

46 a compilation of recent data to show that apatite in the matrix and as inclusions
47 within zircon and titanite is useful for providing insights into the nature and
48 petrogenesis of the parental magma. Trace element modelling from in-situ analyses
49 of apatite and titanite can reliably estimate the original magma composition, using
50 appropriate partition coefficients and careful imaging. This provides a new way to
51 look at magmatic petrogenesis that have been overprinted by metamorphic
52 processes. It also provides the rationale for new investigations of sedimentary
53 provenance using detrital accessory minerals, and could provide a powerful new
54 window into early Earth processes if applied to Archean or Hadean samples.

55 Keywords: apatite, petrogenesis, inclusions in accessory minerals, crustal evolution,
56 provenance.

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Introduction

59 Interest in apatite has recently increased as this mineral seems to be an excellent
60 recorder of Earth and planetary processes (e.g. Bruand et al., 2014; Harlov et al.,
61 2015; Mc Cubbin et al., 2015; Piccoli et al., 2015; Tartèse et al., 2014; Zirner et al.,
62 2015). Development of in situ techniques such as laser ablation (LA)-ICP-MS and the
63 ion microprobe allows analysis of trace elements in different zones within accessory
64 minerals such as apatite that may record different parts of the crystallization
65 history. Apatite has been shown to record petrogenetic processes during
66 crystallisation (in-situ crystal fractionation, mixing, metasomatism) and is a mineral
67 able to highlight events that are not always visible using whole rock compositions
68 (Bruand et al., 2014). Apatite is also a datable mineral (by U-Pb) and recent

69 advances in that field have also been successful (e.g. Chew and Donelick, 2012).
70 Developing petrological tools based on apatite chemistry is of broad interest as it is
71 a common mineral in most igneous rock types (e.g. felsic, mafic, ultramafic; see
72 Piccoli and Candela, 2002 for review), constitutes one of the main carriers of P_2O_5
73 and REE (alongside zircon, titanite, allanite and monazite), contains various
74 elements sensitive to oxidation state (Mn, V, S; E.g. Miles et al., 2014, Parat et al.,
75 2011) and can accommodate halogens in its structure (F and Cl).

76 In this contribution we compile recent findings showing that apatite is a
77 valuable mineral for tracking igneous petrogenesis and is also of great potential use
78 for provenance studies (Foster and Carter, 2007; Morton and Yaxley, 2007). The
79 first part of this paper is dedicated to the use of apatite as a petrogenetic tool within
80 granitoids and its ability to record different processes that are not necessarily
81 visible using whole rock compositions. The second part looks at using apatite
82 inclusions armoured within robust minerals (e.g. zircon, titanite) to provide a new
83 provenance tool via characterization of the original host rock.

84

85 **Apatite: A petrogenetic recorder**

86 **Imaging**

87 Apatite is commonly zoned as a result of its crystallization, dissolution and/or
88 reprecipitation history. Such zoning can be easily identified by imaging using back-
89 scattered (BSE) and/or cathodoluminescence (CL) techniques (Fig. 1) and
90 interpretation of this zoning combined with detailed petrographic study of the
91 surrounding mineral phases can give additional information on the timing and

92 nature of apatite crystallization (e.g. Bruand et al., 2014; Zirner et al., 2015). In
93 Figure 1a, imaging of apatite crystals within a granitoid from high Ba-Sr granites
94 (northern Scotland) reveals distinct core and rim zonation, the significance of which
95 is discussed below. Despite many workers describing the common presence of
96 zoning in apatite and the use of BSE or CL techniques to observe the zoning (e.g.
97 Kempe and Goetze, 2002; Shore and Fowler, 1996), this first stage of apatite
98 description is often omitted and valuable information can therefore be missed.

99

100 **Trace elements**

101 A number of studies have presented detailed trace element chemistry for apatite
102 crystals in various igneous systems using in-situ techniques (e.g. Belousova et al.,
103 2001, 2002; Chu et al., 2009; Hoskin et al., 2000; Sha and Chappell, 1999). These
104 showed that rare earth element (REE) patterns vary with (i) the type of magma (e.g.
105 affected by differentiation, Hoskin et al., 2000), (ii) the presence or absence of other
106 accessory minerals (e.g. Hoskin et al., 2000; Miles et al., 2013) and could give clues
107 about (iii) the geological setting (Belousova et al., 2002; Chu et al., 2009; Sha and
108 Chappell 1999). More recently, detailed imaging associated with in-situ work has
109 shown that an important part of the crystallization history of an igneous body can
110 be observed at the apatite grain scale (e.g. Bruand et al., 2014, Zirner et al., 2015). In
111 the first part of this contribution, we summarize some of those findings and describe
112 their potential importance for a better understanding of petrogenetic processes.
113 Apatite chemistry from the high Ba-Sr granites (Northern Scotland, Bruand et al.,
114 2014) provide an excellent example to observe those new findings. Two localities

115 were studied in detail (the Strontian and Rogart plutons) in which compositions
116 range from tonalitic to granodiorite to granite, with a local ultramafic component
117 (the so-called appinites; Fowler et al., 2001, 2008). Results on the felsic
118 compositions show that in one locality (Rogart) apatite displays oscillatory zoning
119 and that REE content decreases continuously from core to rim, reflecting
120 progressive in-situ crystal fractionation (Fig. 1b). By contrast, apatites from the
121 second locality (Strontian) have oscillatory cores and homogeneous rims. These
122 different zones correlate with an abrupt change in REE and Y, which is also visible in
123 titanite from the same samples (decrease in REE, Nb and Ta). Prowatke and Klemme
124 (2006) showed that apatite partition coefficients for REE are strongly dependent
125 upon the SiO₂ content of the magma. Apatite in felsic systems can host up to almost
126 an order of magnitude more REE than apatite crystallising in mafic systems (Fig. 2).
127 Moreover, changes of REE, Zr, Nb and Ta in titanite and elemental ratios such as
128 Sr/Sm in apatite and titanite match local apatite and titanite ultramafic
129 compositions (See Fig. 6a, 7 and 12 in Bruand et al., 2014). Therefore, these abrupt
130 changes of apatite composition at Strontian are the likely result of a mixing event
131 with local mafic magma, visible at the single grain scale in both apatite and titanite
132 from the studied samples (Bruand et al., 2014), not apparent in whole –rock
133 chemistry (Fowler et al., 2008) but in agreement with field evidence that shows
134 disrupted synplutonic mafic dykes and abundant mafic enclaves.

135

136 Other trace elements in apatite have also proven useful to assess the host rock
137 chemistry. A compilation of data from the literature indicates that the Sr content in

138 apatite is of particular interest (e.g. Jennings et al., 2011), since it correlates well
139 with Sr of the whole rock (Fig. 3a). Importantly, Bruand et al. (2014) also showed
140 that when Sr from the whole rock is affected by feldspar alteration (see altered
141 sample on Fig. 3a), it is possible to estimate the original Sr content based on the
142 SrAp content of the sample using the SrWR-SrAp correlation compiled from the
143 literature . These authors also show that Sr content of apatite and titanite from the
144 same samples correlate along a 10:1 regression line, which seems robust regardless
145 of alteration in the whole rock. Sr in apatite has also been shown to correlate
146 strongly with whole-rock SiO₂ (Fig. 3b; Belousova et al., 2001; Bruand et al., 2014,
147 2016; Jennings et al., 2011). Therefore, SiO₂ and Sr concentrations from the original
148 rock can be derived using SrAp and give information of the original/unaltered host
149 rock. This tool is important for future work on provenance studies (see second part
150 of this paper).

