Accessory Mineral Eu Anomalies in Suprasolidus Rocks: Beyond Feldspar

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Key Points:

- Eu anomalies in suprasolidus rocks record any process that changes the relative availability of Eu^{2+} and Eu^{3+}, not just feldspar growth.

- Disequilibrium is required for feldspar growth to strongly influence accessory mineral Eu anomalies.

- Comparing accessory mineral Eu anomalies and Sr concentrations leads to more robust interpretation than evaluating Eu anomalies alone.

19 **Abstract**

20 Accessory-mineral Eu anomalies (Eu/Eu*) are routinely measured to infer changes in the amount
21 of feldspar over time, allowing accessory mineral U–Pb dates to be linked to the progressive
22 crystallization of igneous and metamorphic rocks and, by extension, geodynamic processes.
23 However, changes in Eu/Eu* can reflect any process that changes the relative availability of Eu^{2+}
24 and Eu^{3+}. We constructed partitioning budgets for Sm, Eu^{2+}, Eu^{3+}, and Gd in suprasolidus
25 metasedimentary rocks to investigate processes that can influence accessory mineral Eu
26 anomalies. We modeled three scenarios: 1) closed-system, equilibrium crystallization; 2)
27 fractionation of Eu by feldspar growth during melt crystallization; and 3) removal of Eu by melt
28 extraction. In the closed-system equilibrium model, accessory-mineral Eu/Eu* changes as a
29 function of fO₂ and monazite stability; Eu/Eu* changes up to 0.3 over a pressure–temperature
30 range of 4–12 kbar and 700–950°C. Fractionation of Eu by feldspar growth is modeled to
31 decreases accessory-mineral Eu/Eu* by ~0.05–0.15 per 10 wt% feldspar crystallized. Melt
32 extraction has a smaller effect; removal of 10% melt decreases accessory mineral Eu/Eu* in the
33 residue by ≤0.05. Although these models demonstrate that fractionation of Eu by feldspar growth
34 can be a dominant control on a rocks Eu budget, they also show that the common interpretation
35 that Eu/Eu* only records feldspar growth and breakdown is an oversimplification that could lead
36 to incorrect interpretation about the duration and rates of tectonic processes. Consideration of
37 other processes that influence Eu anomalies will allow for a broader range of geological
38 processes to be investigated by petrochronology.

39 **Plain Language Summary**
40 Metamorphic rocks—rocks in which new minerals grew in response to increase in pressure and
41 temperature related to deep burial or subduction—and igneous rocks—rocks that formed as
42 magmas cool and crystallize—provide a direct record of how Earth's continents have moved and
43 changed through time. To read this record, geologists need to be able to measure the ages of
44 metamorphism and magmatism: When did it happen? How long did it last? How does it relate to
45 other rocks around the world? A common approach to addressing these questions is using U–Pb
46 dating of the minerals zircon, monazite, and apatite. The elements these minerals incorporate are
47 indicative of how hot and how deep in the Earth they were when they grew. In this paper we
48 explore how geologists can use the concentrations of the element Europium (Eu) in these
49 minerals to provide new insights into the geological significance of U–Pb dates, leading to more
50 robust interpretations of Earth's plate tectonic history.
51

52 **1 Introduction**

53   Trace-element concentrations and ratios in accessory minerals can be used to (semi-
54)quantitatively link accessory-mineral growth to the growth and breakdown of major phases (e.g.
55 Bea & Montero, 1999; Buick et al., 2006; Cioffi et al., 2019; Finger & Krenn, 2007; Foster et al.,
56 2000; Foster et al., 2002; Garber et al., 2017; Hacker et al., 2019; Hermann & Rubatto, 2003;
57 Hokada & Harley, 2004; Kelly et al., 2006; Kelly & Harley, 2005; Mottram et al., 2014; Pyle &
58 Spear, 1999; Rubatto, 2002; Rubatto & Hermann, 2007; Rubatto et al., 2006; Taylor et al., 2015;
59 Warren et al., 2019) (Figure 1). This approach—along with trace-element thermobarometers
60 (Ferry & Watson, 2007; Gratz & Heinrich, 1997; Hayden et al., 2008; Pyle et al., 2001;
61 Seydoux-Guillaume et al., 2002; Thomas et al., 2015; Tomkins et al., 2007; Wark & Watson,
62 2006) and modeling of accessory-mineral stability (Janots et al., 2007; Kelsey et al., 2008; Kohn
63 et al., 2015; Shrestha et al., 2019; Spear, 2010; Spear & Pyle, 2010; Yakymchuk, 2017;

64 Yakymchuk & Brown, 2014; Yakymchuk et al., 2017)—can be combined with *in-situ* U–Pb
65 geochronology to infer *P–T–t–d* paths of crystalline rocks that underpin interpretations of their
66 geodynamic significance (e.g. Engi, 2017; Kohn, 2017; Rubatto, 2017; Zack & Kooijman, 2017).
67 This multilayered approach to assessing the petrological and geological significance of
68 accessory-mineral U–Pb dates forms the foundation of petrochronology (Engi et al., 2017).

69   In this paper, we address one of the trace-element ratios most commonly used in
70 petrochronology: the Eu anomaly ($Eu/Eu^* = Eu_n^{total}/\sqrt{Sm_n \times Gd_n}$, subscript n denotes a
71 normalized concentration; $Eu^{total} = Eu^{3+} + Eu^{2+}$; for this paper, the normalizing values are C.I.
72 chondrite; McDonough & Sun, 1995). Variability in accessory-mineral Eu/Eu* ratios are
73 commonly attributed to the growth and breakdown of plagioclase (e.g. Holder et al., 2015) or
74 alkali-feldspar (e.g. Mottram et al., 2014; Rubatto et al., 2006; 2013; 2016); plagioclase feldspar
75 is particularly sensitive to changes in pressure and useful for investigating high pressure
76 metamorphism (e.g. O'Brien & Rötzler, 2003), whereas the modes and compositions of both
77 feldspars are sensitive to the extent of partial melting in suprasolidus rocks. However, mineral
78 Eu/Eu* might be influenced by a range of factors, including: 1) bulk-rock Eu/Eu*; 2) the
79 stability of minerals that strongly partition either Eu^{2+} or Eu^{3+}; 3) bulk-rock Eu^{3+}/Eu^{2+}, which
80 depends on fO_2, *T*, and *P*; 4) possible differences in the temperature-dependence of partitioning
81 for Eu^{3+} relative to Eu^{2+}; or 5) any other process that fractionates Eu^{3+} from Eu^{2+}. Consequently,
82 accessory-mineral Eu/Eu* might not always be exclusively controlled by feldspar. The purpose
83 of this paper is to highlight the potential complexity of Eu partitioning, by modeling changes in
84 accessory-mineral Eu/Eu* for three simple, plausible scenarios (changes in fO_2, feldspar
85 fractionation, and open-system melting), as a basis for further discussion about interpreting
86 accessory-mineral Eu/Eu* in natural samples.

87

2 Methods

89   2.1 Construction of partitioning models

90   The concentrations of Sm, Eu, and Gd in accessory minerals, major minerals, and melt
91 were calculated for average suprasolidus metapelite and metagreywacke (Figure 2) as functions
92 of pressure and temperature using mineral modes and partition coefficients. Mineral modes were
93 calculated by phase-equilibrium modeling as described by Yakymchuk et al. (2017). Whole-rock
94 mass fractions of Sm, Eu, and Gd were taken to be 5.9, 1.2, and 5.2 µg/g, respectively, reflecting
95 the average values of shales (e.g. Condie, 1993). This corresponds to Eu/Eu*$_{rock}$ = 0.66.

96   There is considerable variability in the availability and quality of partitioning data. In
97 recognition of this uncertainty, models were constructed with two sets of partition coefficients,
98 referred to as "B94"—empirical partition coefficients from Bea et al. (1994)—and "modified
99 composite" (MC)—a dataset of partition coefficients compiled from multiple studies, modified
100 slightly to reduce several discrepancies observed among calculations and observations in the first
101 iterations of the model calculations (zircon and garnet: Rubatto & Hermann, 2007; Taylor et al.,
102 2015; monazite: Stepanov et al., 2012; apatite: Watson & Green, 1981; plagioclase: Sun et al.,
103 2017; alkali-feldspar: Ren, 2004). The partitioning data used in each of these models are

104   described in more detail in Texts S1 and S2 and summarized in Table 1. All partition coefficients
105   (K_d^x, x = element or ion of interest) are mineral:melt unless specifically stated.

106   The advantages of the B94 models are that: (1) The estimated peak metamorphic
107   temperature of the rocks from which the partitioning data were estimated (750°C) is lower than
108   the experimental/magmatic temperatures of most trace-element partitioning studies, and (2) The
109   rocks from which the data were estimated are similar to the modeled compositions of this study
110   (i.e. peraluminous migmatites). The B94 models do not account for the temperature- or pressure-
111   dependence of partitioning or the presence of Eu^{2+} in accessory minerals and their samples are
112   more reduced than many metasedimentary rocks (e.g. Ague, 1991; Diener & Powell, 2010;
113   Spear, 1993). The advantages of the MC models are that they account for the temperature
114   dependence of partitioning and include both Eu^{2+} and Eu^{3+} in each accessory mineral.

115   2.2 Calculating whole-rock Eu valence for partitioning models

116   The Eu species Eu^{3+} and Eu^{2+} were treated independently. Values of K_d^{Eu3+} were taken as
117   the geometric mean of K_d^{Sm} and K_d^{Gd}, whereas it was assumed that $K_d^{Eu2+} = K_d^{Sr}$ (Philpotts,
118   1970) due to the near identical size and ionic radius of Eu^{2+} and Sr^{2+} (Shannon, 1976). We
119   assumed that the bulk-rock Eu^{2+}/Eu^{3+} ratios are reasonably approximated by the equations of
120   Burnham et al. (2015), who measured Eu valence in experimental silicate melts as functions of
121   temperature, fO_2, and melt composition. Burnham et al. (2015) found that contours of constant
122   Eu^{2+}/Eu^{3+} were parallel to the fayalite–magnetite–quartz buffer in plots of fO_2 vs T,
123   demonstrating that Eu valence was controlled by Fe^{2+}–Fe^{3+} redox. This suggests that the *relative*
124   changes in Eu valence should be reasonably approximated by fO_2 for systems in which fO_2 is
125   controlled by Fe^{2+}–Fe^{3+} mineral equilibrium (among magnetite–spinel, ilmenite, biotite, and
126   garnet in our models). However, the *absolute values* of bulk-rock and mineral Eu^{2+}/Eu^{3+} might
127   be different in real (semi-)pelitic systems which differ from the experiments of Burnham et al.
128   (2015) in that they are outside of their investigated compositional range (mostly mafic–
129   intermediate), at lower temperature, and they contain minerals (the experiments of Burnham et
130   al., 2015, were strictly on melts) which might impart their own crystal-chemistry influence on
131   Eu^{2+}/Eu^{3+} in their structures (e.g. Philpotts, 1970). Therefore, the models should only be
132   interpreted semi-quantitatively, in terms of order-of-magnitude change and trends.

133   Models were calculated with fixed O concentrations, corresponding to slightly oxidized
134   bulk compositions (Fe^{3+}/Fe^{total} = 0.15; Yakymchuk et al., 2017) that produce ilmenite±magnetite
135   (e.g. Diener and Powell, 2010), consistent with observations from many natural metapelites.
136   Calculated $\log_{10}fO_2$ in the models varies between ~FMQ$_{+1}$ and FMQ$_{+3}$, where FMQ is the
137   fayalite–magnetite–quartz buffer and the subscript indicates logarithmic deviations from the
138   buffer. Such values are relatively common in metasedimentary granulites (e.g. Boger et al., 2012;
139   Yakymchuk et al., 2019) and typical of many lower-crustal rocks in general (Bucholz &
140   Keleman, 2019). No explicit fO_2 buffer was imposed on the calculations, as that would require
141   that O concentrations vary as a function of T, P, and the compositions of Fe^{2+}–Fe^{3+} solid
142   solutions to maintain the buffer (i.e. not a closed system). Values of Eu^{3+}/Eu^{total} vary
143   approximately linearly over this fO_2 range (Burnham et al., 2015). For significantly more
144   reduced (<FMQ$_{-4}$) or oxidized rocks (>FMQ$_{+8}$), the equations of Burnham et al. (2015) predict
145   Eu to be monovalent: Eu^{2+} or Eu^{3+}, respectively. Our calculations are not applicable to natural

146 systems at these fO₂ extremes (such as graphite–pyrite-bearing metapelites; Connolly & Cesare,
147 1993).

