



HAL
open science

Mineral-whole rock isotope fidelity? A comparative study of Hf-Nd-O from high Ba Sr granitoids

Emilie Bruand, C. Storey, M. Fowler, B. Dhuime, Régis Doucelance

► To cite this version:

Emilie Bruand, C. Storey, M. Fowler, B. Dhuime, Régis Doucelance. Mineral-whole rock isotope fidelity? A comparative study of Hf-Nd-O from high Ba Sr granitoids. *Chemical Geology*, 2023, 624, pp.121425. 10.1016/j.chemgeo.2023.121425 . insu-04029703

HAL Id: insu-04029703

<https://insu.hal.science/insu-04029703>

Submitted on 15 Mar 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1 Mineral-whole rock isotope fidelity? A comparative study of Hf- 2 Nd-O from high Ba-Sr granitoids.

3
4 Bruand^{1,2}, E., Storey³, C., Fowler³, M., Dhuime⁴, B., Doucelance, R.¹

5
6 ¹ Laboratoire Magmas et Volcans, CNRS, Université Clermont Auvergne, France ; ²
7 Laboratoire Geo-Ocean, CNRS, Université de Bretagne Occidentale, France ; ³ University of
8 Portsmouth, School of Environment, Geography and Geosciences, Portsmouth, UK; ⁴ CNRS-
9 UMR 5243, Géosciences Montpellier, Université de Montpellier, France

10
11 Corresponding author: emilie.bruand@univ-brest.fr

12 Laboratoire Geo-Ocean

13 IUEM, Technopôle Brest-Iroise

14 Rue Dumont d'Urville

15 29280 PLOUZANE

16 ORCID ID: 0000-0003-2711-4019

17
18 Abstract

19 It is well-established that lanthanide rare earth elements (REEs) have the potential to record the
20 nature and source characteristics of their host magmas, in both whole-rock and their minerals.
21 Accessory minerals that concentrate REEs are especially useful in crustal evolution studies,
22 both for their elemental and isotopic information; the classic and unrivalled example being
23 zircon. Approaches using a single radiogenic isotopic system, or one radiogenic and one stable
24 isotope system (e.g., Hf and O) in one REE-bearing mineral (usually zircon) are common, but
25 those involving multiple isotopes in several minerals remain scarce despite offering many
26 advantages. Importantly, the latter approaches also allow comparing different techniques and
27 provide evidence on whether isotopic systems were disturbed by secondary processes. This
28 contribution documents several isotopic systems within the abundant accessory mineral of
29 Caledonian high Ba-Sr granitoids from Northwest Scotland. We present a multi-isotope study
30 of titanite, zircon and apatite from two localities (Strontian and Rogart), which were selected
31 for their contrasting whole-rock isotopic signatures - the former deriving from a depleted mantle
32 source, whereas the latter derived from a strongly enriched mantle source. New in-situ Sm-Nd
33 in titanite and apatite and Hf in zircon isotope data are discussed and compared with in-situ

34 oxygen isotope data previously published for the same samples. An internal consistency is
35 observed for Nd isotopes in apatite and titanite. Nd isotopes values for both minerals strongly
36 correlate with Hf isotopes in zircon. Isotopic data at the mineral scale confirm the Strontian and
37 Rogart source characteristics previously defined from whole-rock isotope data, with the Rogart
38 having a more enriched signature than the Strontian source along the “Caledonian Parental
39 Magma Array”(CPMA). In contrast, a significant discrepancy exists between whole-rock and
40 REE-mineral oxygen isotope data as the latter can be affected by post emplacement alteration
41 and hence can be misinterpreted. Importantly, the contribution of sediments in the CPMA
42 source(s) can be estimated from a diagram combining Sm-Nd isotopic signatures and $(La/Sm)_N$
43 in apatite and titanite. Overall, we demonstrate that detailed petrogenetic records are not only
44 available in zircons but also in magmatic titanite and apatite, and we suggest that integrated
45 multi-mineral approaches have potential to maximise constraints from in-situ mineral isotope
46 geochemistry.

47
48

49 Keywords: Nd isotopes, Hf isotopes, O isotopes, titanite, apatite, zircon, high Ba-Sr granitoids,
50 magma petrogenesis.

51

52 1. Introduction

53

54 Advances in analysing various isotope systems in accessory minerals at (sub)-mineral scale
55 have been critical in improving our understanding of the geological processes that shaped the
56 continental crust. For example zircon ($ZrSiO_4$), by way of U-Pb geochronology coupled with
57 radiogenic Hf and stable O isotopes, has provided tight constraints on crust formation processes
58 up to 4.4 billions years ago in the Hadean (e.g. Wilde et al. 2001a; Bell et al. 2011). Isotopic
59 data in zircon also greatly improved our knowledge of the mechanisms and rates of crustal
60 growth, by linking sedimentary and igneous records (e.g. Kemp et al. 2007; Belousova et al.
61 2010; Dhuime et al. 2012). However, there is increasing evidence that by studying zircon only,
62 we are limiting our ability to fully understand a number of geological processes. This is mostly
63 because (i) zircon crystallization is biased toward felsic compositions and (ii) when studying
64 the complex history of ancient terrains, zircon is not very sensitive to important secondary
65 processes, such as metamorphism or metasomatism (Fisher et al. 2019; Hammerli et al. 2019).
66 More recently, significant progress has been made with less studied REE-minerals (e.g. titanite,
67 apatite, monazite, allanite), and it is now possible to interrogate multiple accessory minerals

68 (including zircon) within a given rock. For example, trace elements in REE-minerals record
69 petrogenetic information about granite petrogenesis (e.g., mixing, crystal fractionation; e.g.
70 Miles et al. 2013; Bruand et al. 2014; Laurent et al. 2017). In particular, trace elements in these
71 minerals are sensitive to melt polymerisation (Prowatke and Klemme, 2006, 2005) and hence
72 have potential to constrain the bulk mafic or felsic composition of their host rocks. Strontium
73 concentration in apatite is a good proxy for the whole-rock Sr concentration (Sr_{WR}), and by
74 extrapolation for the SiO_2 content of the magma (e.g., Jennings et al. 2011; Bruand et al. 2016).
75 Other trace elements and halogens can record metasomatic processes (e.g. Harlov, 2015; Zirner
76 et al., 2015). Recent advances with in-situ O isotope analysis have enabled the production of
77 reliable data for a variety of REE-minerals (Bonamici et al., 2014; Bruand et al., 2019; Sun et
78 al., 2016; Wudarska et al., 2020), which can be used to track potential alteration or sediment
79 input to a magma source. Development of Sm-Nd in-situ analysis in various REE-minerals has
80 been widely applied to igneous and metamorphic rocks (e.g. Foster and Vance 2006; Fisher et
81 al. 2011b; Yang et al. 2014; Doucelance et al. 2020). Finally, other in-situ analytical procedures
82 are currently being developed on REE-minerals: for instance Sr isotopes in apatite to trace the
83 source of igneous rocks in the same fashion as Sm-Nd isotopes (Emo et al., 2018; Gillespie et
84 al., 2021). In the context of this burgeoning array of mineral-scale elemental and isotopic new
85 approaches, attention has recently turned to the coherence between mineral and whole-rock
86 data. For example, Gregory et al. (2009) showed that accessory minerals are a faithful proxy
87 for the Sm-Nd isotopic composition of recent calc-alkaline magmas, while Hammerli et al.
88 (2014) quantified the equilibration of the Sm-Nd isotopic system in accessory minerals along a
89 metamorphic gradient. However, a few recent studies have highlighted the decoupling of
90 accessory mineral U-Pb and Sm-Nd isotopes in Archean granitoids. These studies, along with
91 other studies on the decoupling of isotopic systems and/or trace elements in REE-minerals (e.g.,
92 Hf, Sr, U-Pb; Antoine et al., 2020; Fisher et al., 2019; Gordon et al., 2021; Hammerli et al.,
93 2019), have important implications for our ability to reconstruct complex ancient terrains, with
94 more work required to better understand the responsible parameters (P, T, fO_2 , fluid properties).
95 Approaches using a single isotopic system in one REE-mineral are common, but those
96 involving multiple isotope analyses in several accessory minerals remain scarce (e.g. Fisher et
97 al. 2019). The latter allow cross-calibration of different techniques and provide evidence on
98 whether isotopic systems have been disturbed or not by secondary processes. Here we present
99 a multi-isotopic study on selected REE-minerals from late Caledonian high-Ba-Sr granitoids
100 sampled in Northern Scotland. Our data include new in-situ Sm-Nd isotopes in apatite and
101 titanite, Hf isotopes in zircon, as well as O isotopes previously published by (Bruand et al.,

102 2019). This represents the most comprehensive dataset of three isotope systems in three
103 accessory minerals and their host rocks. Our approach allows us to rigorously test mineral
104 versus whole-rock isotopic fidelity, and we show that in undeformed Phanerozoic granitoids
105 selected for this study, radiogenic isotope ratios (Hf and Nd) give consistent values in all phases,
106 while there is a notable discrepancy for O isotopes between whole rocks (O_{WR}) and REE-
107 minerals (O_{REEml}). We emphasise that titanite and apatite are, in the same way as zircon,
108 powerful minerals to track magma sources, refine petrogenetic models and overcome late
109 alteration of O_{WR} data.

110

111 2. Geological and geochemical setting

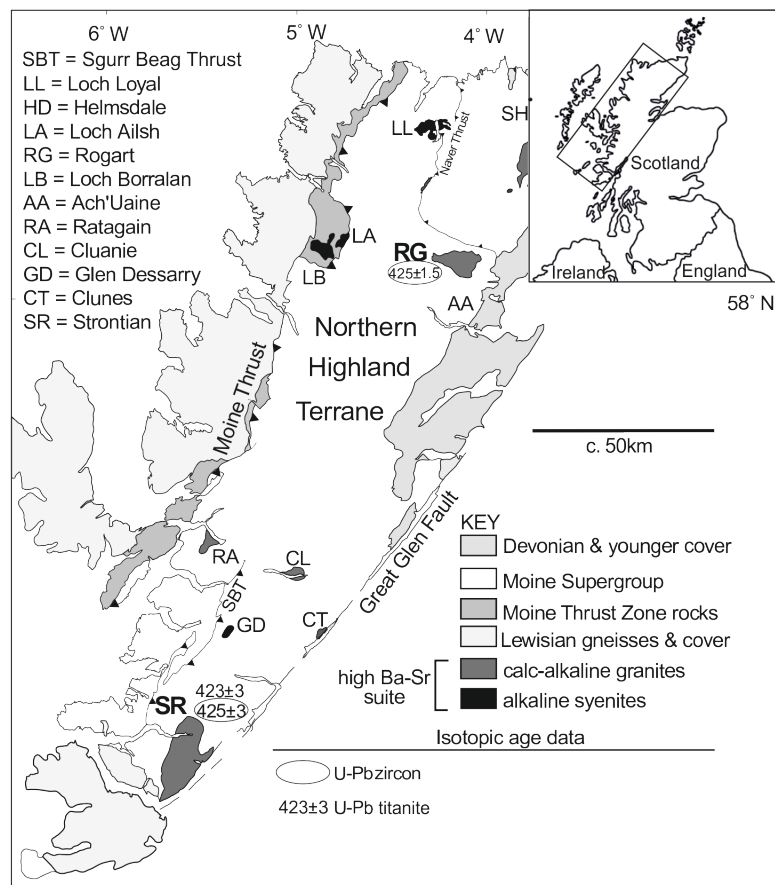
112

113 All samples presented here are from high Ba-Sr granites intruded at the end of the Caledonian
114 orogeny in Scotland. They have been interpreted as the result of a slab break off (Atherton and
115 Ghani, 2002; Fowler et al., 2008, Archibald et al, 2022) consequent upon continental collision
116 between Laurentia and Baltica that followed closure of Iapetus during the Silurian and
117 Devonian (Atherton and Ghani, 2002; Soper et al., 1992). Geological features relevant to this
118 study are described below but readers can refer to previous papers for the tectono-magmatic
119 evolution of Scottish Highlands granites (e.g. Archibald et al., 2022; Brown et al., 2008; Miles
120 et al., 2016; Soper, 1986; Stephens and Halliday, 1984).

