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

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Abstract

Apatite is a common accessory mineral in igneous rocks and is able to readily accommodate a wide range of trace elements and may provide a useful record of magmatic composition and magmatic processes. Relative abundances of redox sensitive elements in apatite could provide a much needed probe of magmatic oxygen fugacity. Examination of a large data set of apatite and whole rock compositions is used to assess the recently proposed, and increasingly used, Mn in apatite oxybarometer. Correlation of apatite whole rock Mn partition coefficients with whole rock SiO₂ and calculated melt polymerisation and aluminosity, support a model where apatite Mn content is largely dependent on melt structure. In more evolved systems, a decrease in availability of non-bridging oxygens in silicate melts drives Mn from being incompatible to increasingly compatible element in apatite. A magmatic fO₂ calculated from Ce concentrations in zircon also shows no discernible correlation with apatite Mn content. Mn content of apatite does not record magmatic fO₂, although it may be useful in indicating the extent of melt evolution. In contrast to concentrations of other trace elements in apatite have a much weaker, or no discernible dependence on melt structure and composition supporting the assertion that apatite records key aspects of magmatic composition.

Eu and Ce anomalies in chondrite normalised Rare Earth Element (REE) data provide an alternative means of using apatite to probe magmatic fO₂. A new method for more reliably comparing the

extent of Eu and Ce anomalies in apatite REEs used to assess control of Eu and Ce content. Apatite Eu content shows a strong dependence on whole rock composition, indicating that Eu anomalies often reflect apatite 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 fO₂ may have some control on apatite Ce content. However, the narrow range of Ce anomalies in apatite data, and lack of reliable control of fO₂, limit the extent to which apatite Ce records magmatic fO₂. As such, REE contents of apatite cannot currently be used to reliably indicate trends in magmatic fO₂.

1. Introduction

Apatite is a widespread accessory mineral found in a range of igneous rocks, metamorphic rocks and sediments. Although nominally $\text{Ca}_5(\text{PO}_4)_3(\text{F,OH,Cl})$, apatites typically contain high concentrations of an extensive range of trace elements, including U, Th, Sr and Rare Earth Elements (REEs) (Belousova et al., 2002; Pan and Fleet, 2002). In magmatic systems, crystallisation of apatite is important in magmatic evolution (Belousova et al., 2002) and the complex chemical fingerprint of detrital apatite may act as a useful provenance indicator in sedimentary rocks (Brugge et al., 2017; Morton et al., 2017). Following Belousova et al. (2002) and earlier studies including Cao et al. (2012), Chen et al. (2014), Ding et al. (2015) and Xu et al. (2015), there has been a considerable recent interest in using apatite geochemistry 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 (Haskin et al., 2000). The composition of apatite is controlled by elemental mineral/melt partitioning, which in turn varies depending on a number of factors,

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 such as pressure and temperature. For multivalent
 elements, partitioning between apatite and melt also depends on oxygen fugacity (for apatite
 trace element chemistry should provide much needed insight into magmatic fO₂ Belousova et al.
 (2002) noted that Mn content of apatite was highly variable due to the effect of fO₂. They
 argued that apatite likely incorporates Mn in preference to either Fe³⁺ or Mn⁴⁺ because on the
 basis of size and charge, it more readily substitutes As for Ca in more reduced magmas as
 increase in the relative proportion of Fe²⁺ 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 would obscure any correlation between apatite
 Mn and magmatic fO₂. Following observations from the zoned Criffel pluton, southern Scotland
 (Miles et al., 2013), Miles et al. (2014) proposed that Mn content of apatite be used to
 determine fO₂ 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 where fO₂ was constrained to propose a simple correlation
 for apatite Mn content and magmatic fO₂. 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
 oxybarometer to intermediate to more silica-rich rocks as an experimental study by Stokes et
 al. (2019) found no evidence for a control of 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, 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

analogue silicate systems were minimal over a range of terrestrially relevant conditions, and that Mn^{2+} dominated as a species in both apatite and coexisting silicates. It is unclear if this is a driving force for a correlation between apatite Mn content and terrestrial systems. Despite this, an increasing number of studies have used the Miles calibration (2014) to constrain magmatic fO₂ in apatite-bearing rocks, sometimes in combination, and in apparent agreement, with other measures of fO₂ (e.g. Sun et al., 2020; Xie et al., 2018a; Xie et al., 2018b; Xie et al., 2019).