148   2.3 Model scenarios

149   (1) In the equilibrium closed-system partitioning models, partition coefficients were used
150 to calculate concentrations of Sm, Eu, and Gd in each relevant mineral as functions of mineral
151 modes, temperature, and Eu^{2+}/Eu^{3+} ratio. (2) The models of Eu fractionation by feldspar
152 crystallization were calculated along an isobaric cooling path at 6 kbar. The models began at
153 950°C with REE-equilibrium among all phases. The REE incorporated into plagioclase and
154 alkali-feldspar as they grew was incrementally removed from the effective whole-rock
155 composition at one-degree-K cooling intervals. All other aspects of these models were assumed
156 to be in equilibrium (e.g. mineral modes, major-element compositions, and REE partitioning
157 among all other phases) to specifically isolate the influence of feldspar fractionation on
158 accessory mineral Eu anomalies. For portions of the modeled cooling path in which the mode of
159 either plagioclase or alkali-feldspar decreased, a proportionate amount of the previously
160 fractionated REE was added back into the effective bulk-composition. (3) For the models of melt
161 extraction during isobaric heating, REE equilibrium was maintained among all phases. When the
162 melt fraction reached 7 mol%, approximately the melt-connectivity threshold (Rosenberg &
163 Handy, 2005), the major-element equivalent of 6 mol% melt was removed from the model
164 composition (leaving 1% remaining) along with proportionate amounts of Sm, Eu, and Gd.
165 Although the exact value of this melt-connectivity threshold will depend on grainsize, grain
166 shape, and deformation, this approach is used for consistency with the now-common melt-
167 reintegration method used by Korhonen et al. (2013) to estimate the protolith composition of
168 residual granulites (this approach is the inverse of theirs). The weight fractions of accessory
169 minerals were also modified by each melt-extraction step in accordance with their solubilities
170 (e.g. Yakymchuk, 2017).

171 **3 Results**

172 Results of the models are tabulated in Data Sets S1–S16, which are available through the
173 EarthChem community data repository (Holder et al., 2020).

174   3.1 Models of equilibrium, unbuffered, closed-system metamorphism

175   Contours of oxygen fugacity ($\log_{10}f$O₂), oxygen fugacity relative to the fayalite–
176 magnetite–quartz buffer ($\log_{10}f$O₂ rock – $\log_{10}f$O₂ FMQ), and Eu valence (Eu^{3+}/Eu^{total}) as functions
177 of pressure and temperature are shown in Figure 3. Contours of $\log_{10}f$O₂ rock – $\log_{10}f$O₂ FMQ
178 (Figure 3c,d) parallel reactions among the Fe^{2+}–Fe^{3+} minerals (ilmenite, magnetite–spinel,
179 garnet, and biotite). At higher pressure, the contours closely parallel the rutile-in reaction, which
180 involves breakdown of ilmenite to form garnet and rutile with increasing pressure; the slope of
181 this reaction changes between 750 and 850°C due to the breakdown of biotite. At lower pressure,
182 the contours become more closely spaced, following magnetite–spinel stability, with a notable
183 "trough" at ~750°C.

184   Contours of Eu^{3+}/Eu^{total} (Figure 3e,f) are similar to the contours of $\log_{10}f$O₂ rock – $\log_{10}f$O₂
185 FMQ (Figure 3c,d), as expected from the Fe-redox-controlled Eu-redox equations used in the

186   models (Burnham et al., 2015). The overall changes in Eu^{3+}/Eu^{total} across the models (675–
187   950°C, 4–12 kbar) is 0.2–0.3 in both pelite and greywacke. The values of Eu^{3+}/Eu^{total} are
188   primarily functions of pressure, due to the pressure-dependence of oxide stability, with slight
189   deflection associated with biotite breakdown, as mentioned in the previous paragraph.

190   Calculated Eu/Eu* in the accessory minerals and garnet in the MC models are shown in
191   Figure 4. The values for each mineral are ~0.6–0.7 at higher pressure and 0.4–0.5 at lower
192   pressure. At lower temperature, where all three accessory minerals are abundant, the contours of
193   Eu/Eu* essentially parallel the contours of whole-rock Eu^{3+}/Eu^{total} (Figure 3e,f). However, at
194   ~850°C (pelite) and ~900°C (greywacke), contours of Eu/Eu* are more temperature-dependent;
195   this change occurs as the mode of monazite decreases exponentially, until it is not stable. For the
196   B94 models, accessory-mineral Eu/Eu* parallels whole-rock Eu^{3+}/Eu^{total} (Figure S1), because
197   accessory-mineral $K_d^{Eu2+} = 0$. Calculated Eu/Eu* anomalies of plagioclase and melt in the MC
198   model are shown in Figure 5. Values of Eu/Eu* in feldspars and melt decrease with increasing
199   temperature and show little pressure dependence, except for the B94 greywacke model (Figure
200   S2) in which plagioclase and melt Eu/Eu* show a stronger pressure dependence near the solidus.

201   Figure 6 shows the proportion of each phase, their total Eu content, and their Eu/Eu*
202   from the MC models along a hypothetical clockwise *P–T* path consisting of isobaric heating at
203   10 kbar to 850°C, isothermal decompression at 850°C to 5 kbar, and isobaric cooling at 5 kbar to
204   675°C. As described above, feldspars and melt Eu/Eu* changes most significantly with
205   temperature, whereas Eu/Eu* of the accessory minerals and garnet ($K_d^{Eu3+} >> K_d^{Eu2+}$) change
206   most significantly with pressure. The total change in accessory mineral Eu/Eu* along such a *P–T*
207   path is similar in all models: approximately –0.1 to –0.2. Pressure–temperature paths that pass
208   through lower pressure and higher temperature conditions, where magnetite–spinel is stable,
209   would result in slightly larger changes in Eu/Eu* for the accessory minerals and garnet (Figure
210   3e,f; e.g. Holder et al., 2018).

211   Figure 7 shows apatite Eu/Eu* as functions of *T*, *P*, feldspar wt%, and Eu^{3+}/Eu^{total} on
212   accessory mineral Eu/Eu* in the closed-system, equilibrium MC models. Apatite is plotted,
213   because it exhibits the largest *P–T* stability range of the accessory minerals; however, monazite
214   and zircon exhibit similar relationships (Figures 4, 6). Viewed together, these plots illustrate that
215   the relationship of accessory mineral Eu/Eu* with feldspar is nonsystematic. In contrast, changes
216   in pressure and temperature show strong consistent effects, due to changes in bulk-rock Eu
217   valence (changes in *f*O$_2$, relative to the FMQ buffer) and monazite stability, respectively. Total
218   changes in accessory mineral Eu/Eu* over the modeled *P–T* conditions are 0.2–0.3.

219   3.2 Models of feldspar fractionation

220   Figure 8 shows the results of the models in which REE are fractionated by feldspars
221   during isobaric cooling and melt crystallization. Models were stopped when the weight fractions
222   of the feldspars became essentially constant, making the fractionation calculations non-
223   applicable. For the pelite model, this occurred at 700°C, slightly above the calculated solidus.
224   For linguistic simplicity, we refer to 700°C as "the solidus" for the pelite models in the following

225 paragraphs. For the greywacke model, the weight fractions of feldspar are essentially constant at
226 $T < 798$°C.

227 In all models, the effective whole-rock Eu/Eu* decreases with cooling, as the amount of
228 feldspar increases. In the MC pelite model, the significant resorption of alkali-feldspar as biotite
229 begins to crystallize (at 813°C) results in a sharp increase in effective whole-rock Eu/Eu*, before
230 continued plagioclase crystallization draws the value back down. The B94 pelite model does not
231 show the same influence of the biotite-in reaction, due to much lower values of K_d^{Eu2+} in the
232 alkali feldspar. Values of Eu/Eu* in accessory minerals and garnet are generally sub-parallel to
233 the whole-rock values, with deviations due to changes in mineral modes and differences in K_d^{Eu3+}
234 and K_d^{Eu2+} among minerals.

235 3.3 Models of melt extraction

236 Figure 9 shows the results of models in which REE were removed by step-wise melt
237 extraction during isobaric heating based on their equilibrium values in melt. The results of the
238 calculations differ substantially between the MC and B94 models.

239 For the MC models, melt extraction changes the bulk-rock Eu/Eu* very little from the
240 initial value of 0.66. Accessory-mineral and garnet Eu/Eu* show a total variability of 0.10–0.15
241 (pelite) and ~0.02 (greywacke). The greywacke models show less variability in Eu/Eu*, because
242 less melt is produced and extracted. For the B94 models, melt extraction changes the bulk-rock
243 Eu/Eu* more appreciably than in the MC models. Bulk-rock Eu/Eu* decreases from 0.66 to 0.53
244 (pelite) or 0.63 (greywacke). Values of accessory-mineral and garnet Eu/Eu* generally follow
245 the effective whole-rock Eu/Eu*, decreasing as melt is extracted.

246 The differences between results of the MC and B94 melt-extraction models are primarily
247 due to differences in the calculated Eu/Eu* of the melt. In the B94 models, the Eu/Eu* of the
248 melt is 14 (greywacke) or 18 (pelite) at the solidus and remains greater than unity for most of the
249 models, allowing for substantial removal of Eu relative to other REE during melt extraction. In
250 the MC models, the Eu/Eu* of the melt is 2.4 (greywacke) or 4.5 (pelite) at the solidus and
251 decreases below unity at 876°C (greywacke) or 830°C (pelite); although melt was extracted
252 multiple times within this temperature range, the draw-down in whole-rock Eu/Eu* is negligible
253 due to the relatively low Eu/Eu* and low total concentrations of REE in the melt.

254 **4 Discussion**

255 4.1 Controls on equilibrium mineral Eu/Eu*

256 Interpreting Eu/Eu* in minerals is complicated by presence of both Eu^{2+} and Eu^{3+} in most
257 metamorphic and igneous environments. The equilibrium Sm–Eu–Gd partitioning calculations
258 shown in Figures 3–7 provide a starting point to understand the processes that control mineral
259 Eu/Eu*.

260 Both feldspars and melt preferentially incorporate Eu^{2+} over Eu^{3+}, resulting in Eu/Eu*
261 consistently greater than the whole-rock value. However, in all models, the values of feldspar
262 and melt Eu/Eu* decrease by approximately an order of magnitude from 700 to 950°C (Figure
263 5). This is due to several effects: 1) temperature- and composition-dependence of feldspar K_d's

264 (e.g. plagioclase K_d^{Eu2+} decreases from 8.4 to 0.33 between 700 to 950°C at 10 kbar in the MC

265 pelite model); 2) increase in the proportion of melt (Eu^{2+} must be shared among feldspars and

266 melt); and 3) dissolution of accessory minerals, most prominently monazite (Figure 6, 7), which

267 requires that their Sm, Gd, and Eu (mostly Eu^{3+}) must be redistributed among the other phases.

268   The accessory minerals and garnet have very large Eu^{3+}/Eu^{2+} ratios (>10–100). Values of

269 Eu/Eu* in these minerals is primarily controlled by the availability of Eu^{3+}. Contours of

270 accessory mineral Eu/Eu* (Figure 4) are sub-parallel to the whole-rock Eu^{3+}/Eu^{total} contours

271 (Figure 3e,f), which is governed by fO_2 (in the B94 models, this is the only control). An

272 exception to this is: at ~850°C (pelite) and ~900°C (greywacke), the amount of monazite

273 decreases exponentially until it becomes fully dissolved in the melt (Figure 4), causing the

274 accessory-mineral Eu/Eu* contours to deviate from the whole-rock Eu^{3+}/Eu^{total} contours.