121 The late Caledonian high Ba-Sr suite intrudes the Northern Highland terrane and can be divided
122 petrographically into a western group of syenites and related rocks and a central-eastern group
123 of granitic plutons and associated appinites (Fig. 1, Fowler et al., 2008 and references therein).
124 In this contribution, we present new isotopic data on REE-bearing minerals (titanite, apatite,
125 zircon) from Rogart and Strontian plutons belonging to the central eastern granitic plutons. We
126 chose these two localities for their contrasting origins from relatively enriched (Rogart) and
127 relatively depleted sources (Strontian) along a “Caledonian Parental Magma Array” (Fowler et
128 al., 2008). The Rogart and Strontian igneous complexes have a broadly concentric geometry
129 and are dominated by biotite-hornblende granodiorite. Strontian has a biotite granodiorite
130 central facies surrounded by hornblende-biotite granodiorite, which grades from porphyritic to
131 non-porphyritic at its margin (Sabine, 1963). The hornblende-biotite granodiorite has been
132 dated at 425 ± 3 Ma (U-Pb on zircon) and 423 ± 3 Ma (U-Pb on titanite; (Rogers and Dunning,
133 1991). The Rogart igneous complex is made up of an inner granodiorite and an outer tonalite,
134 which are cross cut by a later granite. It is coeval with Strontian and has been dated around 420
135 Ma (K-Ar on biotite; Brown et al., 1968) and 425 ± 1.5 Ma (U-Pb on zircon; Kocks et al., 2014).

136 Appinites (Bailey and Maufe, 1916) are mafic magma bodies (from centimetre to hundreds of
 137 metres scale) present in the main facies of both the Strontian and Rogart plutonic bodies.
 138 Scottish appinites are hydrous, mantle-derived rocks with shoshonitic affinities (Fowler, 1988;
 139 Fowler et al., 2008), and are widely believed to be the plutonic equivalents of calc-alkaline
 140 lamprophyres (Murphy, 2013; Rock, 1984). Local mingling and mixing relationships can be
 141 observed between the main plutonic facies and the appinitic bodies in both plutons (Stephenson,
 142 1999). A mingling and intimate mixing event is recorded in the chemistry of apatite and titanite
 143 from the Strontian granite samples (Bruand et al., 2014). On the basis of elemental, stable and
 144 radiogenic isotope evidence, both plutons are believed to have evolved by fractional
 145 crystallisation concurrent with variable assimilation of the surrounding Moine metasediments
 146 (Fowler et al., 2001, 2008).

147

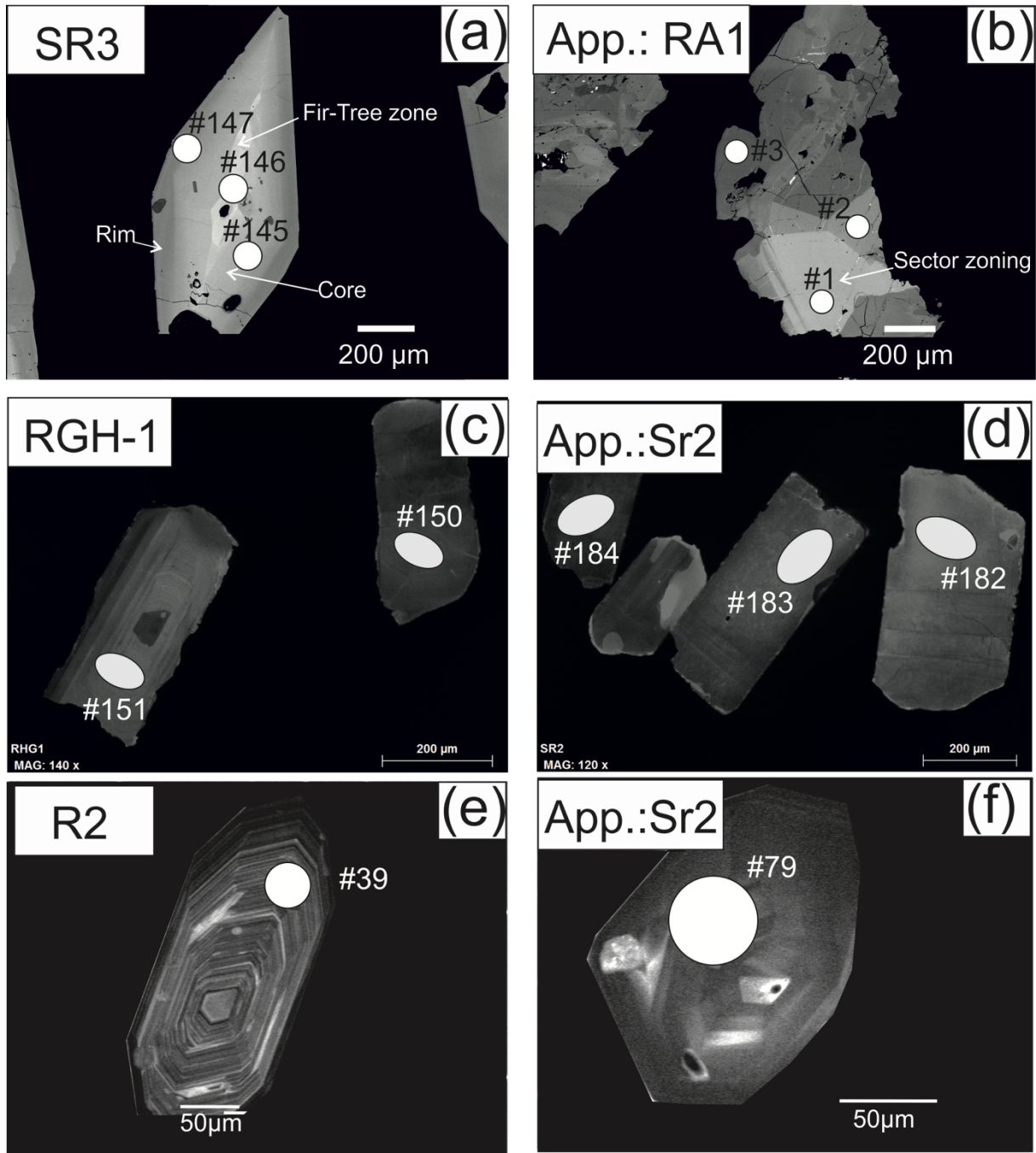


148
 149 **Figure 1: Map from the Northern Highland region (Scotland), modified after Fowler et al. (2008) and**
 150 **showing samples localities and ages from Rogers and Dunning (1991), Brown et al. (1968) and (Kocks et**
 151 **al., 2014). RG (Rogart) and SR (Strontian) granites localities are the focus of this study.**

152

153 3. Sample selection and preparation

154 Eight samples were selected for this study: three hornblende-biotite (hb-bi) granodiorites (SR1,
155 SR3, SR4) and one appinite (SR2) from Strontian; as well as two tonalites (RT1, R2), one
156 granite (RHG1) and one appinite (RA1) from Rogart. All samples from both plutons contain
157 abundant accessory titanite, apatite and zircon (Bruand et al., 2017, 2014). All hb-bi
158 granodiorite samples from Strontian are chemically similar for major and trace element contents
159 while granitoid compositions for major and trace elements contents from Rogart vary more
160 widely. Details on whole rock major and trace elements contents and their interpretation can be
161 found in Fowler et al. (2008) for Strontian and Fowler et al., (2001) for Rogart. Appinites in
162 the central-eastern Northern Highlands carry the high Ba-Sr elemental signature, but are
163 commonly even more enriched in LILEs (e.g. Sr, Ba), HFSEs (e.g. Nb, Th) and transition
164 metals (e.g. Cr, Ni, V) than associated granodiorites and granites (Fowler et al., 2008). These
165 characteristics can be observed in the two appinitic samples studied here (SR2 and RA1).



166
 167 **Figure 2 : Representative back-scattered electron images of titanite (a-b). RA1 and SR2 are appinites, other**
 168 **samples are granitoids. (a-d) Numbers represent Nd isotope analyses done by LA-MC-ICPMS and**
 169 **correspond to the data reported in appendix A. (e-f) Numbers represent Hf isotope analyses (Appendix B)**
 170

171 The samples were crushed (jaw-crusher, ball mill or Selfrag™), sieved (<355 μm, 355-
 172 500 μm and 500-1000 μm fractions) and passed over a Wilfley table. A diamagnetic separator
 173 was then used to obtain fractions of different heavy minerals based on their diamagnetic
 174 properties. Titanite, apatite and zircon were handpicked, mounted in epoxy resin discs and
 175 polished for in-situ chemical analysis. All accessory minerals studied in the different samples

176 have been imaged prior to analysis (Figs. 2) and characterised for their major and trace elements
177 chemistries (Bruand et al., 2017, 2014). Further details concerning the studied samples (Whole
178 rock data, petrography and accessory mineral analyses) can be found in Fowler et al. (2008,
179 2001) and Bruand et al. (2019, 2014), and are not repeated here.

180

181 4. Analytical techniques

182

183 The following text describes the analytical methods for new data presented herein. Associated
184 O isotope procedures are described in Bruand et al. (2019).

185

186 4.1 In-situ Sm-Nd isotope measurements in apatite and titanite

187

188 Neodymium isotope measurements were performed using a Thermo Fisher Scientific™
189 Neptune Plus™ mass spectrometer coupled with a 193-nm wavelength Resonetics™ M-50E
190 laser system at the Laboratoire Magmas et Volcans (LMV, Clermont-Ferrand, France).
191 Analyses were realised with a combination of X-Skimmer and Jet-interface cones and followed
192 the procedure described in Doucelance et al. (2020). For titanite, typical measurements
193 consisted of 70 or 90 cycles with a laser ablation spots of 73 µm in diameter. For apatite, raster
194 analyses were performed (53 µm spot size, 85 µm length) with 130 cycles and an integration
195 time of 1s. The same spot/raster settings were applied on the standards. The first 15 cycles being
196 of every measurement were used to evaluate the baseline level of each Faraday Cup. Oxides
197 were monitored and maintained at <5% (ThO/Th). Baseline and gain reductions were operated
198 online; all other calculations were performed off-line using an in-house Microsoft Excel™
199 spreadsheet. Gain calibration was done at the beginning of each analytical session. Analyses
200 were performed over 5 different analytical sessions. Doped-Jndi glass was analysed regularly
201 during the different sessions to monitor potential $^{147}\text{Sm}/^{144}\text{Nd}$ drift that has been reported
202 previously (Doucelance et al., 2020). Primary standards for apatite (Durango from Doucelance
203 et al., 2020; $^{143}\text{Nd}/^{144}\text{Nd}= 0.512483$ and $^{147}\text{Sm}/^{144}\text{Nd}= 0.076096$) and titanite (SPREN;
204 $^{143}\text{Nd}/^{144}\text{Nd}= 0.512252$ and $^{147}\text{Sm}/^{144}\text{Nd}= 0.1319$ or MKED-1; $^{143}\text{Nd}/^{144}\text{Nd}= 0.51163$ and
205 $^{147}\text{Sm}/^{144}\text{Nd}= 0.127$; Foster and Vance, 2006; Spandler et al., 2016) have been used for
206 normalization and to correct for instrumental drift when necessary. Laser fluence was set to
207 3.8-4.1 J/cm², frequency 6 Hz, He flow rate was 700-875 ml/min and N₂ 1.8-2.6 ml/min
208 depending on the session. All unknowns and standards data acquired can be found in
209 Supplementary data_Table 1. Initial εNd values were calculated using the decay constant of

210 6.54×10^{-12} (Lugmair and Marti, 1978), the CHUR parameters of $^{143}\text{Nd}/^{144}\text{Nd} = 0.512630$ and
211 $^{147}\text{Sm}/^{144}\text{Nd} = 0.1960$ (Bouvier et al., 2008) and an age of 425 Ma for the samples from both
212 localities.

