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Do concentrations of Mn, Eu and Ce in apatite reliably record oxygen fugacity in magmas?

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7   Abstract

8   Apatite is a common accessory mineral in igneous rocks, and its ability to readily accommodate a

9   wide range of trace elements meaning it may provide a useful record of magmatic composition

10   and magmatic processes. Relative abundances of redox sensitive elements in apatite could

11   provide a much-needed probe of magmatic oxygen fugacity. Here, examination of a large data

12   set of apatite and whole rock compositions is used to assess the recently proposed, and increasingly

13   used, Mn-in-apatite oxybarometer. Correlation of apatite-whole rock Mn partition coefficients with

14   whole rock SiO_2 and calculated melt polymerisation and aluminosity, support a model where apatite

15   Mn content is largely dependent on melt structure. In more evolved systems, a decrease in

16   availability of non-bridging oxygens in silicate melts drives Mn from being incompatible to an

17   increasingly compatible element in apatite. Magmatic fO_2 calculated from Ce concentrations in

18   zircon also shows no discernible correlation with apatite Mn content. Mn content of apatite clearly

19   does not record magmatic fO_2, although it may be useful in indicating the extent of melt evolution.

20   In contrast, concentrations of other trace elements in apatite have a much weaker, or no discernible

21   dependence on melt structure and composition, supporting the assertion that apatite records key

22   aspects of magmatic composition.

23   Eu and Ce anomalies in chondrite-normalised Rare Earth Element (REE) data provide an alternative

24   means of using apatite to probe magmatic fO_2. A new method for more reliably comparing the

extent of Eu and Ce anomalies in apatite are used to assess controls on Eu and Ce content

Apatite Eu content shows a strong dependence on whole rock composition, indicating that Eu

anomalies often reflect feldspar crystallisation. Ce anomalies in apatite are much smaller and vary

from weakly positive to weakly negative. Predicted strong negative Ce anomalies in apatite data are

not observed, implying smaller differences in Ce^{3+} and Ce^{4+} compatibility in apatite than in minerals

such as zircon. The cause of small positive Ce anomalies in apatite data is unclear. Comparison of

apatite and zircon data suggests that fO_2 may have some control on apatite Ce content. However,

the narrow range of Ce anomalies in apatite data, and lack of identifiable control of fO_2, limit the

extent to which apatite Ce records magmatic fO_2. As such, REE contents of apatite cannot

currently be used to reliable indicate trends in magmatic fO_2

1. Introduction

Apatite is a widespread accessory mineral found in a range of igneous rocks, metamorphic rocks and

sediments. Although nominally $Ca_5(PO_4)_3(F,OH,Cl)$, apatites typically contain high concentrations of

an extensive range of trace elements, including U, Th, Sr and Rare Earth Elements (REE) (Belousova

et al., 2002; Pan and Fleet, 2002). As such, crystallisation of apatite is important in magmatic

evolution (Belousova et al., 2002) and the complex chemical fingerprint of detrital apatites may act as

a useful provenance indicator in sediments and sedimentary rocks (e.g. Bruand et al., 2017; Morton

). Following Belousova et al. (2002) and earlier studies

including Cao et al. (2012), Chen et al. (2016), Ding et al. (2015) and Xu et al. (2015) there has been

a considerable recent interest in using apatite chemistry to investigate magmatic and hydrothermal

mineralisation processes in a wide range of economic deposits

In magmatic systems, apatite is an early crystallising mineral and reaches saturation during evolution

of a variety of silicate melts (Hoskin et al., 2000). The composition of apatite is controlled by

elemental mineral-melt partitioning, which in turn varies depending on a number of factors,

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including the trace element content of the magma and its evolution during differentiation, the bulk

composition of the magma, which in turn controls melt structure, magma volatile content, apatite

major element chemistry, and external factors including pressure and temperature. For multi-valent

elements, partitioning between apatite and melt also depends on oxygen fugacity (fO_2), and apatite

trace element chemistry could provide much-needed insight into magmatic fO_2. Belousova et al.

(2002) noted that Mn content of apatite was highly variable, in part due to the effect of fO_2. They

argued that apatite likely incorporates Mn^{2+} in preference to either Mn^{3+} or Mn^{4+} because, on the

basis of size and charge, it more readily substitutes for Ca^{2+}. As such, in more reduced magmas, an

increase in the relative proportion of Mn^{2+} should favour greater Mn incorporation in apatite

compared to apatite in more oxidised magmas. However, Belousova et al. (2002) suggested that a

general increase in Mn content during fractionation could obscure any correlation between apatite

Mn and magmatic fO_2. Following observations from the zoned Criffel pluton, southern Scotland

(Miles et al., 2013), Miles et al. (2014) proposed that Mn content of apatite can be used to

determine fO_2 in silica-rich magmas from which apatite crystallised, independent of bulk rock (i.e.

host magma) composition, and largely independent of other factors. Miles et al. (2014) used apatite

data from Criffel and from other studies whose fO_2 was constrained to propose a simple correlation

for apatite Mn content and magmatic fO_2. Although Marks et al. (2016) highlighted the additional

controls that temperature, melt bulk composition, and existing crystallising phases should have on

apatite chemistry, the evidence they presented limits the applicability of Mn in apatite as an

oxybarometer to intermediate to more silicic rocks. In contrast, an experimental study by Stokes et

al. (2019) found no evidence for a control of fO_2 on apatite-melt Mn partitioning in various systems

over a wide range of geologically relevant conditions. Stokes et al. (2019) instead demonstrated that

melt structure has a dominant control on Mn partitioning, and argued that all proposed variations in

Mn content of natural apatite, including those across the zoned Criffel pluton, could be ascribed to

variations in the degree of melt polymerisation inferred from changes in whole rock composition.

They further demonstrated, based on X-ray absorption data, that variations in Mn valence

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76 analogue silicate systems were minimal over a range of terrestrially relevant fO_2 conditions, and that

77 Mn^{2+} dominated as a species in both apatite and coexisting silicate melt, this eliminates

78 any driving force for a correlation between fO_2 and apatite Mn content in terrestrial systems.

79 Despite this, an increasing number of studies have used the Miles et al. (2014) to

80 constrain magmatic fO_2 in apatite-bearing rocks, sometimes in combination, and in apparent

81 agreement, with other measures of fO_2 (e.g. Sun et al., 2020; Xie et al., Xie et al., 2018b: Xie et

82 al., 2019).

83 The ability of apatite to incorporate a wide range of trace elements through various substitution

84 mechanisms (e.g. Pan and Fleet, 2002) means that other multi-valent elements might be useful in

85 determining fO_2 in magmas from which apatite crystallised. Of note here are Eu and the REE.

86 REEs are readily incorporated into apatite and typically present as 3+ cations. However, Eu can be

87 present as either Eu^{2+} or Eu^{3+} in silicate magmas, and Ce as either Ce^{3+} or Ce^{4+} (e.g. Burnham et al.,

88 2015; Burnham and Berry, 2014). The likely preferred substitution of both Eu^{3+} and Ce^{3+} into apatite

89 . in Eu and Ce contents higher or lower than expected concentrations

90 relative to other REEs of fixed 3+ valency, may also be proxies for magmatic fO_2 (Belousova et al.,

91 2002; Pan and Fleet, 2002; Sha and Chappell, 1999). Numerous studies have shown that reducing

92 conditions result in negative Eu anomalies in apatite (Belousova et al., 2002; Cao et al., 2012; Chu et

93 al., 2009; Ding et al., 2015; Duan et al., 2019; Pan and Fleet, 2002; Sha and Chappell, 1999; J. Xie et

94 al., 2018; Zafar et al., 2019). However, any direct oxybarometer based on Eu in apatite is

95 complicated by crystallisation of feldspar, which favours Eu^{2+} and strongly depletes both magma and

96 apatite in Eu (Abdullin et al., 2016; Belousova et al., 2002; Drake and Weill, 1975; Sha and Chappell,

97 1999). In contrast, Ce anomalies in apatite are assumed to be relatively independent of the effects of

98 crystallisation of other phases, with the exception of accessory REE-rich phases. Although

99 apatites variably show positive Ce anomalies, inferred to represent varying degrees of magmatic

100 oxidation, the extent of these are small (Belousova et al., 2002; Chu et al., 2009; Ding et al., 2015;

101 Duan et al., 2019). In notable contrast to zircon, which can exhibit significant positive Ce anomalies in

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102 REE data (Trail et al., 2012), there has been no robust experimental assessment of the extent to

103 which REE anomalies in apatite can be used to probe magmatic fO_2. Despite this, several studies

104 have used apatite REE trends, and the extent of Eu and Ce anomalies, to provide qualitative

105 assessments of magma oxidation.