275   Most importantly for this study, in the equilibrium closed-system models, there is no

276 systematic correlation between feldspar abundance and accessory mineral Eu/Eu*. Apparent

277 correlations occur for some P–T conditions, but these vary in sign and magnitude (Figure 7a,b)

278 and are more appropriately attributed to changes in pressure and temperature, which influence

279 modeled Eu^{3+}/Eu^{total} and the mode of monazite, respectively (Figure 7c,d). This lack of a clear

280 relationship with the amount of feldspar is expected, because feldspars and accessory minerals

281 are mostly competing for difference species of Eu (Eu^{2+} and Eu^{3+}, respectively; e.g. Kohn and

282 Kelly, 2017). Maximum changes in equilibrium accessory-mineral Eu/Eu* are predicted to be

283 ~0.2–0.3 for the modeled suprasolidus conditions. Due to the strong pressure dependence of

284 accessory-mineral Eu/Eu* in the models, clockwise P–T paths are predicted to result in a net

285 decrease in Eu/Eu*, whereas counter-clockwise paths are predicted to result in a net increase in

286 Eu/Eu*.

287   4.2 Open system effects on mineral Eu/Eu*

288   4.2.1 Fractionation of Eu by feldspar crystallization

289   The calculations shown in Figure 8 support the hypothesis that feldspar growth and

290 breakdown can significantly influence accessory mineral Eu/Eu* if the REE incorporated into

291 feldspar are effectively fractionated from the rest of the rock. For the MC models, crystallization

292 of 10% feldspar resulted in a decrease in accessory mineral Eu/Eu* of ~0.15, with a maximum

293 possible decrease of ~0.4; for the B94 models, the corresponding decrease was smaller but not

294 insignificant: ~0.05 for 10% feldspar crystallization, with a maximum possible decrease of

295 ~0.15. However, application of these generalizations to real rocks is complicated by the

296 recognition that alkali-feldspar and plagioclase modes are unlikely to change monotonically

297 during crystallization; they grow/breakdown as functions of their miscibility, and due to

298 reactions with garnet (such as the "GASP" reaction), incongruent versus congruent melting, melt

299 crystallization and reactions with micas. For example, the MC pelite model (Figure 8c) shows

300 accessory mineral Eu/Eu* with increases and decreases of > 0.1 during cooling as a result of

301 feldspar crystallization at high temperature then feldspar resorption and mica crystallization at

302 lower temperature. Another complication is that Eu^{2+} diffusivity in feldspar, if similar to Sr

303 diffusivity, is ~4 orders of magnitude higher than REE^{3+} diffusivity (Cherniak 1995, Cherniak &

304 Watson, 1992; Cherniak & Watson, 1994); fractionation of Eu by feldspar growth might

305 therefore be limited at suprasolidus conditions. Nevertheless, the very large changes in accessory

306 mineral Eu/Eu* observed in some samples (≥0.4, Figure 1; e.g. Rubatto et al., 2006), likely
307 require some degree of Eu fractionation by feldspar growth.

308   4.2.2 Open-system melting

309   In our models, melt Eu/Eu* was greater than whole-rock Eu/Eu* at all conditions.
310 Therefore, extraction of melt from migmatites has the potential to decrease whole-rock Eu/Eu*,
311 but the modeled magnitude of this decrease depends on the partitioning data used. Observations
312 of leucosome:melanosome trace-element ratios in natural samples from Bea et al. (1994) suggest
313 that partial melt extraction can have a substantial influence on Eu/Eu* in residual minerals
314 (Eu/Eu* changes >0.1 in the B94 models; Figure 8). However, the MC models suggest that
315 open-system melting will have essentially no influence on accessory-mineral Eu/Eu*. It is
316 possible that the discrepancy in these results relates to how the partitioning data for the two
317 models were estimated. The partitioning data of Bea et al. (1994) are based on
318 mineral:leucosome trace-element ratios; however, leucosomes rarely record initial melt
319 compositions, due to fractional crystallization of feldspar (physical separation of feldspar from
320 residual melt as the leucosome crystallizes: e.g. Brown et al., 2016; Sawyer, 1987).
321 Consequently, the B94 models might have overpredicted the concentration of Eu^{2+} and Eu/Eu*
322 in the melt.

5 Conclusions

324   As hypothesized by Rubatto et al. (2006), our models predict that growth of feldspar can
325 significantly influence accessory-mineral Eu/Eu*, but only if REE in feldspar are effectively
326 fractionated from the rock. At equilibrium, the mode of feldspar has negligible/subordinate
327 effects on accessory-mineral Eu/Eu* compared to fO$_2$ and the stability of monazite (for the
328 suprasolidus peraluminous rocks modeled). Feldspars do not strongly influence accessory-
329 mineral Eu/Eu* at equilibrium, because feldspars and accessory minerals predominantly
330 incorporate different Eu species (Eu^{2+} and Eu^{3+}, respectively; e.g. Kohn & Kelly, 2017).

331   Whereas Y+HREE partitioning among accessory minerals and garnet is relatively well
332 understood (e.g. Pyle et al., 2001), Eu partitioning is highly complex. This makes interpretation
333 of Eu/Eu* more difficult than Y+HREE, but might allow for a broader range of geological
334 processes to be investigated with petrochronology, particularly open-system processes such as
335 fluid–rock interaction, partial melting, and magma crystallization. The models presented here
336 provide a basis for further study, but are limited in application to suprasolidus peraluminous
337 rocks. The models are also limited in theory by available partitioning data and a lack of
338 quantification on the crystal chemical effects on Eu valence in minerals. To fully understand
339 accessory mineral Eu/Eu*, the roles of other minerals (e.g. allanite, amphibole, titanite in
340 metabasites and intermediate rocks) also needs to be assessed. In addition, systematic
341 assessments of Eu/Eu* in natural samples, as have been undertaken for mineral Y+HREE
342 concentrations, are needed (e.g. Bea & Montero, 1999; Foster et al., 2000; Hermann & Rubatto,
343 2003; Pyle & Spear, 1999).

344

Acknowledgments

References

Ague, J. J. (1991). Evidence for major mass transfer and volume strain during regional metamorphism of pelites. Geology, 19(8), 855–858. https://doi.org/10.1130/0091-7613(1991)019<0855:EFMMTA>2.3.CO;2

Bea, F., & Montero, P. (1999). Behavior of accessory phases and redistribution of Zr, REE, Y, Th, and U during metamorphism and partial melting of metapelites in the lower crust : An example from the Kinzigite Formation of Ivrea-Verbano , NW Italy. *Geochimica et Cosmochimica Acta*, *63*(7/8), 1133–1153. https://doi.org/10.1016/S0016-7037

Boger, S. D., White, R. W., & Schulte, B. (2012). The importance of iron speciation (Fe+2/Fe+3) in determining mineral assemblages: an example from the high-grade aluminous metapelites of southeastern Madagascar. Journal of Metamorphic Geology, 30(9), 997–1018. https://doi.org/10.1111/jmg.12001

Brown, C. R., Yakymchuk, C., Brown, M., Fanning, C. M., Korhonen, F. J., Piccoli, P. M., & Siddoway, C. S. (2016). From source to sink: Petrogenesis of cretaceous anatectic granites from the Fosdick migmatite-granite complex, West Antarctica. *Journal of Petrology*, *57*(7), 1241–1278. https://doi.org/10.1093/petrology/egw039

Bucholz, C. E., & Kelemen, P. B. (2019). Oxygen fugacity at the base of the Talkeetna arc, Alaska. Contributions to Mineralogy and Petrology, 174(10), 1–27. https://doi.org/10.1007/s00410-019-1609-z

Buick, I. S., Hermann, J., Williams, I. S., Gibson, R. L., & Rubatto, D. (2006). A SHRIMP U–Pb and LA-ICP-MS trace element study of the petrogenesis of garnet–cordierite–orthoamphibole gneisses from the Central Zone of the Limpopo Belt, South Africa. *Lithos*, *88*(1–4), 150–172. https://doi.org/10.1016/j.lithos.2005.09.001

Burnham, A. D., Berry, A. J., Halse, H. R., Schofield, P. F., Cibin, G., & Mosselmans, J. F. W. (2015). The oxidation state of europium in silicate melts as a function of oxygen fugacity, composition and temperature. *Chemical Geology*, *411*, 248–259. https://doi.org/10.1016/j.chemgeo.2015.07.002

Cherniak, D. J. (2003). REE diffusion in feldspar. Chemical Geology, 193(1–2), 25–41. https://doi.org/10.1016/S0009-2541(02)00246-2

Cherniak, D. J., & Watson, E. B. (1992). A study of strontium diffusion in K-feldspar, Na-K feldspar and anorthite using Rutherford Backscattering Spectroscopy. Earth and Planetary Science Letters, 113(3), 411–425. https://doi.org/10.1016/0012-821X(92)90142-I

Cherniak, D. J., & Watson, E. B. (1994). A study of strontium diffusion in plagioclase using Rutherford backscattering spectroscopy. Geochimica et Cosmochimica Acta, 58(23), 5179–5190.

383   https://doi.org/10.1016/0016-7037(94)90303-4

384   Cioffi, C. R., Campos Neto, M. da C., Möller, A., & Rocha, B. C. (2019). Titanite petrochronology of the southern

385   Brasília Orogen basement: Effects of retrograde net-transfer reactions on titanite trace element compositions.

386   *Lithos*, *344–345*, 393–408. https://doi.org/10.1016/j.lithos.2019.06.035

387   Condie, K. C. (1993). Chemical composition and evolution of the upper continental crust: Contrasting results from

388   surface samples and shales. *Chemical Geology*, *104*(1–4), 1–37. https://doi.org/10.1016/0009-2541(93)90140-

389   E

390   Connolly, J. A. D., & Cesare, B. (1993). C-O-H-S fluid composition and oxygen fugacity in graphitic metapelites.

391   Journal of Metamorphic Geology, 11(3), 379–388. https://doi.org/10.1111/j.1525-1314.1993.tb00155.x

392   Diener, J. F. A., & Powell, R. (2010). Influence of ferric iron on the stability of mineral assemblages. Journal of

393   Metamorphic Geology, 28(6), 599–613. https://doi.org/10.1111/j.1525-1314.2010.00880.x

394   Engi, M. (2017). Petrochronology Based on REE-Minerals: Monazite, Allanite, Xenotime, Apatite. *Reviews in*

395   *Mineralogy and Geochemistry*, *83*(1), 365 LP – 418. https://doi.org/10.2138/rmg.2017.83.12

396   Engi, M., Lanari, P., & Kohn, M. J. (2017). Significant Ages—An Introduction to Petrochronology. *Reviews in*

397   *Mineralogy and Geochemistry*, *83*(1), 1–12. https://doi.org/10.2138/rmg.2017.83.1

398   Ferry, J. M., & Watson, E. B. (2007). New thermodynamic models and revised calibrations for the Ti-in-zircon and

399   Zr-in-rutile thermometers. *Contributions to Mineralogy and Petrology*, *154*(4), 429–437.

400   https://doi.org/10.1007/s00410-007-0201-0

401   Finger, F., & Krenn, E. (2007). Three metamorphic monazite generations in a high-pressure rock from the

402   Bohemian Massif and the potentially important role of apatite in stimulating polyphase monazite growth along

403   a PT loop. *Lithos*, *95*(1–2), 103–115. https://doi.org/10.1016/j.lithos.2006.06.003

404   Foster, G., Kinny, P., Vance, D., Prince, C., & Harris, N. (2000). The significance of monazite U–Th–Pb age data in

405   metamorphic assemblages; a combined study of monazite and garnet chronometry. *Earth and Planetary*

406   *Science Letters*, *181*(3), 327–340. https://doi.org/10.1016/S0012-821X(00)00212-0

407   Foster, G., Gibson, H. D., Parrish, R., Horstwood, M., Fraser, J., & Tindle, A. (2002). Textural, chemical and

408   isotopic insights into the nature and behaviour of metamorphic monazite. Chemical Geology, 191(1–3), 183–

409   207. https://doi.org/10.1016/S0009-2541(02)00156-0

410   Garber, J. M., Hacker, B. R., Kylander-Clark, A. R. C., Stearns, M. A., & Seward, G. (2017). Controls on trace

411   element uptake in metamorphic titanite: Implications for petrochronology. *Journal of Petrology*, *58*(6), 1031–

412   1057. https://doi.org/10.1093/petrology/egx046

413   Gratz, R., & Heinrich, W. (1997). Monazite-xenotime thermobarometry: Experimental calibration of the miscibility

414   gap in the binary system CePO4-YPO4. *American Mineralogist*, *82*(7–8), 772–780.

415   Hacker, B., Kylander-Clark, A., & Holder, R. (2019). REE partitioning between monazite and garnet: Implications

416   for petrochronology. *Journal of Metamorphic Geology*, *37*(2), 227–237. https://doi.org/10.1111/jmg.12458

417   Hayden, L. A., Watson, E. B., & Wark, D. A. (2008). A thermobarometer for sphene (titanite). *Contributions to*

418   *Mineralogy and Petrology*, *155*(4), 529–540. https://doi.org/10.1007/s00410-007-0256-y

419   Hermann, J., & Rubatto, D. (2003). Relating zircon and monazite domains to garnet growth zones: age and duration

420   of granulite facies metamorphism in the Val Malenco lower crust. *Journal of Metamorphic Geology*, *21*(9),

421   833–852. https://doi.org/10.1046/j.1525-1314.2003.00484.x

422   Hokada, T., & Harley, S. L. (2004). Zircon growth in UHT leucosome: Constraints from zircon-garnet rare earth

423   elements (REE) relations in Napier Complex, East Antarctica. *Journal of Mineralogical and Petrological*

424   *Sciences*, *99*(4), 180–190. https://doi.org/10.2465/jmps.99.180

425   Holder, R. M., Hacker, B. R., Horton, F., & Rakotondrazafy, A. F. M. (2018). Ultrahigh-temperature osumilite

426   gneisses in southern Madagascar record combined heat advection and high rates of radiogenic heat production

427   in a long-lived high- T orogen. *Journal of Metamorphic Geology*, *36*(7), 855–880.