213

214 4.2 In-situ Lu-Hf isotope measurements in zircon

215 The Lu-Hf analyses were performed at the University of Bristol (Bristol Isotope Group)
216 using a ThermoFinnigan Neptune plus multicollector inductively-coupled plasma mass
217 spectrometer (MC-ICP-MS) coupled with a Photon-Machine Analyte G2 Excimer laser (193
218 nm wavelength). Ablation was performed using 50 μm and 40 μm spot sizes, a laser frequency
219 of 4 Hz, and the energy density of the laser beam was c. 6 J/cm². A typical analysis was 90
220 seconds, including a 30 seconds background measurement and a 60 seconds ablation period.
221 Correction for the interferences and mass bias followed the Bristol routine procedure
222 (Hawkesworth and Kemp, 2006; Kemp et al., 2009). The correction for the isobaric interference
223 of Yb and Lu on ^{176}Hf was made following a method detailed in Fisher et al. (2011a). For Yb,
224 the interference-free ^{171}Yb was corrected for mass bias effects using an exponential law and
225 $^{173}\text{Yb}/^{171}\text{Yb} = 1.132685$ (Chu et al., 2002). The mass bias-corrected ^{171}Yb was monitored during
226 the run and the magnitude of the ^{176}Yb interference on ^{176}Hf was calculated using $^{176}\text{Yb}/^{171}\text{Yb}$
227 $= 0.901864$ (Chu et al., 2002). For Lu, the interference-free ^{175}Lu was corrected for mass bias
228 effects assuming $\beta_{\text{Lu}} = \beta_{\text{Yb}}$ and using an exponential law. The mass bias-corrected ^{176}Lu was
229 monitored during the run and the magnitude of the ^{176}Lu interference on ^{176}Hf was calculated
230 using $^{176}\text{Lu}/^{175}\text{Lu} = 0.02655$ (Vervoort et al., 2004). Interference-corrected $^{176}\text{Hf}/^{177}\text{Hf}$ were
231 corrected for mass bias using an exponential law and $^{179}\text{Hf}/^{177}\text{Hf} = 0.7325$ (Patchett and
232 Tatsumoto, 1981), and were finally normalized to JMC-475 = 0.282160. The accuracy and
233 long-term reproducibility of the measurements were gauged by analysing repeatedly three
234 zircon reference standards (Plesovice, Mud Tank and TEMORA 2; Supplementary data_Table
235 2). $^{176}\text{Lu}/^{177}\text{Hf}$ vs $^{176}\text{Yb}/^{177}\text{Hf}$ values of our unknowns plot within the range of standards
236 analysed during analytical session attesting to efficient isobaric correction. Initial ϵ_{Hf} values for
237 this study were calculated using the decay constant of 1.867×10^{-11} (Söderlund et al., 2004), the
238 CHUR parameters $^{176}\text{Hf}/^{177}\text{Hf} = 0.282785$ and $^{176}\text{Lu}/^{177}\text{Hf} = 0.0336$ (Bouvier et al., 2008) and
239 an age of 425 Ma.

240

241 5. Results

242

243 Full data are available in Appendix A, and a summary that also includes published O isotope
 244 data is presented in Table 1 below.

245

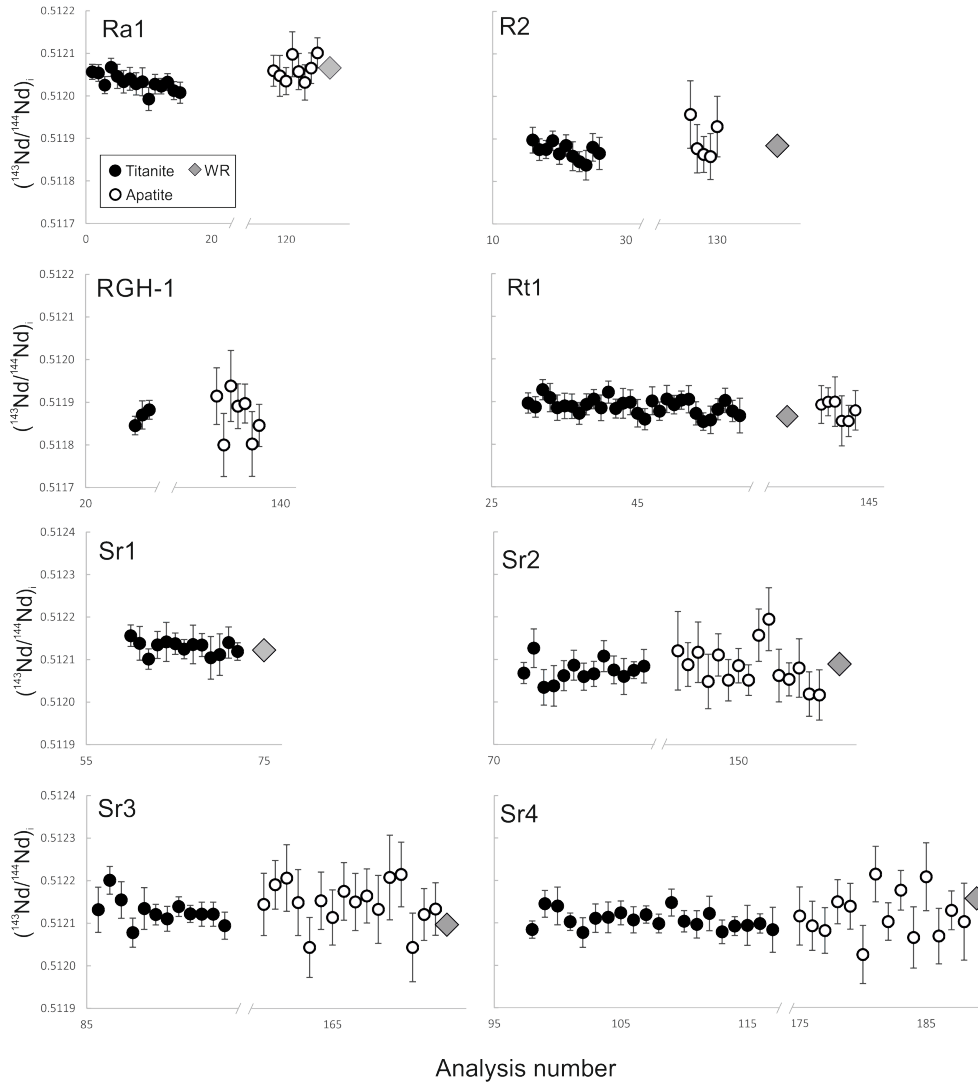
246 **Table 1 : Summary of isotopic data for the studied samples. *Whole rock isotopic analyses are from Fowler**
 247 **et al. (2001, 2008). Reported whole rock uncertainties are based on uncertainties of the standards analysed**
 248 **during the analytical session. The values reported are averages and associated standard deviations for each**
 249 **sample. β Oxygen data are from Bruand et al. (2019). ϵ Hf, $^{87}\text{Sr}/^{86}\text{Sr}_i$ and ϵ Nd are calculated at 425 Ma.**

Sample	RA1	RT1	R2	RGH1	SR1	SR2	SR3	SR4	
	appinite	tonalite	tonalite	granite	granodiorite	appinite	granodiorite	granodiorite	
ϵNd	-0.3	-4.1	-3.9	-	0.7	0.1	0.3	1.4	
2SD	0.5	0.5	0.5	-	0.5	0.5	0.5	0.5	
Whole rock*	$^{87}\text{Sr}/^{86}\text{Sr}_i$	0.70630	0.70633	0.70673	-	0.70527	0.70577	0.70559	0.70559
2SD	0.00002	0.00002	0.00002	-	0.00002	0.00002	0.00002	0.00002	
$\delta^{18}\text{O}$	-	8.5	8.7	-	8	6.7	7.8	6.7	
2SD	-	0.2	0.2	-	0.2	0.2	0.2	0.2	
Av. ϵHf	-	-5.6	-5.9	-5.7	-0.8	-1.7	-0.3	-2.3	
2SD	-	1.2	1.1	0.8	1.2	1.4	1.4	1.2	
Zircon	Av. $\delta^{18}\text{O}_\beta$	5.6	6.2	5.9	6.0	6.0	5.9	6.3	
2SD	0.3	0.5	0.7	0.3	0.3	0.4	0.4	0.2	
Titanite	Av. $\delta^{18}\text{O}_\beta$	4.3	4.8	4.7	5.2	4.8	5.4	5.3	4.3
2SD	0.7	0.4	0.2	0.4	0.8	0.3	0.3	0.3	
Av. ϵNd	-1.0	-3.8	-4.2	-4.3	0.9	-0.2	0.8	0.4	
2SD	0.8	0.7	0.7	0.7	0.6	1.0	1.2	0.8	
Apatite	Av. $\delta^{18}\text{O}_\beta$	5.1	5.3	5.3	5.8	-	6.1	5.8	4.6
2SD	0.4	0.4	0.3	0.4	-	0.6	0.5	0.7	
Av. ϵNd	-0.4	-3.7	-3.7	-4.2	-	0.0	1.2	0.7	
2SD	1.0	0.9	1.7	2.1	-	1.9	2.0	2.1	

250

251

252 5.1 Sm-Nd isotopes in apatite and titanite.



