1 **Accessory mineral constraints on crustal evolution : elemental fingerprints for magma**
2 **discrimination**
3
4 Bruand Emilie, Fowler Mike, Storey Craig, Laurent Oscar, Antoine Clementine, Guitreau
5 Martin, Heilimo Esa, Nebel Oliver
6
7

8 Abstract
9 Somewhat less explored accessory minerals such as titanite and apatite have the potential to
10 give insights into the petrogenesis of their host rock. Their trace element and REE-rich
11 chemistries carry a record of crystallisation history and chemical characteristics of their source.
12 The robust nature of these phases make them ideal candidates to extract such information
13 from Archean rocks that have usually been affected by secondary processes (metamorphism,
14 deformation, hydrothermal activity). Moreover, they are resistant to erosion during multiple
15 sedimentary cycles which makes them ideal to reconstruct the history of long-eroded
16 continental landmasses. Here we report new trace element data on apatite and titanite from
17 granitoids of different Archean cratons and comparative granitoids from the Phanerozoic.
18 Trace elements signatures of both minerals reveal chemical systematics in Y, LREE and Sr
19 contents related to the nature of the host magma, which are used to construct discrimination
20 diagrams delineating Archean TTGs from sanukitoids, and modern adakites from S/I-type
21 granites.
22

23    1.  Introduction
24

25 Rare earth element (REE) bearing minerals have been used widely to date geological events
26 and to understand magmatic petrogenesis. Their ability also to incorporate a range of trace
27 elements in addition to REE make them extremely useful to track geological processes. In the
28 last decade, most studies on accessory minerals have focussed on zircon (e.g. U-Pb, Hf
29 isotopes, O isotopes, trace elements), but the development of in-situ techniques has allowed
30 other phases to be dated (e.g. monazite, Parrish 1990, apatite, Chew et al. 2011), thus
31 providing additional chronological constraints on host rock history. However, despite the
32 impressive number of studies on accessory minerals available today (see Nasdala et al. 2017),
33 knowledge of the behaviour of trace elements within accessory minerals in rocks that make up
34 the continental crust is still limited. The few contributions focussing on less-studied REE-
35 bearing minerals (e.g. apatite and titanite) have shown that trace element concentrations retain
36 considerable information relevant to petrogenesis and provenance. In experimental work
37 focussing on metaluminous compositions, Protwake and Klemme (2005, 2006) have

38    suggested that REE and other trace elements are sensitive to melt evolution. Others (e.g.
39    Belousova et al. 2002; Chu et al. 2009; Jennings et al. 2011; Bruand et al. 2014) have shown
40    that accessory mineral chemistry provides useful information about petrogenetic process and
41    can closely reflect parent magma composition. Recent publications based on a small number
42    of samples (Bruand et al. 2016; 2017; 2019) have shown that apatite and titanite trace element
43    chemistry and isotope systematics have the potential to discriminate different granite types
44    relevant to the ongoing debate about secular evolution of the early Earth and the onset of
45    modern plate tectonics. For this contribution, we have studied the chemical signatures of
46    accessory minerals in a range of granitoids through time, from a relatively hot Archaean Earth
47    producing «tonalites-trondjhemites-granodiorites» (TTG) toward a cooler modern Earth
48    producing plutonic equivalents of the calc-alkaline series (basalt-andesite-dacite-rhyolite –
49    BADR), via the Neoarchaean – Palaeoproterozoic transition to modern tectonics signalled by
50    sanukitoids and related rocks. We demonstrate that their trace element signatures can be used
51    to discriminate between critical magma types and can be robust with respect to metamorphism.
52    We then discuss the causes of consistent differences in accessory mineral chemistry and
53    implications of their robust discrimination for studies of historical evolution of continental crust,
54    for example quantitative source apportionment within mixed-provenance samples provided by
55    the sedimentary cycle (in the manner of detrital zircons).
56
57        2.  Granite samples and their crustal evolution context
58
59    The granitoid record (Fig. 1) has evolved from TTGs throughout the Archean, the products of
60    partial melting of basaltic composition  mafic crust, via sanukitoids and related rocks in the
61    Neoarchean and Palaeoproterozoic that carry the signature of a nascent mantle wedge,
62    towards granodiorites and granites with arc magma compositions (the plutonic equivalents of
63    BADR) plus the typical products of crustal differentiation (S-type granites). Many fundamental
64    questions remain regarding the geodynamics of the early Earth, the growth of the continental
65    crust and the transition to subduction-driven tectonics, some of which may be addressed with
66    a more complete understanding of timings and proportions of granitoid magma genesis. Here
67    we present new geochemical data on titanite and apatite from granitoids selected from this
68    overall temporal progression (i) Archean TTG from three different cratons (Slave Province,
69    Karelia and Kaapvaal), (ii) sanukitoids from the Karelia and Kaapvaal cratons, (iii)
70    Neoproterozoic calc-alkaline granitoids from Guernsey (UK Channel Islands) in the Armorican
71    terrane. In addition to these, we have included likely Phanerozoic equivalents to test the impact
72    of metamorphism on their older counterparts: TTG-like (adakites from Antarctica) and
73    sanukitoid-like (high Ba-Sr granites from Caledonian Scotland). Detailed sample descriptions,
74    geological settings and whole-rock compositions can be found in Supplementary Information.