151 Finally in this section, halogen (F, Cl) contents in apatite in igneous and
152 metamorphic systems may ultimately be used as a proxy for water content of the
153 melt. For example, the halogen content of apatites has been extensively used in the
154 recent years to constrain the amount of water on the Moon (Boyce et al., 2010;
155 Tartèse et al., 2013). However, there are still intense debates in the planetary
156 science community as recent modelling work questions the reliability of water
157 content estimates and infer that H-rich apatite can be generated from a magma poor
158 in hydrogen (Boyce et al., 2014).

159

160 **In situ isotopic analyses**

161 O isotopes analyses in zircon have been used for many years to constrain the
162 nature of the magma source reservoirs and more particularly the input of recycled
163 material in the source or during assimilation (e.g. Valley et al., 2003 and references
164 therein). Zircon has been shown to retain O isotope ratios of the magma source
165 unlike other minerals in which O isotopes can be completely reset when affected by
166 metamorphic or metasomatic events (e.g. quartz). Oxygen isotope data from single
167 grains of other accessory minerals is limited (Bindeman, 2008). Although oxygen
168 isotope analysis in bio-apatite is a common technique to interpret
169 paleoenvironmental conditions (e.g. Zheng, 1996), data concerning metamorphic
170 and magmatic rocks are almost non-existent (Farver and Giletti, 1989). Recent
171 technical advances provide an opportunity to analyse in-situ O (King et al., 2001;
172 Bonamici et al., 2014), Sm-Nd isotopes (Foster & Carter, 2007; Gregory et al., 2009),
173 Cl and H isotopes in accessory minerals (e.g. Greenwood et al. 2011; Tartèse et al.,
174 2014). Similarly, the understanding of oxygen isotope behaviour in other phases
175 such as titanite has recently shown progress (e.g. King et al., 2001 for igneous and
176 metamorphic rocks and Bonamici et al., 2011, 2014, 2015 for titanite in
177 metamorphic rocks). King et al. (2001) show a consistent zircon-titanite
178 fractionation factor of $\sim 1.2 \pm 0.3\text{‰}$ for igneous and of $\sim 2.1 \pm 0.4\text{‰}$ for
179 metamorphic rocks. Bonamici et al. (2011, 2014) recently used oxygen isotope
180 profiles in titanite grains to infer the cooling history of metamorphic rocks. In
181 summary, although there is still a lot to learn about oxygen isotope behaviour in
182 apatite, titanite or monazite, they have comparable potential to zircon (Valley, 2003)
183 to highlight mantle and/or crustal components in the petrological source.

184 In terms of radiogenic isotopes, data are also limited, but Gregory et al.
185 (2009) demonstrated that Sm-Nd isotope analysis at the micrometer scale offers the
186 prospect of developing petrological tools similar to the current Hf isotope studies on
187 zircons. They clearly show that Sm-Nd isotope analyses in titanite and apatite allow
188 the estimation of the isotopic composition of the mantle or the crustal sources.
189 Apatite, monazite and titanite have the advantage over zircon in being more
190 widespread in less evolved magmas (e.g. Piccoli and Candela, 2002; Hoskin and
191 Schaltegger, 2003) and being more responsive to igneous processes and crustal
192 metamorphism (e.g. Bruand et al., 2014 for titanite and apatite; Rubatto et al., 2001
193 for monazite).

194

195 **Potential for provenance studies?**

196 Correlations detailed in Bruand et al. (2016; Sr-Ap vs SrWr, Sr-Ap vs SiO₂, Fig.
197 3) can be used to constrain the host rock composition of the studied minerals, even
198 when they are detrital. Making use of such a tool could therefore be extremely
199 valuable for future provenance studies. The majority of apatite provenance studies
200 have focused on detrital thermochronology of apatite using fission track or U-Th/He
201 thermochronometers (Bernet and Spiegel, 2004) and very little on trace elements.
202 With the recent advances on the understanding of trace elements behaviour in
203 apatite (Hoskin et al., 2000; Belousova et al., 2002; Chu et al., 2002; Jennings et al.,
204 2011; Bruand et al., 2016), there would be merit to test in more details the
205 robustness of trace elements in apatite during erosion, transport and diagenesis.
206 However, apatite has been shown to be affected rapidly by metasomatism and

207 alteration (e.g. Zirner et al., 2015) given little hope to use it on a global scale in old
208 terranes. Indeed, acidic groundwater, weathering and limited mechanical durability
209 can affect the stability of apatite during sediment transport (Morton and Hallsworth,
210 2007). This severely limits its use as a detrital provenance tool. A novel way to look
211 at apatite in the sedimentary record is to analyse apatite inclusions armoured
212 within robust accessory minerals (e.g. zircon, titanite; Bruand et al., 2016; Darling et
213 al., 2009; Jennings et al., 2011). The success of the method depends on the ability of
214 apatite inclusions to record similar chemical features to those described above.

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Apatite inclusions

218 Previously, inclusions present within datable accessory minerals such as zircon
219 were viewed as a common problem, since they might introduce mixed ages and
220 common Pb, which could lead to inaccurate and/or imprecise ages. The grains
221 bearing those inclusions (Fig. 4) were therefore discarded. However, recent work
222 has shown that these inclusions provide valuable insights into the history of a rock
223 (e.g. Bruand et al., 2016; Darling et al., 2009; Jennings et al., 2011). While some
224 inclusions (such as feldspar) have been shown to not reflect the original rock
225 composition (Jennings et al., 2011), elements such as Sr has been shown to correlate
226 with Sr_{WR} and SiO₂_{WR}. In the first part of this contribution, we have shown that
227 apatite composition gives additional petrogenetic information. In this part, we
228 demonstrate how this petrogenetic history is also available *in apatite inclusions*

229 *armoured in zircon and titanite*, from which we can also recover an estimate of
230 whole rock composition.

231

232 **Apatite inclusions in zircons**

233 Apatite, micas, quartz and feldspar are common inclusions in igneous zircon (Fig.
234 5A). However, it has to be noted that careful counting of minerals in a set of samples
235 (Fig. 5A) indicates that the proportions of minerals as inclusions in zircons do not
236 necessary match their modal abundance (Darling et al., 2009). For example, quartz
237 is generally present in greater proportions compared with other phases as an
238 inclusion phase than within the matrix of the same rocks.

239

240 **From apatite inclusions to petrogenesis**

241 Apatite inclusions within titanites from a set of high Ba-Sr granitoids in Scotland
242 (Bruand et al., 2016; Fowler et al., 2001, 2008) have been imaged (Fig. 4) and
243 analysed using ion microprobe and electron microprobe techniques. Trace element
244 results confirm that the Sr concentrations of apatite inclusions and the Ce/Y ratios
245 correlate along a 1:1 correlation with those of apatite in the matrix (Bruand et al.,
246 2016; Fig. 6). Bruand et al. (2016) further demonstrate that the chemistry of apatite
247 provides important petrogenetic constraints for the plutons studied (e.g. insitu
248 crystal fractionation, mixing) that were not visible using whole rock data (Fowler et
249 al., 2001, 2008). In most cases, Sr in apatite has a homogeneous distribution (no
250 zoning), its concentration in apatite has been shown to be a function of plagioclase
251 fractionation during magmatic differentiation (Belousova et al., 2002). In contrast,

