

1 Apatite as a pathfinder to tin mineralisation: prospects and caveats

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28 Abstract

29 Granite-related mineral deposits are major primary sources of the critical metals tin (Sn) and lithium
30 (Li). The utility of accessory minerals such as zircon and apatite as pathfinders to these ore deposits
31 has been a subject of great interest in recent years, with a number of geochemical discriminants
32 having been developed to distinguish barren from metal-fertile and mineralised intrusions. Here, we
33 study the prospects of apatite as an indicator mineral for tin and lithium mineralisation using a
34 compilation of published apatite trace element data as well as new data for the mineralised
35 Cornubian batholith and barren Bhutanese leucogranites. Critical examination of common
36 geochemical discriminants tracing magma fractionation and redox conditions (Mn, Eu/Eu*, La/Yb_N
37 and Sr/Y) shows large and overlapping data scatter for barren and Sn-fertile intrusions. This calls into
38 question the utility of these petrogenetic indicators to pinpoint tin metallogeny, and it suggests that
39 extreme fractionation and reduced conditions in S-type granites are necessary but insufficient
40 conditions for tin mineralisation. Instead, *prima facie* metal concentrations directly related to tin
41 mineralisation (i.e., Sn and Li) are consistently elevated in apatite from fertile and mineralised
42 intrusions, which implies a critical role for source enrichment in tin metallogeny. Based on our data
43 compilation, Li and Sn concentrations in apatite are the most robust indicators for Sn (and Li)
44 mineralisation, and we encourage the community to include Li and Sn in their analytical routines to
45 test this hypothesis further.

46 **Keywords:** Tin mineralisation; apatite; trace elements; exploration

47 1. Introduction

48 Apatite (Ca₅(PO₄)₃(OH,F,Cl)) is a common accessory mineral in magmas across the compositional
49 spectrum. Its stability is primarily controlled by P concentrations in the magma, and it often appears
50 early in the crystallisation sequence of granites (Hoskin et al., 2000; Piccoli and Candela, 2002;
51 Broska et al., 2004; Macdonald et al., 2013; Miles et al., 2013; Zhang et al., 2021). Apatite can
52 accommodate a range of key minor and trace elements such as REE, Sr, U, Pb, and Th (Belousova et

53 al., 2002; Mao et al., 2016); in particular, high apatite-melt partition coefficients for REE, Sr, and Y
54 ($D_{\text{ap/melt}} \sim 3-10$; Prowatke and Klemme, 2006) mean that apatite exerts significant control on the trace
55 element budget of a magma during differentiation. Conversely, its wide stability field and
56 compositional range make apatite a potentially powerful proxy through which to study evolving
57 magma conditions and dynamics (Sha and Chappell, 1999; Miles et al., 2013; 2014; Stock et al. 2018;
58 Li et al. 2021; Lormand et al., 2024; Xu et al. 2024). Moreover, apatite trace element compositions
59 have been used to discriminate between different rock types, such as lherzolites, carbonatites, mafic
60 rocks, granitoids, granite pegmatites, and iron oxides (Belousova et al., 2002), as well as S-type and I-
61 type granites (Sha and Chappell, 1999), highlighting the utility of apatite in provenance studies.

62 Apatite is also a common accessory mineral in granite-hosted mineral deposits, and hence Belousova
63 et al. (2002) highlighted the potential use of apatite as a resistate indicator mineral (RIM) in
64 exploration for critical metals thanks to its widespread occurrence, wide stability field, relative
65 resistance to weathering and surface processes, and ability to incorporate commodity elements such
66 as Ni, Cu, Zn, and As. Since then, discriminant analysis of apatite has been used to distinguish
67 magmatic-hydrothermal mineral deposits from unmineralised rocks (Mao et al., 2016) using a
68 combination of Mg, V, Mn, Sr, Y, REE, Pb, Th, and U concentrations in apatite. The same authors also
69 put forward characteristic apatite compositions for different mineralisation styles, including alkalic
70 porphyry Cu-Au deposits, porphyry Cu \pm Mo \pm Au deposits, and Kiruna-type iron oxide apatite
71 deposits (Mao et al., 2016). Similarly, Ding et al. (2015) distinguished between Cu-Pb-Zn porphyries
72 and W-Sn-bearing granites by tracing the geochemical signatures of their respective magmatic
73 sources (i.e., I-type vs S-type granites) in apatite.

74 Due to efforts to develop new metallogenic models for 'lithophile' granite-related magmatic-
75 hydrothermal deposits, which host Sn, Li and other critical metals such as W and Ta, there has been
76 growing interest in the use of accessory minerals as fertility indicators, which can be used to
77 discriminate barren from metal-fertile deposits, and ultimately be used as pathfinders. Hence, a

78 small number of studies have recently examined the utility of apatite to explore for Sn mineralisation
79 (Azadbakht et al., 2018; Guo et al., 2022; Li et al., 2022). These studies analysed trace elements in
80 magmatic apatite from granitoids associated with Sn-mineralisation and concluded that Mn, Sr, Li,
81 Sn, LREE/HREE and Eu/Eu* can be used to discriminate between Sn-fertile and barren magmas.
82 However, these studies focused on specific case studies, and to date, no global compilation of trace
83 element characteristics of apatite associated with Sn deposits has been produced.

84 Here, we compile published trace element data for apatite from barren and Sn-fertile igneous rocks,
85 and we complement this with new apatite trace element data from Sn-mineralised units in the
86 Cornubian batholith (SW England), as well as for barren 'Himalayan'-style leucogranites from Bhutan.
87 We use the compilation to assess the fidelity of previously suggested trace element signatures in
88 apatite to distinguish barren from Sn-fertile rocks, and we identify the geochemical discriminants
89 which most robustly point towards tin mineralisation.