75

76    3.  Results

77

78    LA-ICPMS chemical data and related analytical protocols obtained are described in
79    Supplementary Information. After initial data interrogation using principal component analysis
80    (PCA), REEs, Y and Sr were found to be most effective for discriminating magma type, so
81    these results are presented and discussed below.

82

83    3.1. Apatite chemistry

84

85    Chondrite-normalized REE patterns of apatite from all studied samples are plotted on Figure
86    2A-E. TTG samples (Fig. 2A) are characterized by a systematic depletion in light REE (LREE)
87    relative to heavy REE (HREE) usually with a significant negative Eu anomaly. The most
88    depleted patterns tend to have a less pronounced to absent Eu anomaly and significant middle
89    REE (MREE) fractionation from HREE. Adakite (TTG-like) apatites (Fig. 2B) have a relatively
90    flat LREE pattern with slightly lower HREE and a significant Eu anomaly. Typical BADR REE
91    patterns (Fig. 2C) show higher LREE content with strong enrichment compared to the HREE,
92    with moderate negative Eu anomalies. Similarly, sanukitoids and high Ba-Sr granite REE
93    patterns (Fig. 2 D-E) reveal a general enrichment in LREE relative to HREE usually with
94    moderate negative Eu anomalies. In the high Ba-Sr group, the most mafic samples often lack
95    Eu anomalies.
96    Following the PCA procedure, a 10*Sr-LREE-10*Y discrimination diagram was constructed
97    (Fig. 3A). Apatite from TTG and TTG-like granitoids are clearly distinguishable from other
98    granite types, defining a distinct cluster towards the 10*Y corner. On the other hand,
99    sanukitoids, sanukitoid-like and BADR samples are characterized by higher LREE and Sr
100   contents and thus form a separate field towards that baseline. Similarly, a $La_N/Sm_N$ versus Y
101   diagram (Fig. 4A) highlights a strong compositional difference. TTG and TTG-like apatites are
102   Y rich (up to 4566 ppm) with low $La_N/Sm_N$ (< 3), while sanukitoid, high Ba-Sr granite and BADR
103   apatites define a field poor in Y (<1000 ppm) and with $(La/Sm)_N$ up to 19.

104

105   3.2. Titanite chemistry

106

107   REE patterns of titanite from the studied samples are presented in figure 2G-J, although titanite
108   is not present in all studied samples (see supplementary information). There are many
109   similarities with those for apatite (Fig. 2A-E). Titanites from one TTG sample (Fig. 2G) are
110   characterized by pronounced LREE depletion relative to HREE. In contrast with apatite, the
111   patterns have variable, usually large Eu anomalies, generally negative for those with higher

112  total REE, positive for lower total REE. Titanite from sanukitoids and high Ba-Sr granites (Fig.

113  2H-I) show strong enrichment of LREE relative to HREE, usually with a convex-upward LREE

114  section and a significant negative Eu anomaly. A few sanukitoid titanites in each of the samples

115  studied have steep downward LREE slopes and/or a positive Eu anomaly (Fig. 2H). The BADR

116  REE patterns (Fig. 2J) are closely comparable with the high Ba-Sr samples, but can be

117  separated into two groups that are sample specific. Sample EG-07 titanites have convex-

118  upward LREE and a negative Eu anomaly while one from sample BD-02 has continually

119  decreasing LREE with no Eu anomaly (Fig. 2J, Appendix A.1).