253

254 **Figure 3 : $^{143}\text{Nd}/^{144}\text{Nd}_{\text{initial}}$ for apatite and titanite from both localities (R = Rogart and S = Strontian), along**
 255 **with whole rock (WR) data from the same samples (Fowler et al. , 2001 and 2008). Error bars on single**
 256 **minerals and whole rock are 2 sigma and are smaller than symbols if not visible. Dashed horizontal lines**
 257 **represents whole rock value.**

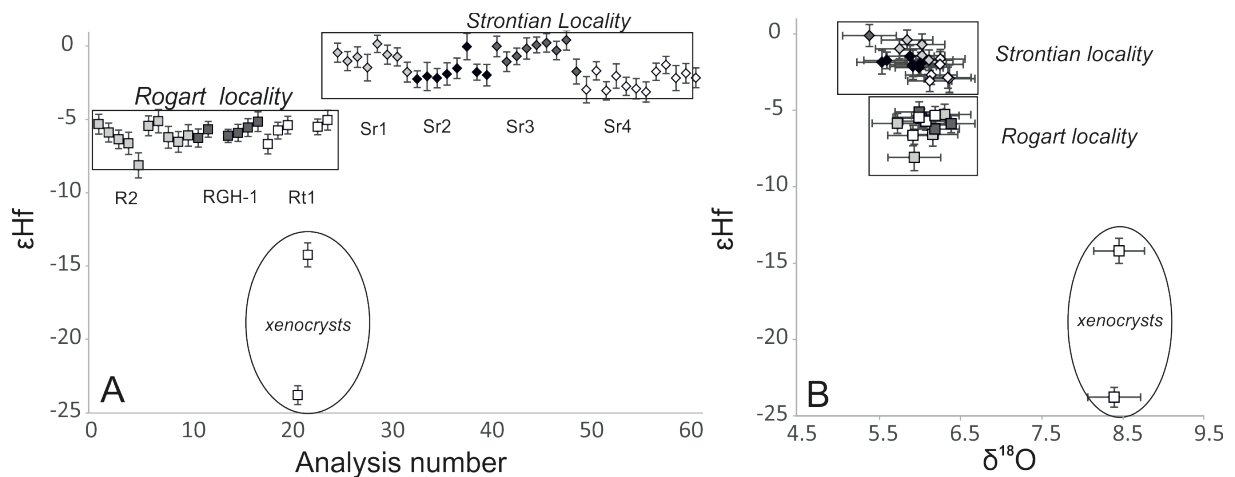
258

259 Overall, Nd isotope data for the high Ba-Sr samples can be split into two groups. The first group
 260 includes Rogart samples RT1, R2 and RGH-1 with similar average $^{143}\text{Nd}/^{144}\text{Nd}_i$ values ranging
 261 between $0.511866 (\pm 0.000038; 2\text{SD})$ and $0.511889 (\pm 0.000036)$ for titanite, and between
 262 $0.511870 (\pm 0.000109)$ and $0.511896 (\pm 0.000087)$ for apatite (Fig. 3 and Appendix_A). The
 263 second group includes all Strontian samples + Rogart apatite RA1, with similar average
 264 $^{143}\text{Nd}/^{144}\text{Nd}_i$ values ranging between $0.512032 (\pm 0.000039)$ and 0.512129 (2SD 0.000032) for
 265 titanite, and $0.512083 (\pm 0.000083)$ and $0.512119 (\pm 0.000109)$ for apatite (Fig. 3 and
 266 Appendix_A). Most data are within uncertainty of the whole-rock associated (Fig. 3). Average
 267 ϵNd_i values for group 1 samples are reported in Table 1. They are between -3.8 ± 0.8 (2SD) and

268 -4.3 ± 0.8 (2SD) for titanite and between -3.7 ± 1.8 (2SD) and -4.20 ± 2.1 (2SD) for apatite.
 269 For group 2 Strontian samples and RA1, average ϵNd_i values are between -1.0 ± 0.8 (2SD) and
 270 0.9 ± 0.6 (2SD) for titanite and -0.4 ± 1.0 (2SD) and 1.2 ± 2.0 (2SD) for apatite.
 271 Rogart apatite and titanite $^{143}\text{Nd}/^{144}\text{Nd}_{\text{initial}}$ values are identical within uncertainty (Fig. 3).
 272 Overall, due to their lower concentration in LREE and the smaller spot required for analyses,
 273 errors on apatite analyses are greater than for titanite. For example, Nd concentrations in titanite
 274 from RA1 vary between 5300 and 11900 ppm, but between 762 and 1700 ppm for apatite
 275 (Bruand et al., 2014). Such differences are present in all samples studied here (Bruand et al.,
 276 2014). Consequently, reproducibility on RA1 titanite $^{143}/^{144}\text{Nd}_i$ is 76 ppm and 102 ppm on
 277 apatite (Appendix_A). For the same reasons, greater errors for apatite measurements are also
 278 observed in Strontian samples. For example, uncertainty on SR3 titanite is 120 ppm, but 200
 279 ppm on apatite (Appendix_A).

280

281 5.2 Lu-Hf isotopes in zircon



282

283 **Figure 4 : ϵHf (A; this study) and $\delta^{18}\text{O}$ (B; from Bruand et al. (2019)) in zircon for both localities. Error**
 284 **bars are 2 sigma and are smaller than symbols if not visible.**

285

286 Hf isotopes have been measured in all samples except RA1 which is an apatite with very few
 287 zircons. Those separated were analysed for trace elements and oxygen isotopes but attempts
 288 with Hf led to unacceptable signal due to the presence of inclusions during ablation. The
 289 remaining data define the same two analytical groups (Fig. 4A). Rogart granitoids (R2, RGH-
 290 1, RT1) have average ϵHf ranging between -5.9 ± 0.6 (1SD) and -5.7 ± 0.6 (1SD), whilst a more
 291 radiogenic group defined by Strontian samples vary between -2.3 ± 0.6 (1SD) and -0.3 ± 0.7
 292 (1SD; Table 1 and Appendix_B). Two data points from RT1 are not included in the average
 293 calculations. They have very negative ϵHf (-23.8 , -14.2) measured in xenocrystic cores (Fig. 4,

294 Appendix_B). These xenocrysts have not been dated and reported ϵ_{Hf} values have been
 295 calculated at 425 Ma for the sake of comparison.

296

297 6. Discussion

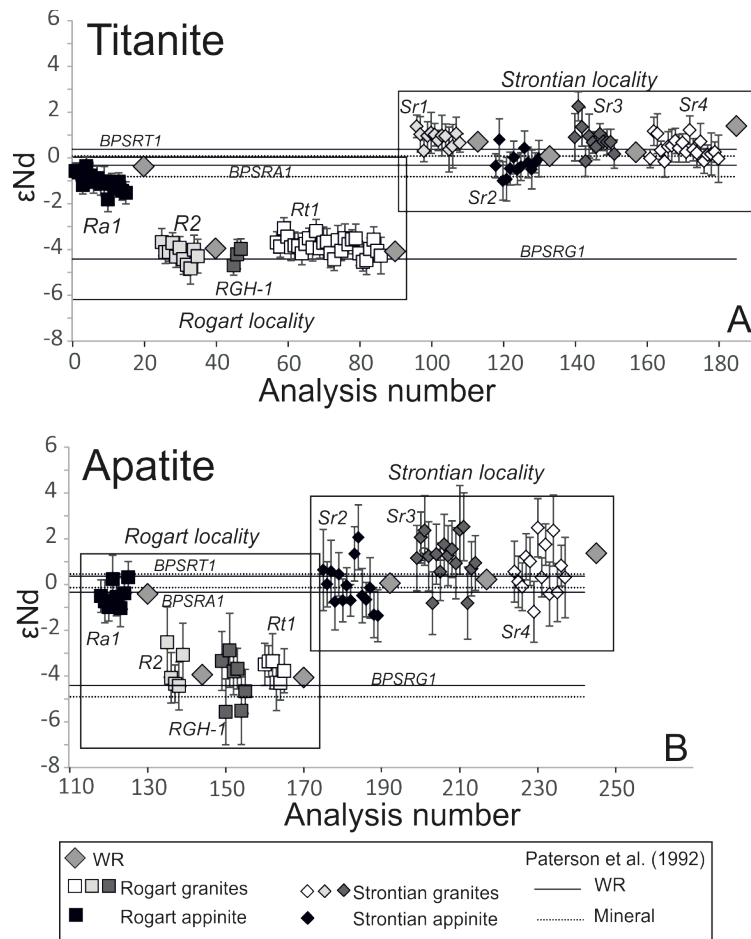
298

299 First we discuss the results for minerals, which are less commonly analysed for their available
 300 isotope systems - apatite and titanite. We then add data for zircon and consider the potential for
 301 enhanced understanding of geological processes with a combined, multi-mineral approach.

302

303 6.1 Apatite and titanite versus whole-rock data.

304



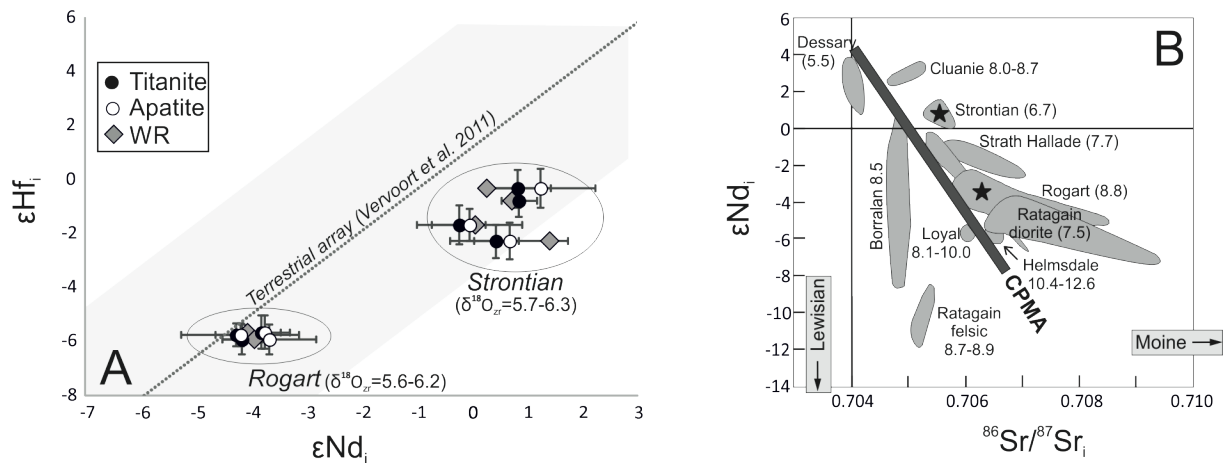
305

306 **Figure 5 : ϵ_{Nd} initial values for titanite (left) and apatite (right) for both localities. Error bars are 2 sigma or**
 307 **within the symbol if not visible. app.= apatite, gr.= granitoid. Black (WR) and dotted lines (a- titanite and**
 308 **b- apatite) are data from Paterson et al. (1992). BPSRT1, BPSRA1 and BPSRG1 are samples from Paterson**
 309 **et al. (1992).**