428   https://doi.org/10.1111/jmg.12316

429   Holder, R. M., Hacker, B. R., Kylander-Clark, A. R. C., & Cottle, J. M. (2015). Monazite trace-element and isotopic

430   signatures of (ultra)high-pressure metamorphism: Examples from the Western Gneiss Region, Norway.

431   *Chemical Geology*, *409*, 99–111. https://doi.org/10.1016/j.chemgeo.2015.04.021

432   Holder, R., Yakymchuk, C., Viete, D. (2020). Modeled mineral Eu anomalies in suprasolidus metasediments,

433   Version 1.0. Interdisciplinary Earth Data Alliance (IEDA). https://doi.org/10.26022/IEDA/111590

434   Janots, E., Brunet, F., Goffé, B., Poinssot, C., Burchard, M., & Cemič, L. (2007). Thermochemistry of monazite-

435   (La) and dissakisite-(La): Implications for monazite and allanite stability in metapelites. *Contributions to*

436   *Mineralogy and Petrology*, *154*(1), 1–14. https://doi.org/10.1007/s00410-006-0176-2

437   Kelly, N. M., Clarke, G. L., & Harley, S. L. (2006). Monazite behaviour and age significance in poly-metamorphic

438   high-grade terrains: A case study from the western Musgrave Block, central Australia11Abbreviations: After

439   Kretz, 1983. *Lithos*, *88*(1–4), 100–134. https://doi.org/10.1016/j.lithos.2005.08.007

440   Kelly, N. M., & Harley, S. L. (2005). An integrated microtextural and chemical approach to zircon geochronology:

441   Refining the Archaean history of the Napier Complex, east Antarctica. *Contributions to Mineralogy and*

442   *Petrology*, *149*(1), 57–84. https://doi.org/10.1007/s00410-004-0635-6

443   Kelsey, D. E., Clark, C., & Hand, M. (2008). Thermobarometric modelling of zircon and monazite growth in melt-

444   bearing systems: examples using model metapelitic and metapsammitic granulites. *Journal of Metamorphic*

445   *Geology*, *26*(2), 199–212. https://doi.org/10.1111/j.1525-1314.2007.00757.x

446   Kohn, M. J. (2017). Titanite Petrochronology. *Reviews in Mineralogy and Geochemistry*, *83*.

447   https://doi.org/10.2138/rmg.2017.83.13

448   Kohn, M. J., Corrie, S. L., & Markley, C. (2015). The fall and rise of metamorphic zircon. *American Mineralogist*,

449   *100*(4), 897–908. https://doi.org/10.2138/am-2015-5064

450   Kohn, M. J., & Kelly, N. M. (2017). Petrology and geochronology of metamorphic zircon. *Microstructural*

451   *Geochronology: Planetary Records Down to Atom Scale*, 35–61. https://doi.org/10.1002/9781119227250.ch2

452   Korhonen, F. J., Brown, M., Clark, C., & Bhattacharya, S. (2013). Osumilite-melt interactions in ultrahigh

453   temperature granulites: Phase equilibria modelling and implications for the P-T-t evolution of the eastern ghats

454   province, India. *Journal of Metamorphic Geology*, *31*(8), 881–907. https://doi.org/10.1111/jmg.12049

455   Mottram, C. M., Warren, C. J., Regis, D., Roberts, N. M. W., Harris, N. B. W., Argles, T. W., & Parrish, R. R.

456   (2014). Developing an inverted barrovian sequence; insights from monazite petrochronology. *Earth and*

457   *Planetary Science Letters*, *403*, 418–431. https://doi.org/10.1016/j.epsl.2014.07.006

458   O'Brien, P. J., & Rötzler, J. (2003). High-pressure granulites: Formation, recovery of peak conditions and

459   implications for tectonics. *Journal of Metamorphic Geology*, *21*(1), 3–20. https://doi.org/10.1046/j.1525-

460   1314.2003.00420.x

461   Philpotts, J. A. (1970). Redox estimation from a calculation of Eu2+ and Eu3+ concentrations in natural phases.

462   *Earth and Planetary Science Letters*, *9*(3), 257–268. https://doi.org/10.1016/0012-821X(70)90036-1

463   Pyle, J. M., & Spear, F. S. (1999). Yttrium zoning in garnet: Coupling of major and accessory phases during

464   metamorphic reactions. *Geological Materials Research*, *1*(6), 1–49.

465   Pyle, J. M., Spear, F. S., Rudnick, R. L., & McDonough, W. F. (2001). Monazite–Xenotime–Garnet Equilibrium in

466   Metapelites and a New Monazite–Garnet Thermometer. *Journal of Petrology*, *42*(11), 2083–2107.

467   https://doi.org/10.1093/petrology/42.11.2083

468   Ren, M. (2004). Partitioning of Sr, Ba, Rb, Y, and LREE between alkali feldspar and peraluminous silicic magma.

469   *American Mineralogist*, *89*(8–9), 1290–1303. https://doi.org/10.2138/am-2004-8-918

470   Rosenberg, C. L., & Handy, M. R. (2005). Experimental deformation of partially melted granite revisited:

471   Implications for the continental crust. *Journal of Metamorphic Geology*, *23*(1), 19–28.

472   https://doi.org/10.1111/j.1525-1314.2005.00555.x

473   Rubatto, D. (2002). Zircon trace element geochemistry: distribution coefficients and the link between U-Pb ages and

474   metamorphism. *Chemical Geology*, *184*, 123–138. Retrieved from www.elsevier.com/locate/chemgeo

475   Rubatto, D. (2017). Zircon: The Metamorphic Mineral. *Reviews in Mineralogy and Geochemistry*, *83*(1), 261 LP –

476   295. https://doi.org/10.2138/rmg.2017.83.10

477   Rubatto, D., Chakraborty, S., & Dasgupta, S. (2013). Timescales of crustal melting in the Higher Himalayan

478   Crystallines (Sikkim, Eastern Himalaya) inferred from trace element-constrained monazite and zircon

479   chronology. *Contributions to Mineralogy and Petrology*, *165*(2), 349–372. https://doi.org/10.1007/s00410-

480   012-0812-y

481   Rubatto, D., & Hermann, J. (2007). Experimental zircon/melt and zircon/garnet trace element partitioning and

482   implications for the geochronology of crustal rocks. *Chemical Geology*, *241*(1–2), 38–61.

483   https://doi.org/10.1016/j.chemgeo.2007.01.027

484   Rubatto, D., Hermann, J., & Buick, I. S. (2006). Temperature and Bulk Composition Control on the Growth of

485   Monazite and Zircon During Low-pressure Anatexis (Mount Stafford, Central Australia). *Journal of*

486   *Petrology*, *47*(10), 1973–1996. https://doi.org/10.1093/petrology/egl033

487   Sawyer, E. W. (1987). The role of partial melting and fractional crystallization in determining discordant migmatite

488   leucosome compositions. *Journal of Petrology*, *28*(3), 445–473. https://doi.org/10.1093/petrology/28.3.445

489   Seydoux-Guillaume, A.-M., Wirth, R., Heinrich, W., & Montel, J.-M. (2002). Experimental determination of

490   Thorium partitioning between monazite and xenotime using analytical electron microscopy and X-ray

491   diffraction Rietveld analysis. *European Journal of Mineralogy*, *14*(5), 869–878. https://doi.org/10.1127/0935-

492   1221/2002/0014-0869

493   Shannon, R. D. (1976). Revised Effective Ionic Radii and Systematic Studies of Interatomie Distances in Halides

494   and Chalcogenides. *Acta Crystallographica*, *A32*, 751–767.

495 Shrestha, S., Larson, K. P., Duesterhoeft, E., Soret, M., & Cottle, J. M. (2019). Thermodynamic modelling of

496   phosphate minerals and its implications for the development of P-T-t histories: A case study in garnet -

497   monazite bearing metapelites. *Lithos*, *334–335*, 141–160. https://doi.org/10.1016/j.lithos.2019.03.021

498 Spear, Frank S. (1993). Metamorphic phase equilibria and pressure-temperature-time paths. Monograph /

499   Mineralogical Society of America. Washington, D.C.: Mineralogical Society of America.

500 Spear, F. S. (2010). Monazite–allanite phase relations in metapelites. *Chemical Geology*, *279*(1–2), 55–62.

501   https://doi.org/10.1016/j.chemgeo.2010.10.004

502 Spear, F. S., & Pyle, J. M. (2010). Theoretical modeling of monazite growth in a low-Ca metapelite. *Chemical*

503   *Geology*, *273*(1–2), 111–119. https://doi.org/10.1016/j.chemgeo.2010.02.016

504 Stepanov, A. S., Hermann, J., Rubatto, D., & Rapp, R. P. (2012). Experimental study of monazite/melt partitioning

505   with implications for the REE, Th and U geochemistry of crustal rocks. *Chemical Geology*, *300–301*, 200–

506   220. https://doi.org/10.1016/j.chemgeo.2012.01.007

507 Sun, C., Graff, M., & Liang, Y. (2017). Trace element partitioning between plagioclase and silicate melt: The

508   importance of temperature and plagioclase composition, with implications for terrestrial and lunar magmatism.

509   *Geochimica et Cosmochimica Acta*, *206*, 273–295. https://doi.org/10.1016/j.gca.2017.03.003

510 Taylor, R. J. M., Harley, S. L., Hinton, R. W., Elphick, S., Clark, C., & Kelly, N. M. (2015). Experimental

511   determination of REE partition coefficients between zircon, garnet and melt: A key to understanding high-T

512   crustal processes. *Journal of Metamorphic Geology*, *33*(3), 231–248. https://doi.org/10.1111/jmg.12118

513 Thomas, J. B., Watson, E. B., Spear, F. S., & Wark, D. A. (2015). TitaniQ recrystallized: experimental confirmation

514   of the original Ti-in-quartz calibrations. *Contributions to Mineralogy and Petrology*.

515   https://doi.org/10.1007/s00410-015-1120-0

516 Tomkins, H. S., Powell, R., & Ellis, D. J. (2007). The pressure dependence of the zirconium-in-rutile thermometer.

517   *Journal of Metamorphic Geology*, *25*(6), 703–713. https://doi.org/10.1111/j.1525-1314.2007.00724.x

518 Wark, D. A., & Watson, E. B. (2006). TitaniQ: A titanium-in-quartz geothermometer. *Contributions to Mineralogy*

519   *and Petrology*, *152*(6), 743–754. https://doi.org/10.1007/s00410-006-0132-1

520 Warren, C. J., Greenwood, L. V., Argles, T. W., Roberts, N. M. W., Parrish, R. R., & Harris, N. B. W. (2019).

521   Garnet-monazite rare earth element relationships in sub-solidus Metapelites: A case study from Bhutan.

522   *Geological Society Special Publication*, *478*(1), 145–166. https://doi.org/10.1144/SP478.1

523 Watson, E. B., & Green, T. H. (1981). Apatite/liquid partition coefficients for the rare earth elements and strontium.