120     Using a similar trivariate diagram  to apatite (Fig. 3B, but note the different Sr multiplier),

121  TTG titanite compositions may be discriminated from all other samples, which themselves

122  overlap – as for apatite. Titanite from TTG define an end member  with high Y and low Sr and

123  LREE contents relative to sanukitoids and BADR samples.

124

125     4. Discussion

126

127  The temporal evolution of granitoids has been well established (Fig. 1, see also Moyen and

128  Martin 2012 for review). TTGs can be discriminated on the basis of several whole-rock

129  chemical indicators, the most obvious of which is strong HREE depletion (Fig.2F). The present

130  study has also shown systematic differences in TTG apatite and TTG titanite compositions

131  relative to sanukitoids and post-Archean granitoids (Figs 2-3), in particular higher Y and HREE

132  contents with low $La_N/Sm_N$ ratio (Fig. 2, 4A). Intriguingly, this is opposite to the whole-rock

133  discrimination (Fig. 2F). In the following text, we attempt to rationalise such observations in

134  terms of possible controls on apatite and titanite chemistry, and in the light of current literature.

135

136  4.1 Effects of metamorphism and/or deformation

137

138  Most Archean rocks have been affected by metamorphism and deformation, so there is the

139  obvious possibility that accessory mineral chemistry has been modified, whereby magmatic

140  crystal-liquid equilibration gives way to metamorphic mineralogical control. The few studies

141  availaible (e.g. Bea and Montero 1999; Garber et al. 2017) describe lithologies (metapelites or

142  orthogneisses) that are very different from our samples. Therefore, in order to test the

143  robustness of magmatic signatures, we have analysed Phanerozoic equivalents of TTG

144  (adakite) and sanukitoid (high Ba-Sr granites), unaffected by any metamorphic event. Their

145  chondrite-normalized REE patterns correspond closely to the Archean equivalents (Fig. 2) and

146  overlap the relevant fields on the discrimination diagrams above (Fig. 3, Fig. 4A).

147     A few TTG apatite patterns show extreme depletion in LREE with no Eu anomaly (Fig

148  2A). Recent work by Antoine et al. (submitted) on apatite inclusions armoured within TTG

149  zircons have the same signature as our most enriched patterns while matrix apatites can also
150  display strong LREE-depletion. This can be explained petrographically, by the observed
151  association of secondary allanite and apatite. The highly LREE-depleted group is therefore
152  interpreted to result from high grade metamorphism, such that typical metamorphic apatite
153  has reduced $La_N/Sm_N$ but retains original HREE signatures.
154
155  4.2 Effects of whole-rock composition
156
157  The systematic chemical differences between the accessory mineral groups studied here, from
158  different types of granitoid, strongly suggest that bulk rock character exerts strong control.
159
160  4.2.1 The influence of whole rock $SiO_2$
161
162  Partition coefficient studies have shown that the magmatic incorporation of REE in apatite and
163  titanite increases with $SiO_2$ (Prowatke and Klemme 2006a,b). TTGs studied herein vary
164  between 65 wt% and 74 wt% $SiO_2$, the other granitoids range between 53 and 77 wt%. Within
165  the former, apatite and titanite total REE contents do not systematically increase with $SiO_2$
166  (Appendix A.1). Furthermore, sanukitoid or BADR samples with similar $SiO_{2WR}$ have apatite
167  and titanite characterised by comparatively higher LREE and lower HREE. Such systematic
168  differences are therefore not controlled simply by silica content.
169
170  4.2.2 The influence of Alumina Saturation Index (ASI).
171
172  The striking dichotomy in the TTG between LREE depletion in the accessory minerals and
173  LREE enrichment in whole rocks suggests that another LREE-bearing phase is required for
174  mass balance. Likely contenders would be allanite and monazite, but since these are also
175  common in many other granitoid types, this is unlikely to be the sole explanation.
176  Figure 4A includes literature data (Sha and Chappell 1999; Belousova et al. 2001; Miles et al.
177  2013), and highlights the presence of two distinct groups of apatite that are strongly dependent
178  on ASI. ASI < 1 samples (metaluminous) correspond to our sanukitoids-BADR apatites (Group
179  1), whereas peraluminous samples (ASI >1) have a comparable chemical signature to TTG
180  apatites (low LREE and high HREE-Y, Group 2). This corroborates previous studies on apatite
181  (Harrison and Watson 1984; Pichavant et al. 1992) and monazite (Montel 1986) solubilities,
182  which suggest that apatite solubility increases with ASI and (to a lesser extent) with $SiO_2$ in
183  metaluminous magmas. Conversely, Montel (1986) has shown that monazite solubility
184  decreases as ASI increases. Therefore, in peraluminous compositions early monazite will

185   strongly partition LREE with the remaining melt relatively enriched in HREE and Y, which will
186   be incorporatred by later apatite and titanite.