90 2. Geochemical discriminants in apatite

91 Geochemical discriminants developed for apatite are empirical in nature and aim to assess magmatic
92 source, degree of fractionation, and oxidation state, since these petrogenetic constraints are
93 considered to control the potential for granite-hosted mineralisation (Blevin and Chappell, 1992;
94 Blevin et al., 1996; Černý et al., 2005, Gardiner et al., 2017). In particular, tin mineralisation is
95 typically associated with highly fractionated, reduced granites derived from melting of crustal
96 sediments (S-type; Taylor, 1979; Lehmann, 1982; Taylor and Wall, 1992; Romer & Kroner, 2016;
97 Lehmann, 2021). Hence, the geochemical tracers proposed as pathfinders to tin mineralisation are
98 those that pinpoint such high degrees of fractionation and low oxygen fugacity:

99 (1) **Sr** and **Y** in apatite are often used in combination to trace the degree of melt fractionation:

100 Whilst Sr generally decreases during melt evolution due to plagioclase fractionation, Y is
101 progressively enriched in the melt (Belousova et al., 2002). These trends in melt composition are
102 thought to be reflected in apatite compositions. However, high melt (and hence apatite) Sr/Y

103 ratios may also reflect a high Sr/Y parental magma source, melting of a garnet-bearing source, or
104 amphibole-dominated fractional crystallisation (Moyen, 2009; Nathwani et al., 2020).

105 (2) **La/Yb** and **other** ratios reflecting the slope of REE patterns also trace the degree of magma
106 fractionation: whilst apatite generally show negative REE slopes, LREE/HREE ratios decrease by
107 about two orders of magnitude during fractionation from primitive to highly evolved
108 compositions; in pegmatites, REE slopes tend to be positive (i.e., LREE/HREE <1; Belousova et
109 al., 2002). A primary reason for the LREE depletion is crystallisation of monazite or allanite,
110 which preferentially incorporate LREE (Tepper and Kuehner, 1999; Miles et al., 2014; Li et al.,
111 2022) thereby passively enriching HREE despite their slightly lower ap-melt partition coefficients
112 (Prowatke and Klemme, 2006). Similar to all fractionation proxies, individual apatite La/Yb ratios
113 therefore depend on the crystallising assemblage and its relative timing within the crystallisation
114 sequence.

115 (3) **Eu anomalies (Eu/Eu^* , where $Eu^* = (Sm_N \cdot Gd_N)^{1/2}$)** are ubiquitously used proxies for magma
116 fractionation in apatite (Belousova et al., 2002; Jia et al., 2020; Nathwani et al., 2020): negative
117 Eu anomalies will increase during melt evolution due to plagioclase fractionation, which controls
118 Eu/Eu^* in apatite. As a result, the most evolved rocks are characterised by apatite with extreme
119 $Eu/Eu^* < 0.1$ (Belousova et al., 2002). However, Miles et al. (2014) point out that Eu^{3+} is more
120 compatible in apatite than Eu^{2+} (Prowatke and Klemme, 2006), and hence negative Eu anomalies
121 could also reflect reducing magma conditions in addition to plagioclase fractionation. Unlike in
122 zircon (Gardiner et al., 2017), Ce anomalies are rare in apatite (Belousova et al., 2002; Miles et
123 al., 2014).

124 (4) **Mn** is **another** element that may reflect both fractionation and redox conditions: Manganese
125 concentrations generally increase in the melt during fractionation, and increasing Mn
126 concentrations in apatite are therefore often interpreted to reflect melt evolution (similar to Y);
127 **Fe** displays analogous trends. However, Belousova et al. (2002) pointed out that Mn is also redox
128 sensitive and that apatite in reduced magmas contains higher Mn concentrations due to the

129 increased availability of the more compatible Mn^{2+} . Based on this effect, Miles et al. (2014)
130 suggested Mn in apatite as a redox proxy in silicic melts.

131 The utility of the above discriminants relies on the implicit assumption that extreme fractionation of
132 S-type granites is sufficient to concentrate Sn enough to form mineralised deposits (Lehmann, 2021).
133 However, as outlined above, a key commonality of such petrogenetic discriminants is that they are
134 sensitive to several magmatic process and variables, and hence their petrogenetic significance is
135 often ambiguous. Other discriminants target volatile compositions (i.e., **F** and **Cl** concentrations in
136 apatite), but most studies find overlapping data and generally extreme enrichment in F and depletion
137 in Cl (Ding et al., 2015; Mao et al. 2016; Azadbakht et al., 2018; Guo et al., 2022; Li et al. 2022).
138 Halogen concentrations will therefore not be further considered in this study.

139 Less commonly, concentrations of the commodity metals themselves – e.g., **Sn** and **Li** concentrations
140 – are reported for apatite. Recent studies indicate that apatite in igneous rocks associated with Sn
141 mineralisation displays elevated Sn and Li concentrations (Azadbakht et al., 2018; Li et al., 2020; Guo
142 et al., 2022), though to date there is not enough data to substantiate this finding. To this end, we
143 analysed an additional 74 apatite crystals from barren and Sn-fertile rocks ($n = 410$ analyses), with
144 particular focus on Sn and Li concentrations.

145 3. Materials and Methods

146 We compiled a dataset of published and new apatite trace element data obtained using laser
147 ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), with particular focus on Sn and
148 Li concentrations in apatite. We categorised the apatite data into (i) *barren*: magmatic apatite from
149 Sn-infertile intrusions); (ii) *Sn-fertile*: magmatic apatite from unmineralised regions of intrusions
150 associated with tin mineralisation. These apatite crystals typically show no evidence for
151 hydrothermal alteration; (iii) *Sn-mineralised*: apatite from altered, cassiterite-bearing regions of
152 intrusions (including pegmatites, aplites and greisens). These apatite crystals have typically been
153 affected by variable degrees of hydrothermal alteration.