The ability of apatite to incorporate a wide range of trace elements through various substitution mechanisms (e.g. Pan and Fleet, 2002) means that other multivalent elements might be useful in determining fO₂ in magmas from which apatite crystallised. Of note here are the REE. REEs are readily incorporated into apatite and typically present as 3+ cations. However, Eu can be 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., 2015; Burnham and Berry, 2014). It is likely that the preferred substitution of both Eu^{2+} and Ce^{3+} into apatite results in Eu and Ce contents higher or lower than the expected concentrations relative to other REEs of fixed 3+ valency, and may also be proxies for magmatic fO₂ (Belousova et al., 2002; Pan and Fleet, 2002; Sha and Chappell, 1999). Previous studies have shown that reducing conditions result in negative Eu anomalies in apatite (Belousova et al., 2002; Cao et al., 2012; Chu et al., 2009; Ding et al., 2015; Duan et al., 2019; Pan and Fleet, 2002; Sha and Chappell, 1999; J. Xie et al., 2018; Zafar et al., 2019). However, any direct oxybarometer based on Eu in apatite is complicated by crystallisation of feldspar, which preferentially depletes both magma and apatite in Eu (Duggan et al., 2016; Belousova et al., 2002; Will, 1975; Sha and Chappell, 1999). In contrast, Ce anomalies in apatite are assumed to be relatively independent of the effects of crystallisation of other phases, with the exception of zircon and zirconium REE phases. Although apatites variably show positive Ce anomalies, interpreted as varying degrees of magmatic oxidation, the extent of these are small (Belousova et al., 2002; Chu et al., 2009; Ding et al., 2015; Duan et al., 2019), in notable contrast to zircons which can exhibit significant positive Ce anomalies in

REE data (Trail et al., 2012). There has been no robust experimental assessment of the extent to which REE anomalies in apatite can be used to probe magmatic fO₂. Despite these studies have used apatite REE trends, and the extent of Eu and Ce anomalies, to provide qualitative assessments of magmatic fO₂.

There is a lack of strong evidence for a Mn in apatite oxybarometer, either from experimental studies on element partitioning, detailed crystal chemical investigations of apatite, or wider review of natural apatite data. Despite this, the preliminary Mn in apatite oxybarometer of Miles et al. (2014) is becoming widely adopted as a method of assessing magmatic fO₂ in apatite-bearing rocks. This perhaps highlights the need for a range of geochemical tools to assess changes in magmatic fO₂, and the general importance of apatite in magmatic, especially, systems. Here, apatite geochemical analyses and whole rock data from an extensive range of geochemical investigations are collated. In addition to data from published studies and wider geochemical studies of apatite chemistry, we assess the validity of Miles et al. (2014) oxybarometer. This dataset is then used to assess other proposed controls on apatite chemistry, with emphasis on cation substitution, including the use of Eu and Ce anomalies to assess the broad extent of changes in magmatic fO₂.

2. Methodology.

Apatite composition data from 26 studies was analysed including, where possibly, whole rock data (Table 1 for details). As apatite is typically an early crystallising accessory phase, whole rock data can be used to assess composition of magmas from which apatite crystallised. In addition, data from study of Transhimalayan apatites by Chatterjee et al. (2009), the extensive study of apatites from a broad range of rock types by Selyukova et al. (2002), and the recent meta-study by (2019) were used. For the latter study, which identifies geochemical fingerprints of apatite provenance (Selyukova et al., 2020), only data from igneous and selected metamorphic apatites were used.

Major and trace elements in the studies were obtained primarily using electron microprobe analysis and laser ablation mass spectrometry to allow ready comparison and were converted to element proportions (by weight). Where Mn concentrations were obtained using both methods, laser ablation data were preferred. For all studies, only REE data obtained from laser ablation were used. In addition to studies of natural samples, apatite Mn composition, and Mn mineral/melt partitioning from available experimental studies was also used (Table 1).

