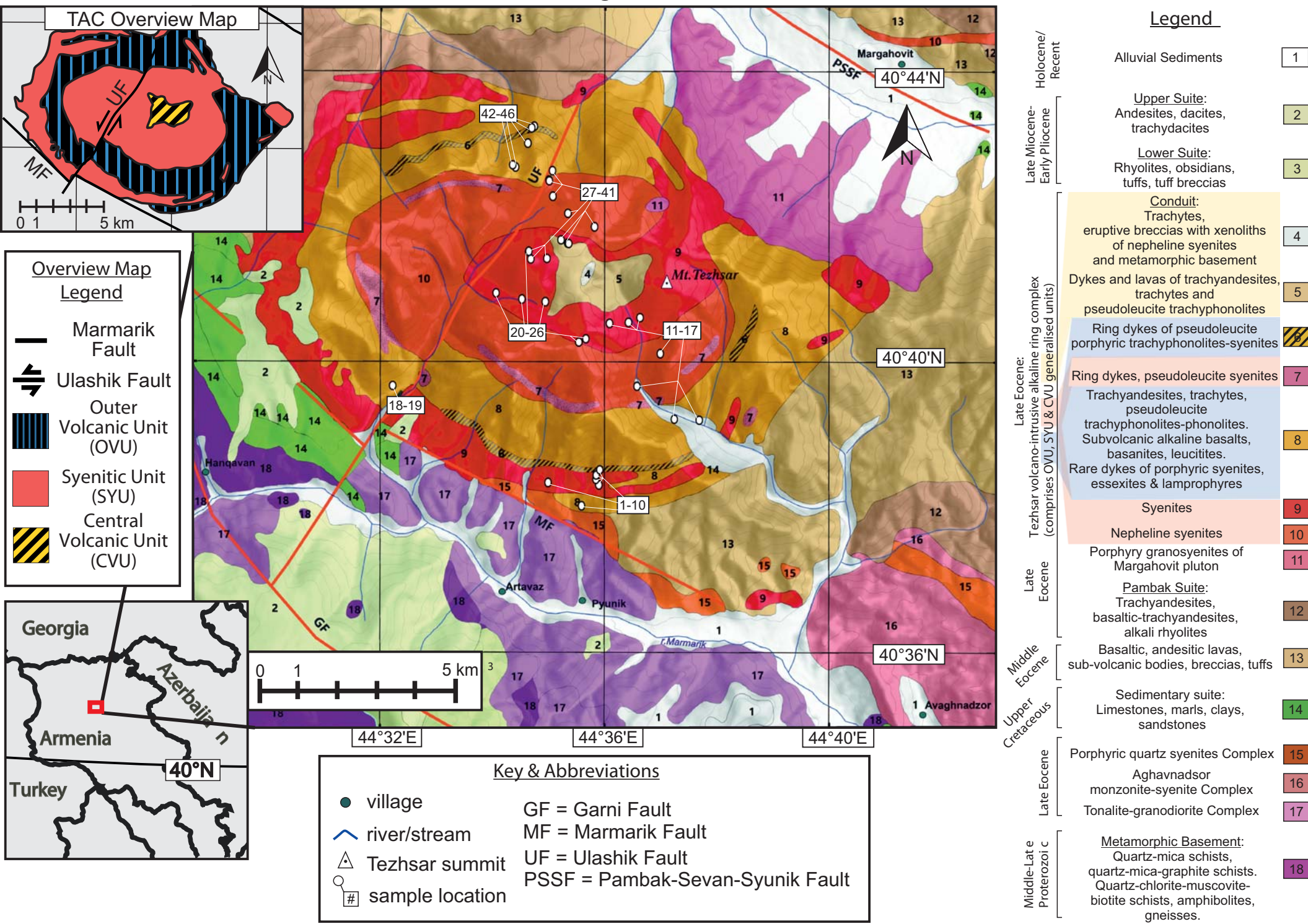


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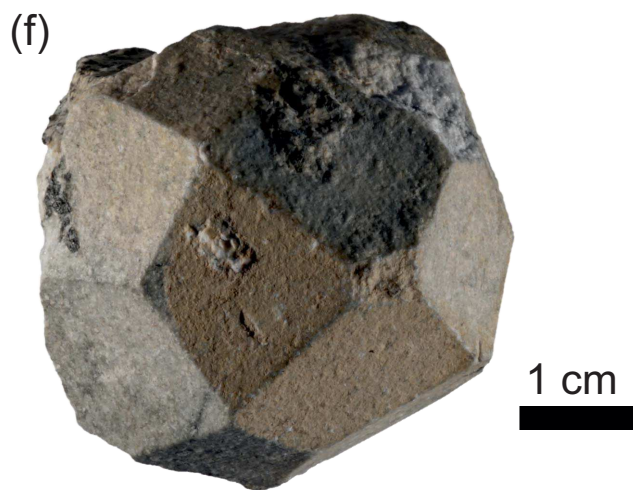
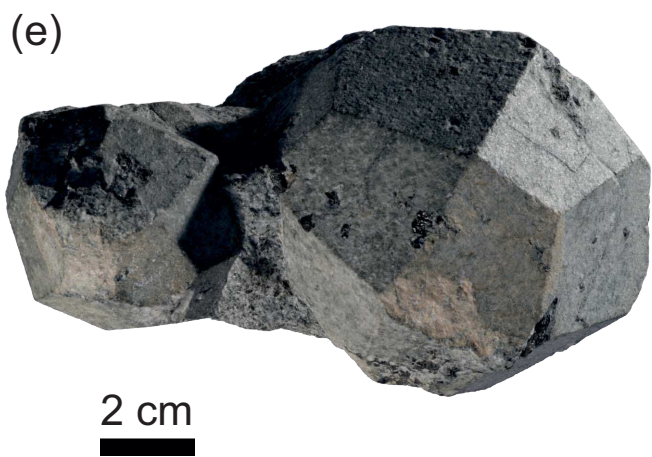
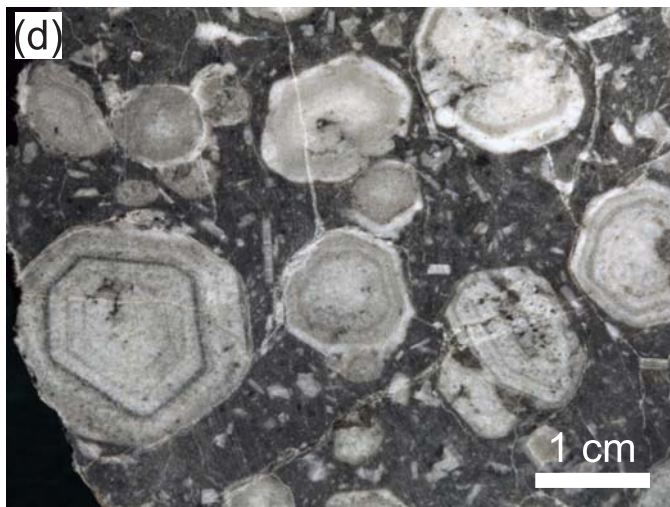
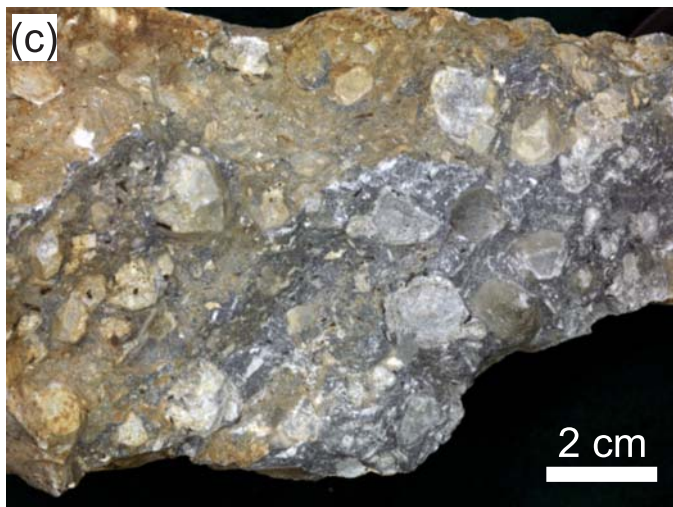
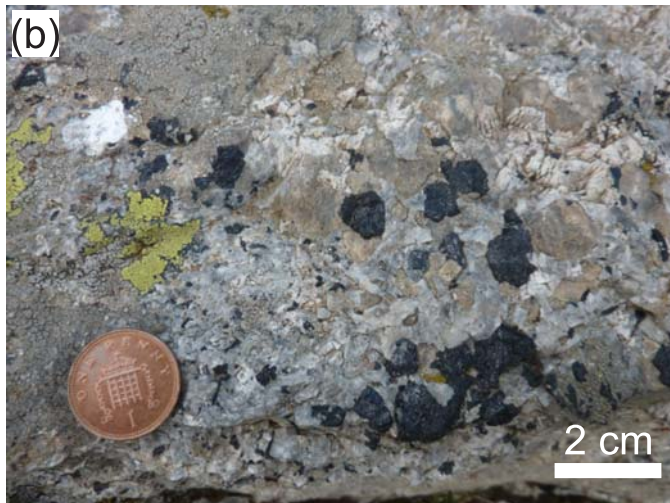