252 REE are extremely sensitive to changes in magmatic conditions. Prowatke and
253 Klemme (2005, 2006) demonstrated that apatite and titanite partition coefficients
254 for REE are dependent upon SiO₂ content. The REE partition coefficients for most
255 felsic rocks are higher than for mafic rocks, particularly for MREE. Therefore, ratios
256 such as Sr/Sm can be particularly helpful to discriminate different magma types. In
257 Figure 7, Sr/Sm of apatite inclusions and their titanite host minerals are reported.
258 They show that Sr/Sm in both minerals can discriminate mafic from felsic
259 (granitoid) compositions. The chemistries of titanite and apatite from the matrix
260 are also reported and show similar values. The studied samples show two different
261 crystallization histories. In Rogart, apatite and associated titanite zones have similar
262 Sr/Sm ratios and plot within a narrow range ($Sr/Sm_{Ttn} \sim 0.05-0.12$ and $Sr/Sm_{Ap} \sim$
263 $3-10$). These results, associated with a continuous decrease of REE from core to rim,
264 suggest in-situ crystal fractionation. In Strontian, titanite cores and apatite
265 inclusions located in these cores plot in the same narrow field. On the other hand,
266 apatite inclusions in titanite rims and the associated titanite rims have systematic
267 higher Sr/Sm ratios (Fig. 7; $Sr/Sm_{Ttn} > 0.15$ and $Sr/Sm_{Ap} \sim 3-27$). As discussed
268 above, this is interpreted to reflect a late influx of mafic magma during the
269 crystallization of Strontian granitoid (Bruand et al., 2014, 2016). Apatite and titanite
270 from the Strontian mafic-ultramafic facies (appinite) plot in the same region as the
271 titanite and apatite rims. In Strontian apatite and titanite record a general decrease
272 of REE from the inner toward the outer core of the titanite and then a late mixing
273 event with the local mafic magma within their rims. In summary, a detailed

274 snapshot of the petrogenetic history of a pluton is preserved within apatite
275 inclusions in titanite or zircon.

276

277 **From apatite inclusions to whole rock chemistry**

278 Apatite chemistry is also extremely powerful for recovering information about the
279 whole rock of their original host. For example, a global compilation of granitoids
280 whole rock and apatite chemistry demonstrate a strong correlation between Sr_{Ap}
281 and Sr_{WR} (Fig. 8), from which it is possible to “back calculate” Sr_{WR} based on apatite
282 chemistry (Fig. 9). In Figure 8B, a compilation of post Archean samples and three
283 average Archean tonalite trondjemite granodiorite (TTG, black stars) compositions
284 have been plotted, showing that Sr_{Ap} correlates with SiO_2 (Fig. 8B). As noted above,
285 the studied high Ba-Sr granites (Bruand et al., 2016) systematically plot above the
286 correlation defined by the other samples. This is consistent with whole-rock data.
287 On Fig. 8C, the high Ba-Sr granites and their Archean equivalent (sanukitoids –
288 Fowler and Rollinson, 2012) define an independent correlation. Based on these
289 observations, a two-step method has been developed to recover original Sr and SiO_2
290 whole rock composition from Sr concentration in apatite.

291 - First, Sr_{WR} is back calculated using Sr_{Ap} and the correlation defined in Fig. 8A.

292 - Second, using this calculated Sr_{WR} value, the SiO_2 can be estimated (Fig. 8B).

293 If $Sr_{WR} > 650$ ppm the correlation based on sanukitoid compilation is used

294 and if $Sr_{WR} < 650$ ppm, the correlation based on the post-Archean trend is

295 used. The 650 ppm cut off is based on the Sr_{WR} value of the most mafic

296 endmember of the post-Archean trend.

297

298 Following this procedure, appropriate partition coefficients can be chosen (e.g. Luhr
299 et al., 1984; Prowatke and Klemme, 2005, 2006) and the REE of the host magma can
300 be calculated, which is broadly equivalent to that of the whole host rock. For
301 example, results for Rogart are shown in Fig. 9 (whole-rock data from Fowler et al.,
302 2008). Apatite and titanite produce similar results and a particularly good fit for
303 sample RHG1. The results from Strontian produce a good fit for sample SR4 for
304 apatite inclusions from the core and the titanite core composition (higher REE
305 contents of the calculated area in Fig. 9). Calculated MREE concentrations for SR1
306 and SR3 are generally lower than that of the whole rock. This could be explained by
307 a slight discrepancy between the partition coefficient for apatite and titanite that we
308 used and our sample. Calculations made with rim compositions plot at much lower
309 REE and their calculated REE patterns give lower values especially for MREE (Fig.
310 9). When this back-calculation method is used on grains that have been affected by
311 the complications of a late influx of mafic magma such as in Strontian (Figs. 1, 7),
312 only the unaffected core composition should be used for calculations. Although
313 clearly not perfect, key elemental ratios such as Ce/Yb and Eu/Eu* are accurately
314 reproduced. Thus, it seems likely that apatite and titanite have the potential to
315 faithfully record their parent melt chemical signature.

316

317 **Apatite inclusions in zircon and titanite – a window to the early Earth?**

318 Robust detrital accessory minerals such as monazite and zircon preserved in
319 sandstones are particularly informative as they can be dated and can then be

320 potentially compared to similar terranes to allow paleogeographic reconstruction
321 (e.g. Samson et al., 2005). Much of what we know about early crustal evolution and
322 the generation of continents is based on such work. However, zircon trace element
323 chemistries have not yet been proven particularly helpful to discriminate different
324 magma compositions and allow a detailed interpretation of their original host rock
325 (e.g. Coogan and Hinton, 2006), which represents a major weakness in the approach.
326 We have shown above that it is possible to reconstruct whole rock chemistry of the
327 parent rock (Belousova et al., 2002; Bruand et al., 2016; Jennings et al., 2011) based
328 on apatite chemistry, even when the crystals are <100 microns inclusions in other
329 accessory minerals. Such work could be applied to inclusions in the detrital zircon
330 archive, such that magmatic composition over time could be recovered. Of particular
331 interest in this regard, is the presence of apatite inclusions reported in the oldest
332 terrestrial zircons from Jack hills (Hopkins et al., 2008; Rasmussen et al., 2011).
333 Rasmussen et al. (2011) report the presence of numerous inclusions that are
334 secondary and have crystallized during one of the later metamorphic events, some
335 of them replacing apatite (e.g. xenotime, monazite, muscovite; Fig. 5B). However,
336 they also report the presence of rare preserved primary apatite, whose petrogenetic
337 affinities would be illuminating.

338

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Implications

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341 Apatite chemistry has the ability to record petrogenetic processes that are not
342 available using whole rock data. It also discriminates different magma composition

343 that are diagnostic of geodynamic changes during crustal evolution (e.g. distinguish
344 sanukitoids from post-Archean granitoids). Between the Archean (4-2.5 Ga ago) and
345 the Phanerozoic (0.54 Ga to present), the magmatic production system changed
346 from a “hot” Earth, producing TTG suites, to a ‘colder’ Earth, producing mainly calc-
347 alkaline andesitic crust (e.g. Martin et al., 2005). This shift of composition has been
348 interpreted by some as reflecting major geodynamic changes of the Earth and
349 ultimately has been linked to the onset of plate tectonic (Martin et al., 2005).
350 Sanukitoids are interpreted as being the product of a metasomatized mantle wedge
351 and have been reported as occurring during the Archean-Proterozoic transition
352 (~2.7-2.5 Ga; Martin *et al.*, 2009). They have been interpreted by various workers
353 (e.g. Martin *et al.*, 2009) as the result of the evolution from a shallow to a steep
354 subduction style in this time interval and therefore might mark the onset of modern
355 plate tectonics. However, there are remaining fundamental unknowns about the
356 conditions of the early Earth as its record is extremely sparse (Bleeker et al., 2005;
357 e.g. composition of the crust, geodynamic regime). The study of accessory minerals
358 and more particularly detailed in-situ work on apatite (trace element and isotopes)
359 provides a potentially pivotal role to gather more information about igneous
360 processes and to interrogate the rock record in ever greater detail (e.g. Hadean
361 zircons, eroded products of ancient cratons). Although there has been a recent
362 increase in work on REE in apatite and other accessory minerals, there is still much
363 to do. For example:

- 364 - Studying in greater detail REE behaviour in the whole set of accessory minerals in
365 various magma compositions. Most studies focus on one of the accessory phases

366 contained within a suite of rocks (e.g. Tepper & Kuehner, 1999; McLeod *et al.*,
367 2011). The comparison of the different accessory phases within a suite of samples
368 is more rarely done (Bruand *et al.*, 20015; Hoskin *et al.*, 2000b). As those minerals
369 all bear REE, systematic comparative studies are essential to understand their
370 behaviour.