3. Controls on the Mn content of apatite

The oxybarometer of Mies et al. (2013) assumes that magmatic fO_2 is the sole control on the Mn content of apatite in less silicic systems. This can be explained in terms of ionic radius: Mn^{2+} has a very similar ionic radius to Ca^{2+} which it likely substitutes in apatite. In contrast, Mn^{3+} is substantially smaller, implying that Mn^{3+} substitution in apatite is minimal. In contrast, both Mn^{2+} and Mn^{3+} can be readily incorporated in silicate melts. A change in fO_2 and proportion of Mn^{2+} vs Mn^{3+} is predicted, therefore, to result in large changes in apatite partitioning. However, experimental data (Stokes et al., 2019) and some observations from studies of natural samples (Bodnar et al., 2010; # demonstrate that apatite Mn content is independent on melt composition, especially SiO_2 content. Stokes (2018) and Stokes et al. (2019) argued that with increasing SiO_2 content, the structure of silicate melts progressively changes, melt polymerisation increases, and the availability of bridging oxygens is markedly reduced. A commonly used measure of melt polymerisation is the ratio NBO/T , defined as $(\text{non-bridging oxygens} / \text{tetrahedral sites})$, where $NBO/T=0$ represents a fully polymerised melt where O sites are shared between neighbouring T sites, and $NBO/T=4$, a fully depolymerised melt where O sites are bound to only one T site. This ratio can be calculated based on measured proportions (Myser et al., 1984, 1982). Stokes (2018) and Stokes et al. (2019) argued that as Mn is not a network former in silicate melts, a reduction in NBOs results in a marked reduction in Mn solubility

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 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 (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 line on Figure 1 is the
 161 calibration of Stokes et al. (2019). As expected, there is considerable scatter in the data use of
 162 whole rock data is a limiting factor here. Apatite crystallisation in most systems involves long
 163 implying that melt composition evolves during apatite crystallisation. Apatite crystallisation also
 164 occurs at different times 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 SiO₂. Experimental data of Stokes et al. (2019) and
 170 al. (2001) is generally consistent with data from natural samples. In contrast, Mn partition
 171 coefficients from van der Auwera et al. (1998) are at least an order of magnitude lower. Given that
 172 these are very low melt fraction experiments with accessory apatite, this data is not considered
 173 further.
 174 Experimentally determined partition coefficients are typically from systems with less polymerised
 175 melts. Those from Stokes et al. (2019) are slightly higher than those from natural
 176 apatite, although the general trend of increasing with increasing melt

polymerisation in the Stokes et al. (2019) data mirrors the overall database. The
 logarithmic algorithm of Stokes et al. (2019) overestimate in highly polymerised
 systems in terms of Mn element proportion (by weight), this algorithm is expressed on figure 1
 as:

$$X_{Mn} = \frac{1}{1 + \exp(-\frac{NBO}{T})} \quad [1]$$

The trend of Stokes et al. (2019) correlation at very low NBO/T is largely consistent with the data
 of Sha and Chappell (1999). From Figure 1 it is apparent that this database tends towards the upper
 end of values for natural samples. A simple exponential relationship based on
 data of Stokes et al. (2019) of the form:

$$X_{Mn} = \frac{1}{1 + \exp(-\frac{NBO}{T})} \quad [2]$$

(Figure 1) provides a better fit to the data. Alternatively, and in addition to this, the Stokes et al.
 (2019) correlation may be systematically offset to higher /lower NBO/T

There are a number of complicating issues with using whole rock data to determine NBO/T and
 assess melt polymerisation. One particular issue is Fe valence. The method of Myschko et al. (1984,
 1982) involves assigning a proportion of Fe sites. Due to a lack of data on current oxidation
 state in whole rocks (i.e. Fe), and oxidation state during apatite crystallisation, all Fe in whole
 rock data is assumed to be Fe²⁺. This likely leads to an overestimation in the extent of melt
 polymerisation as Fe²⁺ is not tetrahedrally coordinated in melt structures. In contrast, Stokes et al.
 (2019) used X-ray absorption data to determine 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 SI (2019) data would be to shift the
 202 data to higher NBO/T. The role of water as a network modifier is 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. 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 $\text{SiO}_2/\text{Al}_2\text{O}_3$ and Aluminium
 208 Saturation Index (ASI). ASI, the molecular ratio $\text{Al}_2\text{O}_3/(\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})$, is a measure of magma
 209 aluminosity and is related to magmatic evolution. As noted by Sha and Chappell (1999), ASI
 210 defines the transition from peraluminous (>1), aluminous (<1), and a change in behaviour of
 211 many major and trace elements in silicate melts. From Figure 2a it is clear that
 212 $\text{SiO}_2/\text{Al}_2\text{O}_3$ increases with increasing ASI, as previously noted by Sha and Chappell (1999) and
 213 et al. (2009). Similarly, Figure 2b demonstrates a clear correlation between $\text{SiO}_2/\text{Al}_2\text{O}_3$ 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 favourable 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 transition in apatite Mn
 224 content from metaluminous to peraluminous systems. This is mirrored in whole rock and NBO/T