Figure 4

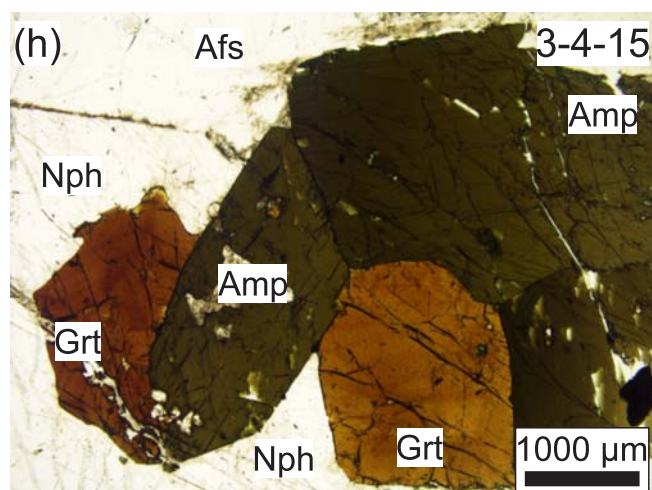
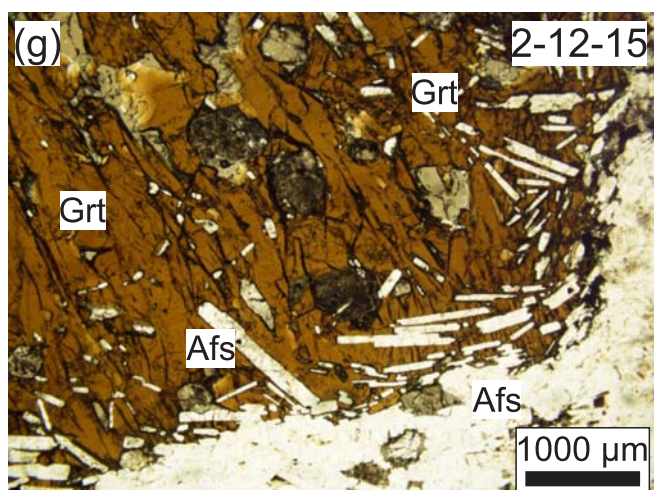
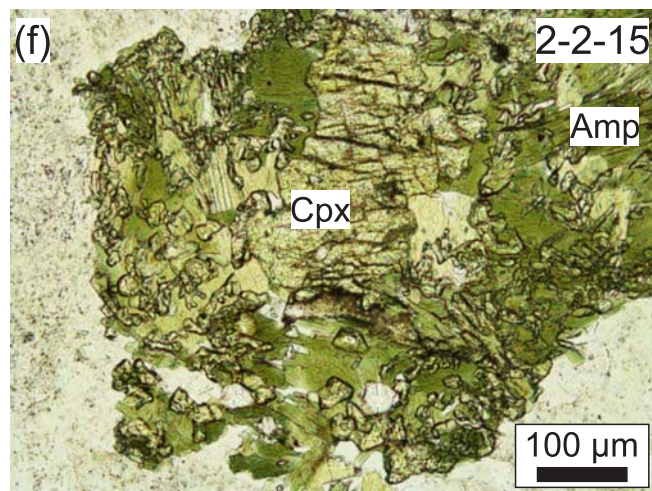
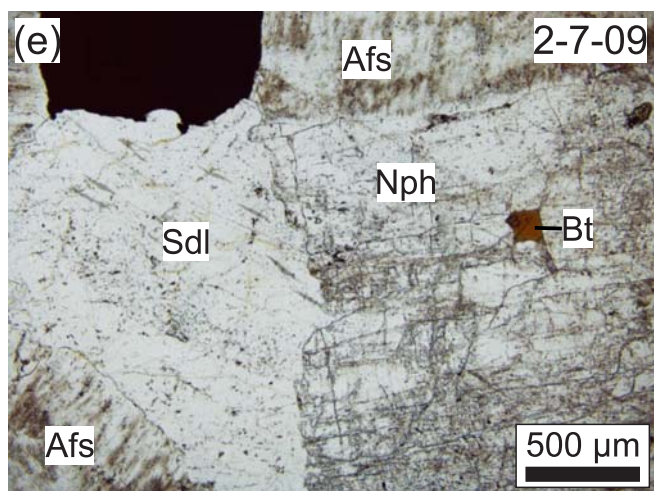
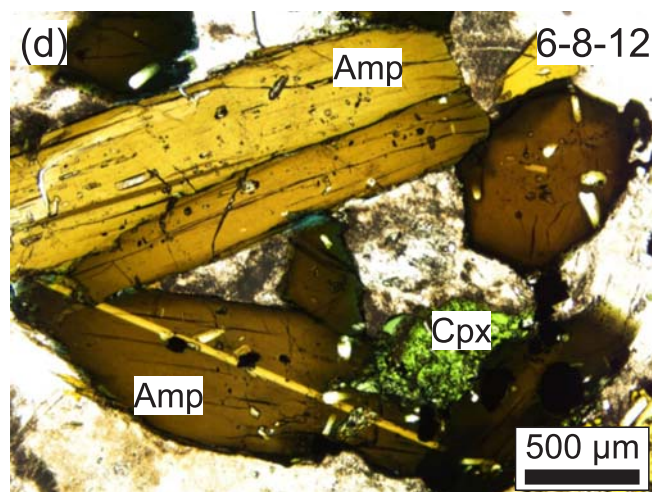
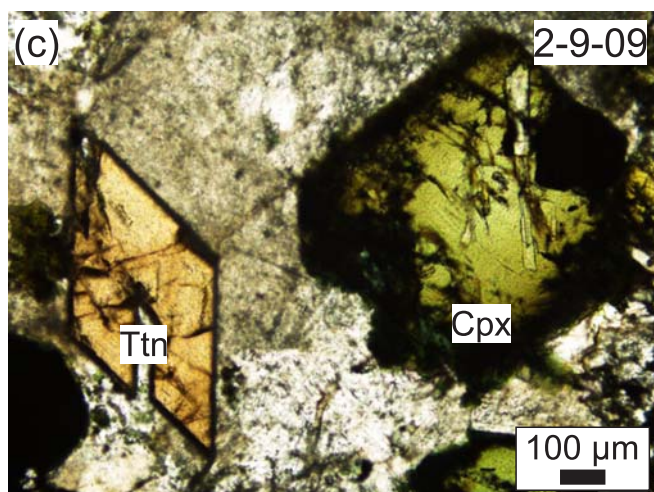
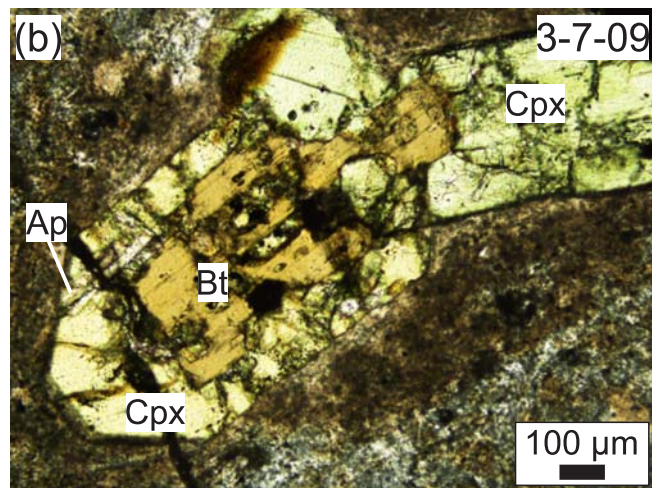
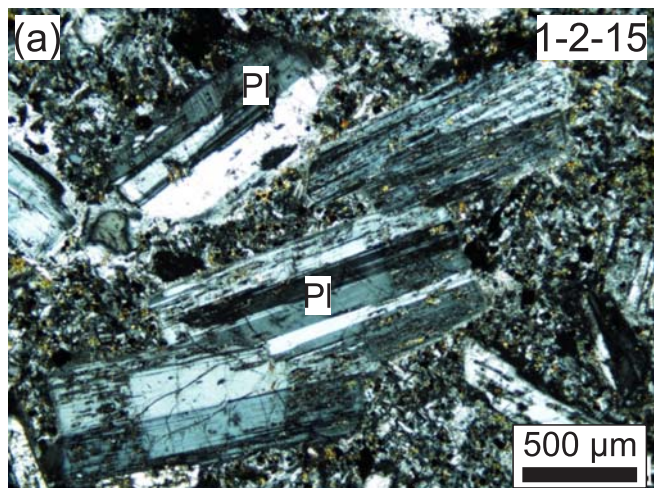