154 In total, the dataset includes 343 datapoints for barren, 188 datapoints for Sn-fertile, and 136
155 datapoints for Sn-mineralised apatite. In addition, we compiled published apatite trace element data
156 from Cu-fertile intrusions for reference ($n = 460$). The compiled data (Supplementary Material 1) was
157 screened for outliers using a 3SD criterion, and results below detection limit are considered a zero
158 result.

159 *3.1 Published data*

160 We compiled apatite trace element data from four studies (Azadbakht et al., 2018; Guo et al., 2022;
161 Li et al., 2022; Ge et al., 2022). Apatite in the selected studies is described as magmatic in all cases,
162 and they are either from barren or Sn-fertile intrusions. The literature compilation includes 109
163 apatite datapoints from Sn-fertile intrusions (three biotite granites from the Geiju Sn polymetallic
164 district, China, Li et al., 2022; two biotite granites from the Dachang Sn polymetallic district, China,
165 Guo et al., 2022; three biotite granites and one syenogranite from Acadia, Canada, Azadbakht et al.,
166 2018) and 148 apatite datapoints from barren intrusions (one gabbro, one monzonite, and three
167 biotite granites from the Dachang Sn polymetallic district, China, Guo et al., 2024; one gabbro-diorite
168 from the Zhuxiling tungsten deposit, China, Ge et al., 2024; and three biotite granites from Acadia,
169 Canada, Azadbakht et al., 2018). For comparison, we also compiled published data from magmatic
170 apatite associated with Cu mineralisation ($n = 460$; Yang et al., 2018; Nathwani et al., 2020; Pan et al.,
171 2020, 2021; Parra-Avila et al., 2022).

172 *3.2 Additional samples*

173 To ensure the representativeness of our global study on apatite as pathfinders to tin mineralisation,
174 we performed additional analyses of apatite crystals from the fertile and mineralised portions of the
175 Cornubian batholith as well as from three barren leucogranites from Bhutan (Supplementary
176 Material 2). The Cornubian batholith samples include two Sn-fertile granites: a biotite granite (CW
177 02; $n = 38$) from the G3 series (Simons et al., 2016), and a G5 topaz granite (Tregonning granite; CW
178 TREG; $n = 41$). In addition, apatite from an Sn-mineralised greisen deposit of the G2 muscovite series

179 (Cligga Head; CW 012; $n = 100$), and from an Sn-mineralised aplite from the G5 topaz series (Meldon
180 aplite; CW MELAP; $n = 36$) were analysed. The barren Bhutanese leucogranites ($n = 195$) are ~15 Ma
181 S-type granites related to melting of pelitic protoliths during the Himalayan orogeny (Hopkinson et
182 al., 2017), and exhibited visible selvages of metapelitic material in the field.