data, although trends are defined in for . This likely indicates the effect of other phases on apatite Mn content. Scatter in data again highlights limitations in using whole rock data, and the influence of other controls, including pressure, temperature, melt volatile content and possibly fO₂ as well as apatite chemistry and, of course, bulk composition. Notably, the correlation of Miles et al. (2014) is based on silicic systems, over which melt composition/structure does have an observable control on apatite Mn content.

Apatite is an important host of Mn in magmatic rocks. However, the control of melt structure and composition on Mn partitioning implies that the correlation of (2014) cannot be used to simply estimate magmatic fO₂. Analysis of a broad dataset, however, supports the use of apatite chemistry as a sensitive probe to the origin of detrital apatite (e.g.), as an indicator mineral in ore exploration and probe to conditions of ore formation (e.g. Beresova et al., 2002) and as an indicator of magmatic conditions (e.g. , 2009). Magmatic apatite with high Mn contents typically reflects crystallisation from more evolved melt. As such, apatite Mn content could be used to assess the onset and duration of crystallisation in an evolving system, with progressive or punctuated periods of growth recorded in distinct increases in apatite Mn content.

Pan and Fleet (2002) noted that the composition of apatite, concentration of Cl and H₂O, can affect substitution mechanisms for various ions in apatite. Notably, some elements such as REEs show changes in preferential incorporation onto the two nonequivalent Ca sites in chloroapatite compared to fluorapatite and hydroxyapatite. However, no clear trends in apatite F/Cl content and either apatite Mn content or were identified. Lack of data on apatite water contents meant that an effect of water on Mn partitioning could not be assessed.

4. Assessing the dependence of apatite Mn content on magmatic fO₂

249 Stokes et al. (2019) provided evidence for a substantial change in Mn valence, and the
 250 proportion of Mn^{3+} to Mn^{4+} in silicate melt and apatite over a broad range of $f\text{O}_2$. This
 251 valence change is required to support any dependence of apatite Mn content on magmatic $f\text{O}_2$
 252 contrast. Stokes et al. (2019) observe consistent changes in the proportions of Fe^{2+} and Fe^{3+} with
 253 $f\text{O}_2$. 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 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. They inferred that differences in Mn valence would
 257 be sufficient to drive changes in Mn partitioning as a function of magmatic $f\text{O}_2$. However, Stokes et
 258 al. (2018) noted that although synthetic and natural spinels contain variable Mn 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 $f\text{O}_2$ 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 $f\text{O}_2$.
 265 It remains possible that some scatter in Figures 1 and 2 is due to an effect of $f\text{O}_2$ on Mn partitioning.
 266 For some studies, independent estimates of magmatic $f\text{O}_2$ are provided. In figure 4A, apatite Mn
 267 content as a function of $\log f\text{O}_2$ 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 $f\text{O}_2$ was experimentally constrained. For other data, $f\text{O}_2$ 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 of Ce^{3+} valence, provides a means of
 273 determining magmatic $f\text{O}_2$ at the point of zircon crystallisation (Trail et al. 2011). Apatite is typically
 274 an earlier crystallising phase than zircon (Duan et al., 2015), so $f\text{O}_2$ recorded by both phases may not