524   *Earth and Planetary Science Letters*, *56*(C), 405–421. https://doi.org/10.1016/0012-821X(81)90144-8

525 White, R. W., Powell, R., & Clarke, G. L. (2002). The interpretation of reaction textures in Fe-rich metapelitic

526   granulites of the Musgrave Block, Central Australia: Constraints from mineral equilibria calculations in the

527   system. Journal of Metamorphic Geology, 20(1), 41–55. https://doi.org/10.1046/j.0263-4929.2001.00349.x

528 Yakymchuk, C. (2017). Behaviour of apatite during partial melting of metapelites and consequences for prograde

529   suprasolidus monazite growth. *Lithos*, *274–275*, 412–426. https://doi.org/10.1016/j.lithos.2017.01.009

530 Yakymchuk, C., & Brown, M. (2014). Behaviour of zircon and monazite during crustal melting. *Journal of the*

531   *Geological Society*, *171*(4), 465–479. https://doi.org/10.1144/jgs2013-115

532   Yakymchuk, C., Clark, C., & White, R. W. (2017). Phase Relations, Reactions Sequences and Petrochronology.

533   *Reviews in Mineralogy and Geochemistry*, *83*, 15–53. https://doi.org/10.2138/rmg.2017.83.2

534   Yakymchuk, C., Rehm, A., Liao, Z., & Cottle, J. M. (2019). Petrochronology of oxidized granulites from southern
535   Peru. Journal of Metamorphic Geology, (December 2018), 839–862. https://doi.org/10.1111/jmg.12501

536   Zack, T., & Kooijman, E. (2017). Petrology and Geochronology of Rutile. *Reviews in Mineralogy and*
537   *Geochemistry*, *83*(1), 443 LP – 467. https://doi.org/10.2138/rmg.2017.83.14
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539

540   **Figure 1**. The most applied interpretations of accessory mineral REE profiles. (a) Schematic illustration of two
541   monazite REE profiles and how they might be interpreted in the context of progressive crystallization during which
542   the abundance of major minerals changes. (b) Example dataset from Rubatto et al. (2006) of monazite core and rim
543   compositions from Mount Stafford, Central Australia. Monazite cores were characterized by low Gd/Lu and high
544   Eu/Eu* compared to monazite rims; this relationship was interpreted to record progressive monazite growth or
545   recrystallization during low-pressure prograde metamorphism as the abundance of alkali-feldspar (preferentially
546   incorporates Eu) and then garnet (preferentially incorporates HREE) increased.

547
548   **Figure 2**. Phase equilibria of (a) average pelite and (b) greywacke used for the partitioning models of this study
549   (Yakymchuk et al., 2017).

550
551   **Figure 3**. (A,B) The $\log_{10}fO_2$ of the modeled compositions. (C,D) Differences between $\log_{10}fO_2$ of the modeled
552   compositions and the fayalite–magnetite–quartz buffer (FMQ). The shape of the contours is influenced by reactions
553   among the Fe^{2+}–Fe^{3+} minerals—ilmenite, magnetite, garnet, and biotite—most notably the rutile-in reaction with
554   increasing pressure (involving ilmenite breakdown and garnet growth), the magnetite–spinel-in reactions with
555   decreasing pressure, and the biotite-out reaction with increasing temperature. (E,F) The ratio Eu^{3+}/Eu^{total} used to
556   calculate Eu partitioning, which was calculated from fO_2, T, and melt composition (Burnham et al., 2015).

557
558   **Figure 4**. Calculated equilibrium Eu/Eu* anomalies of accessory minerals and garnet in the MC models: (A,B)
559   zircon, (C,D) monazite, (E,F) apatite, and (G,H) garnet. Accessory mineral and garnet Eu/Eu* are primarily pressure
560   dependent near the solidus, where the accessory minerals are abundant and the relative availability of Eu^{3+} and Eu^{2+}
561   is controlled by fO_2. With increasing temperature, the fraction of each accessory minerals decreases exponentially,
562   particularly monazite, thereby strongly influencing the distribution of REE, resulting in a stronger temperature
563   dependence on Eu/Eu*.

564
565   **Figure 5**. Calculated equilibrium Eu/Eu* of plagioclase and melt in the MC models: (A,B) plagioclase and (C,D)
566   melt. In contrast to accessory-mineral and garnet Eu/Eu* (Figure 4), feldspar and melt Eu/Eu* are strongly
567   temperature dependent.

568
569   **Figure 6**. Values of Eu/Eu* in each phase are controlled by the temperature-dependent solubilities of accessory
570   minerals and the pressure-dependent Eu^{3+}/Eu^{total} (Figure 3e,f). MC model results along the hypothetical P–T path
571   shown in Figure 4c. Weight percent of phases along the path in (A) pelite and (B) greywacke. Percent of the total Eu
572   in the system hosted by each phase in (C) pelite and (D) greywacke. Values of Eu/Eu* in each phase in (E) pelite
573   and (F) greywacke.

574
575   **Figure 7**. For the closed-system, equilibrium MC models, accessory mineral Eu anomalies exhibit strong positive
576   correlations Eu^{3+}/Eu^{total}, which is primarily a function of pressure (Figure 4), and with monazite stability. In contrast,
577   correlations with the wt% feldspar are inconsistent and variable, illustrating that, at equilibrium, wt% feldspar has
578   minimal influence on accessory mineral Eu/Eu*. (A) Apatite Eu/Eu* as functions of wt% feldspar and temperature
579   at constant pressure. (B) Apatite Eu/Eu* as functions of wt% feldspar and pressure at constant temperature. (C)
580   Apatite Eu/Eu* as functions of whole-rock Eu^{3+}/Eu^{total} and temperature at constant pressure. (D) Apatite Eu/Eu* as
581   functions of whole-rock Eu^{3+}/Eu^{total} and pressure at constant temperature. In all panels, apatite Eu/Eu* is shown
582   because apatite is stable at all modeled P–T conditions; monazite and zircon show similar Eu/Eu* patterns for the P–
583   T conditions at which they are stable (Figure 4).

584
585   **Figure 8**. The fractionation of Eu by feldspar growth can decrease Eu/Eu* in accessory minerals and garnet. (A)
586   Weight fractions of plagioclase, alkali-feldspar, and melt in the model metapelite. (B) Weight fractions of
587   plagioclase, alkali-feldspar, and melt in the model greywacke. (C) Effective whole-rock, garnet, and accessory
588   mineral Eu/Eu* for the MC pelite model. The large increase in Eu/Eu* at ~810°C is due to alkali-feldspar resorption
589   during biotite growth. (D) Effective whole-rock, garnet, and accessory mineral Eu/Eu* for the MC greywacke
590   model. Model was ended at 798°C, because the changes in the weight fractions of feldspars are minimal at lower
591   temperature. (E) Effective whole-rock, garnet, and accessory mineral Eu/Eu* for the B94 pelite model. The smaller
592   overall Eu fractionation relative to the MC model is due to lower feldspar K_d^{Eu2+}, particularly for the alkali feldspar.
593   (D) Effective whole-rock, garnet, and accessory mineral Eu/Eu* for the B94 greywacke model.
594

Table 1. Mineral:melt K_d used for Sm, Eu, and Gd partitioning modeling

model		monazite	zircon	garnet	apatite	plagioclase
B94	Sm^{3+}	75289	3.79	0.45	1105	1.45
	Eu^{2+}	—	—	0.01	—	1.25
	Eu^{3+}	84934	5.91	1.49	1535	1.72
	Gd^{3+}	95815	9.21	4.95	2133	2.05
Modified-Composite	Sm^{3+}	$50 \cdot 10^{(4373.9/T-1.0034)}$	$10^{(4765.0/T-3.3096)}$	$10^{(5424.0/T-4.1211)}$	$10^{(4037.9/T-1.7169)}$	$0.1 \cdot K_d^{Eu2+}$
	Eu^{2+}	$10^{(4317.3/T-3.8397)}$	$10^{(4838.2/T-5.4992)}$	$10^{(4266.1/T-5.0498)}$	$10^{(-738.33/T+0.9258)}$	Sun et al. (2017)
	Eu^{3+}	$50 \cdot 10^{(4317.3/T-1.0125)}$	$10^{(4838.2/T-3.1581)}$	$10^{(4266.1/T-2.8259)}$	$10^{(4359.3/T-1.9877)}$	$0.1 \cdot K_d^{Eu2+}$
	Gd^{3+}	$50 \cdot 10^{(4254.2/T-1.0158)}$	$10^{(5147.7/T-3.2562)}$	$10^{(3470.9/T-1.8673)}$	$10^{(4670.0/T-2.2498)}$	$0.1 \cdot K_d^{Eu2+}$

605
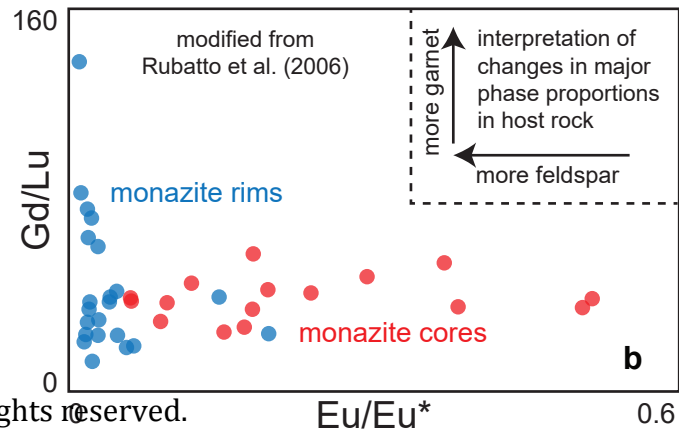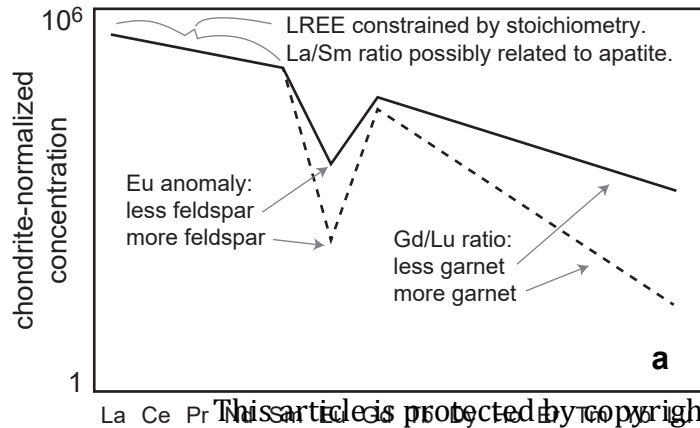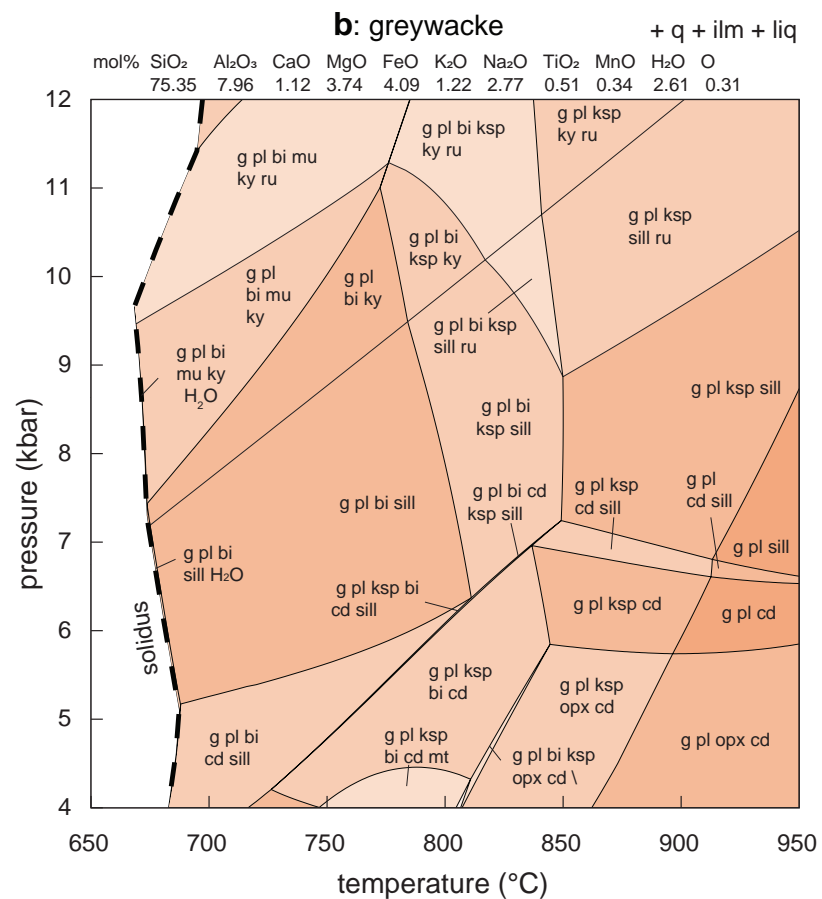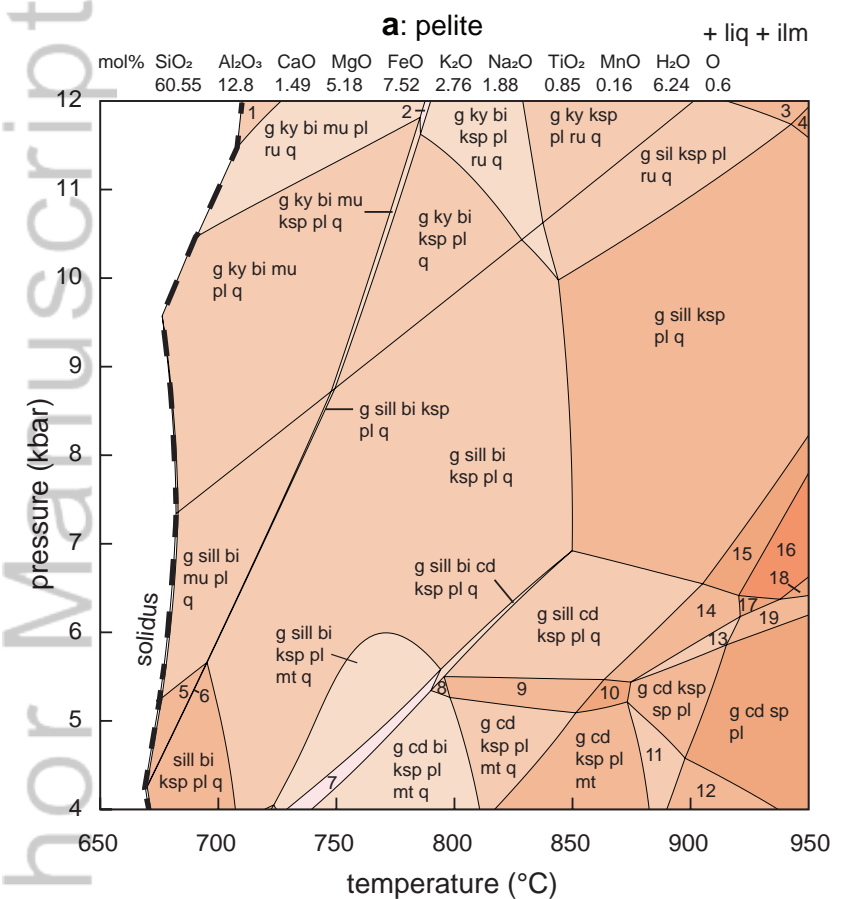
a) LREE constrained by stoichiometry. La/Sm ratio possibly related to apatite. Eu anomaly: less feldspar / more feldspar. Gd/Lu ratio: less garnet / more garnet. chondrite-normalized concentration. La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb