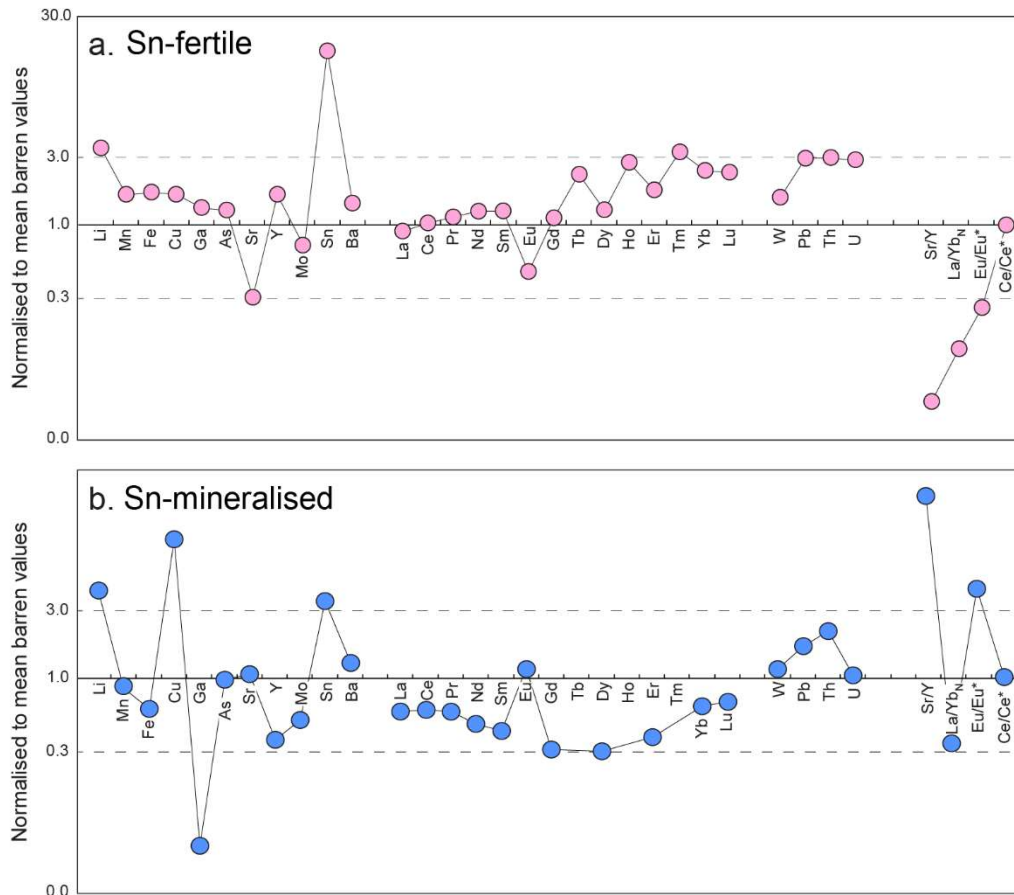
183 *3.3 Analytical methods*

184 Apatite crystals for new analyses were separated from sieved whole rock samples (<250 μm
185 fractions) via heavy liquid and magnetic separation before being mounted in epoxy resin. The
186 mounts were imaged and analysed using a Jeol JXA-iSP100 electron microprobe and Jeol JSM-IT200
187 SEM at the University of St Andrews, UK, to aid targeting suitable crystals. Laser ablation ICP-MS
188 analyses were conducted at the British Geological Survey Keyworth, UK using an ESL 193nm
189 ImageGeo excimer laser ablation system connected to a Nu instruments Attom single-collector
190 sector-field ICP-MS. Spot analyses were acquired using an ablation time of 12 s, a spot size of 30 μm ,
191 a repetition rate of 20 Hz, and a fluence of ~3 J/cm². Ablated material was carried by a 100% He gas
192 composition in chamber before combining with a 50% argon mixture along the sample line. In
193 apatite the following elements were measured: ⁷Li, ²⁷Al, ²⁹Si, ³¹P, ³⁵Cl, ⁴⁴Ca, ⁴⁹Ti, ⁶³Cu, ⁸⁸Sr, ⁸⁹Y, ⁹⁸Mo,
194 ¹²⁰Sn, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴⁶Nd, ¹⁴⁹Sm, ¹⁵³Eu, ¹⁵⁷Gd, ¹⁶³Dy, ¹⁶⁶Er, ¹⁷²Yb, ¹⁷⁵Lu, ¹⁷⁷Hf, ¹⁸¹Ta, ¹⁸⁶W, ²⁰⁶Pb, ²³²Th,
195 ²³⁸U. Data reduction was performed in Lolite 3 (Paton et al., 2011) using the Trace Elements Data
196 Reduction Scheme. Internal standardisation used an assumed stoichiometric Ca concentration of
197 40.04 %, and NIST610 (Jochum et al., 2005) was used as the primary reference material. Data quality
198 was monitored using reference materials Madagascar apatite, McClure apatite, Tiago apatite and
199 Durango apatite. Relative standard deviations are typically between 5% and 20% for elements with
200 concentrations ≥ 1 ppm, and detection limits range between 5 ppb to 2 ppm (Supplementary Material
201 2). Full analytical details and data tables are provided in Supplementary Material 2.

202 4. Results

203 *4.1 Trace elements in apatite: mean values*

204 Mean trace elemental concentrations of apatite from Sn-fertile and Sn-mineralised rocks normalised
205 to respective mean barren values are shown in Figure 1. Apatite in Sn-fertile rocks (Fig. 1a) show, on
206 average, 3.3x lower Sr and 1.6x higher Y concentrations than apatite from barren intrusions, resulting
207 in 18.6x lower Sr/Y values (mean Sr/Y = 0.04). Heavy REE are up to 3x higher in Sn-fertile apatite,
208 whereas LREE concentrations are similar to barren values, resulting in 7.6x lower La/Yb_N values for
209 Sn-fertile apatite (mean La/Yb_N = 2.5) compared to barren apatite (mean La/Yb_N = 18.9). In
210 combination, these signatures appear to confirm a higher degree of fractionation for Sn-fertile
211 intrusions. Slightly elevated Mn and Fe concentrations (enrichment factor of 1.6) as well as more
212 pronounced negative Eu anomalies in apatite from Sn-fertile rocks (mean Eu/Eu* = 0.05) similarly
213 point towards a higher extent of plagioclase fractionation than in barren intrusions (mean Eu/Eu* =
214 0.21). On the other hand, Li and Sn show the highest enrichment factors in apatite from Sn-fertile
215 intrusions: on average, Li is 3.5x higher (mean Li = 21.1 ppm) and Sn is 16.8x higher (mean Sn = 9.6
216 ppm) than in apatite from barren rocks (mean Li = 6.1 ppm; mean Sn = 0.6 ppm). Mean Cu, Ga, As, Ba
217 and W concentrations are enriched by a factor of 1.2 – 1.6 in apatite from Sn-fertile intrusions, and
218 mean Pb, Th and U values are between 1.9 and 4.3x higher than in barren intrusions. No significant
219 Ce anomaly is detected (Ce/Ce* = 1.08).



220

221 **Fig.1:** Mean trace element concentrations in apatite from Sn-fertile and Sn-mineralised granitoids
 222 relative to mean concentrations of apatite from barren rocks. Data compiled from Azadbakht et al.
 223 (2018), Ge et al., (2022), Guo et al. (2024), Li et al. (2022), and this study. The most pronounced
 224 differences between barren and Sn-fertile and -mineralised lithologies are found for Li, Sn, Eu/Eu*,
 225 La/Yb_N, and Sr/Y.