106 There is a lack of strong evidence for a Mn in apatite oxybarometer, either from experimental

107 studies on element partitioning, detailed crystal chemical investigations of apatite, or wider reviews

108 of natural apatite data. Despite this, the preliminary Mn in apatite oxybarometer of Miles et al.

109 (2014) is becoming widely adopted as a method of assessing magmatic fO_2 in apatite-bearing rocks.

110 This perhaps highlights the pressing need for a range of geochemical tools to assess changes in

111 magmatic fO_2, and the general importance of apatite in magmatic, especially porphyry, systems.

112 Here, apatite geochemical analyses and whole rock data from an extensive, wide range of

113 geochemical investigations are collated, in addition to data from published test studies and wider

114 geochemical studies of apatite chemistry, to assess the validity of the Miles et al. (2014)

115 oxybarometer. This dataset is then used to assess other proposed controls on apatite chemistry,

116 with emphasis on cation substitution, including the use of Eu and Ce anomalies to assess the broad

117 extent of changes in magmatic fO_2

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119 2. Methodology.

120 Apatite composition data from 26 studies was analysed including, where possibly, whole rock data

121 (Table 1 for details). As apatite is typically an early crystallising accessory phase, whole rock data can

122 be used to assess composition of magmas from which apatite crystallised. In addition, data from the

123 study of Transhimalayan apatites by Chu et al. (2009), the extensive study of apatites from a broad

124 range of rock types by Belousova et al. (2002), and the recent metastudy by   (2019)

125 were used. For the latter study, which identifies geochemical fingerprints of apatite provenance

126   \ o et al., 2020), only data from igneous and selected metamorphic apatites were used.

127   Major and trace element data in the studies were obtained principally using electron microprobe

128   analysis and laser ablation mass spectrometry. To allow ready comparison, all data were converted

129   to element proportions (by weight). Where Mn concentrations were obtained using both methods,

130   laser ablation data were preferred. For all studies, only REE data obtained from laser ablation were

131   used. In addition to studies of natural samples, apatite Mn composition, and Mn mineral/melt

132   partitioning from available experimental studies was also used (Table 1).

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134   3. Controls on the Mn content of apatite

135   The oxybarometer of Miles et al. (2013) assumes that magmatic fO_2 is the sole control on the Mn

136   content of apatite, at least in more silicic systems. This can be explained in terms of ionic radius.

137   Mn^{2+} has a very similar ionic radius to Ca^{2+} for which it likely substitutes in apatite. In contrast, Mn^{3+}

138   is substantially smaller, implying that Mn^{3+} substitution in apatite is minimal. In contrast, both Mn^{2+}

139   and Mn^{3+} can be readily incorporated in silicate melt. A change in fO_2, and proportion of Mn^{2+}/Mn^{3+},

140   is predicted, therefore, to result in large changes in apatite-melt partitioning. However, experimental

141   data (Stokes et al. 2019) and some observations from studies of natural apatite (Belousova et al.,

142   #   U   demonstrate that apatite Mn   \   o

143   content is also dependent on melt composition, especially SiO_2 content. Stokes (2018) and Stokes et

144   al. (2019) argued that with increasing SiO_2 content, the structure of silicate melts progressively

145   changes, melt polymerisation increases, and the availability of non-bridging oxygens is markedly

146   reduced. A commonly used measure of melt polymerisation is the ratio NBO/T, or non-bridging

147   oxygens/tetrahedral sites, where NBO/T=0 represents a fully polymerised melt, all O sites

148   shared between neighbouring T sites, and NBO/T=4, a fully depolymerised melt where O sites are

149   bound to only one T site. This ratio can be calculated based on measured element proportions

150   (Mysen et al., 1984, 1982). Stokes (2018) and Stokes et al. (2019) argued that as Mn is not a network

151   former in silicate melts, a reduction in NBOs results in a marked reduction in Mn solubility.

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152 ny valence. This effect dominates Mn partitioning. Stokes et al.

153 (2019) derived an empirical double-logarithmic relationship between NBO/T and Mn apatite-melt

154 partition coefficient based on their experimental results and limited data from natural

155 apatite. Using this relationship, Stokes et al. (2019) were able to explain variations in apatite Mn

156 content across the zoned Criffell pluton used by Miles et al. (2014) to derive their oxybarometer.

157 The validity of the assertion that melt structure controls apatite Mn content can be tested using the

158 wider dataset. Figure 1 shows the apatite-whole rock partition coefficient for Mn,

159 , for all samples where whole rock data is available as a proxy for melt

160 composition, and from available experimental studies. The black line on Figure 1 is the

161 calibration of Stokes et al. (2019). As expected, there is considerable scatter in the dataset. Use of

162 whole rock data is a limiting factor here. Apatite crystallisation in most systems is slow and

163 implying that melt composition evolves during apatite crystallisation. Apatite crystallisation also

164 occurs at different points in magmatic evolution in different systems. These, and related factors,

165 mean that NBO/T can only be used to very crudely constrain the extent to which melt structure

166 governs Mn partitioning. Whole rock data in itself is also an approximation of melt composition.

167 Despite this, clearly increases by at least an order of magnitude as NBO/T

168 approaches zero. This implies an increase in apatite Mn content with progressive magmatic

169 differentiation, or with increasing melt SiO_2. Experimental data of Stokes et al. (2019) and Prowatke et

170 al. (2001) is generally consistent with data from natural samples. In contrast, Mn partition

171 coefficients from Vander Auwera et al. (1998) are at least an order of magnitude lower. Given that

172 these are very low melt fraction experiments with only accessory apatite, this data is not considered

173 further.

174 Experimentally determined partition coefficients are typically from systems with less polymerised

175 melts. from Stokes et al. (2019) are slightly higher than those from natural

176 apatite, although the general trend of increasing with increasing melt

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177 polymerisation in the Stokes et al. (2019) data mirrors the overall dataset. The proposed double

178 logarithmic algorithm of Stokes et al. (2019) overestimate   in highly polymerised

179 systems. In terms of Mn element proportion (by weight), this algorithm is expressed on figure 1

180 as:

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182 ¨ « £   [1]

183

184 The trend of the Stokes et al. (2019) correlation at very low NBO/T is largely constrained by the data

185 of Sha and Chappell (1999). From Figure 1 it is apparent that this dataset also lies towards the upper

186 end of   values for natural samples. A simple exponential relationship based on

187 data of Stokes et al. (2019) of the form:

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189 ¨ « £   —   [2]

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191 (Figure 1c) provides a better fit to the data. Alternatively, and in addition to this, the Stokes et al.

192 (2019) correlation may be systematically offset to higher   /lower NBO/T.

193 There are a number of complicating issues with using whole rock data to determine NBO/T and

194 assess melt polymerisation. One particular issue is Fe valence. The method of Mysen et al. (1984,

195 1982) involves assigning a proportion of Fe^{3+} to T sites. Due to a lack of data on current oxidation

196 state in whole rocks (i.e. Fe^{3+}/Fe), and oxidation state during apatite crystallisation, all Fe in whole

197 rock data is assumed here to be Fe^{3+}. This likely leads to an overestimation in the extent of melt

198 polymerisation as Fe^{2+} is not tetrahedrally coordinated in melt structures. In contrast, Stokes *et al.*

199 (2019) used X-ray absorption data to determine Fe^{3+}/Fe ratios in quenched melts, and more

200 accurately constrain NBO/T. This may partly explain offset between experimental and natural apatite

201 data, as the effect of recalculating NBO/T for the Stokes (2019) data would be to shift the

202 data to higher NBO/T. The role of water as a network modifier is also not considered here, which

203 complicates comparison between data. Varying water contents in natural systems will result in

204 variations in NBO/T not captured in calculations here. Higher concentrations of fluids in later stages

205 of magmatic evolution also mean a disproportionate error in NBO/T calculations in more evolved

206 systems.