310

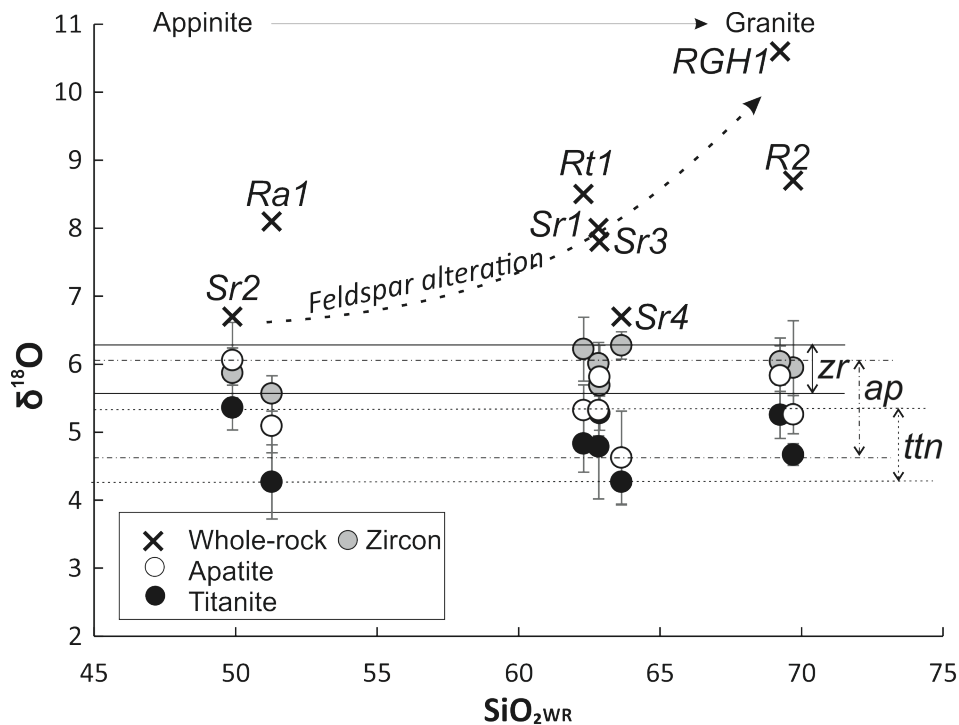
311 Detailed pioneer work was carried out by Paterson et al. (1992) on different granitoid samples
312 from Strontian. They presented Sm-Nd isotopic analyses for both whole-rocks and fractions of
313 multiple grains (apatite, titanite, +/- monazite and zircon). They obtained an $\epsilon\text{Nd}_{\text{WR}}$ of 0.4 (± 1.2 ,
314 2SD), $\epsilon\text{Nd}_{\text{ap}}$ -0.1 (± 1.2 , 2SD), $\epsilon\text{Nd}_{\text{titanite}}$ 0.1 (± 0.8 , 2SD) for Strontian granodiorite (BPSRT1),
315 and they reported ϵNd values for one sample in the center of the pluton with an $\epsilon\text{Nd}_{\text{WR}}$ value
316 of -4.4 (± 0.8 , 2SD) (cf. Table 1). These results are in line with our new data (Figure 5).
317 Interestingly, Paterson et al. (1992) also reported Sm-Nd analyses in zircon in disequilibrium
318 with the other accessory phases (titanite, monazite) and the whole-rocks, and they concluded to
319 a potential inherited contribution from some zircons. Over the last three decades, the
320 development of in-situ techniques has allowed to analyse smaller zones of single minerals with
321 better uncertainties, to refine (i) our understanding of chemical and isotopic behaviour of
322 accessory minerals and (ii) petrogenetic processes affecting magmas. Our new data reveal a
323 close consistency between ϵNd in apatite and titanite within the same sample and, importantly,
324 with previous whole-rock determinations (Table 1). As highlighted in Section 5, ϵNd values
325 obtained in Rogart granites (RT1, R2 and RGH-1) are similar and range between -3.8 and -4.3
326 for titanites, and between -3.7 and -4.2 for apatite (Table 1), while the appinitic sample from
327 the same locality (RA1) give higher ϵNd values for titanite (about -1.0) and for apatite (about -
328 0.4). Overall, this last sample is comparable with ϵNd from Strontian (Fig. 5). Appinitic samples
329 from both localities tend to have slightly lower titanite average ϵNd (-0.2 for SR2 and -1.0 for
330 RA1, Table 1) than for Strontian granitoids ($\epsilon\text{Nd}=0.4-0.9$, Fig. 5A). This is however not fully
331 resolvable considering uncertainties on the data. While more scattered, apatites show exactly
332 the same tendency (Fig. 5B). When disaggregated by locality, some familiar differences emerge
333 (Fig. 5). On the basis of whole-rock data isotopes only, Fowler et al. (2008) argued that the
334 parent magmas of the high Ba-Sr granitoids derived from a Caledonian Parental Magma Array
335 (CPMA, Fig. 6b) that extended from isotopically depleted to isotopically enriched
336 compositions, broadly from the southwest toward the northeast of the Northern Highland
337 Terrane (Fig. 1). A number of high Ba-Sr granites, including Strontian and Rogart, fall on well-
338 defined ϵNd vs $^{87}\text{Sr}/^{86}\text{Sr}_i$ trajectories suggesting assimilation of host rock Moine
339 metasediments, from either end of the CPMA (Fig. 6b). For Rogart, Fowler et al. (2001)
340 proposed that AFC was the controlling process and that the isotopic values limited Moine input
341 to ca. 25%. Later, Fowler et al. (2008) suggested that Strontian evolved via similar processes
342 but originated from less-enriched mantle-derived parent magmas. One key observation that the

343 most mafic samples were often the most “contaminated” is confirmed by our RA1 appinite in-
 344 situ data (Fig. 5). This was interpreted as the consequence of a complex building of the plutonic
 345 body involving several batches of magma with different routes within the crust.



346 **Figure 6: A- $\epsilon\text{Nd}_{\text{initial}}$ for titanite, apatite and WR versus $\epsilon\text{Hf}_{\text{initial}}$ in zircon for Rogart and Strontian**
 347 **localities. $\delta^{18}\text{O}_{\text{Zr}}$ ranges are also reported on the figure. Appinite RA1 sample is not reported on this figure**
 348 **due to the lack of Hf data. Error bars are 1 SD. B- from Fowler et al. (2001): ϵNd versus $^{87}\text{Sr}/^{86}\text{Sr}_i$ for**
 349 **Caledonian high Ba-Sr granitoids from the NHT including Strontian and Rogart (black stars), annotated**
 350 **with $\delta^{18}\text{O}_{\text{WR}}$. CPMA= Caledonian Parental Magma Array.**
 351

352
 353 In contrast to the fidelity with which radiogenic isotopes in accessory minerals record the
 354 primary composition of the source magma from which they crystallised, the oxygen signature
 355 is not so clear cut. Fowler et al (2008) observed higher whole-rock O isotope values for Rogart
 356 ($\delta^{18}\text{O} = 8.5-10.6\text{‰}$) than for Strontian ($\delta^{18}\text{O} = 6.7-8\text{‰}$, Fig. 7), apparently correlated with
 357 increasing $^{86}\text{Sr}/^{87}\text{Sr}_i$ and decreasing ϵNd (Fig. 6b) and unrelated to LOI (Fowler et al., 2008,
 358 their Fig. 10). These were originally interpreted as the consequence of higher pelagic sediment
 359 input to the Rogart mantle source (Fowler et al., 2008). A subsequent study of the same samples
 360 using in-situ O isotopes in accessory minerals (Bruand et al., 2019 – the source of the O data
 361 considered here) recorded homogeneous oxygen isotopes across all minerals (apatite, titanite
 362 and zircon) from both localities (Fig. 7). This decoupling between whole rock and in-situ
 363 oxygen data was interpreted as the consequence of feldspar alteration (visible in thin section),
 364 being stronger in Rogart and in the most differentiated samples (Bruand et al., 2019). The
 365 petrogenetic consequence is that required pelagic sediments input previously estimated at about
 366 10% for these samples is not a preferred model anymore (Fowler et al., 2008).



367
 368 **Figure 7: $\delta^{18}\text{O}$ versus $\text{SiO}_{2\text{WR}}$ for high Ba-Sr samples modified after Brand et al. (2019).** RGH1 has a
 369 **higher $\delta^{18}\text{O}$ whole-rock value (10.6 ‰), which is interpreted to be the result of late feldspar alteration**
 370 **(Fowler et al., 2001; Bruand et al., 2014). No variations of oxygen isotopic values are resolvable between the**
 371 **less and the most differentiated samples for apatite and titanite. zr: zircon, ap: apatite, ttn: titanite.**

372
 373 6.2 Hf in zircon vs Sm-Nd in apatite and titanite.

374
 375 The Hf and Nd isotope systems are very closely related, an obvious result of their parentage.
 376 Plotting average ϵ_{Hf} in zircon versus ϵ_{Nd} in titanite and apatite for both localities plot close to
 377 the terrestrial array (Fig. 6a). The datasets reveal two groups of samples – Rogart and Strontian,
 378 relatively “enriched” and “depleted” respectively in both isotope systems, directly comparable
 379 with the traditional whole-rock treatment of Nd and Sr isotopes (Fig. 6b). Both diagrams
 380 illustrate that the juvenile component increase from Rogart to Strontian. Strontian samples are
 381 plotting slightly lower than the terrestrial array line itself but is still within the original field
 382 defined by the data in Vervoort et al. (2011, grey field on figure 6a). These slightly lower values,
 383 could also be interpreted as the consequence of residual xenocrysts preventing the full
 384 homogenisation of the magma source during the incorporation of rocks rich in zircons. Both
 385 localities present xenocrysts but dissolution of zircon in the magma source might have been
 386 less efficient than in Rogart.

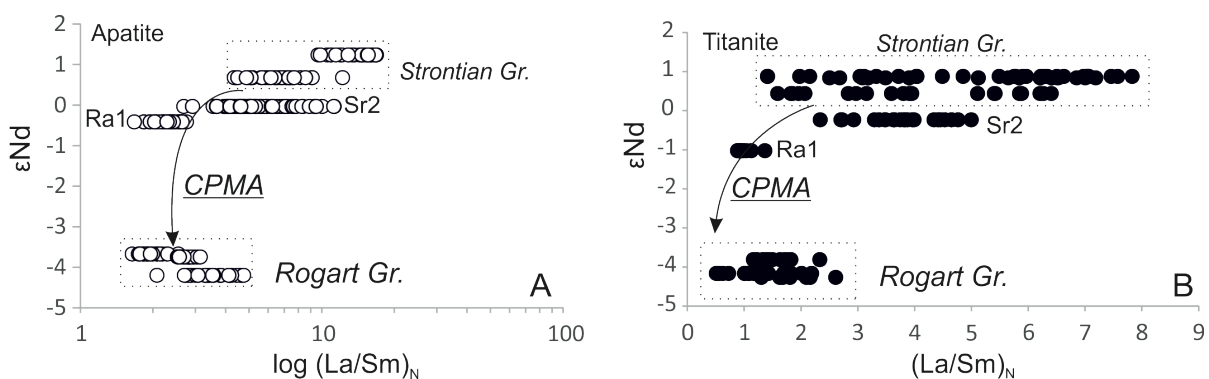
387

6.3 Tracking sediment/crustal assimilation by combining isotopes and elements in apatite and titanite

388
389
390
391 Mineral chemical data gathered from the same accessory minerals (Bruand et al, 2014, 2020)
392 provide the opportunity to investigate variations in elemental ratios that are key for petrogenetic
393 studies. Earlier studies have demonstrated the potential of using REE-bearing minerals and the
394 Sm-Nd systems in crustal evolution studies (Fisher et al., 2017; Gregory et al., 2009; Hammerli
395 and Kemp, 2021). In particular, Gregory et al. (2009) have shown that in-situ Nd isotopes in
396 REE-minerals could faithfully record the source characteristics of a suite of plutons in the
397 Bergell pluton (Italy). Later, Hammerli et al., (2018) used a combination of Nd-Hf-O isotopes
398 in accessory minerals and whole rock to trace melt source in the crust. Although the Nd
399 signature of the magma source was very successfully recovered, they failed to find trace
400 elements systematics tracking crustal assimilation. From the present dataset, we provide an
401 index of crustal assimilation, which is given by the $(La/Sm)_N$ ratio. The $(La/Sm)_N$ ratio in
402 apatite has been shown sensitive to the Aluminium Saturation Index (ASI) of igneous rocks
403 (e.g. Belousova et al., 2001; Bruand et al., 2020; Miles et al., 2013), with apatite from
404 peraluminous magmas ($ASI > 1$) having lower $(La/Sm)_N$ ratios than apatite from metaluminous
405 magmas ($ASI < 1$). In the present sample suite, all studied samples are metaluminous, but
406 $(La/Sm)_N$ variations reveal interesting features seemingly related to the source of the studied
407 granitoids. In figure 8, the $(La/Sm)_N$ versus ϵNd for apatite and titanite shows consistent
408 differences between the plutons - positive ϵNd (ca. 0.5) with relatively high $(La/Sm)_N$ (up to
409 7.8 in titanite and 20 in apatite) at Strontian versus negative ϵNd (ca. -4) with relatively low
410 $(La/Sm)_N$ (between 0.5 and 2.3 in titanite and < 5 in apatite) at Rogart. Part of the $(La/Sm)_N$
411 variation observed within accessories in a given sample has been attributed to in-situ crystal
412 fractionation (Bruand et al. 2014). Additionally, part of this scatter within a given sample can
413 also occasionally reflect competition with other accessory phases and/or delay of crystallization
414 of certain phases. For example, titanite (interstitial in texture) is crystallising late in the
415 appinites while apatite is crystallising early. Even if the scatter of data is relatively pronounced
416 in each sample, there is a clear difference between the 2 granitoid localities that cannot account
417 for in-situ crystal fractionation. This interpretation is confirmed by whole rock data as both
418 localities have similar whole rock SiO_2 -MgO ranges and have been shown to have encountered
419 similar crystallization fractionation process (Fowler et al., 2001, 2008). Whole rock $(La/Sm)_N$
420 for both granitoids localities have a similar range and show no correlations with ϵNd .