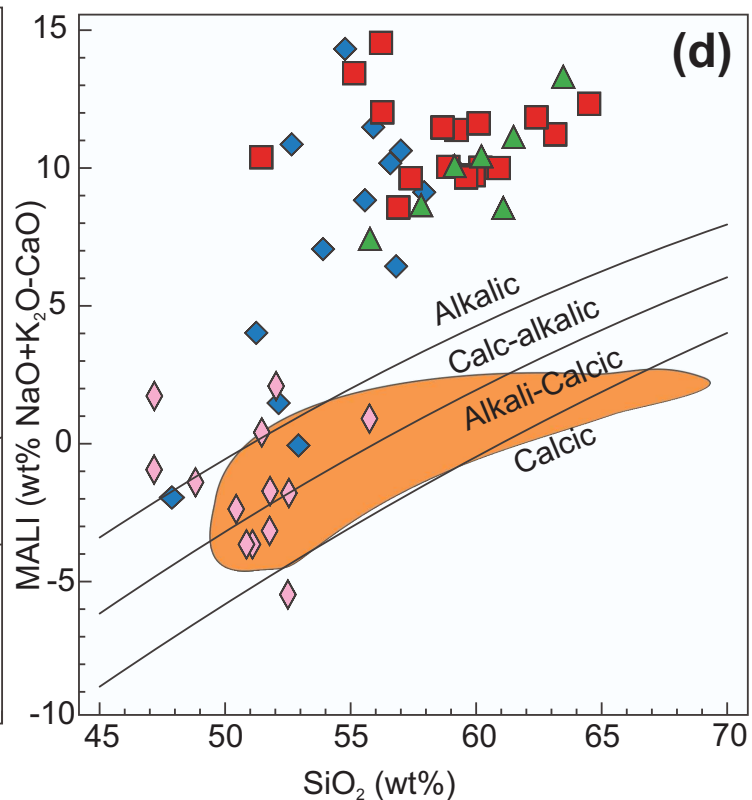
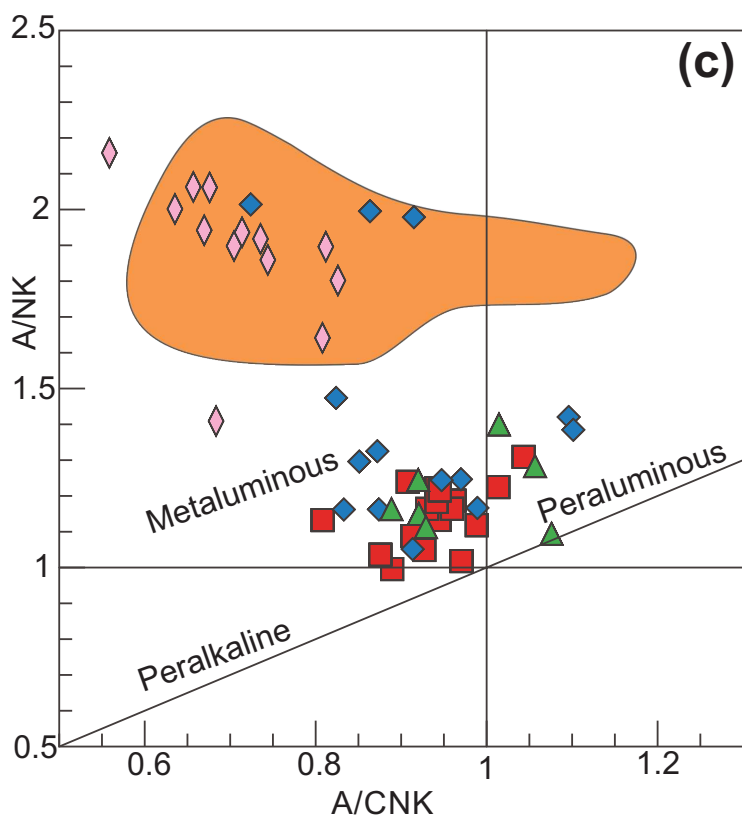
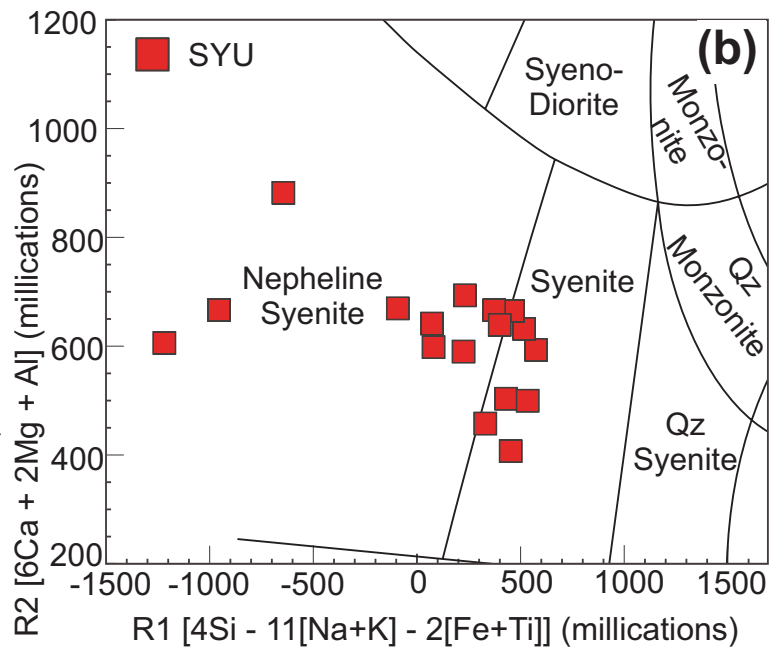
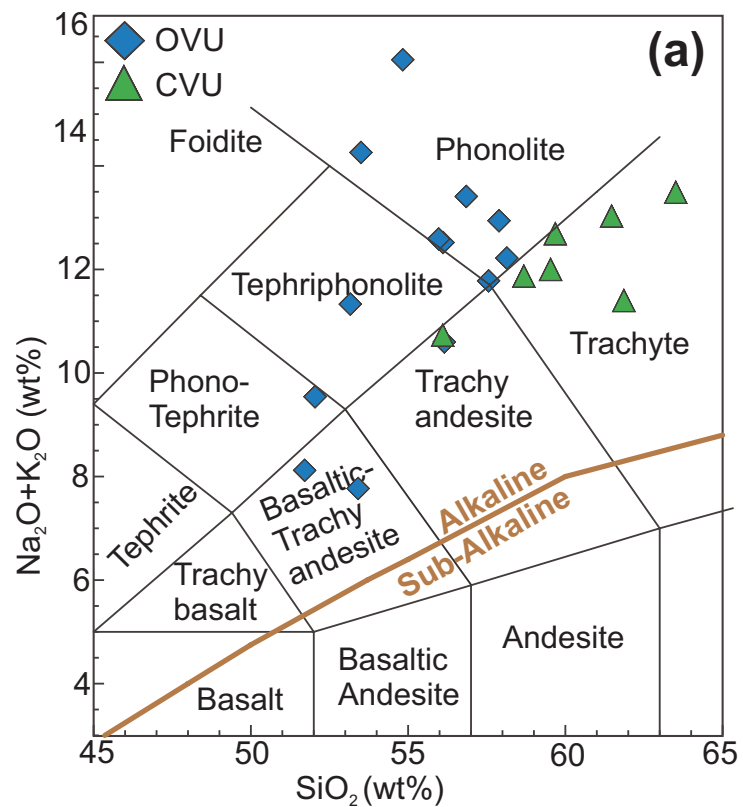
Figure 5