207 Stokes et al. (2019) noted a weaker correlation between   and Aluminium

208 Saturation Index, ASI. ASI, the molecular ratio $Al_2O_3/(CaO+Na_2O+K_2O)$, is a measure of magma

209 aluminousity and also related to magmatic evolution. As noted by Sha and Chappell (1999), ASI 0

210 defines the transition from peraluminous (>1) to metaluminous (<1), and a change in behaviour of

211 many major and trace elements in silicate melts. From Figure 2a it is clear that

212   increases with increasing ASI, as previously noted by Sha and Chappell (1999) and Chu

213 et al. (2009). Similarly, Figure 2b demonstrates a clear correlation between   and whole

214 rock SiO_2. Both correlations support a model where melt structure and availability of NBOs has a

215 strong control on Mn partitioning between apatite and melt, especially in more evolved systems.

216 Melt evolution during fractionation results in marked decreases in the proportion of NBOs, and the

217 ability of melts to incorporate Mn. This progressive change drives Mn from being an incompatible

218 element (<1) in less evolved systems to a variably compatible element in evolved

219 systems. As such, increased Mn incorporation in apatite simply reflects less favourably incorporation

220 of the element in more polymerised melts.

221 The correlation of Miles et al. (2014) is based on Mn content of apatite, rather than partitioning

222 between apatite and melt. Figure 3 shows how apatite Mn content varies with ASI, NBO/T, and

223 whole rock SiO_2. As suggested by Sha and Chappell (1999) there is a general transition in apatite Mn

224 content from metaluminous to peraluminous systems. This is mirrored in whole rock and NBO/T

225 data, although trends are less defined than for . This likely indicates the effect of other

226 phases on apatite Mn content. Scatter in data again highlights limitations in using whole rock data,

227 and the influence of other controls, including pressure, temperature, melt volatile content and

228 possibly fO_2, as well as apatite chemistry, and of course, bulk composition. Notably, the correlation

229 of Miles et al. (2014) is based on silicic systems, over which melt composition/structure does

230 have an observable control on apatite Mn content.

231 Apatite is an important host of Mn in magmatic rocks. However, the control of melt structure and

232 composition on Mn partitioning implies that the correlation of Miles (2014) cannot be used to

233 simply estimate magmatic fO_2. Analysis of a broad dataset does, however, support the use apatite

234 chemistry as a sensitive probe to the origin of detrital apatite (e.g.), as an

235 indicator mineral in ore exploration and probe to conditions of ore formation (Belousova et al.,

236 2002) and as an indicator of magmatic conditions (Chu et al., 2009). Magmatic apatite with high

237 Mn contents typically reflects crystallisation from more evolved melts. As such, apatite Mn content

238 could be used to assess the onset and duration of crystallisation in an evolving system, with

239 progressive or punctuated periods of apatite growth recorded in distinct increases in apatite Mn

240 content.

241 Pan and Fleet (2002) noted that X ion composition of apatite, i.e. concentration of Cl, F and H_2O, can

242 affect substitution mechanisms for various cations in apatite. Notably, some elements such as REEs

243 show changes in preferential incorporation onto the two nonequivalent Ca sites in chloroapatite

244 compared to fluorapatite and hydroxyapatite. However, no clear trends in apatite F/Cl content and

245 either apatite Mn content or were identified here. Lack of data on apatite water

246 contents meant that an effect of O content on Mn partitioning could not be assessed

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248 4. Assessing the dependence of apatite Mn content on magmatic fO_2

249 Stokes et al. (2019) failed to observe evidence for a substantial change in Mn valence, and the

250 proportion of Mn^{2+} to Mn^{4+} in silicate melt and apatite over a broad range of fO_2 conditions. This

251 valence change is required to support any dependence of apatite Mn content on magmatic fO_2. In

252 contrast, Stokes et al. (2019) did observe consistent changes in the proportions of Fe^{3+} and Fe^{2+} with

253 fO_2. This is surprising as it suggests minimal changes in Mn valence in natural (terrestrial) systems.

254 Changes in Mn valence in analogue magmatic systems have, however, been observed. Bromiley et

255 al. (2015), for example, determined site proportions of Mn^{2+} and Mn^{3+} in synthetic hercynite, a Fe-

256 Mn bearing spinel, and coexisting silicate melt. They inferred that differences in Mn valence would

257 be sufficient to drive changes in Mn partitioning as a function of magmatic fO_2. However, Stokes et

258 al. (2018) noted that although synthetic and natural spinels contain variable Fe^{2+}, Mn^{3+} and even

259 Mn^{4+}, relationships between Mn valence and other factors were complicated by the influence of site

260 chemistry on Mn incorporation and possibly valence. They further demonstrated that consistent

261 changes in Mn valence with fO_2 were only noted in Fe-rich spinels. It is possible that these changes

262 are driven by coupled changes in Fe valence, combined with the effects of crystal site constraints

263 (Stokes, 2018). This might be the case generally, implying that consistent changes in Mn valence are

264 only expected in certain Fe-rich phases, and provide limited insight into magmatic fO_2.

265 It remains possible that some scatter in Figures 1 and 2 is due to an effect of fO_2 on Mn partitioning.

266 For some studies independent estimates of magmatic fO_2 are provided. In figure 4A, apatite Mn

267 content as a function of $log fO_2$ is shown. The Miles et al. (2014) calibration is shown on this figure,

268 along with data on which it was derived. Also shown is a subset of data from Stokes et al. (2019) for

269 low bulk Mn contents, where fO_2 was experimentally constrained. For other data, fO_2 is determined

270 from Ce anomalies in zircon, following the method of Trail et al. (2012, 2011). Ce^{4+} is considerably

271 more compatible in zircon than Ce^{3+}, and thus the extent of positive Ce anomalies in normalised REE

272 zircon data, i.e. relative enrichment of Ce compared to REE fixed 3+ valence, provides a means of

273 determining magmatic fO_2 at the point of zircon crystallisation (Trail et al. 2011). Apatite is typically

274 an earlier crystallising phase than zircon (Duan et al., 2019), so fO_2 recorded by both phases may not

275   be strictly comparable. Miles et al. (2014) and (Zhong Jie et al., 2019) further observe that errors in

276   calculating Ce anomalies in zircon REE data using conventional methods result in significant

277   uncertainties. Despite this, it is clear from Figure 4A that no meaningful correlation between fO_2 and

278   apatite Mn content can be observed beyond data presented by Miles et al. (2014). This point is

279   further emphasised in Figures 4B and 4C, which consider the extent of Eu anomalies in zircon, and

280   inferred zircon Ce^{4+}/Ce^{3+}, based on zircon and whole rock (i.e. coexisting melt) data. Under reducing

281   conditions, the proportion of Eu^{2+} to Eu^{3+} in magmatic systems increases. Eu^{2+} is highly incompatible

282   in zircon, meaning that reducing conditions result in a marked negative Eu anomaly compared to

283   calculated Eu content based on chondrite-normalised concentrations of 3+ REE concentrations (Trail

284   *et al*, 2012). However, in this instance, relative Eu depletion in zircon can also be inherited from the

285   magma, as Eu^{2+} is readily incorporated into feldspars. Eu anomalies can, therefore, only be used

286   under certain conditions to estimate magmatic fO_2. Despite this, it is clear from Figure 4B that there

287   is no relationship between the extent of zircon Eu anomalies and apatite Mn content, either within

288   the dataset or, importantly, within data from individual studies. Ce^{3+}/Ce^{4+} in Figure 4C is estimated

289   based on zircon and melt composition (Trail et al., 2012, 2011) and is a measure of Ce partitioning

290   driven by valence change, corrected for the effect of melt composition/structure. Figure 4C again

291   shows scatter in Mn apatite data which cannot be ascribed to any effect of magmatic fO_2. As such,

292   although data available here is limited, there is again no evidence to support the oxybarometer of

293   Miles et al. (2013).

294

295   5. Controls on the partitioning of trace elements into apatite.