421 In their whole-rock study, Fowler et al. (2008) defined a “Caledonian Parental Mantle Array”
 422 as a variable source for Scottish Caledonian granitoids (Fig. 6b), defined by variable sediment
 423 input in the source. In this study, we show that the variations of up to 5 ϵNd recorded between
 424 both localities in both phases are clearly recording the influence in sediments along the
 425 Caledonian Parental Magma Array previously defined as the main reservoir of Caledonian
 426 granitoids in Northwest Scotland (Fig 8b). On the other hand, $\delta^{18}\text{O}_{\text{Zr}}$ in the same samples show
 427 limited variations (5.6-6.3 ‰, Table 1) close to a mantle-like source ($\delta^{18}\text{O}_{\text{Zr mantle}}=5.3\pm 0.6$ 2SD,
 428 Valley and Kita, 2009). The maximum estimated AFC contamination (based on radiogenic
 429 isotopes) is of the order of 25% (Fowler et al., 2001). On the other hand, the maximum
 430 estimated Moine metasediment input into the source, using an average Moine $\delta^{18}\text{O}$ value of
 431 about 8‰ to attain the maximum $\delta^{18}\text{O}$ of our sample, is about 15%. This interesting discrepancy
 432 is currently unresolved, but could perhaps relate to fractionation from incongruent dynamic
 433 melting reactions during assimilation, a sample spot bias towards early-crystallising zones in
 434 the accessory phases or be related to the analytical uncertainty. Using Sr isotopes, Fowler et
 435 al. (2008) could distinguish two clear sources of subsequent crustal contamination moving the
 436 granitoids signatures away from the CPMA: (i) Moine metasediment contamination affecting
 437 the granites (e.g., Rogart, Strontian) and (ii) Lewisian basement contamination affecting the
 438 syenites (Fig. 6b). Based on whole rock isotope data, both localities sampled here have been
 439 affected by Moine metasediments assimilation, which created small ϵNd variations (< 3 ϵNd ;
 440 Fowler et al., 2008).

441



442

443 **Figure 8: $\epsilon\text{Nd}_{\text{initial}}$ versus $\log(\text{La}/\text{Sm})_N$ in apatite (A) and titanite (B) for both localities. $\epsilon\text{Nd}_{\text{initial}}$ values are**
 444 **averages values per samples (Table 1) and $(\text{La}/\text{Sm})_N$ are from Bruand et al. (2014, 2020). Ra1 and Sr2 are**
 445 **appinites while Rogart Gr. and Strontian Gr. are granitoids. CPMA= Caledonian Parental Magma Array.**
 446 **Both minerals record the influence of the CPMA source in their elemental and isotopic signatures. Trace**
 447 **elements data are from Bruand et al. (2014) and can be found in Appendix_C.**

448

449 Gregory et al. (2009) and Sun et al. (2021) reported internal variation of ϵNd within apatite,
450 interpreted as evidence of local crustal assimilation preserved at the grain scale. To our
451 knowledge, there are no such reports using titanite. In our case, confirmation of at least some
452 crustal assimilation is provided by the presence of xenocrysts in zircons. Thus, while trace
453 element chemistry in zircon from granitoids is less amenable to petrogenetic interpretation, its
454 well-known capacity to preserve xenocrysts can add important additional constraints. In both
455 locations reported here, xenocrysts in zircon have been described (Bruand et al., 2014).
456 Unfortunately, Hf measurements could be performed only in one sample (from Rogart). ϵHf
457 results for two xenocrysts are strongly negative and may suggest contamination with a strongly
458 enriched component (Fig. 4b). As the xenocryst could not be dated, the ϵHf values are minimum
459 values. Oxygen isotope measurements ($\delta^{18}\text{O}$ up to 8.5‰) are consistent with this interpretation.
460 Other xenocrysts have been analysed for O but not Hf isotopes, due to their small size. They
461 range between 5.9‰ and 8.7‰, which is a slightly larger variation than that observed in the
462 granites (5.5-6.5‰; Bruand et al., 2019). Very few literature data combining O and Hf
463 measurements exist for the local Moine metasediments, but two samples in the Morar formation
464 analysed by Lancaster et al. (2011) show similar values to the xenocrysts of this study.

465

466 6.4. Implication for ancient terranes

467 Earlier studies (e.g. Iizuka et al., 2011) have proved that Sm-Nd isotopes in accessory minerals
468 constitute the only robust record of the evolution of the Sm-Nd system in eroded or disturbed
469 ancient terranes. However, accessory minerals in granitoids can also be reactive to
470 metamorphism. They may record past metamorphic events under certain conditions: (i) a
471 temperature above the closure temperature of the accessory mineral has to be attained; (ii)
472 whole-rock characteristics and/or fluid-assisted metamorphic event can promote their
473 dissolution and reprecipitation (e.g. Rapp and Watson, 1986; Watson, 1996; Wolf and London,
474 1994).

475 As a consequence, metamorphic events affecting ancient terranes have potential to reopen
476 isotopic systems in accessory minerals, and to erase their primary igneous history leading to
477 anomalous whole-rock isotopic signatures. This has been recently discussed in two studies on
478 accessory minerals within Archean grey gneisses (Hammerli et al., 2019; Fisher et al., 2020),
479 and this may explain apparent contradictory findings in the recent literature. Indeed,
480 contradictory radiogenic signatures for Hf isotopes in zircon and Nd isotopes in bulk-rock have

481 been at the core of major speculations about early Earth's evolution. The discovery of super-
482 chondritic Nd isotope ratios was used to infer the presence of a highly depleted mantle early in
483 Earth history, and which could reflect the extraction of large volumes of crust (Bennett et al.,
484 1993). However, chondritic Hf isotope ratios in zircon point towards no/little mantle depletion
485 over the same period of time (Vervoort and Kemp, 2016). Recent measurements (Hammerli *et*
486 *al.*, 2019) on accessory minerals from Eoarchean gneisses suggest that these minerals can record
487 LREE mobility during HT metamorphic events that can shift whole-rock Nd radiogenic value.
488 It is important to note that although these studies rely only on few heavily disturbed samples,
489 they highlight several limitations in our current knowledge of the effect of metamorphism on
490 LREE behaviour in accessory phases, which needs to be better addressed in the future. For
491 example in Fisher et al. (2020), while the U-Pb system in apatite dates a younger event from
492 the Slave craton (1.8-1.9 Ga, Wopmay orogeny), its Sm-Nd signature preserves a much older
493 event (at about 2.65 Ga). This observation highlights that the reopening of the U-Pb system
494 could be much more sensible than the Sm-Nd isotopic system. Another key observation in
495 Fisher et al. (2020) is that different accessory minerals can record different timing of the
496 reopening of the Sm-Nd system. Indeed, in Acasta while the apatite Sm-Nd isochron records a
497 2.65 Ga event, titanite records a much older Sm-Nd signature (3.3 Ga) consistent with zircon
498 U-Pb age. This study (Fisher et al., 2020) is consistent with recent trace elements data collected
499 on apatite and titanite in Archean TTG affected by greenschist to amphibolite facies, which
500 reveal that trace elements in titanite are less prone to be disturbed by metamorphism than in
501 apatite (Bruand et al., 2020). Indeed, Bruand et al. (2020) have demonstrated that trace elements
502 in accessory minerals from Archean granitoids affected by later greenschist to amphibolite
503 facies from different cratons (Kaalvaal, Slave, Karelia) could preserve under certain conditions
504 original/igneous trace elements concentrations. The major impact of metamorphism on titanite
505 and apatite chemistry was demonstrated to induce a decrease of LREE concentration. They
506 could clearly show that in the Slave craton, secondary apatite were depleted in LREE when
507 compared to primary apatite (e.g. apatite inclusions armoured in zircon). Under greenschist to
508 amphibolite facies, the same chemical systematic on apatite chemistry has also been
509 convincingly demonstrated on other lithologies (e.g. metapelite: Henrichs et al., 2018;
510 O'Sullivan et al., 2020). Combining the ability of the Sm-Nd system to date the geological
511 process recorded, its source tracer potential and trace element signatures within the accessory
512 phases, give new opportunities to refine geological event affecting igneous rocks (e.g. later
513 metamorphic event, mixing event with another magma, etc.). Once the igneous origin of the
514 accessory minerals have been confirmed using recent trace elements discriminators (e.g.

515 O’Sullivan et al., 2020; Bruand et al., 2020), the ϵNd associated to element ratios such as
516 $(\text{La}/\text{Sm})_{\text{N}}$ in apatite or titanite could help to refine the source characteristics of a given magma
517 (Fig. 8). Ultimately this will allow to observe the crustal/sediment component in its source at
518 the grain scale.

519 7 Conclusion

520

521 In this contribution we document several isotope systems within zircon, apatite and titanite. We
522 show close agreement between radiogenic isotopes (Hf and Nd) within the accessory minerals
523 and with previous whole rock data (Nd) to confirm an unbiased radiogenic isotope record in
524 the accessory phases. A main point of this study being that while Nd isotopes and associated
525 $(\text{La}/\text{Sm})_{\text{N}}$ in apatite and titanite are powerful indicator of the CPMA source variabilities present
526 in the northwest Scotland Caledonian granites, the assimilation of the host Moine sediments is
527 only clearly visible by the presence of xenocrysts in zircons.

528

529 Acknowledgements

530 We are grateful to M. Gannoun for the help provided with the LA-MC-ICPMS analyses. This
531 work was partly supported by the Natural Environment Research Council (grant
532 NE/I025573/1), by the French Government Laboratory of Excellence initiative n° ANR-10-
533 LABX-0006, and by the French National Research Agency (grant ANR-21-CE49-0001-01,
534 AMNESIA, PI EB). This is Laboratory of Excellence ClerVolc contribution number 586. This
535 manuscript benefited from constructive reviews by two anonymous reviewers. We thank Balz
536 Kamber for his editorial handling.

537

538 References

539

- 540 Antoine, C., Bruand, E., Guitreau, M., Devidal, J.-L., 2020. Understanding Preservation of
541 Primary Signatures in Apatite by Comparing Matrix and Zircon - Hosted Crystals From
542 the Eoarchean Acasta Gneiss Complex (Canada). *Geochemistry, Geophysics,*
543 *Geosystems* 1–21. <https://doi.org/10.1029/2020GC008923>
544 Archibald, D.B., Murphy, J.B., Fowler, M., Strachan, R.A., Hildebrand, R.S., 2022. Testing
545 petrogenetic models for contemporaneous mafic and felsic to intermediate magmatism
546 within the “Newer Granite” suite of the Scottish and Irish Caledonides. *New*
547 *Developments in the Appalachian-Caledonian-Variscan Orogen.*
548 [https://doi.org/10.1130/2021.2554\(15\)](https://doi.org/10.1130/2021.2554(15))

549 Atherton, M.P., Ghani, A.A., 2002. Slab breakoff: A model for Caledonian, Late Granite syn-
550 collisional magmatism in the orthotectonic (metamorphic) zone of Scotland and
551 Donegal, Ireland. *Lithos* 62, 65–85. [https://doi.org/10.1016/S0024-4937\(02\)00111-1](https://doi.org/10.1016/S0024-4937(02)00111-1)

552 Bailey, E.B., Maufe, H.B., 1916. The geology of Ben Nevis and Glen Coe and the
553 surrounding country (revised by EB Bailey). *Memoirs of the Geological Survey of Great*
554 *Britain*. Edinburgh, Her Majesty's Stationery Office.