be strictly comparable (Miles et al. (2014) (ZhongJie et al., 2019)) then observe that errors in
 calculating Ce anomalies in zircon REE data using conventional methods results in significant
 uncertainties. Despite this, it is clear from Figure 4A that no correlation between apatite
 apatite Mn content can be observed beyond data presented by Miles et al. (2014). This point is
 further emphasised in Figures 4B and 4C, which consider the extent of Eu anomalies in zircon, and
 inferred zircon Ce^{3+} , based on zircon and whole rock (i.e. coexisting melt) data. Under reducing
 conditions, the proportion of Eu^{3+} in magmatic systems increases. Eu^{3+} is highly incompatible
 in zircon, meaning that reducing conditions result in a marked negative Eu anomaly compared to
 calculated Eu content based on chondrite-normalised concentrations of REE concentrations (Trail
 et al. 2012). However, in this instance, relative Eu depletion in zircon is inherited from the
 magma, as Eu^{3+} is readily incorporated into feldspars. Eu anomalies can only be used
 under certain conditions to estimate magmatic fO₂. Despite this, it is clear from Figure 4B that there
 is no relationship between the extent of zircon Eu anomalies and apatite Mn content, either within
 the dataset, or importantly within data from individual studies. Ce^{3+} in Figure 4C is estimated
 based on zircon and melt composition (Trail et al., 2012, 2014) and is a measure of Ce partitioning
 driven by valence change, corrected for the effect of melt composition/structure. Figure 4C again
 shows scatter in Mn apatite data which cannot be ascribed to any effect. As such,
 although data available here is limited, there is no evidence to support the barometer of
 Miles et al. (2013).

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

Analysis of data from a large number of studies supports a model where the partitioning of apatite
 controlled by the effect of melt structure on Mn partitioning, such that apatite only contains
 appreciable Mn when it cannot be readily incorporated in highly polymerised, peraluminous silicate
 melts. Additional variations in Mn partitioning are expected as a function of pressure, temperature, and

and possibly factors such as magmatic volatile content can be tested to a certain extent by considering controls of melt structure/composition on partitioning of elements. A summary of various trends is shown in Figures 5 and 6.

The marked shift of Mn from incompatible to compatible in apatite is not noted for other trace elements, partly because of the ease with which apatite does incorporate a range of commonly

The REEs, for example, are among the most incompatible elements which provide insight into the effects of ionic radius on mineral/melt partitioning. REEs are incorporated onto the two nonequivalent Ca sites in apatite, the coordinated₁ site, and 7-fold

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

Contents in apatite reflect magmatic sources (Belousova et al., 2002), though there are some

exceptions. REE patterns in apatite can be affected by crystallisation of phases such as Xie

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

(Chu et al., 2009; Sha and Chappell, 1999). Eu anomalies, driven by f₇₀ changes, are

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

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

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

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

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

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

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

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

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

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

enrichment of LREE. Some apatites have flat trends, and some have slight enrichment in REE mid

The latter is inconsistent with experimental data; mid-REE (MREE) from Sm to Gd, show slightly

325 elevated partition coefficients compared to light REE (HREE) (Prowatke and Klemme,
326 2006; Watson and Green 1981)

327 are relatively uniform from LREE to HREE. Function of whole rock
328 composition as demonstrated for La, Sm and Lu in Figure 5. Consistencies in values

329 within studies suggest that scatter is due to external effects such as
330 temperature, pressure, presence of volatiles, other aspects of apatite chemistry. There is a

331 general trend of MREE > HREE > LREE, consistent with data from ext
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 > (Figure 5D). 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 in polymerised/silica

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

339 in contrast to the observations of Ahn (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. 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 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

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

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

348 much less control over REE partitioning

Eu and Ce contents of apatite can differ from those of other REE due to changes in valence. Across the dataset, there is only a slight decrease in apatite Ce and Eu content with increasing whole rock SiO_2 and ASI, mirroring trends in other REEs. Partition coefficients for both are broadly comparable independent of any change in melt composition/structure. For some studies there are differences in D_{Ce} and D_{Eu} of up to several orders of magnitude, consistent with control by an external factor such as D_{Ce} and D_{Eu} are generally compatible in apatite.