296   Analysis of data from a large number of studies supports a model where the Mn content of apatite is

297   controlled by the effect of melt structure on Mn partitioning, such that apatite only contains

298   appreciable Mn when it cannot be readily incorporated in highly polymerised, peraluminous silicate

299   melts. Additional variations in Mn partitioning are expected as a function of pressure, temperature

300 and, possibly, factors such as magmatic volatile contents. This model can be tested to a certain extent

301 by considering controls of melt structure/composition on partitioning in other trace elements. A

302 summary of various trends is shown in Figures 5 and 6.

303 The marked shift of Mn from incompatible to compatible in apatite is not noted for other trace

304 elements, partly because of the ease with which apatite does incorporate a range of commonly

305 The REEs, for example, are a group of incompatible elements which

306 provide insight into the effects of ionic radius on mineral-melt partitioning. REEs are incorporated

307 onto the two non-equivalent Ca sites in apatite, the 9-fold coordinated Ca site, and 7-fold

308 coordinated Ca site (see Pan and Fleet, 2002, for a discussion of substitution mechanisms). REE

309 contents in apatite reflect magmatic source (Belousova et al., 2002), although there are some

310 exceptions. REE patterns in apatite can be affected by co-crystallisation of phases such as zircon (Xie

311 et al., 2019) and Nd depletion may be due to preferential incorporation in phases such as monazite

312 (Chu et al., 2009; Sha and Chappell, 1999) and Eu anomalies, driven by fO_2 changes, are

313 considered below. Apatites typically exhibit enrichment in LREE over HREE, resulting in right-inclined

314 REE trends (e.g. Belousova et al., 2002; Cao et al., 2012; Chu et al., 2009). Belousova et al (2002)

315 suggested that Ce/Yb ratios a fingerprint of the magmatic source of apatite, due to consistent

316 trends in the slopes of REE data from ultramafic to mafic/intermediate to highly fractionated granite.

317 Occasionally, apatites exhibit flat trends over the whole-REE region (Cao et al., 2012). Chu et al.(2009)

318 suggested that this relative HREE enrichment in apatite from peraluminous rocks might be due to an

319 absence of other HREE-incorporating phases. This work continues to be extended to develop use of

320 apatite as a powerful magmatic probe (Bruand et al., 2020).

321 Figure 7 shows a selection of chondrite-normalised REE patterns from apatite, chosen to highlight

322 variability across the dataset. Apatite REE data are typically variably right-inclined, with relative

323 enrichment of LREE. Some apatites have flat trends, and some have slight enrichment in HREE.

324 The latter is consistent with experimentally data; mid-REE (MREE), from Sm to Gd, show slightly

325 elevated partition coefficients compared to light- and heavy-REE (HREE) (Prowatke and Klemme,

326 2006; Watson and Green, 1981)

327   are relatively uniform from LREE to HREE as a function of whole rock

328 composition, as demonstrated for La, Sm and Lu in Figure 5C. Consistencies in values for

329   within studies suggests that scatter is due to external effects such as

330 temperature, pressure, presence of volatiles and other aspects of apatite chemistry. There is a

331 general trend in   of MREE>HREE>LREE, consistent with data from experimental

332 studies (Prowatke and Klemme, 2006; Watson and Green, 1981). It is possible, however, that there is

333 a slight decrease in   with increasing melt polymerisation and SiO₂ content

334 Concentrations of REE in apatite follow the general trend La>Sm>Lu (Figure 5D-F). There is no clear

335 change in relative concentrations of LREE, MREE and HREE which would explain a systematic change

336 in slope in chondrite-normalised REE plots with magmatic fractionation. There is, possibly, a slight

337 decrease in overall apatite REE concentrations with magmatic evolution, i.e. in polymerised/silica-

338 rich systems, and absolute concentration of REEs in apatite generally decreases with increasing ASI,

339 in contrast to the observations of Chu al. (2009). This is counterintuitive, as increases in melt

340 polymerisation should increase   . However, the fact that all REE are compatible in

341 apatite lessens the effect of systematic changes in melt composition/structure. It is also likely

342 that apatite content in more evolved systems is partly controlled by REE incorporation in other

343 phases, and depletion in REE in magmas from which apatite crystallises. As such, apatite is a useful

344 magmatic probe, and provides insight into magmatic composition independent of the effects of

345 magmatic evolution, as suggested by Hoskin et al. (2000). This behaviour is in marked contrast to

346 Mn. However, REE are generally compatible in natural apatites in a range of systems, whilst Mn is

347 incompatible except in more evolved systems. Systematic changes in melt structure have, therefore,

348 much less control on REE partitioning.

349 Eu and Ce contents of apatite can differ from those of other REE due to changes in valence. Across

350 the dataset, there is only a slight decrease in apatite Ce and Eu content with increasing whole rock

351 SiO_2 and ASI, mirroring trends in other REEs. Partition coefficients for both are broadly comparable,

352 independent of any change in melt composition/structure (Fig. 6A,B). For some studies, there are

353 differences in   and   of up to several orders of magnitude,

354 consistent with control by an external factor such as fO_2. Both REE are, again, generally compatible

355 in apatite.

356 With increasing fractionation, Y content of apatite increases and Sr content decreases (Figure 6C,D),

357 as previously noted (Belousova et al., 2002; Chu et al., 2009). Importantly, these changes are

358 independent of any control of melt chemistry on either   or   .

359 Both Y and Sr are compatible in apatite. Changes in apatite Y and Sr content, therefore, represent

360 progressive enrichment of the generally incompatible Y, and depletion of Sr, during magmatic

361 fractionation. This is consistent with the suggestion of Belousova et al. (2002) that low Sr in apatites

362 from more evolved rocks is due to plagioclase crystallisation. Once again, trends in Sr and Y imply

363 that apatite provides a useful probe of magmatic composition.

364 Figure 6E,F shows how the concentration of Zr in apatite and   vary with extent of

365 polymerisation. Zr is, like Mn, an incompatible element in apatite in less evolved systems. However,

366 in contrast to Mn, progressive fractionation does not result in an increase in the partitioning of Zr

367 into apatite, and the element remains incompatible in highly evolved, peraluminous, silica-rich

368 melts. This is likely due to the ability of other accessory minerals to incorporate Zr, such as zircon. In

369 fact, examination of all trace elements commonly measured in apatite reveals that the behaviour of

370 Mn as a function of melt composition/structure is distinct. Firstly, Mn is a relatively incompatible

371 element in apatite, as opposed to many other typically incompatible elements. Secondly, a marked

372 change in melt structure in more evolved systems drives partitioning of Mn into apatite, as the

373 element is not readily incorporated in other phases at the point of apatite crystallisation. Some

15

374 phases, such as magnetite, biotite and amphibole, can incorporate appreciable Mn (Miles et al.,

375 2014), although partitioning of Mn into these phases is apparently not sufficient to fully

376 accommodate a reduction in the ability of evolved melts to accommodate Mn at the point of apatite

377 crystallisation.