371 - Improving the understanding of redox sensitive elements in apatite (S, Mn; Miles *et*
372 *al.*, 2014; Parat *et al.*, 2011)

373 - Studying less investigated elements such as Pb, Sr, Th, Nb, U, V and Ta that are also
374 sensitive to changes in magma composition.

375

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387 **References cited**

- 388 Belousova, E. A., Walters, S., Griffin, W. L. and O'Reilly, S. Y. (2001) Trace-element
389 signatures of apatites in granitoids from the Mt Isa Inlier, northwestern Queensland.
390 Australian Journal of Earth Sciences, 48, 603-619.
- 391 Belousova, E.A., Griffin, W.L., O'Reilly, S.Y. and Fisher, N.I. (2002) Apatite as an
392 indicator mineral for mineral exploration: trace-element compositions and their
393 relationship to host rock type. Journal of Geochemical Exploration, 76, 45-69.
- 394 Bindeman, I. (2008) Oxygen isotopes in mantle and crustal magmas as revealed by single
395 crystal analysis. Reviews in Mineralogy and Geochemistry, 69, 445-478.
- 396 Bonamici, C., Kozdon, R., Ushikubo, T. and Valley, J.W. (2011) High-resolution P-T-t
397 paths from $\delta^{18}\text{O}$ zoning in titanite: A snapshot of late-orogenic collapse in the
398 Grenville of New York. Geology, 39, 959-962.
- 399 Bonamici, C., Kozdon, R., Ushikubo, T. and Valley, J.W. (2014) Intragrain oxygen
400 isotope zoning in titanite by SIMS: Cooling rates and fluid infiltration along the
401 Carthage-Colton Mylonite Zone, Adirondack Mountains, NY, USA. Journal of
402 metamorphic Geology, 32, 71-92.
- 403 Bonamici, C., Fanning, C.M., Kozdon, R., Fournelle, J.H. and Valley, J.W. (2015)
404 Combined oxygen-isotope and U-Pb zoning studies of titanite: new criteria for
405 age preservation. Chemical Geology, 398, 70-84.
- 406 Boyce, J.W., Liu, Y., Rossman, G.R., Guan, Y., Eiler, J.M., Stolper, E.M. and Taylor,
407 L.A., (2010) Lunar apatite with terrestrial volatile abundances. Nature, 466, 466-
408 69.
- 409 Boyce, J.W., Tomlinson, S.M., McCubbin, F.M., Greenwood, J.P. and Treiman, A.H.
410 (2014). The Lunar apatite paradox. Science, 344, 400-402.

- 411 Bruand, E., Storey, C. and Fowler, M. (2014) Accessory mineral chemistry of High Ba-Sr
412 granites from northern Scotland: constraints on petrogenesis and records of
413 whole-rock signature. *Journal of Petrology*, 55, 1619-1651.
- 414 Bruand, E., Storey, C. and Fowler, M. (2016) Apatite inclusions within zircon and titanite
415 as a window into the early Earth. *Geology*, 44, 91-94.
- 416 Chew, D. and Donelick, R. (2012) Combined apatite fission track and U-Pb dating by
417 LA-ICP-MS and its application in apatite provenance analysis. *Mineralogical
418 Association of Canada Short Course*, 42, 219-247.
- 419 Chu, M.F., Wang, K.L., Griffin, W.L., Chung, S.L., O'Reilly, S.Y., Pearson, N.J. and
420 Iizuka, Y. (2009) Apatite Composition: Tracing Petrogenetic Processes in
421 Transhimalayan Granitoids. *Journal of Petrology*, 50, 1829-1855.
- 422 Coogan, L.A. and Hinton, R. (2006) Do the trace element compositions of detrital zircons
423 require Hadean continental crust? *Geology*, 34, 633-636.
- 424 Darling, J., Storey, C. and Hawkesworth, C. (2009) Impact melt sheet zircons and their
425 implications for the Hadean crust. *Geology*, 37, 927-930, DOI:10.1130/G30251A.1.
- 426 Farver, J.R. and Giletti, B.J. (1989) Oxygen and strontium diffusion kinetics in apatite
427 and potential applications to thermal history determinations. *Geochimica and
428 Cosmochimica Acta*, 53, 1621-1631.
- 429 Foster, G. and Carter, D. (2007) Insights into the patterns and locations of erosion in the
430 Himalaya - A combined fission-track and in situ Sm-Nd isotopic study of detrital
431 apatite. *Earth Planetary Science Letters*, 257, 407-418.

- 432 Fowler, M. B., Henney, P. J., Darbyshire, D. P. F. and Greenwood, P. B. (2001)
433 Petrogenesis of high Ba-Sr granites: the Rogart pluton, Sutherland. Journal of the
434 Geological Society, 158, 521-534.
- 435 Fowler, M. B., Kocks, H., Darbyshire, D. P. F. and Greenwood, P. B. (2008) Petrogenesis
436 of high Ba-Sr plutons from the Northern Highlands Terrane of the British
437 Caledonian Province. Lithos, 105, 129-148.
- 438 Fowler, M. and Rollinson, H. (2012) Phanerozoic sanukitoids from Caledonian Scotland:
439 Implications for Archean subduction. Geology, 40, 1079-1082.
- 440 Greenwood, J. P., Itoh, S., Sakamoto, N., Warren, P., Taylor L. A. and Yurimoto H.
441 (2011) Hydrogen isotope ratios in lunar rocks indicate delivery of cometary water
442 to the Moon. Nature Geoscience, 4, 79–82.
- 443 Gregory, C.J., McFarlane, C.R.M., Hermann, J. and Rubatto, D. (2009) Tracing the
444 evolution of calc-alkaline magmas: In-situ Sm-Nd isotope studies of accessory
445 minerals in the Bergell Igneous Complex, Italy. Chemical Geology, 260, 73-86.
- 446 Harloy, D. E. (2015) Apatite; a fingerprint for metasomatic processes (in Apatite; a
447 mineral for all seasons). Elements Magazine, 11(3),171-176
- 448 Hopkins, M.D., Harrison, T.M. and Manning, C.E. (2010) Constraints on Hadean
449 geodynamics from mineral inclusions in >4 Ga zircons. Earth and Planetary
450 Science Letters, 298, 367-376.
- 451 Hoskin, P.W.O. and Ireland, T.R. (2000a) Rare earth element chemistry of zircon and its
452 use as a provenance indicator. Geology, 28, 627-630.