555 Bell, E.A., Harrison, T.M., Mcculloch, M.T., Young, E.D., 2011. Early Archean crustal
556 evolution of the Jack Hills Zircon source terrane inferred from Lu – Hf , 207 Pb / 206 Pb
557 , and d 18 O systematics of Jack Hills zircons. *Geochim Cosmochim Acta* 75, 4816–
558 4829. <https://doi.org/10.1016/j.gca.2011.06.007>

559 Belousova, E.A., Kostitsyn, Y.A., Griffin, W.L., Begg, G.C., O'Reilly, S.Y., Pearson, N.J.,
560 2010. The growth of the continental crust: Constraints from zircon Hf-isotope data.
561 *Lithos* 119, 457–466. <https://doi.org/10.1016/j.lithos.2010.07.024>

562 Belousova, E.A., Walters, S., Griffin, W.L., O'Reilly, S.Y., 2001. Trace-element signatures of
563 apatites in granitoids from the Mt Isa Inlier, Northwestern Queensland. *Australian*
564 *Journal of Earth Sciences* 48, 603–619. [https://doi.org/10.1046/j.1440-](https://doi.org/10.1046/j.1440-0952.2001.00879.x)
565 [0952.2001.00879.x](https://doi.org/10.1046/j.1440-0952.2001.00879.x)

566 Bennett, V.C., Nutman, A.P., Mcculloch, M.T., 1993. Nd isotopic evidence for transient ,
567 highly depleted mantle reservoirs in the early history of the Earth. *Earth Planet Sci Lett*
568 119, 299–317.

569 Bonamici, C.E., Kozdon, R., Ushikubo, T., Valley, J.W., 2014. Intragrain oxygen isotope
570 zoning in titanite by SIMS: Cooling rates and fluid infiltration along the Carthage-Colton
571 Mylonite Zone, Adirondack Mountains, NY, USA. *Journal of Metamorphic Geology* 32,
572 71–92. <https://doi.org/10.1111/jmg.12059>

573 Bouvier, A., Vervoort, J.D., Patchett, P.J., 2008. The Lu-Hf and Sm-Nd isotopic composition
574 of CHUR: Constraints from unequilibrated chondrites and implications for the bulk
575 composition of terrestrial planets. *Earth Planet Sci Lett* 273, 48–57.
576 <https://doi.org/10.1016/j.epsl.2008.06.010>

577 Brown, P.E., Miller, J.A., Grasty, R.L., 1968. Isotopic ages of late Caledonian granitic
578 intrusions in the British Isles. *Proceedings of the Yorkshire Geological Society* 36, 251–
579 276.

580 Brown, P.E., Ryan, P.D., Soper, N.J., Woodcock, N.H., 2008. The Newer Granite problem
581 revisited: a transtensional origin for the Early Devonian trans-suture suite. *Geol Mag*
582 145, 235–256.

583 Bruand, E., Fowler, M., Storey, C., Darling, J., 2017. Apatite trace element and isotope
584 applications to petrogenesis and provenance. *American Mineralogist* 102.
585 <https://doi.org/10.2138/am-2017-5744>

586 Bruand, E., Fowler, M., Storey, C., Laurent, O., Antoine, C., Guitreau, M., Heilimo, E.,
587 Nebel, O., 2020. Accessory mineral constraints on crustal evolution: elemental
588 fingerprints for magma discrimination. *Geochemical Perspectives Letters* .
589 <https://doi.org/http://dx.doi.org/10.7185/geochemlet.2006>

590 Bruand, E., Storey, C., Fowler, M., 2016. An apatite for progress: Inclusions in zircon and
591 titanite constrain petrogenesis and provenance. *Geology* 44.
592 <https://doi.org/10.1130/G37301.1>

593 Bruand, E., Storey, C., Fowler, M., 2014. Accessory mineral chemistry of high Ba-Sr granites
594 from Northern Scotland: Constraints on petrogenesis and records of whole-rock
595 Signature. *Journal of Petrology* 55. <https://doi.org/10.1093/petrology/egu037>

596 Bruand, E., Storey, C., Fowler, M., Heilimo, E., 2019. Oxygen isotopes in titanite and apatite
597 , and their potential for crustal evolution research. *Geochim Cosmochim Acta* 255, 144–
598 162. <https://doi.org/10.1016/j.gca.2019.04.002>

599 Chu, N.C., Taylor, R.N., Chavagnac, V., Nesbitt, R.W., Boella, R.M., Milton, J.A., German,
600 C.R., Bayon, G., Burton, K., 2002. Hf isotope ratio analysis using multi-collector
601 inductively coupled plasma mass spectrometry: An evaluation of isobaric interference
602 corrections. *J Anal At Spectrom* 17, 1567–1574. <https://doi.org/10.1039/b206707b>

603 Dhuime, B., Hawkesworth, C.J., Cawood, P.A., Storey, C.D., 2012. A Change in the
604 Geodynamics of Continental Growth 3 Billion Years Ago. *Science* (1979) 335, 1334 LP
605 – 1336.

606 Doucelance, R., Bruand, E., Matte, S., Bosq, C., Auclair, D., Gannoun, A., 2020. In-situ
607 determination of Nd isotope ratios in apatite by LA-MC-ICPMS : Challenges and
608 limitations. *Chem Geol* 550.

609 Emo, R.B., Smit, M.A., Schmitt, M., Kooijman, E., Scherer, E.E., Sprung, P., Bleeker, W.,
610 Mezger, K., 2018. ScienceDirect Evidence for evolved Hadean crust from Sr isotopes in
611 apatite within Eoarchean zircon from the Acasta Gneiss Complex. *Geochim Cosmochim*
612 *Acta* 235, 450–462. <https://doi.org/10.1016/j.gca.2018.05.028>

613 Fisher, C.M., Bauer, A.M., Vervoort, J.D., 2020. Disturbances in the Sm – Nd isotope system
614 of the Acasta Gneiss Complex — Implications for the Nd isotope record of the early
615 Earth. *Earth Planet Sci Lett* 530, 115900.

616 Fisher, C.M., Hanchar, J.M., Miller, C.F., Phillips, S., Vervoort, J.D., Whitehouse, M.J.,
617 2017. Combining Nd isotopes in monazite and Hf isotopes in zircon to understand
618 complex open-system processes in granitic magmas. *Geology* 45, 267–270.
619 <https://doi.org/10.1130/G38458.1>

620 Fisher, C.M., Hanchar, J.M., Samson, S.D., Dhuime, B., Blichert-Toft, J., Vervoort, J.D.,
621 Lam, R., 2011a. Synthetic zircon doped with hafnium and rare earth elements: A
622 reference material for in situ hafnium isotope analysis. *Chem Geol* 286, 32–47.
623 <https://doi.org/10.1016/j.chemgeo.2011.04.013>

624 Fisher, C.M., McFarlane, C.R.M., Hanchar, J.M., Schmitz, M.D., Sylvester, P.J., Lam, R.,
625 Longerich, H.P., 2011b. Sm-Nd isotope systematics by laser ablation-multicollector-
626 inductively coupled plasma mass spectrometry: Methods and potential natural and
627 synthetic reference materials. *Chem Geol* 284, 1–20.
628 <https://doi.org/10.1016/j.chemgeo.2011.01.012>

629 Foster, G.L., Vance, D., 2006. In situ Nd isotopic analysis of geological materials by laser
630 ablation 288–296. <https://doi.org/10.1039/b513945g>

631 Fowler, M.B., 1988. Elemental evidence for crustal contamination of mantle-derived
632 Caledonian syenite by metasediment anatexis and magma mixing. *Chem Geol* 69, 1–16.
633 [https://doi.org/10.1016/0009-2541\(88\)90154-4](https://doi.org/10.1016/0009-2541(88)90154-4)

634 FOWLER, M.B., HENNEY, P.J., DARBYSHIRE, D.P.F., GREENWOOD, P.B., 2001.
635 Petrogenesis of high Ba-Sr granites: the Rogart pluton, Sutherland. *J Geol Soc London*
636 158, 521–534. <https://doi.org/10.1144/jgs.158.3.521>

637 Fowler, M.B., Kocks, H., Darbyshire, D.P.F., Greenwood, P.B., 2008. Petrogenesis of high
638 Ba-Sr plutons from the Northern Highlands Terrane of the British Caledonian Province.
639 *Lithos* 105, 129–148. <https://doi.org/10.1016/j.lithos.2008.03.003>

640 Gillespie, J., Nemchin, A.A., Kinny, P.D., Martin, L., Aleshin, M., Roberts, M.P., Ireland,
641 T.R., Whitehouse, M.J., Jeon, H., Cavosie, A.J., Kirkland, C.L., 2021. Strontium isotope
642 analysis of apatite via SIMS. *Chem Geol* 559, 119979.
643 <https://doi.org/10.1016/j.chemgeo.2020.119979>

644 Gordon, S.M., Kirkland, C.L., Reddy, S.M., Blatchford, H.J., Whitney, D.L., Teyssier, C.,
645 Evans, N.J., McDonald, B.J., 2021. Deformation-enhanced recrystallization of titanite
646 drives decoupling between U-Pb and trace elements. *Earth Planet Sci Lett* 560, 116810.
647 <https://doi.org/10.1016/j.epsl.2021.116810>

648 Gregory, C.J., McFarlane, C.R.M., Hermann, J., Rubatto, D., 2009. Tracing the evolution of
649 calc-alkaline magmas: In-situ Sm-Nd isotope studies of accessory minerals in the Bergell
650 Igneous Complex, Italy. *Chem Geol* 260, 73–86.
651 <https://doi.org/10.1016/j.chemgeo.2008.12.003>

652 Hammerli, J., Kemp, A.I.S., 2021. Combined Hf and Nd isotope microanalysis of co-existing
653 zircon and REE-rich accessory minerals: High resolution insights into crustal processes.
654 *Chem Geol* 581, 120393. <https://doi.org/10.1016/j.chemgeo.2021.120393>

655 Hammerli, J., Kemp, A.I.S., Shimura, T., Vervoort, J.D., Dunkley, D.J., 2018. Generation of
656 I-type granitic rocks by melting of heterogeneous lower crust. *Geology* 46, 907–910.

657 Hammerli, J., Kemp, A.I.S., Spandler, C., 2014. Neodymium isotope equilibration during
658 crustal metamorphism revealed by in situ microanalysis of REE-rich accessory minerals.
659 *Earth Planet Sci Lett* 392, 133–142. <https://doi.org/10.1016/j.epsl.2014.02.018>

660 Hammerli, J., Kemp, A.I.S., Whitehouse, M.J., 2019. In situ trace element and Sm-Nd isotope
661 analysis of accessory minerals in an Eoarchean tonalitic gneiss from Greenland :
662 Implications for Hf and Nd isotope decoupling in Earth ' s ancient rocks. *Chem Geol*
663 524, 394–405.