378

379 6. Eu and Ce anomalies in apatite as a probe of magmatic fO_2

380 6.1 Defining Eu and Ce anomalies in apatite, and crystal chemical controls

381 It is commonly suggested that changes in valence of Eu and Ce should result in changes in

382 , and anomalies in chondrite normalised concentrations of Eu and Ce in apatite

383 compared. The extent of relative depletion or enrichment can be quantified by calculating

384 concentrations for Eu and Ce based on normalised concentrations of neighbouring REEs je

385 expected concentrations of Ce and Eu if both were 100% trivalent. There are several methods for

386 doing this. For example, Eu anomalies (Eu_N/Eu_N*), or ratio of normalised Eu content to a calculated

387 Eu content based on trivalent REE can be calculated based on the arithmetic mean of chondrite

388 normalised Sm and Gd concentrations (Eu_N*) (Sha and Chappell, 1999)

389

390 ——— ———   [3]

391

392 or based on a geometric mean of normalised Sm and Nd concentrations (Mao et al., 2016)

393

394 —— ·——   [4]

395

396 Likewise, Ce anomalies can be calculated compared to concentrations of adjacent normalised REEs

397 (Cao et al., 2012)

398

399 —— ——   [5]

400

401 or again based on geometric averages of similar radius REEs. There remains some lack of clarity

402 within the literature regarding which methods are most suitable for determining anomalies in

403 apatite data. Apatites typically show variable, negative Eu anomalies, due to an effect of fO_2 on

404 apatite–melt partitioning, and/or inherited from magma, due to preferential incorporation of Eu^{2+}

405 into feldspar (Belousova et al., 2002; Cao et al., 2012; Chu, 2009; Ding et al., 2015; Li et al.,

406 2016; Pan and Fleet, 2002; Sha and Chappell, 1999). Ca in the $Ca[9]$ site and the $Ca[7]$ site in

407 apatite has ionic radii of 1.18 Å, and 1.06 Å, respectively (Shannon, 1976). Eu^{3+} has radii of 1.12 Å

408 and 1.01 Å in 9-fold and 7-fold coordination, respectively. In contrast, Eu^{2+} is considerably larger,

409 with ionic radii of 1.30 Å and 1.20 Å. Therefore, on the basis of size Eu^{3+} should be compatible in

410 apatite and Eu^{2+} substitution rather limited. Under reducing conditions, an increase in the proportion

411 of Eu^{2+} over Eu^{3+} will lower   compared to other REEs, resulting in a pronounced

412 negative Eu anomaly. In contrast, oxidising conditions, where all Eu is trivalent, would produce no

413 apatite Eu anomaly. This is a reasonable geochemical argument as REEs are clearly compatible in

414 apatite and melt composition has a minor influence on partitioning. However, Eu anomalies in

415 apatite can also reflect depletion in Eu relative to other REEs inherited from magmatic sources, for

416 example due to feldspar crystallisation (Drake and Weill, 1975).

417 Ce partitioning should show a contrasting effect with a change from reducing to oxidising conditions.

418 Under typical magmatic conditions Ce^{3+} dominates, and Ce should behave similarly to other REEs.

419 Under more oxidising conditions Ce^{4+} is increasingly stabilised. Ce^{4+} has an ionic radius very close to

17

420 that of Ca (1.196Å and 1.07Å in 9- and 7-fold coordination), and should readily substitute into the

421 apatite structure. Ce⁴⁺ is substantially smaller (0.97 Å in 8-fold coordination) and not favoured in 9-

422 or 7-fold coordination. As such, oxidising conditions should result in negative Ce anomalies in

423 normalised apatite REE data. However, although a potential control of fO_2 on Ce valence and

424 partitioning behaviour has been noted in studies of apatite chemistry, explanation of Ce anomalies

425 based on partitioning behaviour is less straightforward. Ce anomalies in normalised apatite REE are

426 typically much smaller than Eu anomalies, and range from slightly negative to slightly positive (e.g.

427 Cao et al., 2012; Mao et al., 2016). Contradictory negative Ce anomalies coupled with negative Eu

428 anomalies have been explained by preferential Ce incorporation in other phases such as monazite

429 and allanite (Puchelt and Emmermann, 1976). However, despite recent observed negative

430 correlations of Eu and Ce anomalies in apatite (Chen et al., 2019; Zafar et al., 2019), it remains

431 unclear whether Ce anomalies in apatite are of use as an indicator of magmatic fO_2. This is in marked

432 contrast to zircon, which preferentially incorporates Ce⁴⁺, leading to marked positive Ce anomalies in

433 zircon under more oxidising conditions (Ballard et al., 2002).

434

435 6.2. A new procedure for determining REE anomalies in apatite

436 Examples of trends in normalised apatite REE data are shown in Figure 7. Consistent with previous

437 observations, there are variable, sometimes large, negative Eu anomalies. Ce anomalies are subtle to

438 absent, and range from slightly negative to slightly positive where present. Quantification of Eu and

439 Ce anomalies using simple calculations based on normalised data for neighbouring REEs (e.g.

440 equations [3] to [5]) is unreliable due to variations in normalised REE trends. For Eu anomalies, the

441 best procedure for calculating Eu* depends on the extent of right-inclined REE slope and relative

442 enrichment of MREE. This may explain why different procedures are used in the literature. For Ce,

443 the subtleness of any anomaly also necessitates a more robust approach to modelling Ce*. Choice

444 of method for calculating normalised Ce content has a significant effect and can produce spurious

445   results. Zhong et al (2019) proposed a more robust procedure for determining Ce anomalies in

446   normalised zircon REE data based on fitting MREE to HREE data to a logarithmic function. However,

447   this procedure is unsuitable for fitting apatite REE data. Instead, anomalies are calculated here based

448   on an alternative method of fitting all normalised REE3+ data, shown in figure 8. Chondrite-

449   normalised REE concentrations, excluding Ce and Eu, are fitted to a polynomial function of the

450   general form:

451

452   ¨ « £   [6]

453

454   where x is ionic radius (Shannon, 1976). A 6 order polynomial is sufficient to consistently fit all

455   apatite data here and minimise residuals about 0, although for most data a 4th order polynomial is

456   sufficient. Eu* and Ce* are then calculated based on the fitted function, for Eu^{3+} and Ce^{3+} ionic

457   radii. In accordance with previous methods, the extent of anomalies can then be calculated based on

458   the ratios of measured and calculated normalised Eu and Ce contents, i.e. Eu$_N$/Eu* and Ce$_N$/Ce*.

459   This method of calculating Eu* and Ce* is less arbitrary than other procedures, and able to take

460   account of variations in overall REE trends, which is key when comparing diverse datasets. The

461   method is also less susceptible to errors arising from individual REE analyses, and proved to be more

462   reliable at calculating anomalies for all data.

463   Figure 9 compares Ce and Eu anomalies calculated with the polynomial method and using equations

464   [3] and [4] for Eu, and [5] for Ce. For the whole dataset, there is good overall consistency between

465   estimated extent of anomalies using the different approaches (Figure 9). Although as expected,

466   considerable scatter about 1 (no anomaly). A polynomial approach results in a greater proportion

467   of apatites with small positive, as opposed to negative, Ce anomalies. Both methods show that

468   apatites can have small positive and negative anomalies, and that a small proportion of apatites can

19

469 have much larger anomalies. Examination of individual datasets demonstrates improvements in

470 quantifying small Ce anomalies using the polynomial fitting method. For example, apatite data from

471 Sun et al. (2020) show flattening in normalised concentrations over the MREE clear,

472 positive Ce anomaly, as identified with the polynomial fitting method. Determination of Ce_N

473 using an arithmetic mean produces an incorrect negative anomaly. Similarly, determinations of

474 Ce_N/Ce_N^* for apatite data from Xie et al. (2018b) using an arithmetic mean often imply a negative Ce

475 anomaly for data in which a small positive Ce anomaly is correctly identified using the polynomial

476 method. Given the limited extent of Ce anomalies in normalised apatite REE data, a polynomial

477 approach is preferred for comparing different datasets. However, no fitting method is ideal, and

478 work here clearly demonstrates the importance of ground truthing any method for determining the

479 extent of Ce anomalies.

480 Eu anomalies in apatite are typically larger, generally negative, and more variable. There is good

481 general consistency between methods for determining Eu anomalies (Fig. 9B,C), although

482 considerable scatter. Examination of individual apatite data demonstrates again that contrasts in the

483 extent of Eu anomalies determined using different methods typically arise from inaccuracies in

484 estimating Eu^* in samples with non-linear REE trends. Traditional methods result in erroneous

485 calculation of the extent of Eu anomalies for a subset of the data which is detrimental to

486 identification of trends in the broad dataset. This is especially true for calculations of Eu^* using a

487 geometric mean based on Sm and Nd concentrations, where non variations in normalised REE

488 concentrations can result in significant errors in calculated Eu concentrations.