- 453 Hoskin, P.W.O., Kinny, P.D., Wyborn, D. and Chappell, B.W. (2000b) Identifying
454 accessory mineral saturation during differentiation in granitoid magmas: an
455 integrated approach. *Journal of Petrology*, 41, 1365-1396.
- 456 Iizuka, T., Nebel, O. and McCulloch, M.T. (2011) Tracing the provenance and
457 recrystallization processes of the Earth's oldest detritus at Mt. Narryer and Jack
458 Hills, Western Australia: An in situ Sm-Nd isotopic study of monazite. *Earth and
459 Planetary Science Letters*, 308, 350-358.
- 460 Jennings, E.S., Marschall, H.R., Hawkesworth, C.J. and Storey, C.D. (2011)
461 Characterization of magma from inclusions in zircon: Apatite and biotite work
462 well, feldspar less so. *Geology*, 39, 863-866.
- 463 King, E.M., Valley, J.W., Davis, D.W. and Kowallis, B.J. (2001) Empirical
464 determination of oxygen isotope fractionation factors for titanite with respect to
465 zircon and quartz. *Geochimica et Cosmochimica Acta*, 65, 3165-75.
- 466 Kempe, U. and Götze, J. (2002) Cathodoluminescence (CL) behaviour and crystal
467 chemistry of apatite from rare-metal deposits. *Mineralogical Magazine*, 66, 135–
468 156.
- 469 Luhr, J. F., Carmichael, I. S. E. and Varekamp, J. C. (1984) The 1982 eruptions of el-
470 chichon volcano, chiapas, mexico - mineralogy and petrology of the anhydrite-
471 bearing pumices. *Journal of Volcanology and Geothermal Research*, 23, 69-108.
- 472 Martin, H., Moyen, J.F. and Rapp, R. (2009) The sanukitoid series: Magmatism at the
473 Archean-Proterozoic transition. *Earth and Environmental Science Transactions of
474 the Royal Society of Edinburgh*, 100, 15–33, DOI:10.1017/S1755691009016120.

- 475 McCubbin, F.M. and Jones, R.H. (2015) Extraterrestrial apatite: Planetary geochemistry
476 to astrobiology. *Elements Magazine*, 11, 183–188,
477 DOI:10.2113/gselements.11.3.183.
- 478 McDonough, W.F., and Sun, S.S. (1995) The Composition of the Earth. *Chemical*
479 *Geology*, 120, 223–253, DOI:10.1016/0009-2541(94)00140-4.
- 480 Miles, A. J., Graham, C. M., Hawkesworth, C. J., Gillespie, M. R. and Hinton, R. W.
481 (2013) Evidence for distinct stages of magma history recorded by the compositions
482 of accessory apatite and zircon. *Contributions to Mineralogy and Petrology*, 166, 1-
483 19.
- 484 Miles, A.J., Graham, C.M., Hawkesworth, C.J., Gillespie, M.R. and Hinton, R.W. (2014)
485 Mn in apatite: A new redox proxy for silicic magmas? *Geochimica et*
486 *Cosmochimica Acta*, 132, 101-119.
- 487 Morton, A. and Hallsworth, C. (2007) Stability of detrital heavy minerals during burial
488 diagenesis, in Mange, M., and Wright, D.K., eds., *Heavy Minerals in Use:*
489 *Amsterdam, Elsevier, Developments in Sedimentology*, 58, 215–245,
490 DOI:10.1016/S0070-4571(07)58007-6.
- 491 Parat F., Holtz F. and Streck M. (2011) Sulfur-bearing magmatic accessory minerals. In :
492 Behrens H, Webster JD (eds) *Sulfur in Magmas and Melts and Its Importance for*
493 *Natural and Technical Processes. Reviews in Mineralogy and Geochemistry*, 73,
494 285-314.
- 495 Piccoli, P., Candela, P. and Rivers, M. (2000) Interpreting magmatic processes from
496 accessory phases: titanite- a small scale recorder of large-scale processes.
497 *Geological Society of America Special Papers*, 350, 257-267.

- 498 Prowatke, S. and Klemme, S. (2005) Effect of melt composition on the partitioning of
499 trace elements between titanite and silicate melt. *Geochimica Et Cosmochimica*
500 *Acta*, 69, 695-709.
- 501 —, (2006) Trace element partitioning between apatite and silicate melts. *Geochimica Et*
502 *Cosmochimica Acta*, 70, 4513-4527.
- 503 Rasmussen, B., Fletcher, I.R., Muhling, J.R., Gregory, C.J. and Wilde, S. (2011)
504 Metamorphic replacement of mineral inclusions in detrital zircon from Jack Hills,
505 Australia: Implications for the Hadean Earth. *Geology*, 39, 1143-1146.
- 506 Rubatto, D., Williams, I.S. and Buick, I.S. (2001) Zircon and monazite response to
507 prograde metamorphism in the Reynolds Range, central Australia. *Contributions*
508 *to Mineralogy and Petrology*, 140, 458-468.
- 509 Sha, L. K. and Chappell, B. W. (1999) Apatite chemical composition, determined by
510 electron microprobe and laser-ablation inductively coupled plasma mass
511 spectrometry, as a probe into granite petrogenesis. *Geochimica Et Cosmochimica*
512 *Acta* 63, 3861-3881.
- 513 Shore, M. and Fowler, A.D. (1996) Oscillatory zoning in minerals; A common
514 phenomenon. *Canadian Mineralogist*, 34, 1111–1126.
- 515 Tartèse, R., Anand, M., McCubbin, F.M., Elardo, S.M., Shearer, C.K. and Franchi, I.A.
516 (2014) Apatites in lunar KREEP basalts: The missing link to understanding the H
517 isotope systematics of the Moon. *Geology*, 42, 363-66.
- 518 Tepper, J. H. and Kuehner, S. M. (1999) Complex zoning in apatite from the Idaho
519 batholith: A record of magma mixing and intracrystalline trace element diffusion.
520 *American Mineralogist*, 84, 581-595.

- 521 Valley, J.W. (2003) Oxygen isotopes in zircon. *Reviews in Mineralogy and*
522 *Geochemistry*, 53, 343-385.
- 523 Webster, J.D. and Piccoli, P.M. (2015) Magmatic apatite: a powerful yet deceptive,
524 *Mineral. Elements Magazine*, 11, 177-182.
- 525 Wilde, S.A., Valley, J.W., Peck, W.H. and Graham, C.M. (2001) Evidence from detrital
526 zircons for the existence of continental crust and oceans on the Earth 4.4 Gyrs
527 ago. *Nature*, 409, 175-178.
- 528 Zheng, Y-F. (1996) Oxygen isotope fractionations involving apatites: Application to
529 paleotemperature determination. *Chemical Geology*, 127, 177-187.
- 530 Zirner, A., Marks, M., Wenzel, T., Jacob, D. and Markl, G. (2015) Rare earth elements in
531 apatite as a monitor of magmatic and metasomatic processes: The Ilimaussaq
532 complex, South Greenland. *Lithos*, 228-229, 12-22.

533

534 **Figure Captions**

535 Figure 1. Modified after Bruand et al. (2014). Cathodoluminescence images of
536 apatites crystals for granitoids (A-B). A- Apatites from Strontian granitoids are
537 made up of oscillatory cores and unoscillatory rims. These two zones correspond to
538 a sudden change of apatite chemistry and more particularly a decrease of REE. The
539 rim records a mixing event with local mafic magma. B- Apatites from Rogart
540 granitoids are characterized by an oscillatory zoning. Apatite REE concentration
541 continuously decreases from core to rim reflecting progressive in situ crystal
542 fractionation.

543

544 Figure 2. Apatite/ melt partition coefficient for apatite for felsic and mafic
545 compositions (modified after Prowatke & Klemme, 2006).

546

547 Figure 3. SrAp-SrWR and SrAp-SiO₂ compilation. Data from Hoskin et al., 2000b
548 (black dot), Chu et al., 2009 (grey dot), Jennings et al., 2011 (colourless dot),
549 Belousova et al., 2001 (cross) and Bruand et al., 2014 (square). A- SrAp-SrWR
550 showing close correlation. B- SrAp-SiO₂WR showing broad correlation. Obvious
551 outliers are the high Ba-Sr granites from Bruand et al. (2014).

552 Figure 4. Apatite inclusions and host minerals (zircon and titanite). Analysis
553 numbers available in tables DR1-DR2 in Bruand et al., (2016).