187

188        Interestingly, apatites from two metaluminous samples are Y-rich and LREE poor (Fig.
189   4A), which is inconsistent with the general trend. These exceptions have the highest $SiO_2$
190   content (>73 wt%), a phenomenon also described by Sha and Chappell (1999). High melt $SiO_2$
191   content increases apatite solubility (Harrison and Watson 1984) and therefore delays its
192   saturation. Consequently, apatite may grow late, allowing early LREE phases (monazite and/or
193   allanite) to incorporate most of the LREE.

194

195   4.2.3 Other variables

196

197   We have shown above that aluminosity and consequent timing of mineral saturation is a first
198   order control. However, our TTG apatite compositions have systematically even lower LREE
199   concentrations than published data for peraluminous rocks (Fig. 4A) so other variables must
200   also be important. For example, previous authors have inferred that differences in magmatic
201   apatite composition could be related to magma $fO_2$ (Sha and Chappell 1999; Belousova et al.
202   2001). It remains unclear whether this is linked to TTG source parameters (e.g. composition,
203   $fO_2$, temperature, $H_2O$-saturated or undersaturated melting) or is another effect of co-
204   crystallising accessory phases. Experimental constraints are currently lacking.

205

206   4.2.4 The significance of Sr

207

208   In this section, we rationalise the utility of Sr concentration in apatite and titanite, in association
209   with REEs to discriminate magma type. Previous work has distinguished high-pressure TTG,
210   corresponding to a deep source in equilibrium with garnet and rutile but no plagioclase, from
211   low-pressure TTG consistent with residual plagioclase. As a direct consequence of residual
212   mineralogy, HP-TTG have low HREE, Nb and Ta and high Sr while LP-TTG show the opposite
213   signature for comparable bulk compositions. Previous authors (Belousova et al. 2001;
214   Jennings et al. 2011; Bruand et al. 2014) have shown a strong correlation between Sr in apatite
215   and in the corresponding whole-rock. Accordingly, in our apatite dataset, two TTG and our
216   adakite samples that have typical HP-TTG signature have systematic higher Sr concentrations
217   than the others that have MP-LP TTG signature (Fig. 4C). Figure 4C also shows that the HP-
218   TTG apatites have lower Y (and by analogy, HREE). All these observations confirm that apatite
219   Sr content can allow discrimination between HP and LP TTG.

220

221   4.4 Implications for historical evolution of continental crust

223    The preservation of magmatic trace element signatures in apatite and titanite from

224    metamorphosed terranes provides a new methodology to  reconstruct their magmatic history.

225    In addition, the ability to distinguish parent magma type encourages application to the detrital

226    mineral record. Voluminous data exist from zircons, but the results described above promise

227    much tighter constraints on parent rock identity, thus providing vital access to the primary

228    history of old eroded terranes and helping to reconstruct the parameters of the historical

229    evolution of continental crust from the early Earth to the present day.

230

231 **Figure Captions**

232 Fig. 1 Cartoon of continental crust evolution, from TTG and sanukitoid in the Archean

233 towards typical arc magma in the Phanerozoic, plus samples studied in this contribution.

234 Fig. 2 Chondrite-normalised REE patterns for apatite (A-E) and titanite (G-J). F is modified

235 after Moyen and  Martin (2012).

236 Fig. 3 Ternary discrimination diagrams; 10*Sr-LREE-10*Y for apatite and 100*Sr-LREE-10*Y

237 for titanite.

238 Fig.4 Apatite compositions: A - La vs Y diagram discriminating 2 groups of apatite, B -

239 $La_N/Sm_N$ vs ASI (nAl/((nCa-3.33*nP)+nNa+nK))),discriminating peraluminous from

240 metaluminous compositions and C - Sr vs Y, discriminating HP- and LP-TTG magmas.

241

242 **References**

243 Antoine, C., Bruand, E., XX

244 Bea F, Montero P (1999) Behavior of accessory phases and redistribution of Zr, REE, Y, Th,

245      and U during metamorphism and partial melting of metapelites in the lower crust: An

246      example from the Kinzigite Formation of Ivrea-Verbano, NW Italy. Geochim Cosmochim

247      Acta 63:1133–1153. doi: 10.1016/S0016-7037(98)00292-0

248 Belousova E, Griffin W, O'Reilly SY, Fisher N (2002) Igneous zircon: trace element

249      composition as an indicator of source rock type. Contrib to Mineral Petrol 143:602–622.