Figure 6

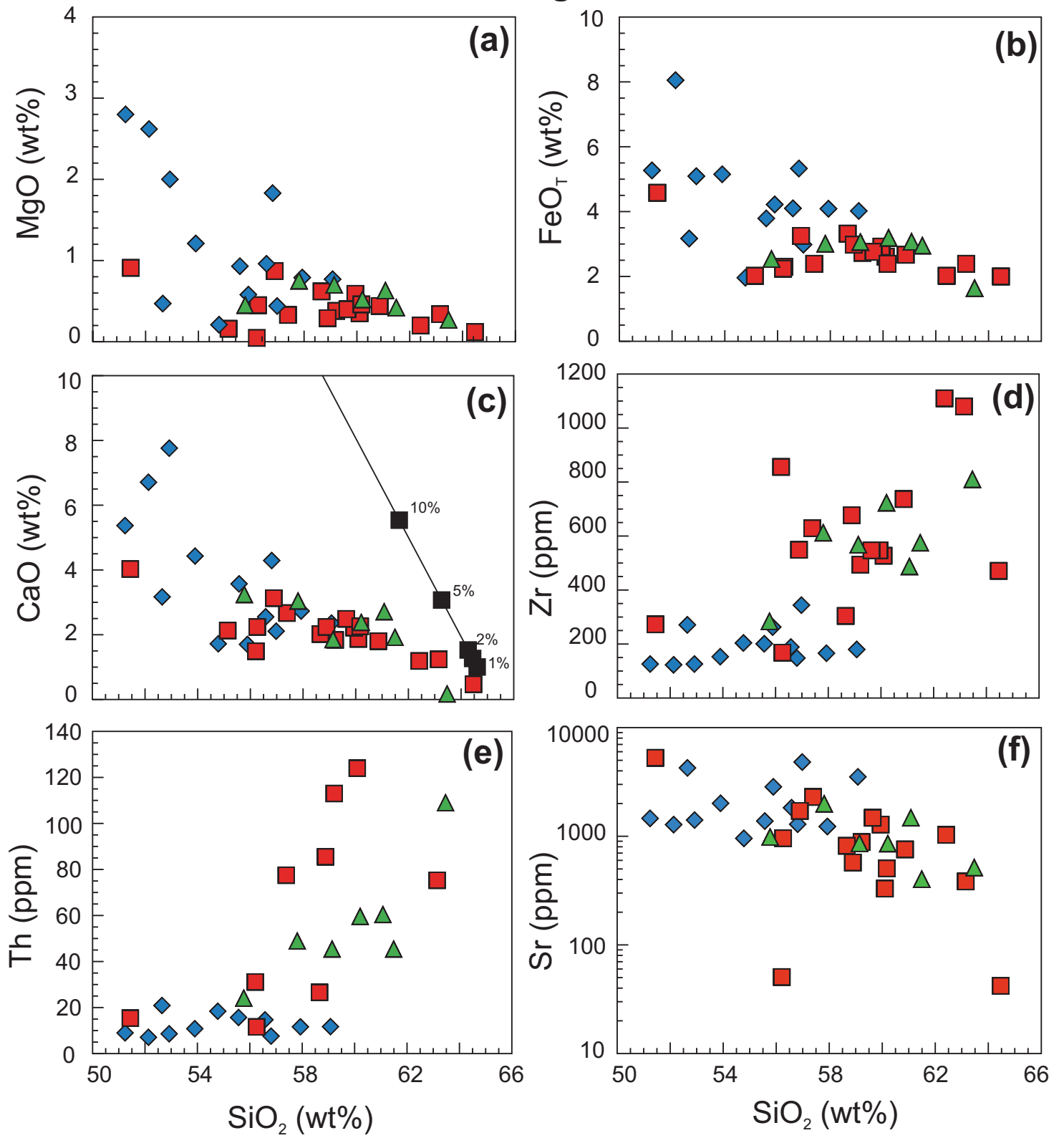


Figure 7

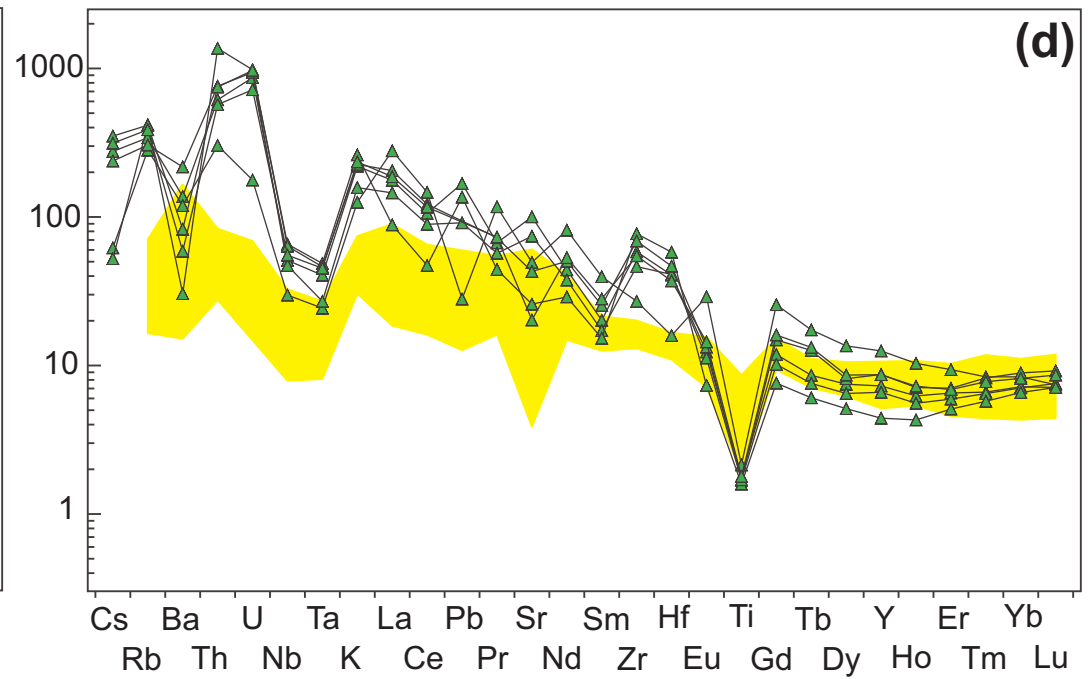
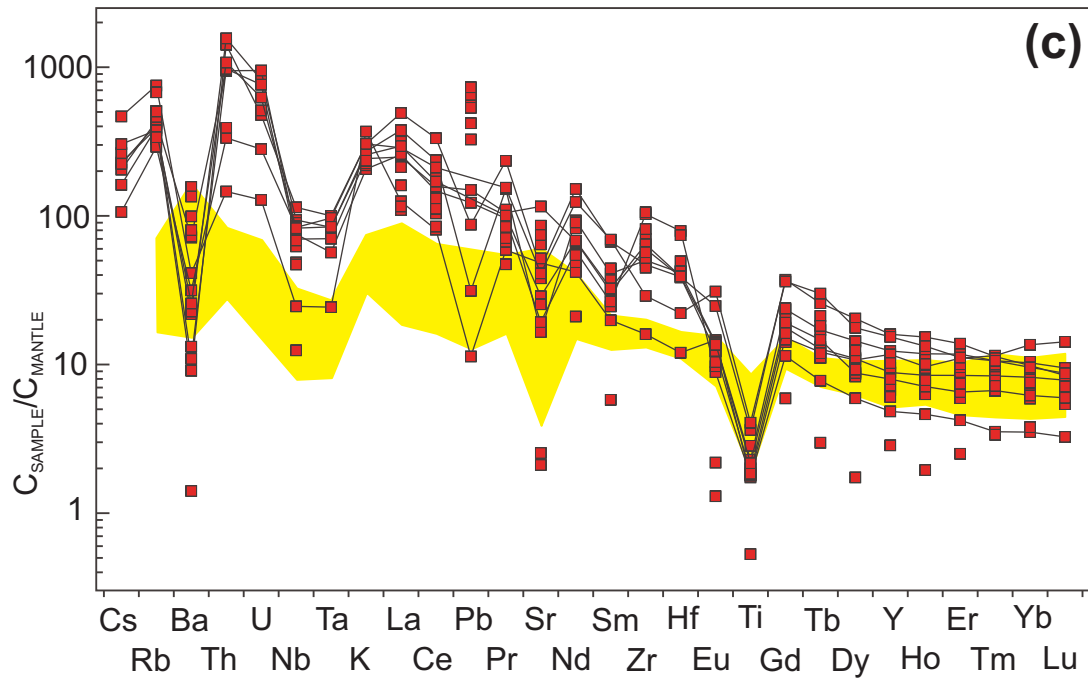
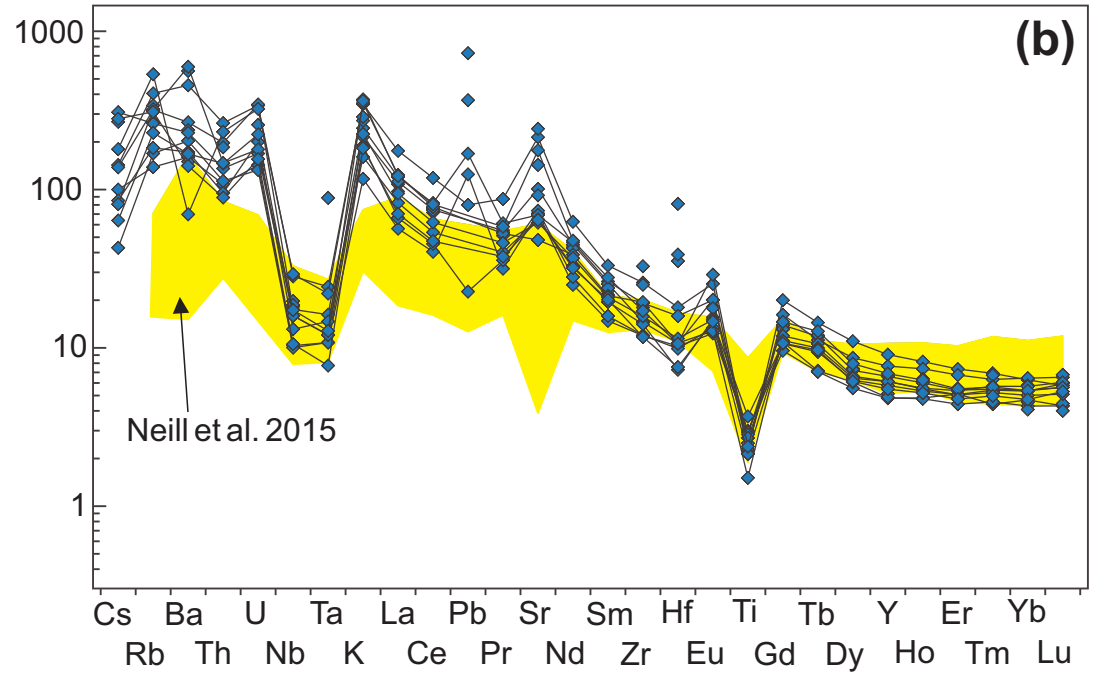
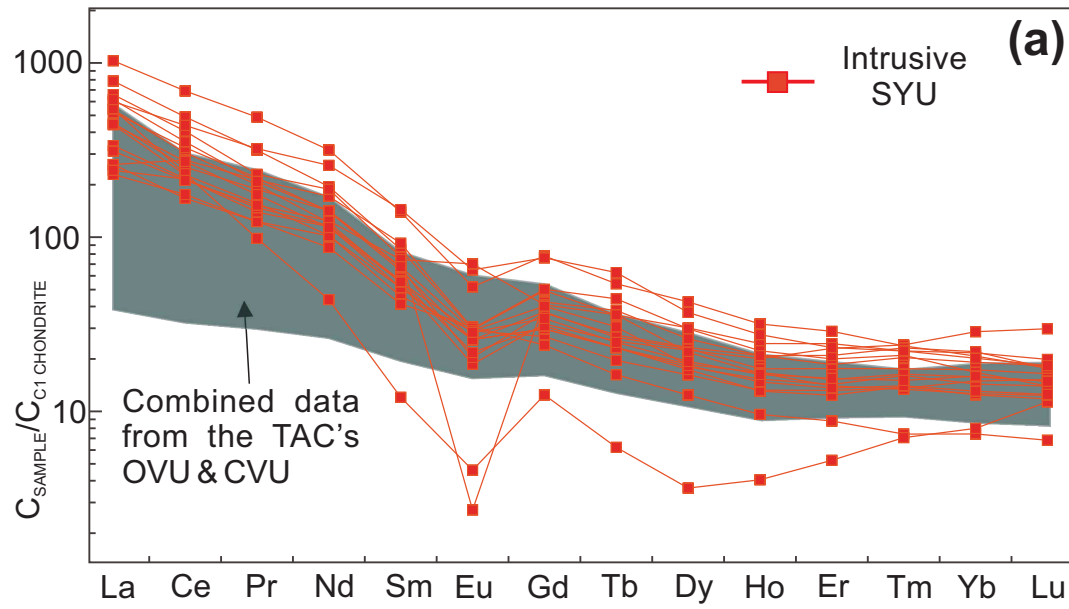