554

555 Figure 5. Zircon inclusion populations. A- After Darling et al. (2009). Left: relative
556 frequency of main inclusion phases in various rock types. Right: Streckeisen
557 diagram showing rock and inclusion mineralogy for each sample. Arrows indicate
558 different proportion of minerals from whole rock to zircon inclusions. B-After
559 Rasmussen et al. (2011) in repository material. Mineral and mineral inclusions data
560 for the Jack Hills (JH) and the Narryer Gneiss Complex (NGC).

561

562 Figure 6. Inclusions in zircon-titanite versus rock matrix. Data are average
563 compositions given with 2 sigma errors. A) Ce/Y apatite. B) Sr apatite. After Bruand
564 et al. (2016)

565

566 Figure 7. Petrogenetic processes and the nature of the parent magma (granitoid
567 versus mafic) using Sr/Sm ratios in apatite inclusions and host titanite. For
568 comparison, apatite and titanite average compositions from the matrix have also
569 been reported (error bars are 1σ , Bruand et al., 2014, 2016).

570

571 Figure 8. A- $Sr_{Ap_{incl}}$ average compositions versus Sr_{WR} (error bars are 2σ). Available
572 data on post Archean granitoids (crosses – Jennings et al., 2011; Belousova et al,
573 2002; Chu et al., 2009; Hoskin et al., 2000; square- Rogart locality and diamond-
574 Strontian locality in high Ba-Sr granites from Bruand et al., 2016) have been added.
575 B- Sr_{Ap} vs SiO_{2WR} with apatite inclusions in the grey field of the studied high Ba-Sr
576 samples (sanukitoid-like, 2σ error bars) and two sanukitoids from the Karelian
577 Province analyzed by electron microprobe, and Post-Archean apatite data set in the
578 white field. C- Sr_{WR} vs SiO_{2WR} with the sanukitoid compilation (Fowler and Rollinson,
579 2012 ; $SiO_{2WR}>46\%$), the high Ba-Sr granites (Fowler et al., 2001, 2008), average
580 TTG compositions from Martin et al. (2005) and the Post-Archean data set. This
581 Figure is after Bruand et al. (2016).

582

583 Figure 9. Back-calculation of parent magma composition using single apatite
584 inclusions and titanite in host rock analysis (Bruand et al., 2016 dataset). KD values
585 of Luhr et al., (1984) for apatite and titanite. For comparison, sanukitoid data set
586 from Martin et al. (2009) has been added. Chondrite values are from Mc Donough
587 and Sun (1995).

588

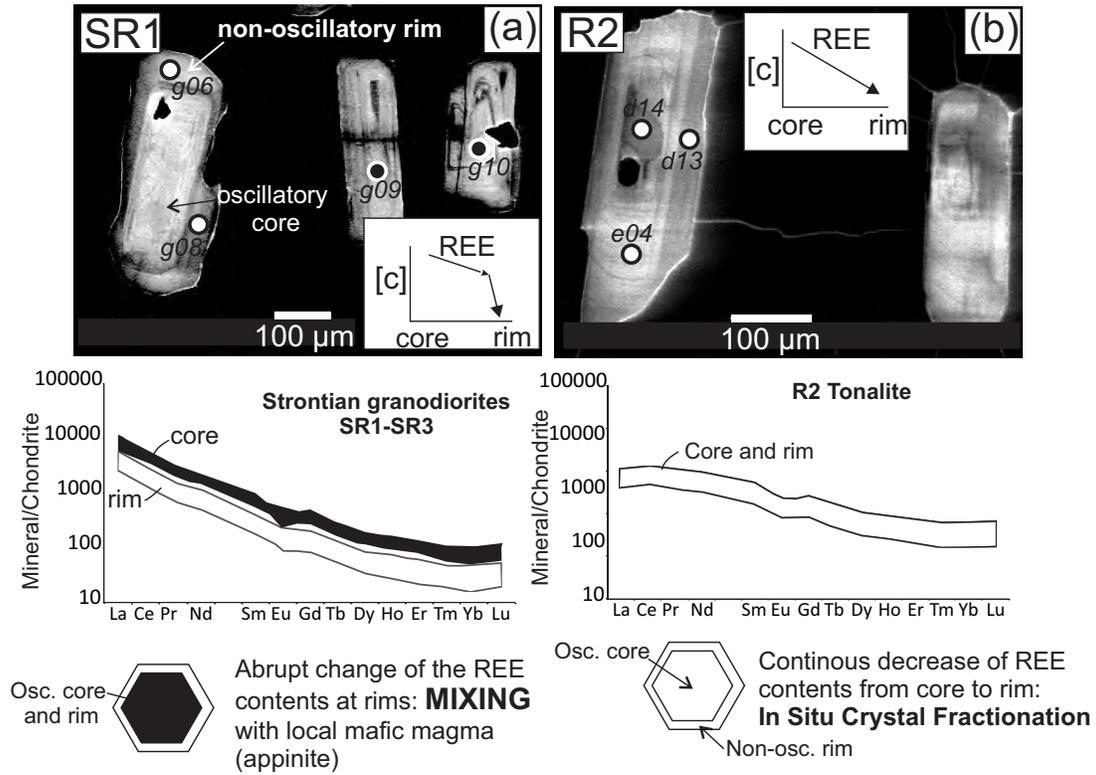


Fig. 1

Fig. 1, Bruand et al. (2016)

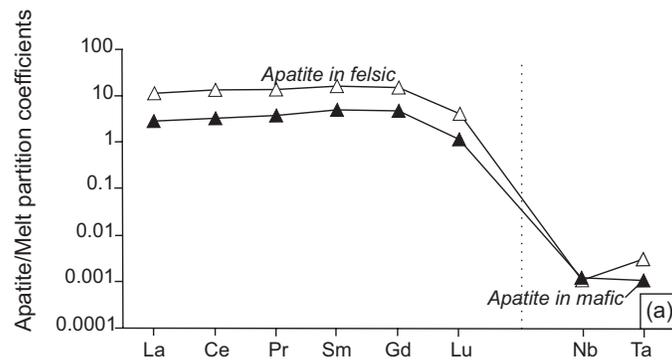


Fig. 2 Bruand et al. (2016)