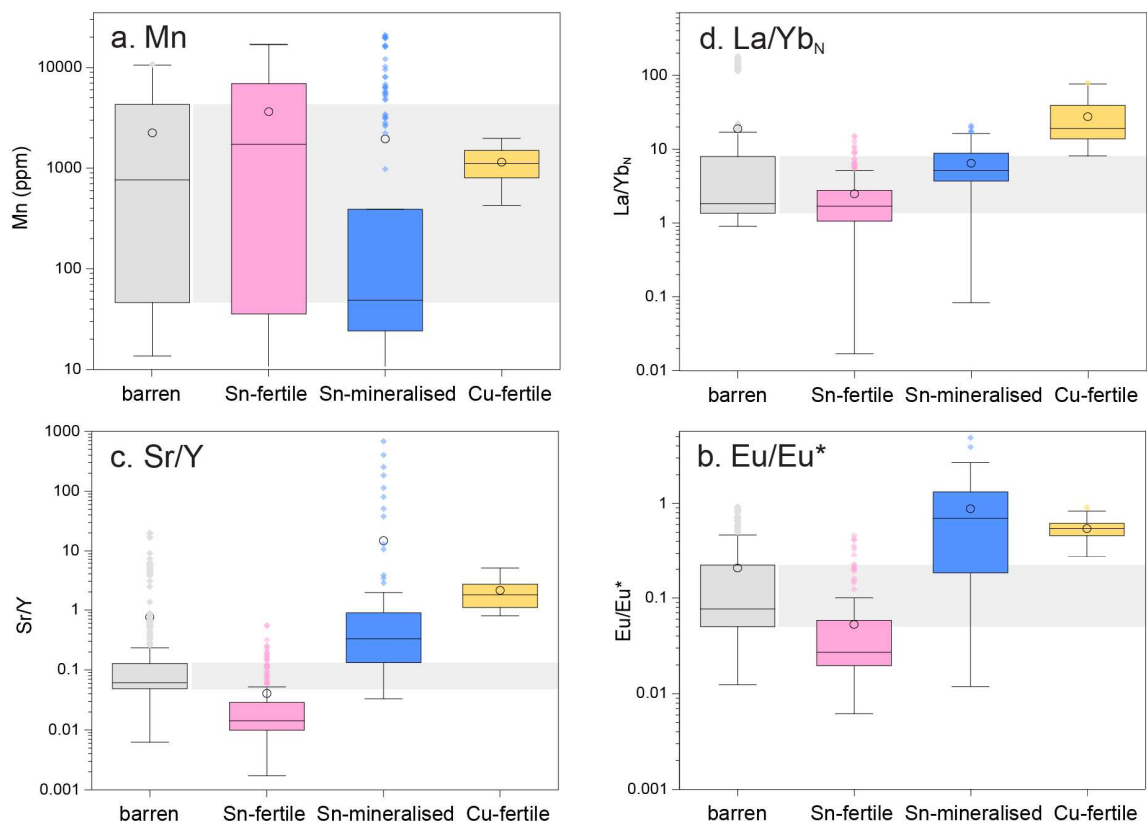
226 Apatite in Sn-mineralised rocks shows a general pattern of trace element depletion relative to mean
 227 barren values (Fig. 1b). This observation is consistent with Bouzari et al. (2016) and Mao et al. (2016),
 228 who found that apatite in hydrothermally altered rocks (i.e., hydrothermally altered magmatic
 229 apatite or true hydrothermal apatite) has higher Ca concentrations and lower trace element
 230 concentrations (REE, Y, Mn, Sr, Pb, Th, U) and suggested that this was due to trace element loss
 231 during the hydrothermal stage. Our compilation supports their observation for REE, Y and Mn,
 232 however mean Sr and U concentrations in apatite from Sn-mineralised rocks are indistinguishable

233 from barren ones, and Pb and Th concentrations are 1.7 and 1.4x higher, respectively (Fig. 1b). The
234 relative depletion of Y results in high Sr/Y ratios (mean Sr/Y = 14.5) compared to apatite from barren
235 and Sn-fertile rocks. Overall REE slopes in apatite from Sn-mineralised intrusions are slightly steeper
236 than in Sn-fertile rocks (mean La/Yb_N = 6.4), but La/Yb_N is 2.9x lower than in apatite from barren
237 intrusions. Europium anomalies are weaker in apatite from Sn-mineralised rocks (Eu/Eu* = 0.88) than
238 in apatite from barren and Sn-fertile intrusions, which may indicate oxidising conditions during
239 mineralisation (e.g., Lehmann, 2021) or widespread feldspar dissolution. Consistent with Sn-fertile
240 patterns, the most important enrichments in apatite from Sn-mineralised rocks are displayed for Li
241 (4.1x enrichment), Sn (3.5x) and Cu (9.5x). Similar to the Sn-fertile samples, no significant Ce anomaly
242 is observed (Ce/Ce* = 1.12).

243 *4.2 Trace elements in apatite: data distributions*

244 Mean concentrations can be misleading, particularly in case of skewed data distributions. Moreover,
245 the utility of apatite as a pathfinder for tin mineralisation depends on data *ranges* (rather than
246 means or medians) being distinguishable for different groups. In other words, a discriminant with
247 distinct mean values but large scatter in each group is not a viable discrimination tool. For example,
248 median Mn concentrations in apatite from barren, Sn-fertile, and Sn-mineralised rocks appear
249 distinctive (Fig. 2a), but the data is heavily scattered for all three groups, producing widely
250 overlapping concentration ranges. In fact, apatite from barren and Sn-fertile rocks shows almost
251 identical upper and lower quartile ranges. As a result, if detrital apatite data were being examined
252 with view to Sn mineralisation, Mn concentrations would not be a useful discriminant. Even apatite
253 from Cu-fertile intrusions shows an overlapping range (yellow boxplot in Fig. 2a). A similar issue is
254 present for La/Yb_N (Fig. 2b): while distinct mean and median values indicate that La/Yb_N in apatite is
255 a useful tool to distinguish barren from Sn-fertile and -mineralised rocks, the range of data related to
256 barren intrusions is large and substantially overlaps with Sn-fertile and -mineralised data,
257 compromising its utility as a metallogenic discriminant. Better discrimination is achieved using Sr/Y
258 (Sr shows similar results), where 75% of apatite from Sn-fertile intrusions have Sr/Y ≤ 0.029, while