489

490 6.3. Comparison of Ce and Eu anomalies in apatite and zircon.

491 A number of studies provide data on coexisting zircon. Correlations between relative zircon Ce

492 content and magmatic fO_2 have been more robustly demonstrated, and are supported by

493 experimental data (Trail et al., 2012). Therefore, comparison with zircon Ce data allows investigation

494 of the extent to which magma affects the extent of Ce anomalies in apatite. Comparison is

495 made here between reported Ce^{4+}/Ce^{3+} ratios in zircon calculated from zircon and whole rock data

496 Ballard et al. (2002) and . Eu_N/Eu_N* data for zircon is compared to .

497 Figure 10A demonstrates that Ce^{4+}/Ce^{3+}_{zircon} and Ce_N/Ce_N* in apatite are inversely correlated. This is

498 expected based on contrasting compatibility of Ce^{4+} in zircon and apatite. High Ce^{4+}/Ce^{3+}_{zircon} (>400)

499 are consistent with $Ce_N/Ce_N*_{apatite}$ of 0.98 to 1.02. There is a weak linear correlation in data at high

500 Ce^{4+}/Ce^{3+}_{zircon} which may imply that small apatite Ce anomalies are only due to scatter about

501 zero. Higher Ce^{Ap}_{anom}, >0.2, correlate with samples which have low Ce^{4+}/Ce^{3+}_{zircon}, <200. There is

502 obvious scatter in the data, and magma fO_2 recorded by the two phases may not, strictly, be

503 comparable as apatite is typically an earlier crystallising phase. Both phases might also record

504 progressive changes in fO_2 and both phases do not directly coexist in all samples. Horizontal trends

505 in Figure 10A, for example in Xie et al. (2018b) data, probably mask progressive changes in Ce

506 anomalies as a function of fO_2 or some other control. Despite this, the observed correlation

507 between the datasets is notable. A similar, although weaker, correlation is observed when

508 comparing zircon data to Ce anomalies calculated from apatite REE data normalised to whole rock

509 REE composition. This implies that systematic changes in the extent of Ce anomalies in apatite are

510 not simply inherited from the magma but reflect a change in partitioning behaviour. However,

511 greater scatter limits use of apatite/whole rock ratios.

512 In contrast, Figure 10B demonstrates that there is no obvious relationship between Eu anomalies

513 in apatite and zircon. Eu^{2+} incorporation in zircon is unfavourable (Trail et al., 2012). Therefore,

514 under reducing conditions an increase in the proportion of Eu^{2+} should result in large negative

515 Eu anomalies in both zircon and apatite normalized REE data. Again, there are limitations in this,

516 although the clear lack of any correlation, especially considering the relative magnitude of Eu

517 anomalies, suggests that other factors control Eu concentration in zircon and apatite. Most likely

518 this again emphasises the influence of fractional crystallisation. This is demonstrated in plots of

21

519   Eu_N/Eu_N^* (apatite) and Ce_N/Ce_N^* (apatite) as a function of whole rock SiO_2 (Figure 11). There is a

520   broad trend in apatite data where increasingly negative Eu anomalies are noted with increasing

521   whole rock SiO_2 above a value of ~65%. Similar trends are noted if other measures of magmatic

522   fractionation are used, such as ASI, as noted by Chu et al. (2009). This is consistent with enhanced

523   feldspar crystallisation and Eu^{2+} depletion in more evolved magmatic systems. In contrast, Ce_N/Ce_N^*

524   in apatite shows no dependence on whole rock SiO_2 or other measures of magmatic evolution.

525   Importantly, this suggests that melt structure also has little discernible influence on Ce compatibility in

526   apatite.

527

528   6.4. Dependence of the extent of Ce and Eu anomalies in apatite on magmatic fO_2

529   Eu and Ce anomalies in apatite should be coupled, with highly reducing conditions resulting in large,

530   negative Eu anomalies which progressively decrease with increasing fO_2, and more oxidising

531   conditions resulting in negative Ce anomalies. Valence changes in both Eu and Ce will depend on the

532   system in question, and there is a lack of data on how Eu^{2+}/Eu^{3+} and Ce^{3+}/Ce^{4+} vary in apatite as a

533   function of fO_2. Figure 12 gives approximate ranges of valence changes in magmatic systems,

534   illustrating that Eu valence changes occur under more reducing conditions, and that Ce valence

535   changes occur under oxidising conditions atypical for terrestrial magmas. Negative Eu anomalies for

536   apatite are expected for more reduced magmas, but Eu^{3+} will dominate in most conditions in

537   terrestrial magmas, so the presence of notable Eu anomalies in most apatite data implies that a

538   small proportion of Eu^{2+} exists to higher fO_2, and/or that incorporation of Eu in feldspars is able to

539   drive Eu depletion in magmas over a wide range of magmatic fO_2. Rare positive Eu anomalies in

540   apatite must reflect magmatic sources rather than any control of apatite on Eu partitioning. Ce^{4+} is

541   predicted to be stabilised only under very oxidising conditions. X-ray absorption data demonstrate

542   that very small proportions of Ce^{4+} in various silicate melts can be stabilised above the QFM buffer

543   (Burnham and Berry, 2014; Smythe and Brenan, 2015). The presence of large Ce anomalies in zircon

544 demonstrates that small changes in proportions of Ce^{4+}/Ce^{3+} have a significant effect on zircon REE

545 composition, due to large differences in the compatibilities of each species into zircon. As an

546 extension of this argument, Ce anomalies in apatite might also be expected over a similar range of

547 fO_2 to zircon. This would reduce the range of magmatic fO_2 for which neither Eu and/or Ce

548 anomalies in apatite are predicted based on observations of redox couples in magma shown in

549 Figure 12. However, the extent of fO_2 driven changes in apatite Ce content will depend on

550 differences in compatibility of Ce^{3+} and Ce^{4+}. As noted by Ballard et al. (2002) there is an order of

551 magnitude difference in Ce^{3+} and Ce^{4+} partitioning in zircon. The extent of difference in Ce

552 partitioning in apatite can be estimated using experimental partitioning data from Prowatke and

553 Klemme (2006). Capsule design used by Prowatke and Klemme (2006) constrained log fO_2 at

554 approximately FMQ-1 log units, corresponding to a Ce^{4+}/Ce^{3+} ratio of approximately 0.004, according

555 to melt speciation data of Smythe and Brenan (2015). As apatite-melt Ce partition coefficients

556 from the Prowatke and Klemme (2006) data set are consistent with $D_{Ce3+}^{apatite/melt}$ of approximately

557 10. Their partitioning data for 4+ elements suggests that $D_{Ce4+}^{apatite/melt}$ is likely to range from

558 0.01 to 0.1. As such, although there is a large difference in Ce^{3+} and Ce^{4+} compatibility in apatite, this

559 difference is much smaller than in zircon. Correspondingly, Ce anomalies in apatite are probably

560 smaller and much harder to detect, especially given the low proportions of Ce^{4+} in terrestrial

561 systems

562 Comparison of calculated Ce and Eu anomalies across the entire dataset demonstrates that simple

563 site and ionic radius arguments fail to explain trends in normalised REE data for apatite (Figure 13).

564 Aside from a few exceptionally metamorphosed Archaen samples, apatites display negative Eu

565 anomalies, likely due to a combination of the effects of magmatic fO_2 and crystallisation of feldspar.

566 This implies that at least a proportion of Eu is stable in magmas over a large range of fO_2. The

567 extent of Ce anomalies is significantly less, ranging from 0.8 to 1.2, as opposed to 0 - 1.2 for

568 Eu. Despite predictions of negative Ce anomalies, a significant majority of apatites display weak,

569 positive anomalies. Scatter in data about zero cannot be used to simply explain this as an artefact in

570   the data. Even if all Ce anomalies from 0.92 to 1.08 are discounted there is a clear dominance of

571   small, positive Ce anomalies, and absence or larger negative Ce anomalies in oxidised systems.