250      doi: 10.1007/s00410-002-0364-7

251 Belousova EA, Walters S, Griffin WL, O'Reilly SY (2001) Trace-element signatures of

252      apatites in granitoids from the Mt Isa Inlier, Northwestern Queensland. Aust J Earth Sci

253      48:603–619. doi: 10.1046/j.1440-0952.2001.00879.x

254 Bruand E, Storey C, Fowler M (2016) An apatite for progress: Inclusions in zircon and titanite

255      constrain petrogenesis and provenance. Geology.

256 Bruand E, Storey C, Fowler M (2014) Accessory mineral chemistry of high Ba-Sr granites

257      from Northern Scotland: Constraints on petrogenesis and records of whole-rock

258      Signature. J Petrol. doi: 10.1093/petrology/egu037

259    Chew DM, Sylvester PJ, Tubrett MN (2011) U-Pb and Th-Pb dating of apatite by LA-ICPMS.
260        Chem Geol 280:200–216. doi: 10.1016/j.chemgeo.2010.11.010
261    Chu MF, Wang KL, Griffin WL, et al (2009) Apatite composition: Tracing petrogenetic
262        processes in Transhimalayan granitoids. J Petrol 50:1829–1855. doi:
263        10.1093/petrology/egp054
264    Garber JM, Hacker BR, Kylander-Clark ARC, et al (2017) Controls on Trace Element Uptake
265        in Metamorphic Titanite : Implications for Petrochronology. J Petrol 58:1031–1058. doi:
266        10.1093/petrology/egx046
267    Harrison TM, Watson EB (1984) The behavior of apatite during crustal anatexis: Equilibrium
268        and kinetic considerations. Geochim Cosmochim Acta 48:1467–1477. doi:
269        10.1016/0016-7037(84)90403-4
270    Jennings ES, Marschall HR, Hawkesworth CJ, Storey CD (2011) Characterization of magma
271        from inclusions in zircon: Apatite and biotite work well, feldspar less so. Geology
272        39:863–866. doi: 10.1130/G32037.1
273    Li H, Hermann J (2017) The e ff ect of fl uorine and chlorine on trace element partitioning
274        between apatite and sediment melt at subduction zone conditions. Chem Geol 473:55–
275        73. doi: 10.1016/j.chemgeo.2017.10.016
276    Miles AJ, Graham CM, Hawkesworth CJ, et al (2013) Evidence for distinct stages of magma
277        history recorded by the compositions of accessory apatite and zircon. Contrib to Mineral
278        Petrol 166:1–19. doi: 10.1007/s00410-013-0862-9
279    Montel JM (1986) Experimental determination of the solubility of Ce-monazite in SiO2-Al2O3-
280        K2O-Na2O melts at 800°C, 2kbar, under H2O-saturated conditions. Geology 14:659–
281        662.
282    Moyen J, Martin H (2012) Forty years of TTG research. LITHOS 148:312–336. doi:
283        10.1016/j.lithos.2012.06.010
284    Nasdala L, Broska I, Harlov DE, Macdonald R (2017) Recent progress in the study of
285        accessory minerals. Mineral Petrol 102:431–433. doi: 10.1007/s00710-017-0526-y
286    Pichavant M, Montel JM, Linda R (1992) Apatite solubility in peraluminous liquids :
287        Experimental data and an extension of the Harrison-Watson model. Geochemica
288        Cosmochim Acta 56:3855–3861.
289    Prowatke S, Klemme S (2006a) Trace element partitioning between apatite and silicate
290        melts. Geochim Cosmochim Acta 70:4513–4527. doi: 10.1016/j.gca.2006.06.162
291    Prowatke S, Klemme S (2006b) Rare earth element partitioning between titanite and silicate
292        melts: Henry's law revisited. Geochim Cosmochim Acta 70:4997–5012. doi:
293        10.1016/j.gca.2006.07.016
294    Sha L-K, Chappell BW (1999) Apatite chemical composition, determined by electron
295        microprobe and laser-ablation inductively coupled plasma mass spectrometry, as a

296     probe into granite petrogenesis. Geochim Cosmochim Acta 63:3861–3881. doi:

297     10.1016/S0016-7037(99)00210-0

298