With increasing fractionation, Y content of apatite increases and Sr content decreases (Figure 6C) as previously noted (Belousova et al., 2002; Chu et al., 2009). Importantly, these changes are independent of any controlled chemistry on either D_{Y} or D_{Sr} . Both Y and Sr are compatible in apatite. Changes in apatite content therefore, represent progressive enrichment of the generally incompatible depletion of Sr, during magmatic fractionation. This is consistent with the suggestion of Belousova et al. (2002) that low Sr in apatites from more evolved rocks due to plagioclase crystallisation. One can gain, trends in Sr and imply that apatite provides a useful probe of magmatic composition.

Figure 6E,F shows how the concentration of Zr in apatite and D_{Zr} vary with extent of polymerisation. Zr is, like Mn, an incompatible element in apatite in systems evolved, however, in contrast to Mn, progressive fractionation does not result in an increase in the partitioning of Zr into apatite, and the element remains incompatible in highly evolved, silica-rich melts. This is likely due to the ability of other accessory minerals to incorporate Zr, zircon. In fact, examination of all trace elements commonly measured in apatite reveals that the behaviour of Mn as a function of melt composition/structure is distinct. Firstly, Mn is a relatively incompatible element in apatite, as opposed to many other typically compatible elements. Secondly, a marked change in melt structure in more evolved systems drives partitioning of Mn into apatite, as the element is not readily incorporated in other phases at the point of apatite crystallisation.

phases, such as magnetite, biotite and amphibole, can incorporate appreciable Mn (Miles et al., 2014), although partitioning of Mn into these apparently not sufficient to fully accommodate reduction in the ability of evolved melts to accommodate Mn at the point of apatite crystallisation.

6. Eu and Ce anomalies in apatite as a probe of magmatic fO₂

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

It is commonly suggested that changes in valence of Eu and Ce should result in changes in $\frac{Eu}{Ce}$, and anomalies in chondrite-normalised concentrations of Eu and Ce in apatite compared. The extent of relative depletion or enrichment can be quantified by calculating concentrations for Eu and Ce based on normalised concentrations of neighbouring REEs expected concentrations of Ce and Eu if both were 100% trivalent. There are several methods for doing this. For example, Eu anomalies (Eu/Eu^*), or ratio of normalised Eu to a calculated Eu content based on trivalent REEs, can be calculated based on the arithmetic mean of chondrite normalised Sm and Co concentration (Eu^*) (Sha and Chappell, 1999)

$$Eu^* = \frac{Sm}{(Sm/Co)} + \frac{Co}{2} \quad [3]$$

or based on a geometric mean of normalised Sm and Nd concentrations (Conrath, 2016)

$$Eu^* = \sqrt{\frac{Sm}{(Sm/Nd)} \times \frac{Nd}{2}} \quad [4]$$

396 Likewise, Ce anomalies can be calculated compared to concentrations of adjacent 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 f0
404 apatite/melt partitioning, and inherited from magmas due to preferential incorporation² of Eu
405 into feldspar (Belousova et al., 2002; Cao et al., 2012a,b, 2009; Ding et al., 2015; Li et al.,
406 2016; Pan and Fleet, 2002; Sha and Chappell, 1999). The Gd³⁺ site and the Gd³⁺ site
407 apatite has ionic radii of 1.18 Å, and 1.06 Å, respectively (Shannon, 1976). Eu³⁺ has radii of 1.12 Å
408 and 1.01 Å in 9-fold and 7-fold coordination, respectively. In contrast, Eu²⁺ is considerably larger,
409 with ionic radii of 1.30 Å and 1.20 Å. Therefore, on the basis of size, Eu³⁺ should be compatible in
410 apatite and Eu²⁺ substitution is rather limited. Under reducing conditions, an increase in the proportion
411 of Eu²⁺ over Eu³⁺ will lower the partition coefficient 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 and is clearly compatible in
414 apatite and melt composition has a minor influence on partitioning. However, Eu anomalies in
415 apatite can also reflect depletion of Eu relative to other REEs inherited from magmatic sources
416 for 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 Ce³⁺ dominates and Ce should behave similarly to other REEs.
419 Under more oxidising conditions Ce is increasingly stabilised as Ce⁴⁺ has an ionic radius very close to