Figure 8

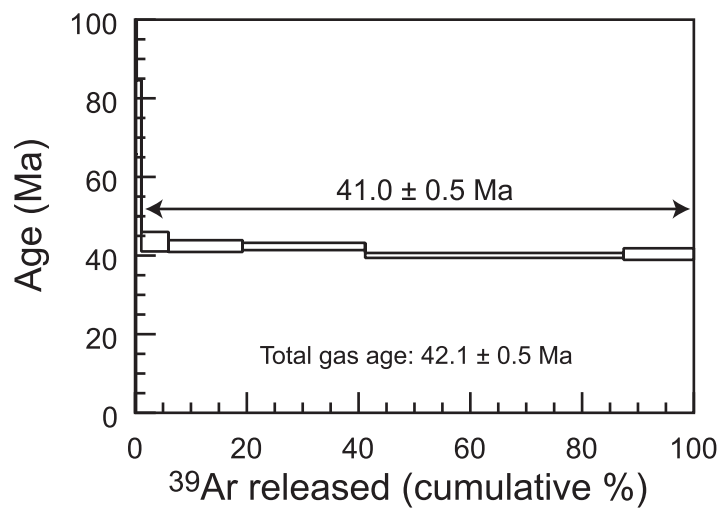


Figure 9

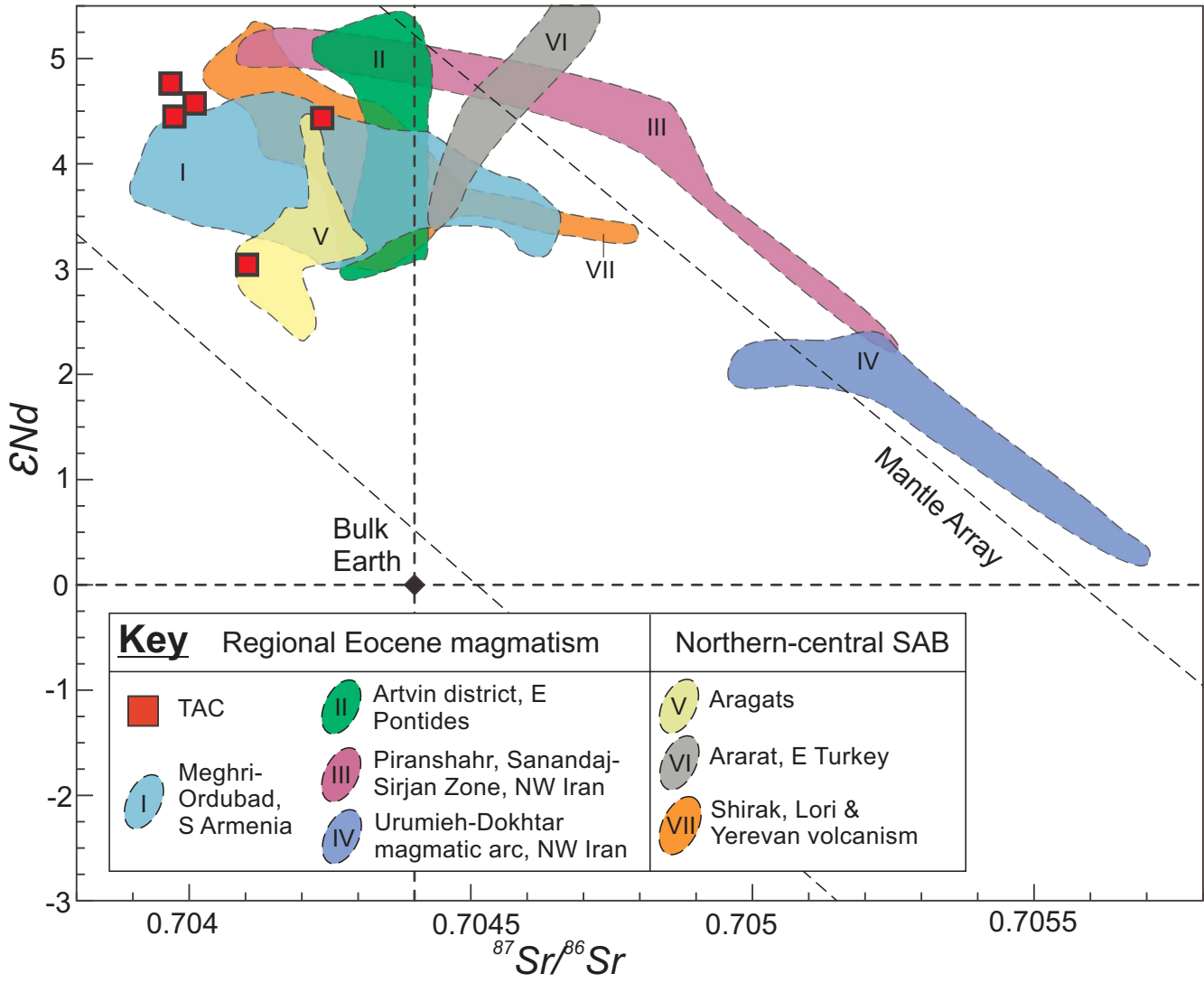


Figure 10

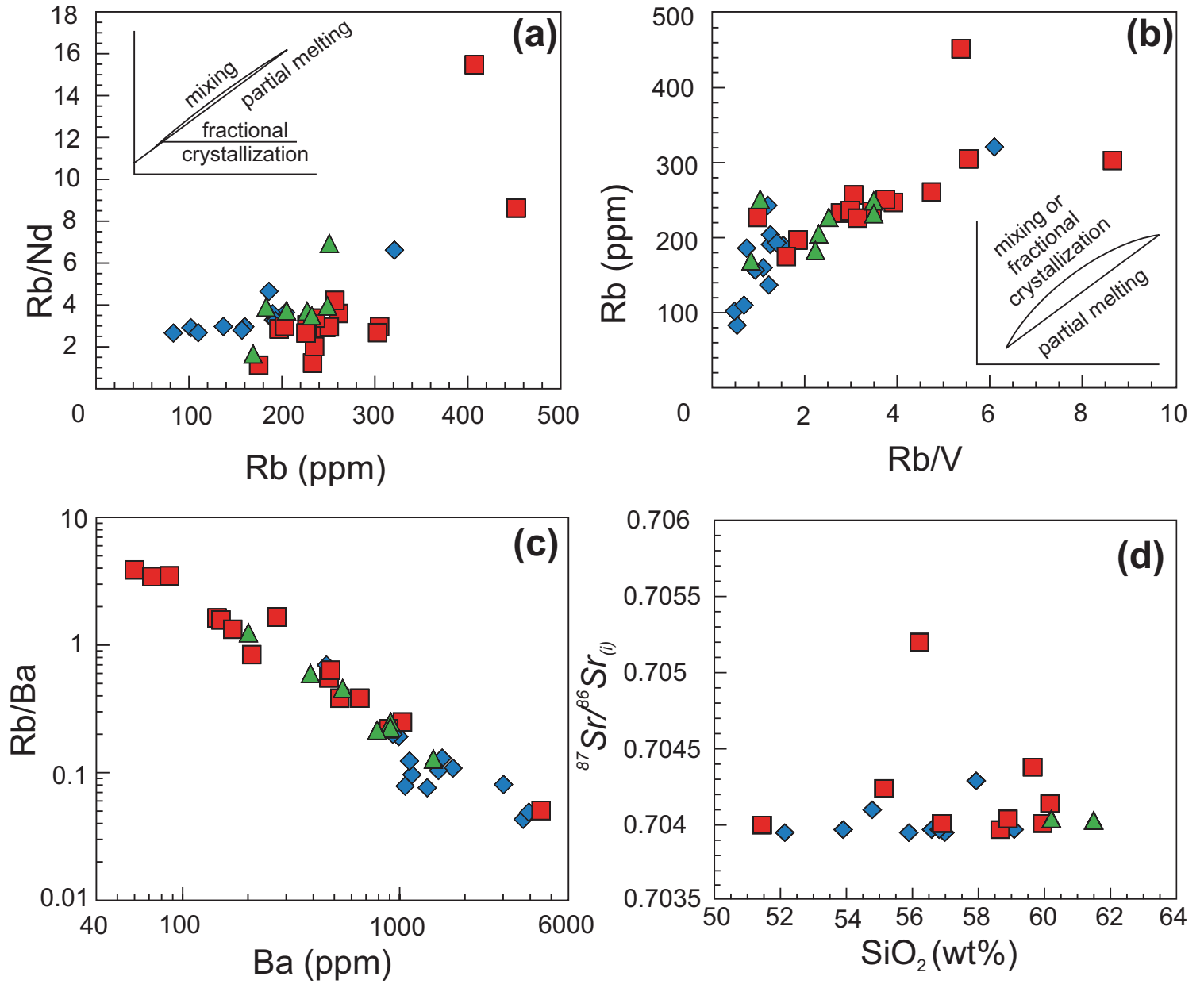