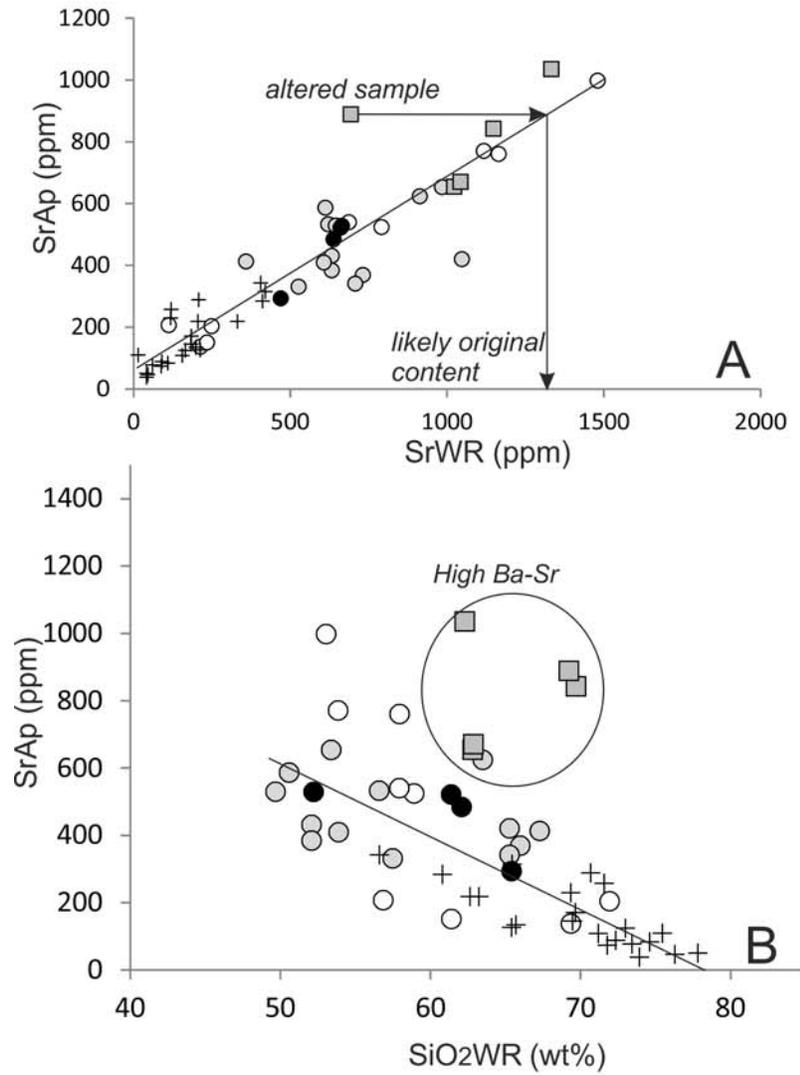


Fig. 3, Bruand et al (2016)

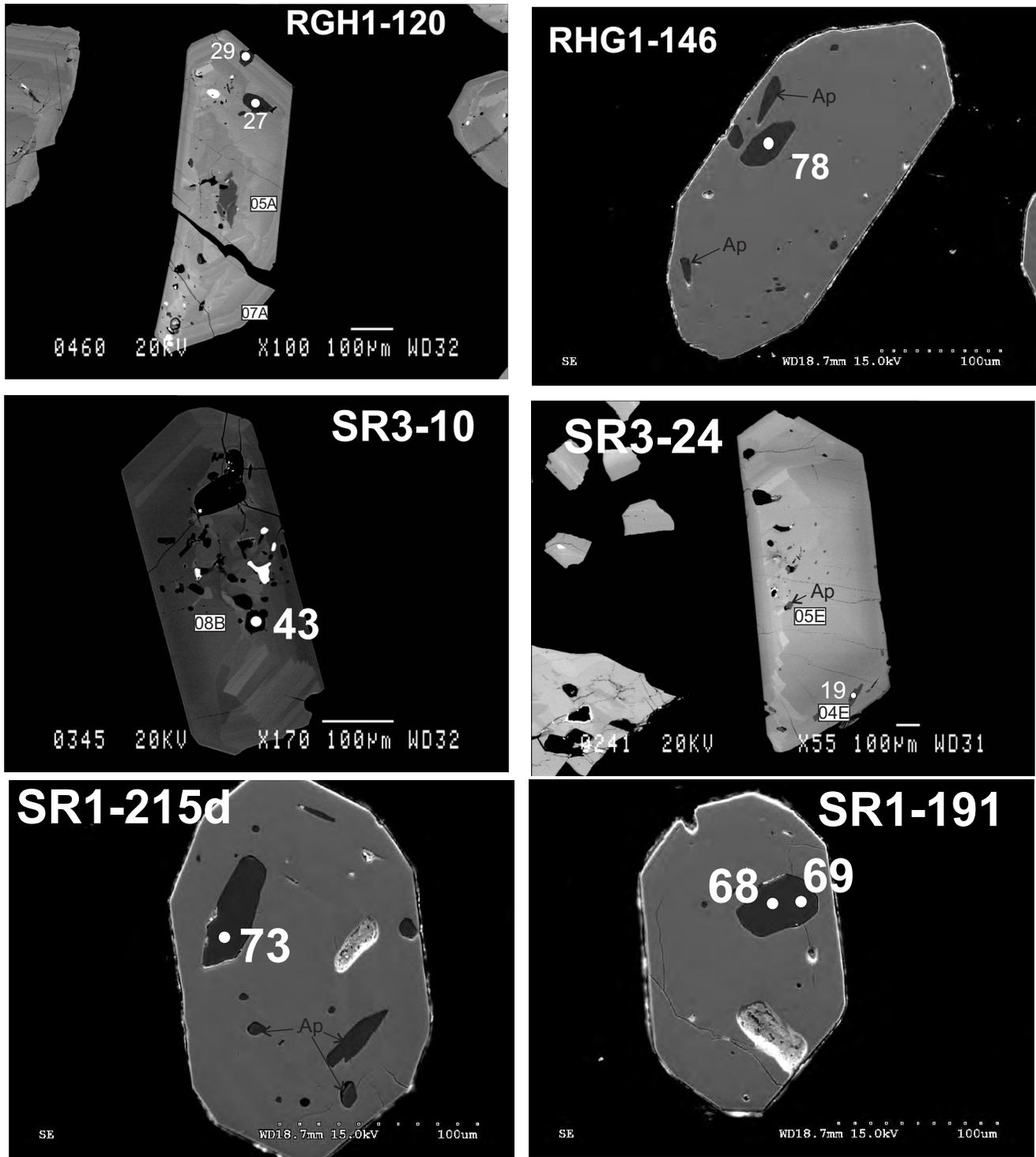


Fig. 4, Bruand et al. (2016)

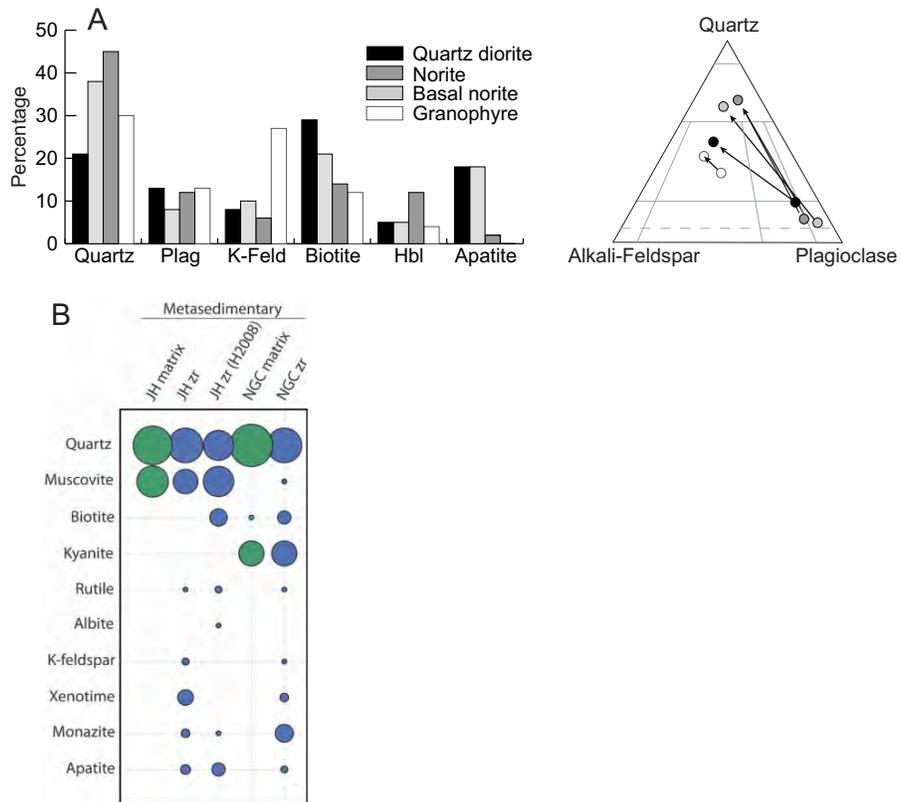


Fig. 5, Bruand et al (2016)