572   Large, positive Ce anomalies in samples with no Eu anomaly in Figure 13 are from carbonatite

573   hosted apatites, for which Ce anomalies are generally assumed to reflect enrichment in host magma

574   (Mao et al., 2016). In general, contrary to expectations, apatites simultaneously display negative Eu

575   anomalies and small positive Ce anomalies. In part this may reflect a strong control of magmatic

576   composition on normalised Eu concentrations in apatite. However, predicted negative Ce anomalies

577   in normalised apatite REE data are, generally, not observed.

578   Contrasting Eu and Ce anomalies in apatite have been documented previously. Puchelt and

579   Emmermann (1976) observed coupled Eu and Ce depletion in apatite, which they assigned to an

580   effect of fO_2 and the occurrence of Ce rich phases such as monazite and allanite. The presence of

581   such phases should also result in overall depletion in REE in apatite, coupled to Ce anomalies.

582   However, Ce_N/Ce_N^* appears to be independent of overall REE concentrations in apatite, suggesting

583   that any effect due to crystallisation of Ce rich phases is of limited importance. Similarly, no

584   correlation between Ce_N/Ce_N^* and either whole rock or apatite fO_2 is observed, as might be

585   expected if apatite Ce trends were assigned to crystallisation and preferential Ce^4 Ce

586   depletion from magma. It is more likely that negative Ce anomalies reflect relatively oxidised

587   magmatic systems, and that contradictory Eu anomalies are simply due to preferential incorporation

588   of Eu in plagioclase.

589   It is feasible that positive Ce anomalies in apatite reflect Ce enrichment in host magma. To test this,

590   the same polynomial fitting method can be used to quantify the extent of Ce and Eu anomalies in

591   whole rock data. Comparison of apatite and whole rock Ce_N/Ce_N^* and Eu_N/Eu_N^* is shown in figure 14

592   for a subset of data for which corresponding whole rock data is available. For the compiled dataset,

593   whole rock Ce_N/Ce_N^* scatter about 1, with some displaying small positive and negative anomalies.

594   This contrasts with apatite data, and there is no clear dependence of apatite Ce_N/Ce_N^* on whole rock

24

composition. Apatite and whole rock Eu/Eu^* by contrast, show a reasonable correlation. Both

typically show negative Eu anomalies, consistent with a control of feldspar on fractionation

magmatic composition, although Eu depletion in apatite is typically larger. Whole rock data only

gives an approximate measure of magma composition at the point of apatite crystallisation.

However, given that Ce^{3+} is more compatible in apatite than Ce^{4+}, it should be readily apparent from

whole rock data if small positive Ce anomalies in apatite are inherited from magma. A clear, positive

Ce anomaly in whole rock data would be required to account for small anomalies in apatite data,

and this is not observed.

From limited data available (Figure 10A) it appears that positive Ce anomalies in apatite are only

noted in rocks which record low zircon Ce^{4+}/Ce^{3+}, and that high zircon Ce^{4+}/Ce^{3+} results in negligible

Ce anomalies in apatite. Examination of the dataset fails to identify any correlation of apatite Ce

content with other aspects of apatite or whole rock chemistry. The cause of small positive Ce

anomalies in apatite remains unexplained. What is clear, however, is that apatite Ce content cannot

currently be used to assess magmatic fO_2

7. Mn, Ce and Eu in apatite as an indicator of magmatic fO_2

The ability of apatite to incorporate a range of trace elements means that it is, potentially, a useful

indicator of magmatic process. However, there is a clear dependence of melt partitioning of

Mn on melt structure, and the proposed oxybarometer of Miles et al. (2014) is unreliable.

Experimental studies, and analysis of compositional data at large numbers of sample suites, fail

to demonstrate any systematic change in apatite Mn content, or in apatite-melt partitioning, which

support an oxybarometer. This is consistent with X-ray absorption data from Stokes et al. (2019) and

with experimental data on forsterite-silicate melt Mn partitioning (Watson 1977) which imply that

Mn does not significantly change valence in terrestrial magmatic systems.

619

620 Systematic changes in Eu and Ce valence in terrestrial systems suggest an alternative means of using

621 apatite chemistry to determine magmatic fO_2. Natural apatites typically demonstrate significant,

622 negative Eu anomalies in normalised REE data. However, this correlation is overprinted by a strong

623 control of bulk rock composition, such that the extent of Eu anomalies increases in more silicic

624 systems. This most likely arises due to ready substitution into feldspar, implying that apatite

625 Eu anomalies can also be inherited from the magma from which they crystallise. A similar effect is

626 noted for Eu incorporation in zircon (Trail et al., 2012). If the effects of feldspar crystallisation can be

627 discounted, for example in systems where apatite is an early crystallising phase, Eu anomalies

628 provide a means of estimating relative changes in fO_2. However, given that other factors such as

629 temperature are also likely to influence apatite REE composition, it is unlikely that a general Eu in

630 apatite oxybarometer is feasible. Eu anomalies in apatite remain an unreliable recorder of magmatic

631 fO_2.

632 The extent of Ce anomalies in normalised apatite REE data appears to be independent of any control

633 of bulk or melt composition. In contrast to zircon, oxidising conditions and an increase in proportion

634 of Ce^{4+} are predicted to result in negative Ce anomalies in apatite. However, Ce anomalies in apatite

635 are considerably smaller than those in zircon, or compared to Eu anomalies, because the contrast in

636 apatite-melt partitioning of Ce^{3+} and Ce^{4+}, while large, is significantly smaller than in zircon. Small Ce

637 anomalies in normalised apatite data are not reliably determined by simple comparison with similar

638 radii REE pairs, partly due to variations in overall REE trends in apatite data. The extent of Ce and

639 anomalies in apatite can be more accurately constrained by fitting whole REE apatite data using a

640 polynomial fitting approach, although all methods of identifying anomalies in normalised REE have

641 limitations. Reexamination of literature data suggests that a small proportion of apatites have

642 negative Ce anomalies, but that a larger proportion have small positive Ce anomalies. The cause of

643 this relative enrichment in Ce compared to other REEs remains unclear. Comparison of apatite and

zircon Ce data does suggest that there may be some control of fO_2 on apatite Ce content. However,

the limited extent of Ce anomalies in natural apatite would limit application of any

oxybarometer, and the control of fO_2 on REE behaviour in apatite remains unexplained. Although

apatite composition provides a useful record of the chemical characteristics of magma from which it

crystallised it provides, at best, an unreliable indicator of the oxidation state of magmas.

654 Table 1 Sources of data used

Reference	Host (rock type/magma composition)	Locality/details
Alavijeh et al., 2019	Gabbro	Nodoushan plutonic complex, Sananda-Sirjan Zone, Central Iran
Azadbakht et al., 2018	Series of felsic intrusions: granodiorite to granite	Arcadian-related granitoids, New Brunswick, Canada
Belousova et al., 2002	Metastudy: granite, larvikite, dolerite, carbonatite, Iron ore deposits, lherzolite	Metastudy: various
Birski et al., 2019a	Nakhlite meteorites (Martian)	NWA 10153 and NWA 10645 Martian meteorites
Birski et al., 2019b	Phosphates: cherts, BIFs, silicif felsic volcaniclastics, igneous derived detrital apatites	Barberton greenstone belt, Kapva Craton, S. Africa.
Bruand et al., 2014	Granites; appinite, granodiorite	Rogart and Strontian plutons, N Highlands, Scotland.
Bruand et al., 2020	Various granitoids	Various Archaen granitoids, plus comparative Phanerozoic granit
Cao et al., 2012	Granites, granodiorites, diorite porphyries	Various granitic ore deposits, Central Kazakhstan
Chen et al., 2019	Quartz diorite and diorite porphyry, diabase, granodiorite	Xietongmen ore-bearing porphyries S. Gangdese Belt, S. Tibet
Chu et al., 2009	Suite of rocks, categorised as type granites type granites and adakites	Trashimalayan igneous plutonic suite, Tibet
Duan et al., 2019	Granodiorites	Wushan granitoid, Middle-lower Yangtze Metallogenic Belt, and Zhuxiling granitoid Jiangnan Orogenic Belt, E. China.
Fabbrizio et al., 201	Volcanic despoits: granular, leucocractic, lithic breccia (itali	Colli Albani Volcanic District, Cer Italy
Hoskin et al., 2000	Zoned pluton: adamellite, granodiorite, diorite, quartz monzodiorite and aplite	Boggy Plain pluton, E. Australia
Kogarko, 2018	Ijolite-urtite; peralkaline intrusio	Khibina alkaline complex, Kola Peninsula, Russia
Miles et al., 2013	Granodiorites, granite	Criffell pluton, S. Scoltand
\ o 2019,2020	Metastudy: various (igneous an metamorphosed igneous derive apatite only)	Metastudy: various
Qian et al., 2019	Mineralised granodiorite	S. Anhui Province, China
Qu et al., 2019	I-type granite	# 8 Œ China
Richards et al., 2017	Broad range of igneous intrusio associated with IOCG and porp deposits (Cu mineralisation)	Mesozoic Coastal Cordillera, N. C
Sha and Chappell, 1999	I-type and S-type granites	Lachlan Fold Belt, SE Australia