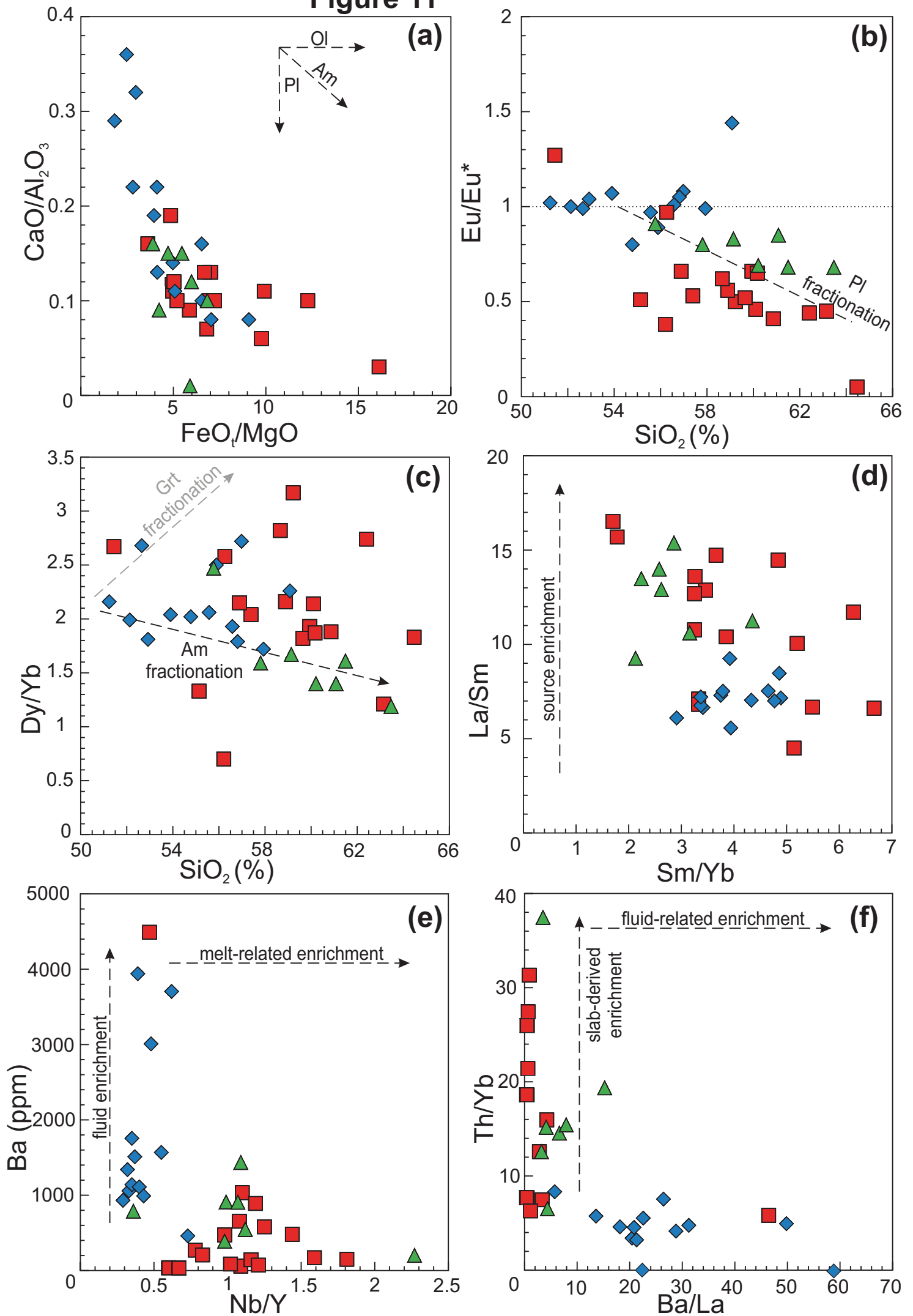
Figure 11

Figure 12

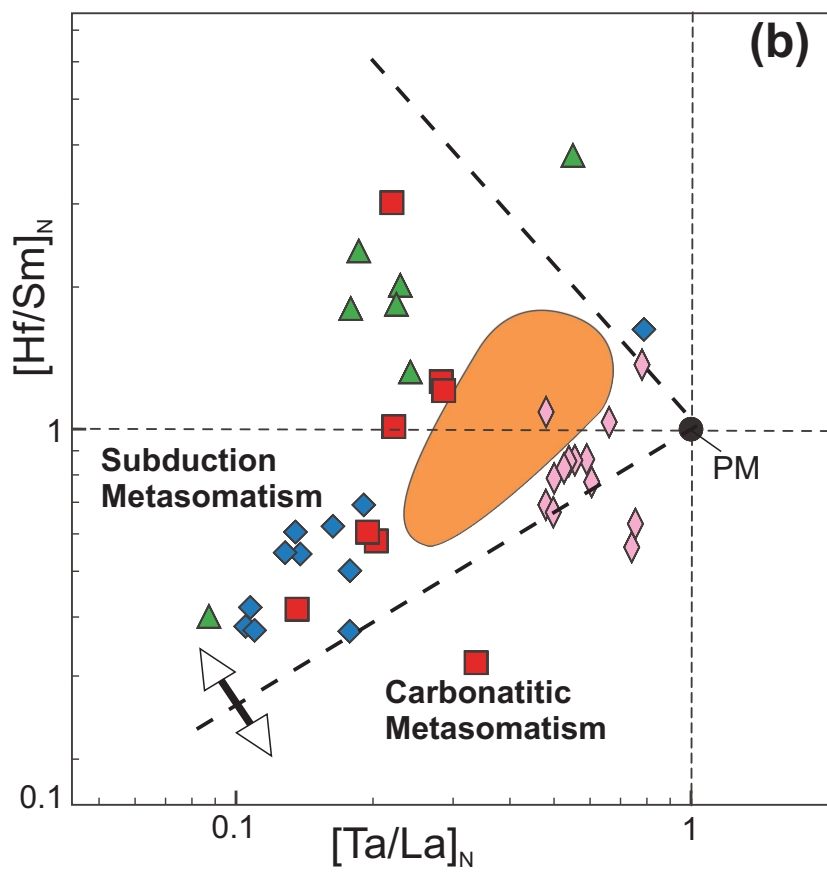
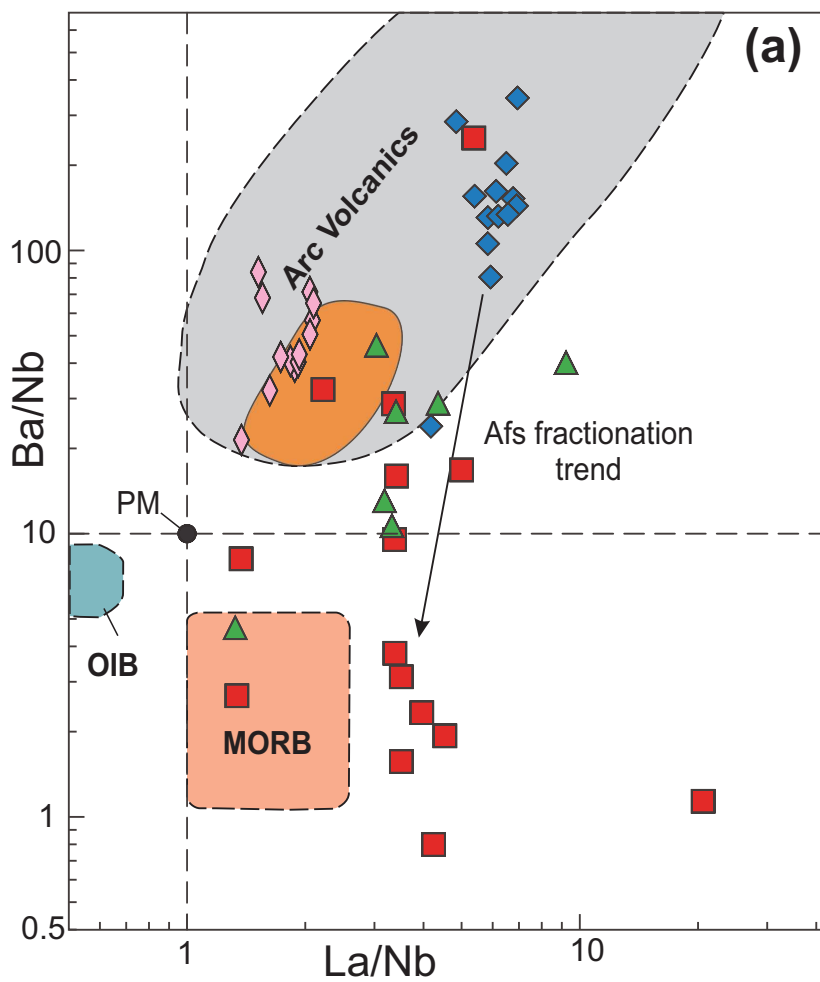


Figure 13

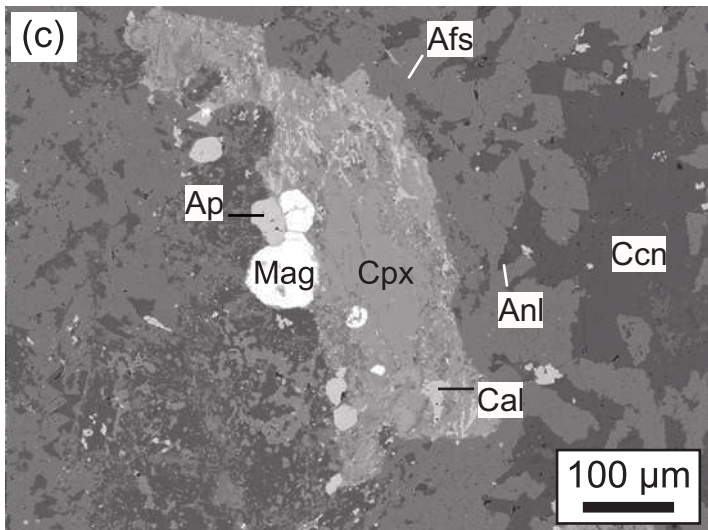