b) modified from Rubatto et al. (2006). more garnet / more feldspar. interpretation of changes in major phase proportions in host rock. Gd/Lu. monazite rims. monazite cores. Eu/Eu*

a: pelite   + liq + ilm

mol%	SiO₂	Al₂O₃	CaO	MgO	FeO	K₂O	Na₂O	TiO₂	MnO	H₂O	O
	60.55	12.8	1.49	5.18	7.52	2.76	1.88	0.85	0.16	6.24	0.6

b: greywacke   + q + ilm + liq

mol%	SiO₂	Al₂O₃	CaO	MgO	FeO	K₂O	Na₂O	TiO₂	MnO	H₂O	O
	75.35	7.96	1.12	3.74	4.09	1.22	2.77	0.51	0.34	2.61	0.31

1: g bi mu pl ru q   5: sill bi mu pl q   9: g cd ksp pl q   13: g sill cd ksp sp pl   17: g sill cd pl
2: g ky bi mu ksp pl ru q   6: sill ksp bi mu pl q   10: g cd ksp pl   14: g sill cd ksp pl   18: g sill sp pl
3: g sill ksp ru q   7: g sill cd bi ksp pl mt q   11: g cd ksp sp pl mt   15: g sill ksp pl   19: g sill cd sp pl
4: g sill ksp q   This article is protected by copyright. All rights reserved.

a: log₁₀ (*f*O₂ rock), pelite
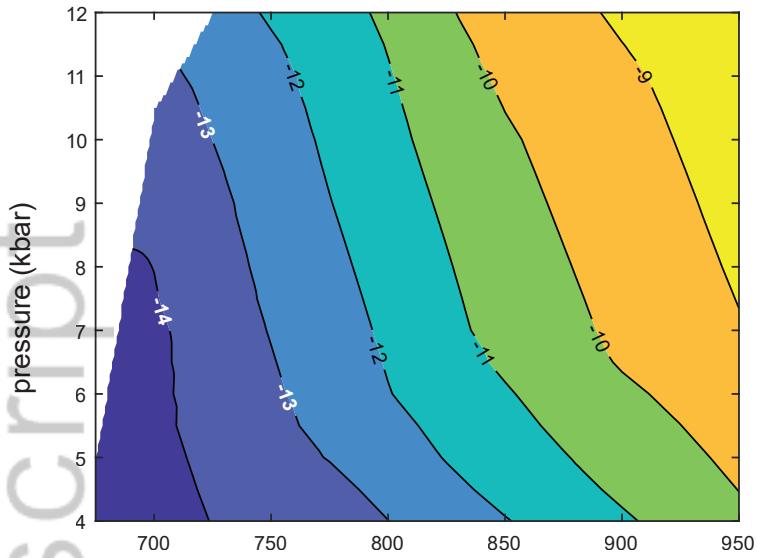
b: log₁₀ (*f*O₂ rock), greywacke
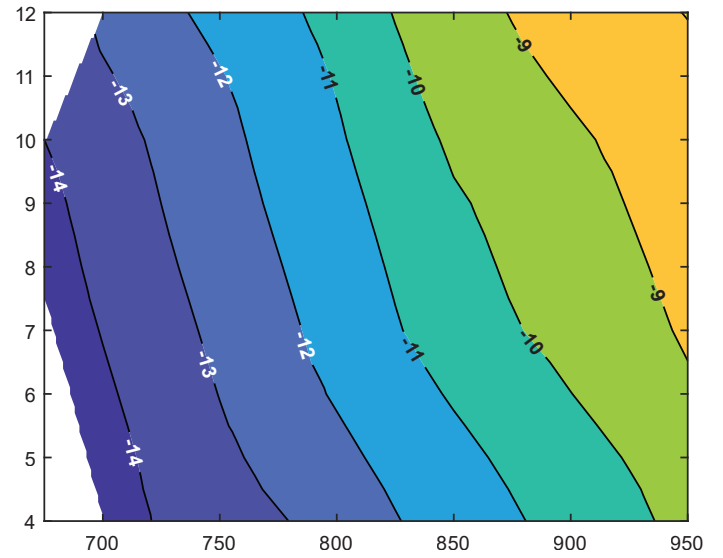
c: log₁₀ (*f*O₂ rock) − log₁₀ (*f*O₂ FMQ), pelite
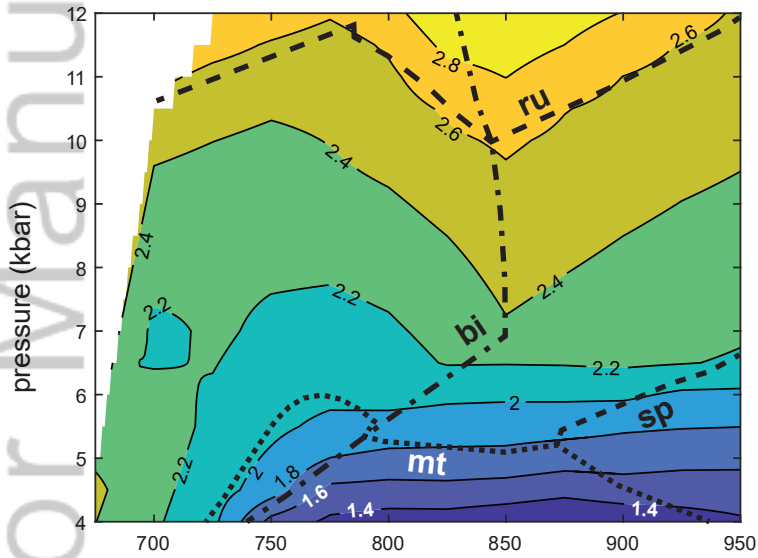
d: log₁₀ (*f*O₂ rock) − log₁₀ (*f*O₂ FMQ), greywacke
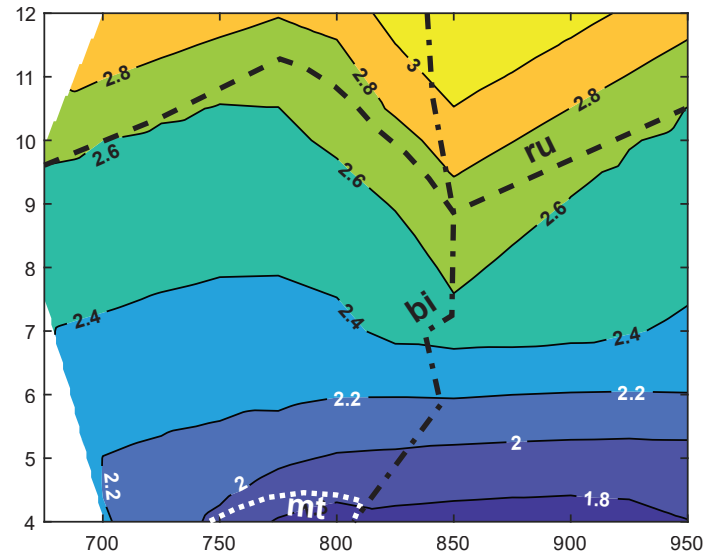
e: Eu³⁺/Euᵗᵒᵗᵃˡ, pelite
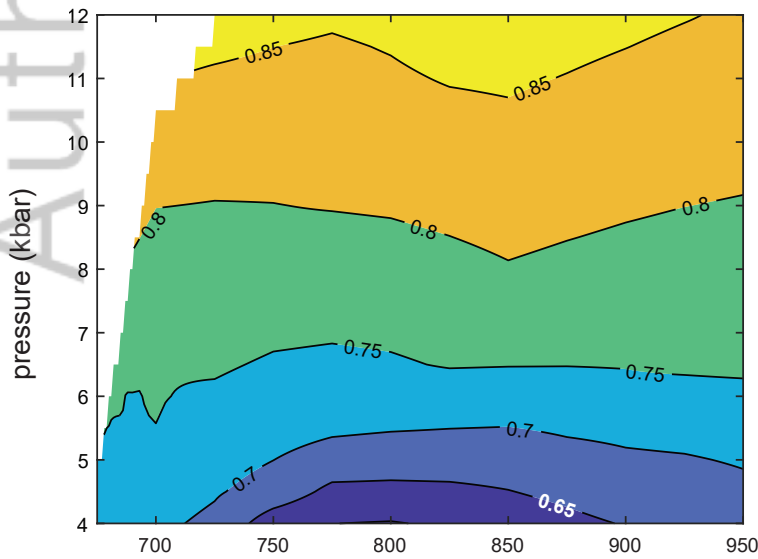
f: Eu³⁺/Euᵗᵒᵗᵃˡ, greywacke

a: zircon, pelite

b: zircon, greywacke

c: monazite, pelite

d: monazite, greywacke

e: apatite, pelite

f: apatite, greywacke

g: garnet, pelite

h: garnet, greywacke

temperature (°C)

temperature (°C)