664 Harlov, D.E., 2015. Apatite: A fingerprint for metasomatic processes. *Elements* 11, 171–176.
665 <https://doi.org/10.2113/gselements.11.3.171>

666 Hawkesworth, C.J., Kemp, A.I.S., 2006. Using hafnium and oxygen isotopes in zircons to
667 unravel the record of crustal evolution. *Chem Geol* 226, 144–162.
668 <https://doi.org/10.1016/j.chemgeo.2005.09.018>

669 Henrichs, I.A., Sullivan, G.O., Chew, D.M., Mark, C., Babechuk, M.G., Mckenna, C., Emo,
670 R., 2018. The trace element and U-Pb systematics of metamorphic apatite. *Chem Geol*
671 483, 218–238. <https://doi.org/10.1016/j.chemgeo.2017.12.031>

672 Iizuka, T., Nebel, O., McCulloch, M.T., 2011. Tracing the provenance and recrystallization
673 processes of the Earth's oldest detritus at Mt. Narryer and Jack Hills, Western Australia:
674 An in situ Sm-Nd isotopic study of monazite. *Earth Planet Sci Lett* 308, 350–358.
675 <https://doi.org/10.1016/j.epsl.2011.06.006>

676 Jennings, E.S., Marschall, H.R., Hawkesworth, C.J., Storey, C.D., 2011. Characterization of
677 magma from inclusions in zircon: Apatite and biotite work well, feldspar less so.
678 *Geology* 39, 863–866. <https://doi.org/10.1130/G32037.1>

679 Kemp, A.I.S., Foster, G.L., Scherstén, A., Whitehouse, M.J., Darling, J., Storey, C., 2009.
680 Concurrent Pb–Hf isotope analysis of zircon by laser ablation multi-collector ICP-MS,
681 with implications for the crustal evolution of Greenland and the Himalayas. *Chem Geol*
682 261, 244–260.

683 Kemp, A.I.S., Hawkesworth, C.J., Foster, G.L., Paterson, B.A., Woodhead, J.D., Hergt, J.M.,
684 Gray, C.M., Whitehouse, M.J., 2007. Magmatic and Crustal Differentiation History of
685 Granitic Rocks from Hf-O Isotopes in Zircon. *Science* (1979) 315, 980 LP – 983.

686 KOCKS, H., STRACHAN, R., EVANS, J., FOWLER, M., 2014. Contrasting magma
687 emplacement mechanisms within the Rogart igneous complex, NW Scotland, record the
688 switch from regional contraction to strike-slip during the Caledonian orogeny. , 151(5), .
689 *Geol Mag* 151, 899–915.

690 Lancaster, P.J., Storey, C.D., Hawkesworth, C.J., Dhuime, B., 2011. Understanding the roles
691 of crustal growth and preservation in the detrital zircon record. *Earth Planet Sci Lett* 305,
692 405–412. <https://doi.org/10.1016/j.epsl.2011.03.022>

693 Laurent, O., Zeh, A., Gerdes, A., Villaros, A., 2017. How do granitoid magmas mix with each
694 other ? Insights from textures , trace element and Sr – Nd isotopic composition of apatite
695 and titanite from the Matok pluton (South Africa). [https://doi.org/10.1007/s00410-017-](https://doi.org/10.1007/s00410-017-1398-1)
696 1398-1

697 Lugmair, G.W., Marti, K., 1978. Lunar initial $^{143}\text{Nd}/^{144}\text{Nd}$: Differential evolution of the
698 lunar crust and mantle. *Earth Planet Sci Lett* 39, 349–357.
699 [https://doi.org/https://doi.org/10.1016/0012-821X\(78\)90021-3](https://doi.org/https://doi.org/10.1016/0012-821X(78)90021-3)

700 Miles, A.J., Graham, C.M., Hawkesworth, C.J., Gillespie, M.R., Hinton, R.W., 2013.
701 Evidence for distinct stages of magma history recorded by the compositions of accessory
702 apatite and zircon. *Contributions to Mineralogy and Petrology* 166, 1–19.
703 <https://doi.org/10.1007/s00410-013-0862-9>

704 Miles, A.J., Woodcock, N.H., Hawkesworth, C.J., 2016. Tectonic controls on post-subduction
705 granite genesis and emplacement: The late Caledonian suite of Britain and Ireland.
706 *Gondwana Research* 39, 250–260. <https://doi.org/10.1016/j.gr.2016.02.006>

707 Murphy, J.B., 2013. Appinite suites: A record of the role of water in the genesis, transport,
708 emplacement and crystallization of magma. *Earth Sci Rev* 119, 35–59.

709 O’Sullivan, G., Chew, D., Kenny, G., Henrichs, I., Mulligan, D., 2020. The trace element
710 composition of apatite and its application to detrital provenance studies. *Earth Sci Rev*
711 201, 103044. <https://doi.org/10.1016/j.earscirev.2019.103044>

712 Patchett, P.J., Tatsumoto, M., 1981. A routine high-precision method for Lu-Hf isotope
713 geochemistry and chronology. *Contributions to Mineralogy and Petrology* 75, 263–267.

714 Paterson, B.A., Rogers, G., Stephens, W.E., 1992. Evidence for inherited Sm - Nd isotopes in
715 granitoid zircons 378–390.

716 Prowatke, S., Klemme, S., 2006. Trace element partitioning between apatite and silicate
717 melts. *Geochim Cosmochim Acta* 70, 4513–4527.
718 <https://doi.org/10.1016/j.gca.2006.06.162>

719 Prowatke, S., Klemme, S., 2005. Effect of melt composition on the partitioning of trace
720 elements between titanite and silicate melt. *Geochim Cosmochim Acta* 69, 695–709.
721 <https://doi.org/10.1016/j.gca.2004.06.037>

722 Rapp, R.P., Watson, E.B., 1986. Monazite solubility and dissolution kinetics : implications for
723 the thorium and light rare earth chemistry of felsic magmas. *Contributions to Mineralogy
724 and Petrology* 94, 304–316.

725 Rock, N.M.S., 1984. Nature and origin of calc-alkaline lamprophyres: minettes, vogesites,
726 kersantites and spessartites. *Earth Environ Sci Trans R Soc Edinb* 74, 193–227.

727 Rogers, G., Dunning, G.R., 1991. Geochronology of appinitic and related granitic magmatism
728 in the W Highlands of Scotland: constraints on the timing of transcurrent fault
729 movement. *J Geol Soc London* 148, 17–27.

730 Sabine, P.A., 1963. The Strontian granite complex, Argyllshire. *Bulletin of the Geological
731 Survey of Great Britain* 20, 6–42.

732 Söderlund, U., Patchett, P.J., Vervoort, J.D., Isachsen, C.E., 2004. The ^{176}Lu decay constant
733 determined by Lu–Hf and U–Pb isotope systematics of Precambrian mafic intrusions.
734 *Earth Planet Sci Lett* 219, 311–324.

735 Soper, N.J., 1986. The Newer Granite problem: a geotectonic view. *Geol Mag* 123, 227–236.

736 Soper, N.J., England, R.W., Snyder, D.B., Ryan, P.D., 1992. The Iapetus suture zone in
737 England, Scotland and eastern Ireland: a reconciliation of geological and deep seismic
738 data. *J Geol Soc London* 149, 697–700.

739 Spandler, C., Hammerli, J., Sha, P., Hilbert-Wolf, H., Hu, Y., Roberts, E., Schmitz, M., 2016.
740 MKED1: A new titanite standard for in situ analysis of Sm-Nd isotopes and U-Pb
741 geochronology. *Chem Geol* 425, 110–126.
742 <https://doi.org/10.1016/j.chemgeo.2016.01.002>

743 Stephens, W.E., Halliday, A.N., 1984. Geochemical contrasts between late Caledonian
744 granitoid plutons of northern, central and southern Scotland. *Earth Environ Sci Trans R
745 Soc Edinb* 75, 259–273.

746 Stephenson, D., 1999. Caledonian igneous rocks of Great Britain. Joint Nature Conservation
747 Committee.

748 Sun, J.-F., Yang, J.-H., Zhang, J.-H., Yang, Y.-H., Zhu, Y.-S., 2021. Apatite geochemical and
749 SrNd isotopic insights into granitoid petrogenesis. *Chem Geol* 566, 120104.
750 <https://doi.org/https://doi.org/10.1016/j.chemgeo.2021.120104>

751 Sun, Y., Wiedenbeck, M., Joachimski, M.M., Beier, C., Kemner, F., Weinzierl, C., 2016.
752 Chemical and oxygen isotope composition of gem-quality apatites : Implications for
753 oxygen isotope reference materials for secondary ion mass spectrometry (SIMS). *Chem*
754 *Geol* 440, 164–178. <https://doi.org/10.1016/j.chemgeo.2016.07.013>

755 Valley, J.W., Kita, N.T., 2009. In-situ oxygen isotope geochemistry by Ion Microprobe.
756 *Mineralogical Association of Canada Short Course* 41, 19–63.

757 Vervoort, J.D., Kemp, A.I.S., 2016. Clarifying the zircon Hf isotope record of crust – mantle
758 evolution. *Chem Geol* 425, 65–75. <https://doi.org/10.1016/j.chemgeo.2016.01.023>

759 Vervoort, J.D., Patehett, P.J., Söderlund, U., Baker, M., 2004. Isotopic composition of Yb and
760 the determination of Lu concentrations and Lu/Hf ratios by isotope dilution using MC-
761 ICPMS. *Geochemistry, Geophysics, Geosystems* 5.
762 <https://doi.org/10.1029/2004GC000721>

763 Watson, E.B., 1996. Dissolution, growth and survival of zircons during crustal fusion: kinetic
764 principals, geological models and implications for isotopic inheritance. *Trans R Soc*
765 *Edinb Earth Sci* 87.

766 Wilde, S. a, Valley, J.W., Peck, W.H., Graham, C.M., 2001. Evidence from detrital zircons
767 for the existence of continental crust and oceans on the Earth 4.4 Gyr ago. *Nature* 409,
768 175–178. <https://doi.org/10.1038/35051550>

769 Wolf, M.B., London, D., 1994. Apatite dissolution into peraluminous haplogranitic melts : An
770 experimental study of solubilities and mechanisms. *Geochim Cosmochim Acta* 58,
771 4127–4145.

772 Wudarska, A., Wiedenbeck, M., Słaby, E., Harris, C., Joachimski, M.M., Lécuyer, C.,
773 MacLeod, K.G., Pack, A., Vennemann, T., Couffignal, F., Glodny, J., Kusebauch, C.,
774 Lempart, M., Sun, Y., Wilke, F., 2020. SIMS- and IRMS-based study of apatite
775 reference materials reveals new analytical challenges for oxygen isotope analysis, in:
776 EGU General Assembly Conference Abstracts, EGU General Assembly Conference
777 Abstracts. p. 18841.

778 Yang, Y.-H., Wu, F.-Y., Yang, J.-H., Chew, D.M., Xie, L.-W., Chu, Z.-Y., Zhang, Y.-B.,
779 Huang, C., 2014. Sr and Nd isotopic compositions of apatite reference materials used in
780 U–Th–Pb geochronology. *Chem Geol* 385, 35–55.
781 <https://doi.org/10.1016/j.chemgeo.2014.07.012>

782 Zirner, A.L.K., Marks, M.A.W., Wenzel, T., Jacob, D.E., Markl, G., 2015. Rare earth
783 elements in apatite as a monitor of magmatic and metasomatic processes: The
784 Il??mausseq complex, South Greenland. *Lithos* 228–229, 12–22.
785 <https://doi.org/10.1016/j.lithos.2015.04.013>
786