28

Sun et al., 2020	Monzonitic mafic enclaves and host granites	Qianjia pluton, Hainan Island, Ch
Wang et al., 2019	Carbonatite veins associated w aegirine syenite	Weishan carbonatite, Shandong province, E. China
F. Xie et al., 2018a	Quartz diorite prophyries	Xiongcun district, southern Gangdese porphyry Cu belt, Tibe
F. Xie et al., 2018b	Granite porphryr, granodiorite, granodiorite porphyry, monzoni	S. Lhasa subterrane, Tibet
J. Xie et al., 2018	Monzodiorite, granodiorite	Tongling region, E. China
Xie et al., 2019	Granodiorites (porphyries) (peraluminous, I-type)	Chizhou Cu-Mo deposits, Middle and lower Yangtze metallogenic belt, E. China
Xu et al., 2019	Granitic plutons (mineralised quartz syenite porphyry and unmineralized)	Tongchang and Shilicun plutons, China
Zafar et al., 2019	Granite	Kukaazi granite, W. Kunlun oroge belt, NW China
Zirner et al., 2015	Granodiorite, augite syenites, phonolites, pulaskite, agpaite	Ilímaussaq complex, S. Greenland
Zhang et al., 2020	Granite, monzodiorite; quartz diorite, granodiorite and diorite minor mafic intrusions	Yunmengshan, Fangshan, Tiantangzhai, Dabie, and Shichen intrusions, North China Craton
Apatite-melt Mn partitioning data: experimental studies		
Danni et al., 2001	Analogue Shergotty (Martian) meteorite system (water-bearing, halogen-free)	Phase equilibria (high melt fract fixed pressure/temperature/fO2
Stokes et al., 2019	Basaltic andesite to rhyolitic m compositions saturated with apatite	Apatite-melt Mn partitioning at fixed pressure/temperature/fO2
Vander Auwera et al., 1998	natural jotunite starting composition: accessory apatite with low fraction melt	Phase equilibria at fixed pressure/temperature, some fO buffered

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869   Figure captions

870   Figure 1. Variation in apatite-whole rock Mn partitioning (based on element proportions by weight)

871   as a function of NBO/T, calculated from whole rock data, assuming all Fe as Fe^{3+} in accordance

872   with protocol of Mysen et al. (1984, 1982). Crosses are apatite-melt partition coefficients from

873   experimental studies where melt data is available. Dashed line is correlation of Stokes et al. (2019

874   A. shows all data, and B a magnified view of scatter at low values of NBO/T where data cluster. In

875   C. shows an alternative, simple exponential correlation based only on the experimental data in

876   Stokes et al. (2019). Same colour key used in all plots.

877

878   Figure 2. Variation in apatite-whole rock Mn partitioning as a function of A. ASI (based on whole rock

879   data, or melt compositions for experimental studies), and B. whole rock (or melt for experimental

880   studies) SiO_2 by weight, normalised to 100%, not including loss of ignition or low electron

881   microprobe totals due to the presence of water. Same key as Figure 1

882

883   Figure 3. Comparative plots of Mn content of apatite (recalculated as ppm by weight) as function

884   whole rock or melt A. ASI, B. SiO_2 content (by weight), and C. NBO/T.

885

886   Figure 4. Dependence of apatite Mn content on: A. $log(fO_2)$ determined from chemistry of other

887   phases (see references for detail) or as constrained in experiments; larger data points are those u

888   by Miles et al. (2013) to constrain their oxybarometer (solid line); B. (Eu/Eu^*) in zircon,

889   i.e. calculated Eu anomaly compared to general REE trend in chondrite normalised data, defined as

890   $(Eu/Eu^*)_N = \dfrac{}{}$, where   is the chondrite normalised concentration of Eu; C.

891 Calculated Ce^{4+}/Ce^{3+} ratio in zircon (Ballard et al., 2002) based on normalised zircon and whole rock

892 data.

893

894 Figure 5: Apatite-whole rock partitioning and apatite concentration (chondrite normalised) of key

895 REE as a function of NBO/T (A,D), whole rock SiO_2 (B,E) and ASI (C,F).

896

897 Figure 6. Variations in concentration of various trace elements in apatite with NBO/T (from whole

898 rock data) and whole rock SiO_2 (by weight).

899

900 Figure 7. Selected Chondrite normalised REE patterns from apatite, offset vertically for clarity (same

901 scale). Single analyses are shown to illustrate full variability in apatite REE patterns. Sun et al. (2020)

902 shows data from granite-hosted apatite, Xie et al. (2018a) quartz diorite-hosted, Alavijeh et al.

903 (2019) from alkaline gabbro-hosted, and Qian et al. (2019) from granodiorite-hosted apatite, all

904 showing typical LREE over HREE enrichment and variable negative Eu anomalies. Bruand et al. (2020)

905 is data from TTG-hosted apatite showing reverse pattern of LREE depletion relative to MREE and HREE,

906 and data from Xie et al. (2019b) from granodiorite-hosted apatite which show minor MREE

907 enrichment and HREE depletion. Sullivan et al. (2019) shows MREE enrichment in upper greenschist

908 facies metapelite. Azadbakht et al. (2018) is data from a felsic granodiorite-hosted apatite showing a

909 flat REE pattern with large negative Eu anomaly and small positive Ce anomaly. Binski et al. (2019)

910 data is from apatite in dacite-derived volcaniclastic sediment from the Barbeton Greenstone belt,

911 showing MREE enrichment and no negative Eu anomaly.

912

913 Figure 8. Procedure for fitting REE data and quantifying Eu and Ce anomalies used here. Chondrite

914 normalised REE concentrations plotted as a function of ionic radius (squares), and data (not

915 including Eu and Ce concentration) fitted to a general polynomial function. Line shows cal

916 REE concentrations based on fitted polynomial, with residuals shown in figure above.

917

918 Figure 9. Ce and Eu anomalies in apatite calculated using a whole REE polynomial fitting method

919 compared to traditional approaches (eq [3], [4] and [5] in text.)

920

921 Figure 10. Comparison of extent of Ce (A) and Eu (B) anomalies in apatite calculating using the

922 polynomial fitting method, with data from coexisting zircons.

923

924 Figure 11. Calculated Eu and Ce anomalies (polynomial fitting) in apatite as a function of whole rock

925 SiO$_2$ content.

926

927 Figure 12. Approximate positions of valence changes for Eu, Fe and Ce in magmatic systems, after

928 (Herd, 2008), with data for Ce from (Schreiber, 1987) relative to the IW-FeO) solid buffer.

929

930 Figure 13. Calculated Eu and Ce anomalies in apatite for the whole dataset, determined by

931 polynomial fitting.

932

933 Figure 14. Comparison of Ce and Eu anomalies in apatite and corresponding whole rock data, both

934 determined by polynomial fitting. Key same as Figure 13.

935

936

937   Figure 1

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