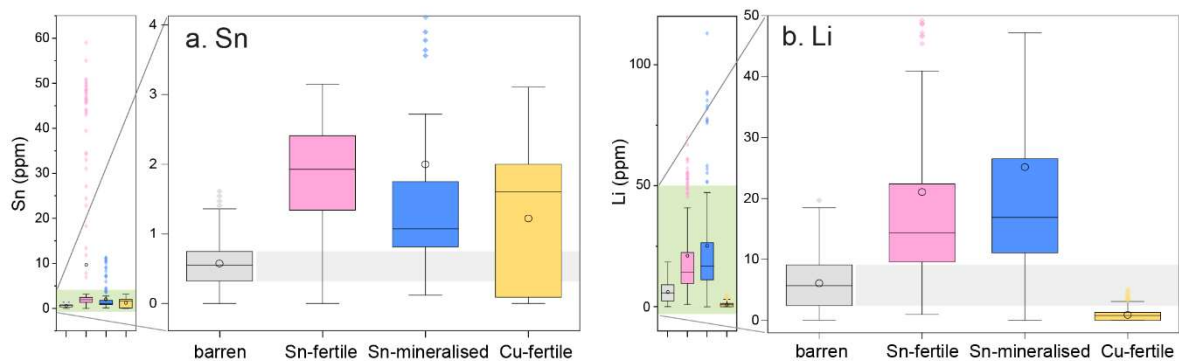
259 83% of barren apatite have $Sr/Y > 0.029$ (Fig. 2c; Supplementary Material 1). Tin-mineralised
 260 intrusions can also be distinguished from barren rocks using Sr/Y , as 75% of apatite in Sn-mineralised
 261 rocks have $Sr/Y \geq 0.13$, whereas 75% of apatite in barren intrusions have Sr/Y ratios lower than that.
 262 Europium anomalies show a similar but less clear discrimination (Fig. 2d), with apatite from Sn-fertile
 263 rocks showing generally lower values (75% show $Eu/Eu^* \leq 0.058$) than those in barren rocks (68%
 264 show $Eu/Eu^* > 0.058$), and apatite from Sn-mineralised rocks showing generally higher values (75%
 265 show $Eu/Eu^* \geq 0.18$) than barren rocks (72% show $Eu/Eu^* < 0.18$).



266
 267 **Fig. 2:** Boxplots showing data distributions of four commonly used geochemical discriminants in
 268 apatite. Median (dashed lines) and mean (circles) values are distinct for apatite from barren, Sn-
 269 fertile and Sn-mineralised rocks, however their core (lower to upper quartile) ranges (boxes and grey
 270 areas) overlap significantly in many cases. This compromises the utility of Mn and La/Yb_N to
 271 fingerprint tin mineralisation. Apatite from Cu-fertile intrusions generally exhibits distinct data
 272 ranges.

273 This compilation shows that when entire data distributions are considered, established discriminants
 274 Mn and La/Yb_N in apatite are unreliable pathfinders for tin mineralisation. On the other hand, Sr/Y
 275 and Eu/Eu* signatures offer more robust discrimination, even though significant overlap remains at
 276 least in the case of Eu/Eu*. Finally, we note that Sr/Y and La/Yb_N can be used to identify magmatic
 277 apatite from Cu-fertile intrusions, as all three ratios are systematically higher than those of barren
 278 and Sn-fertile systems (Fig. 2).

279 In contrast to magma fractionation and redox proxies, metal concentrations in apatite directly related
 280 to tin mineralisation (Sn and Li) unambiguously distinguish between barren intrusions and those
 281 associated with tin mineralisation (Fig. 3). Specifically, Sn concentrations in apatite from Sn-fertile
 282 intrusions are consistently higher than those in barren rocks (Fig. 3a), with 75% of apatite from Sn-
 283 fertile intrusions showing Sn ≥1.3 ppm (maximum value: 59 ppm), whereas 97% of apatite from
 284 barren rocks show Sn <1.3 ppm (maximum value: 1.6 ppm). Apatite from Sn-mineralised rocks also
 285 display relatively elevated tin concentrations, with 75% showing Sn ≥0.8 ppm, which is higher than
 286 80% of barren apatite.



287 **Fig. 3:** Boxplots showing data distributions of Sn and Li concentrations in apatite from barren, Sn-
 288 fertile, Sn-mineralised, and Cu-fertile rocks. The core ranges (lower to upper quartile = boxes and
 289 grey areas) of Sn and Li concentrations in apatite from barren intrusions are lower than those of Sn-
 290 fertile and Sn-mineralised apatite, facilitating robust discrimination between barren granitoids and
 291 those associated with tin deposits. Our data compilation further indicates that Li in apatite can also
 292 be used to identify Cu-fertile intrusions.
 293

294 Similarly, lithium shows distinctively high concentrations in both Sn-fertile and Sn-mineralised apatite
295 (Fig. 3b): 75% of apatite from Sn-fertile and Sn-mineralised rocks show $\text{Li} \geq 9.7$ ppm and $\text{Li} \geq 11$ ppm,
296 respectively, whereas 81% of apatite from barren intrusions have $\text{Li} < 9.7$ ppm. Lithium and tin
297 concentrations are therefore the most robust geochemical discriminants to fingerprint Sn
298 mineralisation using both magmatic and hydrothermal (or hydrothermally altered) apatite. Based on
299 our data compilation, Li in apatite can also be used to identify Cu-fertile intrusions (Fig. 3b).

300 5. Discussion

301 Our data compilation is consistent with our current understanding of tin metallogeny: the distinctly
302 low Sr/Y and Eu/Eu* signatures of apatite from Sn-fertile intrusions confirm that Sn mineralisation
303 requires a high degree of fractionation and reducing conditions. On the other hand, elevated Sr/Y
304 and Eu/Eu* for apatite from Sn-mineralised rocks likely reflects removal of REE, Y and other
305 incompatible elements under more oxidising conditions during hydrothermal alteration. However,
306 beyond these first order trends, the data scatter for traditional geochemical discriminators is
307 significant, and there remains significant overlap between barren and Sn-fertile and -mineralised
308 rocks, in particular for Mn and La/Yb_N . Above all, this overlap between barren and Sn-fertile rocks
309 speaks to the fact that extreme fractionation of reduced S-type granites (cf. Lehmann, 2021) is a
310 *necessary* but, on its own, *insufficient* condition for tin mineralisation. Beyond this observation,
311 which implies that source enrichment is a crucial factor controlling tin mineralisation (Romer &
312 Kroner, 2015; 2016), the scatter in each group, as well as overlaps between barren and fertile groups
313 may be due to a number of factors, which we discuss in the following section.