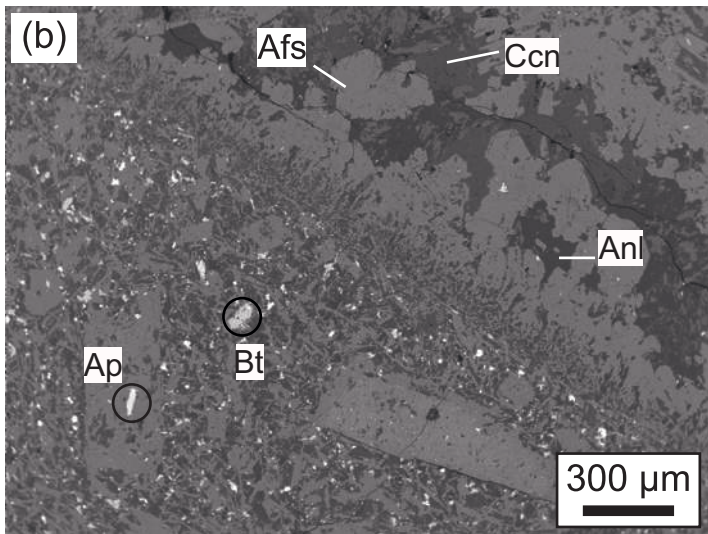
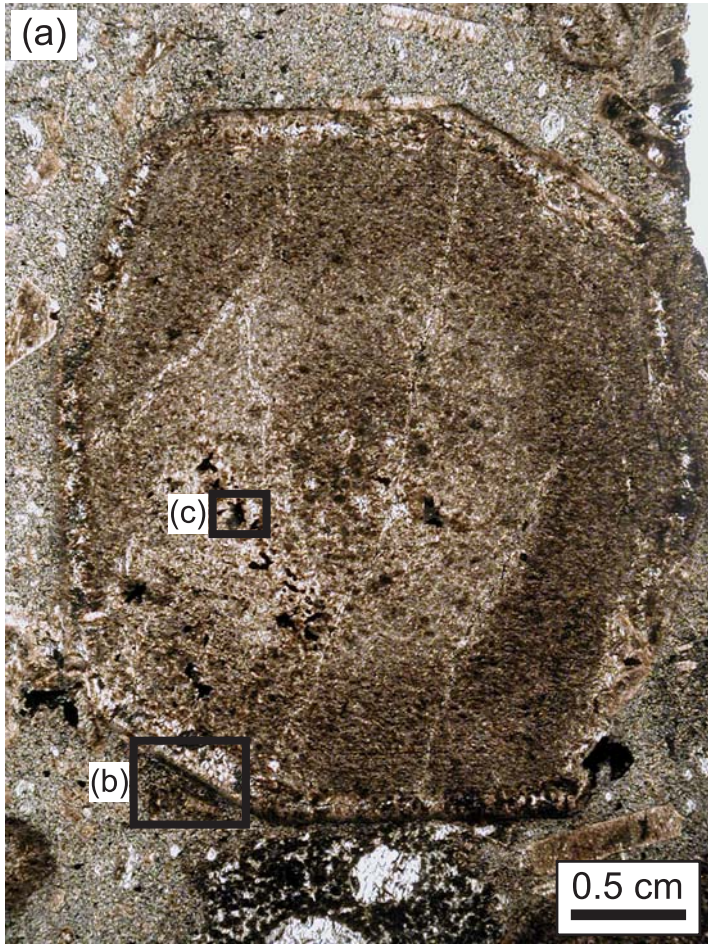


Table 2: Argon isotopic data for an amphibole separate of syenite sample 6-8-12.