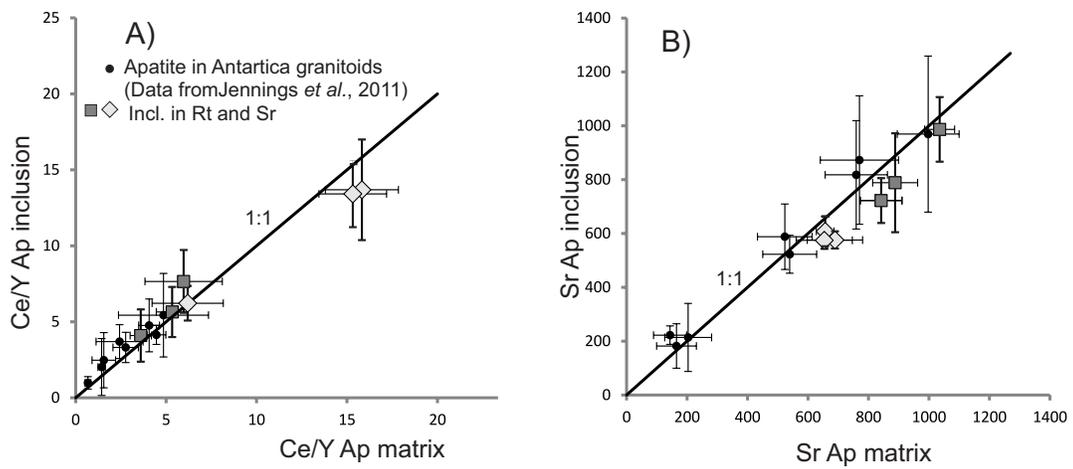


Fig. 6, Bruand et al. (2016)

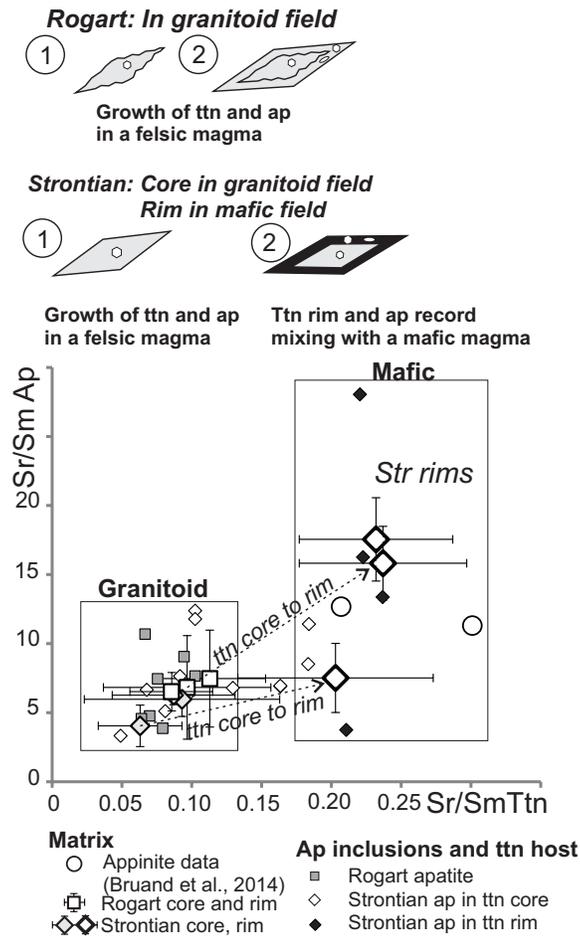


Fig.7 Bruand et al., 2016

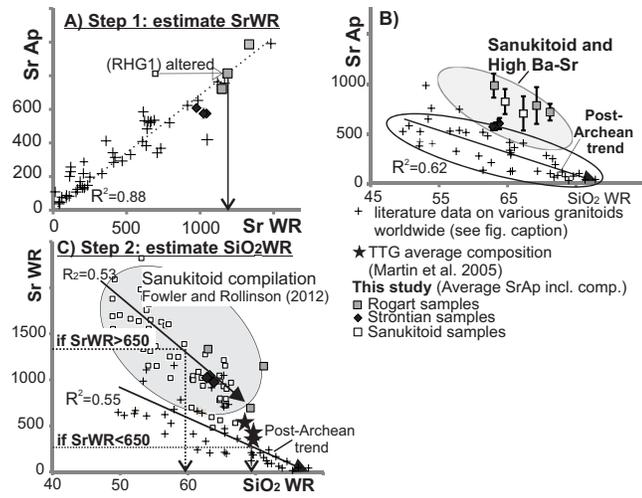


Fig. 8 Bruand et al. (2016)

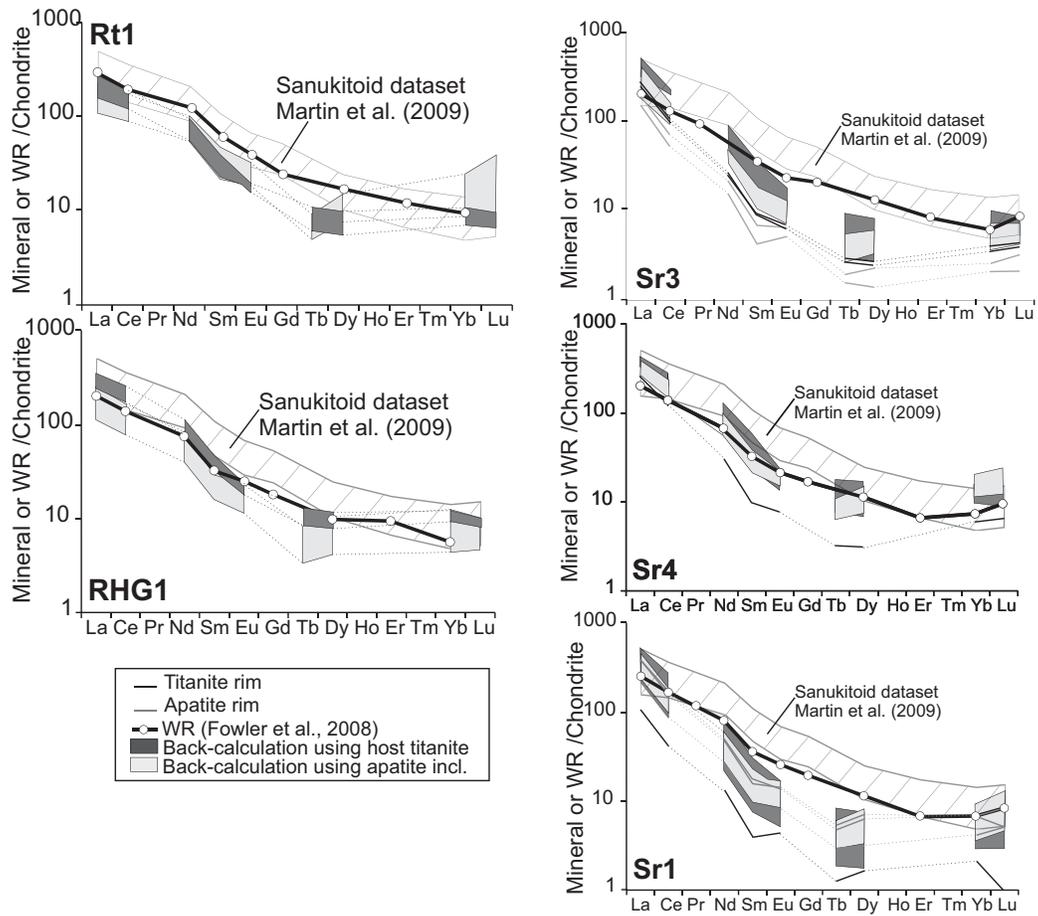


Fig. 9, Bruand et al (2016)