314 5.1 Petrogenetic and metallogenic ambiguity of apatite compositions

315 The wide ranges of Mn, Eu/Eu*, La/Yb_N and Sr/Y in apatite are not surprising given the multitude of
316 source rocks, magmatic conditions and processes these geochemical proxies may represent. These
317 include:

318 (1) *Source rocks and melt evolution histories are unique to each magmatic system.* Protoliths and
319 melting conditions and degrees impart geochemical characteristics on a magma which may
320 affect discriminants such as Sr/Y (Moyen, 2009; Roberts et al., 2024). Similarly, the geochemical
321 evolution of a melt is controlled by its crystallisation sequence. Since apatite reflects evolving
322 melt composition, trace element concentrations in apatite will vary depending on primary melt
323 composition and crystallisation history (i.e., mineral phases which crystallise before or during
324 apatite crystallisation). For example, the typical LREE depletion in apatite is controlled by
325 crystallisation of monazite, allanite or titanite, which fractionate LREE (Tepper and Kuehner,
326 1999; Chu et al., 2009; Miles et al., 2013; Li et al., 2022). On the other hand, trends of
327 decreasing Y and Yb concentrations in apatite of the Criffell granitic pluton in Scotland have
328 been interpreted to represent zircon and earlier apatite crystallisation (Miles et al., 2013). Major
329 mineral phases may also fractionate trace elements of interest, such as amphibole or biotite
330 (Putzolu et al., 2024). Furthermore, apatite-melt partition coefficients can vary as a function of
331 magmatic conditions; for example, Mn and Eu partition coefficients depend on redox conditions
332 (e.g., Miles et al., 2014). Apatite trace element compositions therefore reflect igneous processes
333 from source to final emplacement, and they will be different for each batch of magma.

334 (2) *Apatite crystals do not merely record the final stages of fractionation.* Apatite often appears
335 early in the crystallisation sequence of silicic magmas, as evidenced by their common inclusion
336 in rock-forming minerals (e.g., biotite, feldspar and zircon; Hoskin et al., 2000; Piccoli and
337 Candela, 2002; Broska et al., 2004; Macdonald et al., 2013; Miles et al., 2013; Zhang et al., 2021;
338 Li et al., 2022). Apatite may therefore record magma fractionation from early to late stage in any
339 given rock sample, which will be reflected in its compositional range. This is useful to
340 reconstruct magma petrogenesis but poses a problem from an exploration point of view: a rock
341 from a Sn-fertile magma will likely contain apatite crystals which formed early (and long before
342 mineralisation), and those crystals will therefore not reflect extreme fractionation; if such

343 apatite is then analysed as a detrital grain, it will not indicate tin mineralisation using
344 petrogenetic discriminants such as Eu/Eu^* , La/Yb_N or Sr/Y .

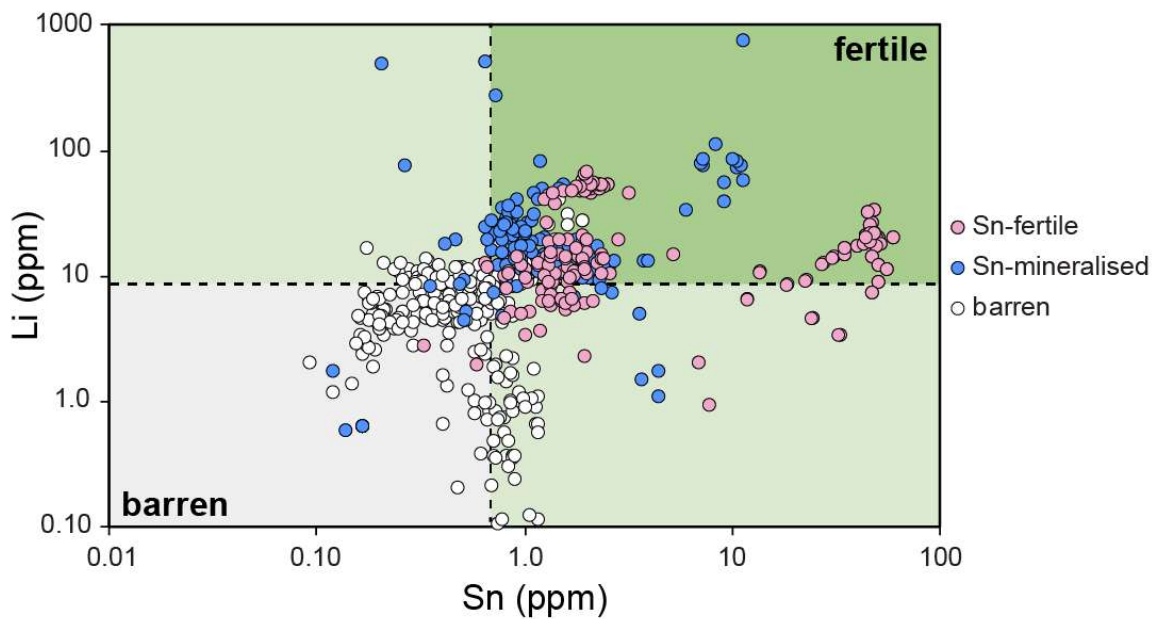
345 (3) *Diffusion and hydrothermal alteration may modify and obscure primary trace element*
346 *concentrations.* Mineral-scale diffusion ($>10\ \mu\text{m}$ scale) in apatite at magmatic temperatures
347 likely operates in timescales of days to decades for many elements (Ca, Pb, Sr, Mn, U, Li, F, Cl,
348 OH; Cherniak, 2010). Diffusive re-equilibration of apatite with their host (melt or mineral) may
349 therefore alter its trace element composition and obscure primary magmatic signatures.
350 Similarly, fluid-moderated overprinting during and after the magmatic-hydrothermal transition
351 may disturb or replace primary compositions. For example, Bouzari et al. (2016) found that
352 hydrothermally altered apatite has higher Ca and lower trace element concentrations than
353 apatite from unaltered rocks, which they attributed to trace element loss during alteration. If
354 considered within its petrogenetic context, apatite can be an insightful tool to study these
355 metasomatic processes (e.g., Harlov et al., 2015), but in an exploration context it adds an
356 additional layer of complexity.