pressure (kbar)
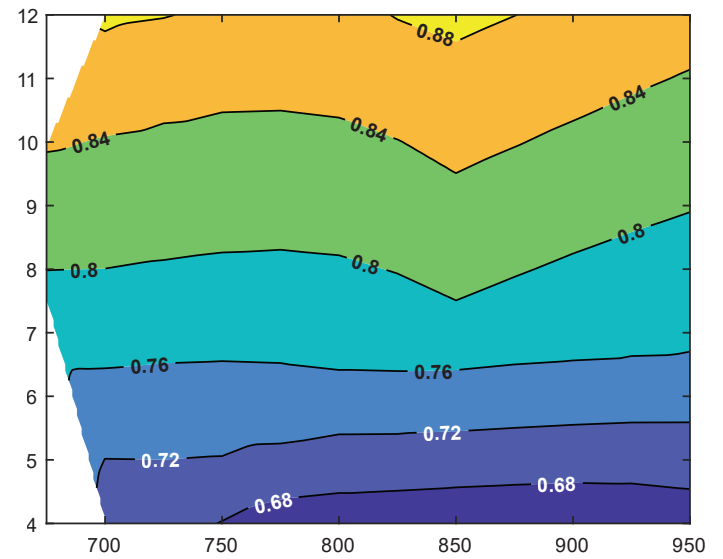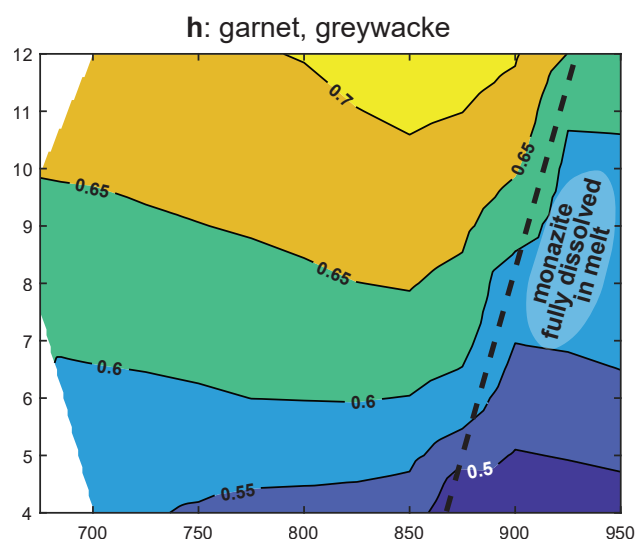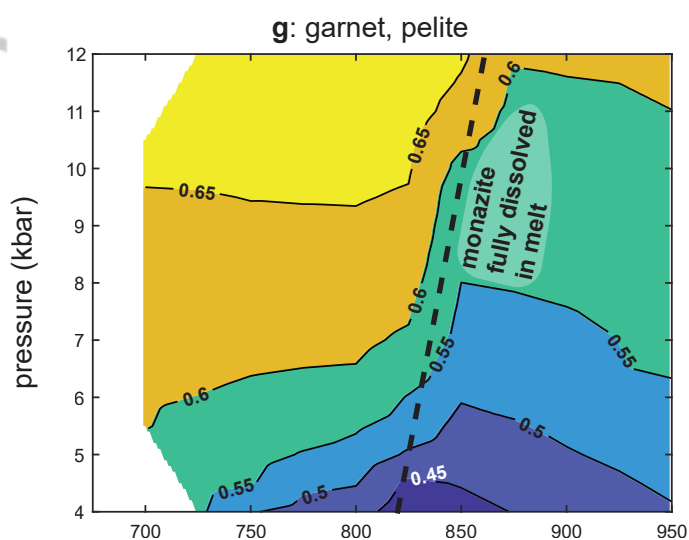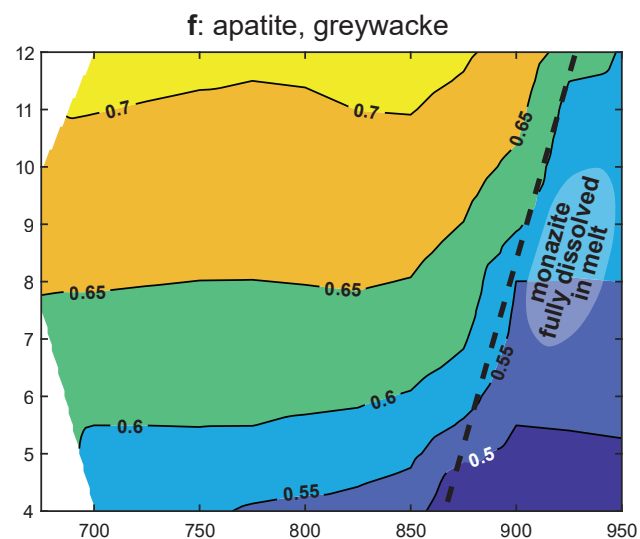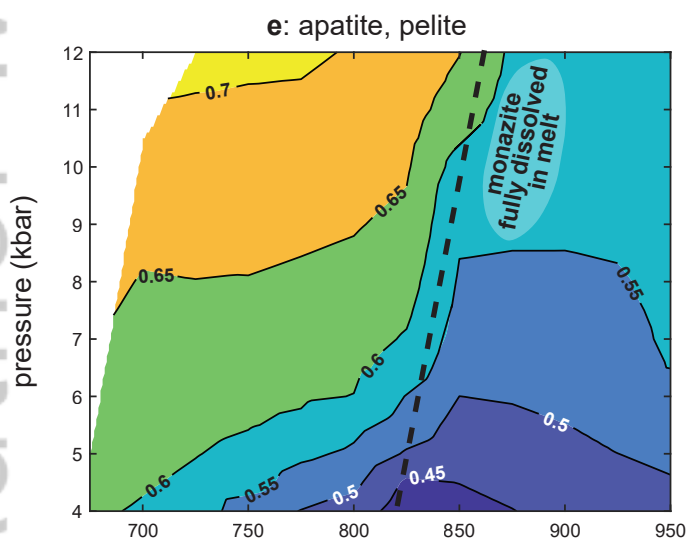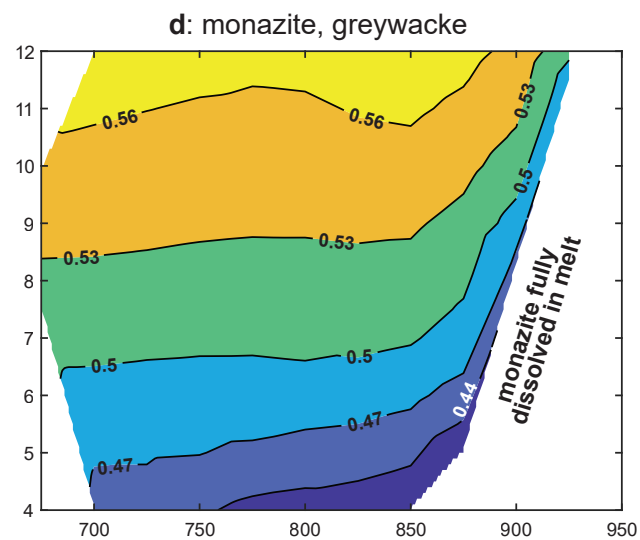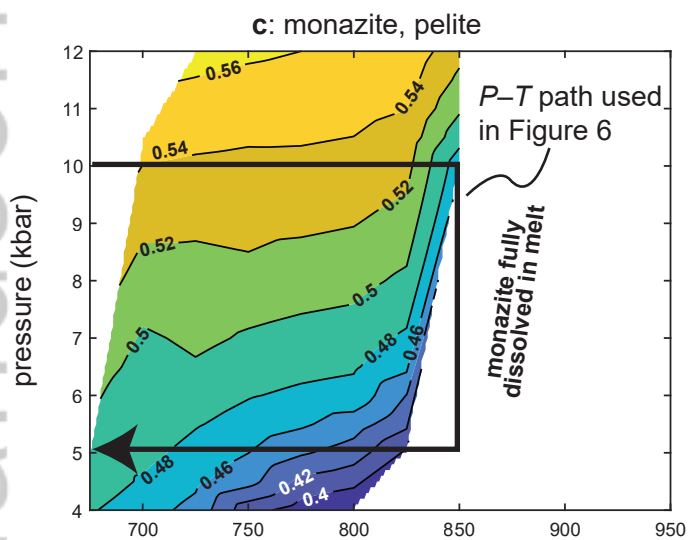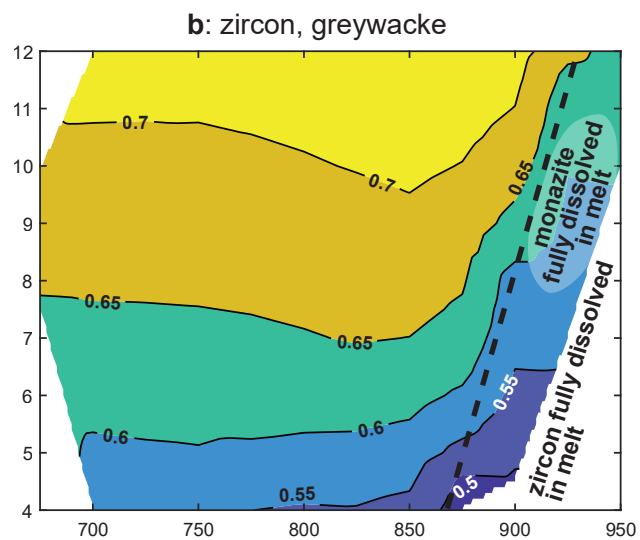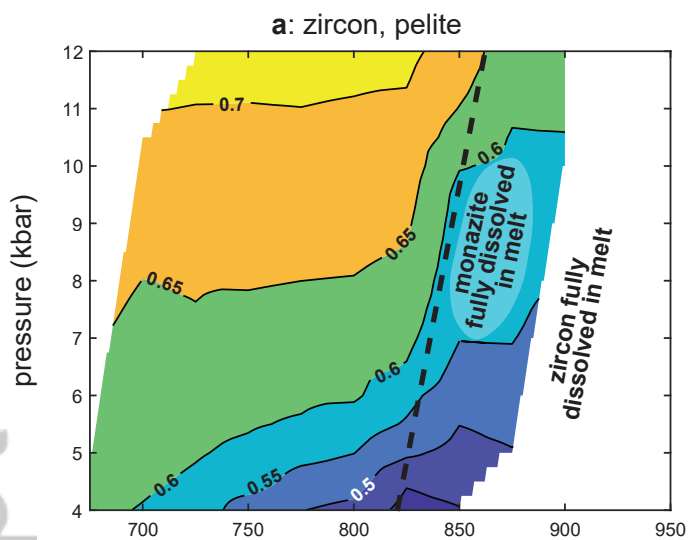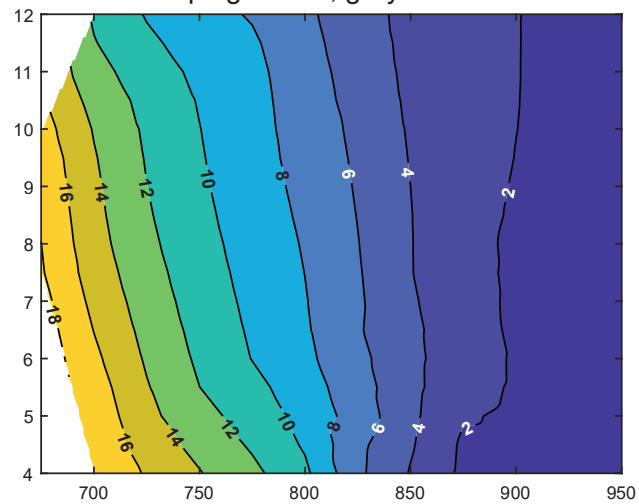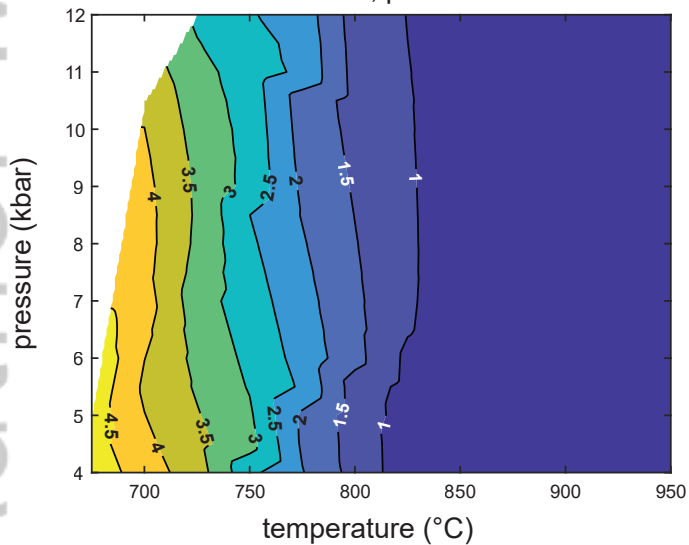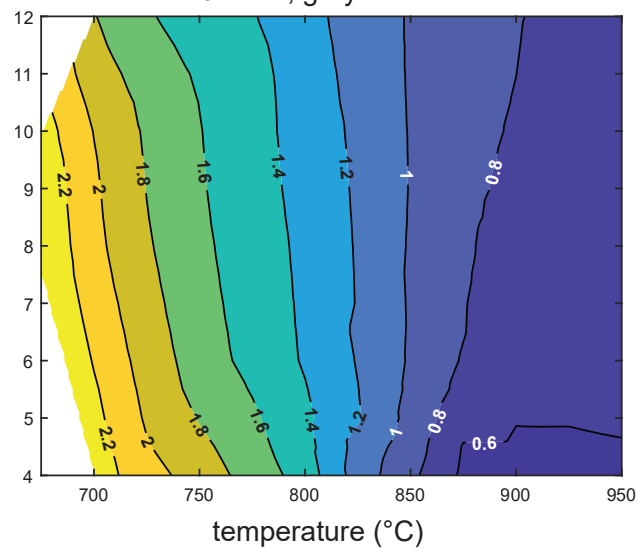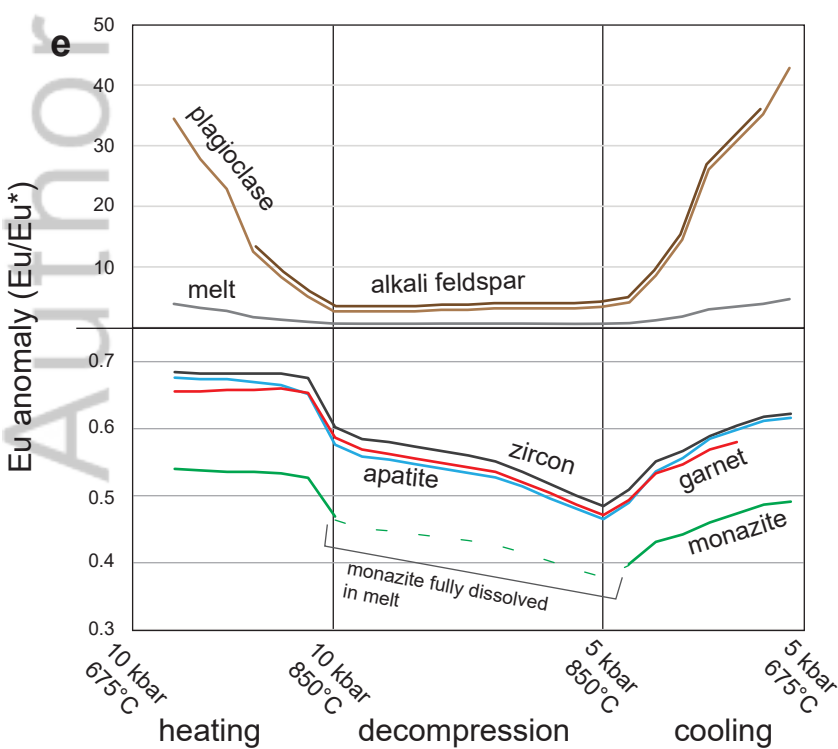
a: plagioclase, pelite
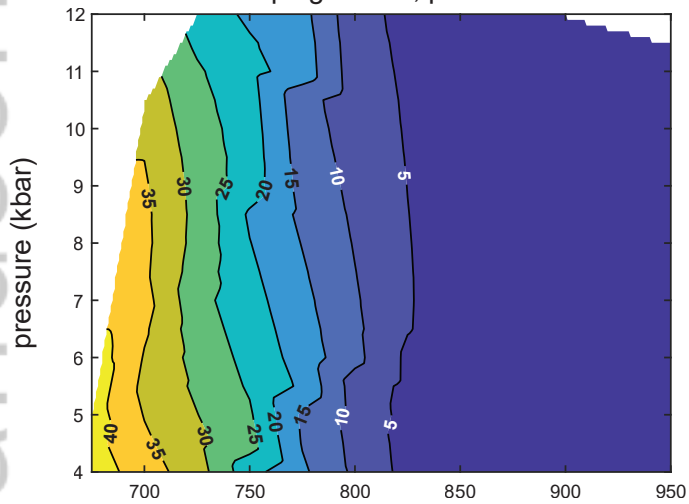
b: plagioclase, greywacke