TZ-6-8-12		Laboratory ID: C15038		Irradiation ID: PO-2														
$^{40}\text{Ar}/^{39}\text{Ar}$		$^{37}\text{Ar}/^{39}\text{Ar}$		$^{36}\text{Ar}/^{39}\text{Ar}$			K/Ca	$^{40}\text{Ar}^*$	$^{39}\text{Ar}_K$	$^{40}\text{Ar}^*/^{39}\text{Ar}_K$		Age		±	1s			
				(×10 ⁻³)				(%)	fraction (%)			(Ma)						
J=0.0009720																		
Laser output																		
1.8%	1397	±	251	7.4	±	137	3703	±	710.85	0.08	21.73	0.13	305	±	98	469	±	132
2.0%	1385	±	938	141	±	566	4558	±	3110	0.00	3.54	0.03	54	±	147	93	±	245
2.4%	352	±	60	6	±	149	919	±	203	0.10	22.92	0.14	81	±	44	137	±	71
2.8%	77	±	3	39	±	15	141	±	33	0.01	49.59	0.82	39	±	10	67	±	17
3.1%	37.0	±	0.4	7	±	4	42	±	5	0.09	67.55	4.85	25.1	±	1.4	44	±	2
3.3%	29.79	±	0.16	6	±	2	20	±	3	0.10	81.79	13.29	24.5	±	0.9	42.4	±	1.5
3.5%	29.80	±	0.14	1.6	±	1.7	18.7	±	1.7	0.37	81.82	21.93	24.4	±	0.5	42.3	±	0.9
3.7%	30.8	±	0.2	2.4	±	0.6	26.9	±	1.0	0.25	74.79	46.26	23.1	±	0.4	40.0	±	0.6
3.9%	31.1	±	0.4	2.4	±	1.9	27	±	3	0.25	74.67	12.56	23.3	±	0.9	40.4	±	1.5
												Total gas age		42.05	±	0.52		
												Plateau age (step 5-9: 98.8% of total ³⁹Ar)		40.96	±	0.46		
												Normal isochron age (step 5 to 9)		41.32	±	2.51		
												Inverse isochron age (step 5 to 9)		41.25	±	2.11		

Supplementary material

Whole rock major and trace element analyses

1. Royal Holloway University, London, UK

Fourteen samples were analysed by inductively coupled plasma atomic emission spectrometry (ICP-AES) for major elements and some high abundance trace elements (Sr, Zr, Cr, Sc, Zn, Co, Li, V, Be and Ni) and by inductively coupled plasma mass spectrometry (ICP-MS) for low abundance trace elements (Rb, Nb, Y, Mo, Cs, Ba, Hf, Ta, Tl, Pb, Th, U, and all REE) using a Perkin Elmer instrument. The analytical work followed the methodology described by Walsh et al. (1981) and Garbe-Schönberg (1993), respectively. The relative standard deviation (RSD) typically was $\leq 2\%$ for major elements and $\leq 5\%$ for minor and trace elements.

2. Institute of Geosciences, Kiel University, Germany

Three samples were analysed by X-ray fluorescence (XRF) on fused glass discs using a Philips PW1480 XRF spectrometer for major elements and by ICP-MS using an Agilent 7500c instrument for trace elements. For major element oxides, the RSD is $\leq 1.3\%$ based on multiple analyses of reference material BHVO-1. The RSD for trace elements is generally $\leq 2\%$ based on multiple analyses of one sample solution. Details about sample preparation and instrument calibration are given in Garbe-Schönberg (1993) and John et al. (2008), and representative data for precision and accuracy during the course of this study are provided by Laeger et al. (2013).

3. GeoForschungsZentrum (GFZ) Potsdam and Potsdam University, Germany

Nine samples were analysed for major and some trace elements (Ba, Cr, Ga, Nb, Ni, Rb, Sr, V, Y, Zn and Zr) by XRF using a Siemens SRS303-AS XRF spectrometer at the GFZ and for REE by ICP-AES using a Varian Vista MPX instrument following the methods described by Zuleger and Erzinger (1998). RSD values are in the range of 1-3% for major oxides and $\leq 5\%$ for trace elements and REE (Moazzen and Oberhänsli, 2008; Hadj Zobir et al., 2014).

4. AcmeLabs, Bureau Veritas Minerals, Vancouver, Canada

Fifteen samples were analysed for major elements by XRF using a Panalytical Axios Max instrument and by ELAN 9000 ICP-MS for trace elements and REE. The RSD is <1.2% for major oxides based on the analyses of SY-4(D) diorite gneiss and OREAS72B VMS ore standards, while for trace elements and REEs the RSD was <3.8%.

Strontium (Sr) and neodymium (Nd) isotope analyses

Strontium (Sr) and neodymium (Nd) isotope analyses were performed on a Thermo Finnigan Triton multicollector mass spectrometer at the School of Earth and Environment, University of Leeds. About 30 to 60 mg of powdered whole-rock material (same was used for the major and trace element work) was dissolved in concentrated ultra-clean HF-HNO₃-HCl acids and Sr and Nd were extracted from the unspiked solutions by conventional ion-exchange chromatographic techniques (see Halama et al. 2013 for details of the analytical protocol). ⁸⁷Sr/⁸⁶Sr and ¹⁴³Nd/¹⁴⁴Nd ratios were normalized for mass fractionation to ⁸⁶Sr/⁸⁸Sr = 0.1194 and ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219. The average ⁸⁷Sr/⁸⁶Sr obtained from replicate measurements of NIST SRM-987 during this study was 0.710254 and all data were corrected for the offset from the generally accepted value 0.710250 (McArthur et al. 2000). Similarly, Nd isotope data were corrected for the offset from the LaJolla reference material (¹⁴³Nd/¹⁴⁴Nd = 0.511853; Weis et al. 2005). Initial ⁸⁷Sr/⁸⁶Sr isotope ratios were calculated using the ⁸⁷Rb decay constant 1.3972 x 10⁻¹¹ a⁻¹ (Villa et al. 2015). For the calculations of the εNd values, the following parameters were used: ¹⁴⁷Sm decay constant λ = 6.54 x 10⁻¹² a⁻¹, present-day (¹⁴³Nd/¹⁴⁴Nd)^{CHUR} = 0.512638, (¹⁴⁷Sm/¹⁴⁴Nd)^{CHUR} = 0.1966.

⁴⁰Ar/³⁹Ar dating

About 1 mg of amphibole from syenite sample 6-8-12 was used for ⁴⁰Ar/³⁹Ar analysis by the CO₂ laser stepwise heating technique at the Institute of Earth and Environmental Science,

Universität Potsdam. For details of the analytical protocol see Wilke et al. (2010) and Halama et al. (2014). Mineral grains were obtained by crushing, sieving and selecting the size fraction between 250-500 μm mesh size for magnetic separation and finally by hand-picking under the binocular. Separated amphiboles were cleaned ultrasonically in 10% HNO_3 for 15 minutes and then washed in de-ionized water and dried. Samples, the Fish Canyon Tuff sanidine age standard, prepared by the Geological Survey of Japan (27.5 Ma: Uto et al., 1997; Ishizuka, 1998) and salts of K_2SO_4 and CaF_2 were irradiated at the Oregon State TRIGA Reactor for 4 hours under a neutron flux of $2.5 \times 10^{13} \text{ n cm}^{-2} \text{ s}^{-1}$. Argon isotope ratios of the gas from the samples were analyzed by stepwise heating until total fusion using a New Wave Research DualWave laser ablation system comprising a 50W CO_2 continuous laser with 10.6 μm wavelength. The extracted gas is purified in the ultra-high vacuum line via SAES getter pumps and a cold trap for 10 min. The high sensitivity Micromass 5400 noble gas mass spectrometer used for Ar isotopic analysis is equipped with an electron multiplier pulse counting system for analyzing small amounts of Ar. Raw data were corrected for procedural blank contributions, mass discrimination by analysis of atmospheric Ar, interferences of Ar isotopes derived from Ca and K and decay of radiogenic ^{37}Ar and ^{39}Ar isotopes produced by irradiation. Calculation of ages and errors was performed following Uto et al. (1997) using the total ^{40}K decay constant of $5.543 \times 10^{-10} \text{ a}^{-1}$ (Steiger and Jäger, 1977) as well as decay constants of $1.978 \times 10^{-2} \text{ d}^{-1}$ for ^{37}Ar and $2.58 \times 10^{-3} \text{ a}^{-1}$ for ^{39}Ar .

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