357 (4) *Apatite may host small inclusions of other minerals which may bias analyses.* For example,
358 monazite and zircons inclusions are commonly observed in apatite (Tepper and Kuehner, 1999;
359 Farley and Stockli, 2002). REE-rich minerals monazite and xenotime are often found as inclusions
360 in hydrothermally altered apatite zones, where they likely formed in response to the
361 metasomatic removal of REE from apatite (e.g., Harlov et al., 2005; 2011; Zirner et al., 2015).
362 Larger inclusions may be avoided or detected in the ablation signal, but small, dispersed mineral
363 or fluid inclusions may not be resolvable in the signal and bias the results.

364 In summary, common geochemical discriminants in apatite which empirically relate tin mineralisation
365 to petrogenetic processes (e.g., fractionation and oxidation state) show large scatter because they
366 record magmatic evolution over a temporal and spatial extent much beyond that of any mineralising
367 process. Moreover, it indicates that barren and fertile granitoids undergo similar petrogenetic
368 processes, which points towards source enrichment as a crucial pre-requisite for tin mineralisation.

369 5.2 Li and Sn as robust tracers of mineralisation

370 We argue that many common geochemical discriminants are petrogenetically ambiguous and often
371 of limited use as robust discriminants for tin mineralisation. Instead, prima facie concentrations of Sn
372 and Li in apatite offer a more satisfactory discrimination between barren granites and intrusions
373 associated with Sn deposits (Figs. 3 & 4). This is a somewhat surprising result considering that apatite
374 is not a primary host for either Li or Sn, which are more likely to be fractionated by micas (Ellis et al.,
375 2022; Putzolu et al., 2024). Furthermore, Li is known to be a fast-diffusing element in most rock-
376 forming minerals including apatite (Audétat et al., 2018, Li et al., 2020), which may obscure primary
377 elemental signatures. This illustrates that Sn and Li are subject to the same processes that
378 compromise the utility of common metallogenic indices, yet they retain distinctively elevated
379 concentrations in apatite through differentiation.



380
381 **Fig. 4:** Lithium and tin concentrations in magmatic apatite from barren intrusions, Sn-fertile and Sn-
382 mineralised intrusions. 75% of apatite from barren intrusions have $Li \leq 9.1$ ppm and $Sn \leq 0.7$ ppm,
383 while >77% of apatite from Sn-fertile and -mineralised granitoids have $Li > 9.1$ ppm, and >82% show
384 $Sn > 0.7$ ppm. This demonstrates the utility of Sn and Li concentration in apatite to fingerprint tin
385 mineralisation.

386 While we show that classical fractionation and oxidation indices fail to unambiguously point to Sn
387 mineralisation, Li and Sn concentrations in apatite can “see through” complex petrogenetic and
388 metallogenetic processes. This suggests that source enrichment and elevated primary Sn and Li
389 concentrations are crucial aspects of tin mineralisation.

390 Our database shows that Sn and Li in apatite hold promise to be developed as robust discriminants
391 for Sn mineralisation (Fig. 4). Specifically, apatite crystals with Li >9.1 ppm and Sn >0.7 ppm are highly
392 likely to stem from a Sn-fertile or Sn-mineralised intrusion: 75% of apatite from barren granitoids fall
393 below these thresholds, whereas 77% of apatite from Sn-fertile and 83% of apatite from Sn-
394 mineralised rocks have higher Li concentrations, and 95% of apatite from Sn-fertile and 82% of
395 apatite from Sn-mineralised rocks have higher Sn concentrations. For the new data presented in this
396 study, mean analytical uncertainties are 22% (2SE) for Li and 13% for Sn (Supplementary Material 2);
397 assuming more conservative uncertainties of 30% 2SE on analytical results dilutes the significance of
398 the Li-Sn discriminant system. Despite this, based on our data compilation, we consider Li and Sn the
399 most meaningful pathfinders to tin mineralisation using apatite.

400 6. Conclusions

401 Our apatite trace element data compilation reveals large variability of widely used geochemical
402 fractionation and redox proxies for both barren, Sn-fertile and Sn-mineralised intrusions (Fig. 2),
403 which leads to significant overlap between the groups. In part, this overlap implies that while
404 extreme fractionation and reduced conditions in S-type granites are *necessary* conditions for tin
405 mineralisation, they are, on their own, not *sufficient*. The much more distinctive character of Li and
406 Sn concentrations in apatite (Figs. 3 & 4) indicates that source enrichment may be an additional
407 precondition for tin mineralisation. These findings call into question the utility of petrogenetic
408 indicators like Mn and La/Yb_N in tin exploration, at least for the case of apatite. Instead, our data
409 suggests that Li and Sn in apatite are a more robust discriminant for Sn mineralisation. We therefore
410 encourage the tin exploration community to exercise caution when using common petrogenetic

411 indicators (Mn, Eu/Eu*, La/Yb_N and Sr/Y), and we instead recommend including Sn and Li in their
412 apatite trace element analyses in order to optimise use of apatite as an indicator mineral for Sn
413 mineralisation.

414 [Data Availability](#)

415 All data underlying this study is available in the Supplementary Material.

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418 [References](#)

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