c: melt, pelite

d: melt, greywacke

temperature (°C)

pressure (kbar)

pelite

greywacke

a

weight percent of each phase

melt
garnet
alk.-feldspar
plagioclase

zircon, monazite

monazite
apatite
zircon
apatite

b

plagioclase
melt
garnet
alkali-feldspar

apatite
monazite
zircon
apatite

c

percent of total Eu in each phase

monazite
garnet
apatite
alkali feldspar
plagioclase
melt

d

monazite
apatite
melt
garnet
plagioclase
alkali feldspar

e

Eu anomaly (Eu/Eu*)

plagioclase
melt
alkali feldspar

apatite
zircon
garnet
monazite

monazite fully dissolved in melt

f

plagioclase
melt
alkali feldspar

apatite
zircon
garnet
monazite

10 kbar 675°C   10 kbar 850°C   5 kbar 850°C   5 kbar 675°C

heating   decompression   cooling

10 kbar 675°C   10 kbar 850°C   5 kbar 850°C   5 kbar 675°C

heating   decompression   cooling

a: isobaric, closed-system, equilibrium

mnz stable at low T →

Eu/Eu* decreases 0.1–0.2 as monazite breaks down

12 kbar

8 10 6 4

← mnz unstable at high T

Eu/Eu* changes little with T or wt% feldspar

arrows: increasing T

700°C

950°C

apatite Eu/Eu*

wt% feldspar (pl+kfs)

b: isothermal, closed-system, equilibrium

725 750 775 800 825
700°C 950 925 900 875 850

arrows: increasing P

12 kbar 12 kbar
4 kbar

Eu/Eu* increases with P, correlation with wt% feldspar changes with T

apatite Eu/Eu*

wt% feldspar (pl+kfs)

c: isobaric, closed-system, equilibrium

12 kbar
8 9 10 11

monazite stable

4 5 6 7

monazite unstable

Eu/Eu* decreases as T increases due to monazite breakdown

arrows: increasing T

700°C

950°C

apatite Eu/Eu*

whole-rock Eu^{3+}/Eu^{total}

d: isothermal, closed-system, equilibrium

700°C 750 800
850 900 950

monazite stable

monazite unstable

Eu/Eu* increases with whole-rock Eu^{3+}/Eu^{total} and P

arrows: increasing P

12 kbar

4 kbar

apatite Eu/Eu*

whole-rock Eu^{3+}/Eu^{total}

pelite

greywacke

a — weight fraction

melt

biotite in

plagioclase + alkali feldspar

alkali feldspar

plagioclase

b — weight fraction

biotite in

plagioclase + alkali feldspar

plagioclase

melt

alkali feldspar

c — Eu anomaly (Eu/Eu*) MC model

biotite in

garnet

apatite

zircon

monazite

effective whole rock

d — Eu anomaly (Eu/Eu*) MC model

biotite in

insignificant change in weight fractions of alkali-feldspar or plagioclase at T<798°C

garnet
zircon

apatite

monazite

effective whole rock

e — Eu anomaly (Eu/Eu*) B94 model

biotite in

garnet

effective whole rock

monazite, apatite, zircon

f — Eu anomaly (Eu/Eu*) B94 model

biotite in

garnet

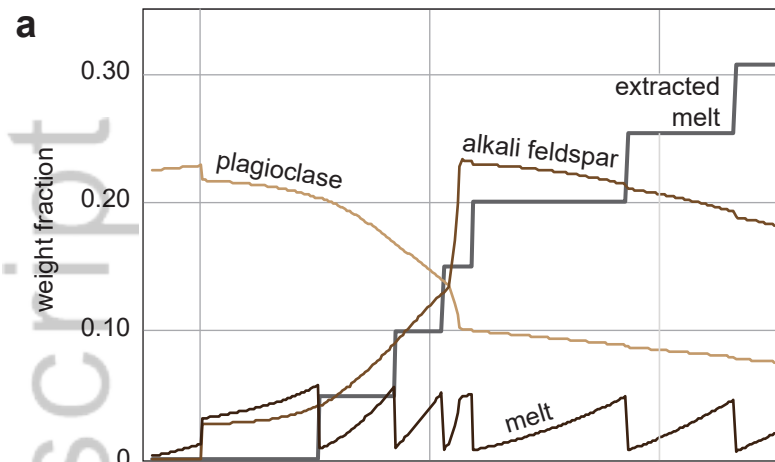effective whole rock

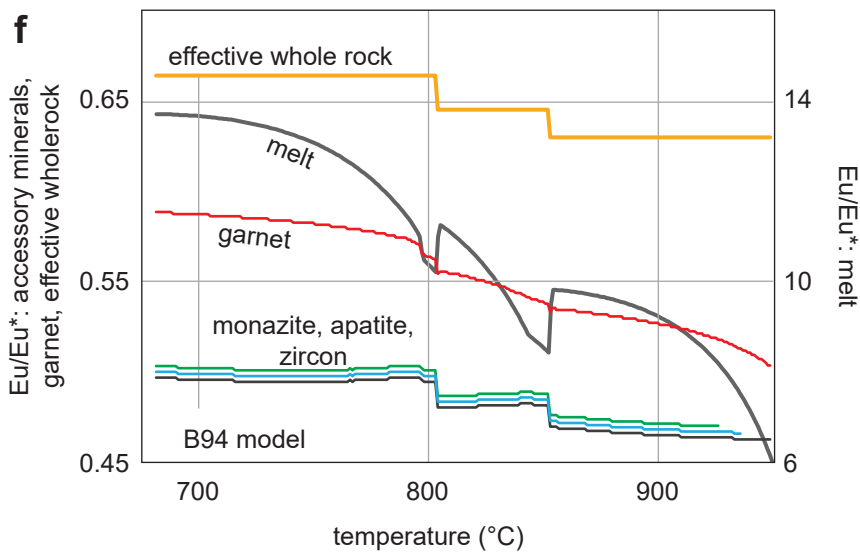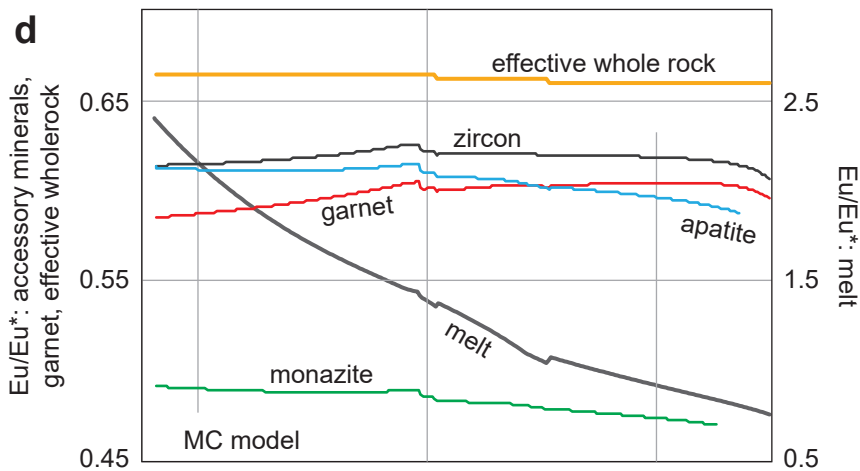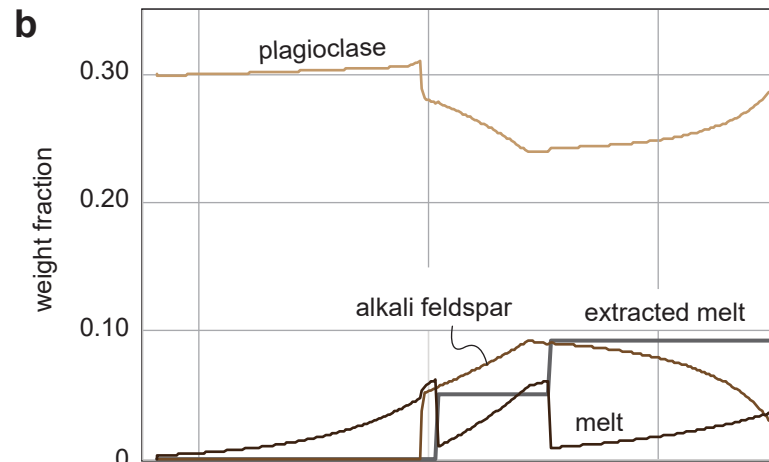monazite, apatite, zircon

temperature (°C)

temperature (°C)

← feldspar fractionation of REE during isobaric cooling

← feldspar fractionation of REE during isobaric cooling

pelite | greywacke

a plagioclase, extracted melt, alkali feldspar, melt

b plagioclase, alkali feldspar, extracted melt, melt

c MC model — effective whole rock, zircon, garnet, apatite, melt, monazite

d MC model — effective whole rock, zircon, garnet, apatite, melt, monazite

e B94 model — melt, garnet, effective whole rock, monazite, apatite, zircon

f B94 model — effective whole rock, melt, garnet, monazite, apatite, zircon

temperature (°C)

batch melt extraction during isobaric heating →   batch melt extraction during isobaric heating →