that of Ca (1.196 Å and 107 Å in 9- and 7-fold coordination), and should readily substitute into the apatite structure. Ce is substantially smaller (0.97 Å in 8-fold coordination) and not favoured in 9- or 7-fold coordination. As such, oxidising conditions should result in negative Ce anomalies in normalised apatite REE data. However, although potential control of Fe on Ce valence and partitioning behaviour has been noted in studies of apatite chemistry, explanation of Ce anomalies based on partitioning behaviour is less straightforward. Ce anomalies in normalised apatite REE are typically much smaller than Eu anomalies, and range from slightly negative to slightly positive (e.g. Cao et al., 2012; Mao et al., 2016). Contradictory negative Ce anomalies coupled with negative Eu anomalies have been explained by preferential Ce incorporation in other phases as monazite and allanite (Puchelt and Enmermann 1976). However, despite recent observed negative correlations of Eu and Ce anomalies in apatites (Al., 2019; Zafar et al., 2019), it remains unclear whether Ce anomalies in apatite are an indicator of magmatic Fe. This is in marked contrast to zircon, which preferentially incorporates Ce, leading to marked positive Ce anomalies in zircon under more oxidising conditions (Behar et al., 2002).

6.2. A new procedure for determining REE anomalies in apatite

Examples of trends in normalised apatite REE data are shown in Figure 7. Consistent with previous observations, there are variable, sometimes large, negative Eu anomalies. Ce anomalies are subtle to absent, and range from slightly negative to slightly positive. Quantification of Eu and Ce anomalies using simple calculations based on normalised neighbouring REEs, e.g. equations [3] to [5], is unreliable due to variations in normalised REE trends. For Eu anomalies, the best procedure for calculating depends on the extent of right-tined REE slope and relative enrichment of MREE. This may explain why different procedures are used in the literature. For Ce, the subtleness of any anomalies also necessitates a more robust approach to modelling. Choice 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 REE data based on fitting MREE to HREE data to a logarithmic function. However,
 447 this procedure is unsuitable for fitting apatite REE data as anomalies are calculated here based
 448 on an alternative method of fitting normalised REE3+ data, shown in figure 8. Chondrite
 449 normalised REE concentrations including Ce and Eu are fitted to a polynomial function of the
 450 general form:

$$451 \quad \text{[6]}$$

454 where x is ionic radius (Shannon, 1976). A 6th order polynomial is sufficient to consistently fit all
 455 apatite data here and minimise residuals about 0, although data 4th order polynomial is
 456 sufficient. Eu and Ce* are then calculated based on the fitted function for Eu^{2+} and Ce^{2+} 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, Eu^*/Eu and Ce^*/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 REE individualisation, 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 and doubling 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). As expected, there is
 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 show that
 468 apatites can have small positive and negative anomalies, and that a small proportion of apatites can

have much larger anomalies. Examination of individual datasets demonstrates improvements in quantifying small Ce anomalies using the polynomial fitting method. For example, apatite data from Sun et al. (2020) show flattening in normalised REE concentrations over the REE, a clear, positive Ce anomaly, as identified with the polynomial fitting method. Determination of Ce using an arithmetic mean produces an incorrect negative anomaly. Similarly, determinations of Ce_N/Ce^* for apatite data from Xie et al. (2018b) using an arithmetic mean often imply a negative Ce anomaly for data in which a small positive Ce anomaly is correctly identified using the polynomial method. Given the limited extent of Ce anomalies in normalised apatite REE data, a polynomial approach is preferred for comparing different datasets. However, no fitting method is ideal, and work here clearly demonstrates the importance of ground truthing any method for determining the extent of Ce anomalies.

Eu anomalies in apatite are typically generally negative and more variable. There is good general consistency between methods for determining Eu anomalies (Fig. 9B), although considerable scatter. Examination of individual apatite data against the REE diagram demonstrates that contrasts in the extent of Eu anomalies determined using different methods typically arise from inaccuracies in estimating Eu in samples with non-linear REE trends. Traditional methods result in erroneous calculation of the extent of Eu anomalies for a subset of the data which is detrimental to identification of trends in the broad dataset. This is especially true for calculations using a geometric mean based on Sm and Nd concentrations, where variations in normalised REE concentrations can result in significant errors in calculated Eu concentrations.

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

A number of studies provide data on coexisting zircon. Correlations between relative zircon Ce content and magmatic age have been more robustly demonstrated, and are supported by experimental data (Trail et al., 2012). Therefore, comparison with zircon Ce data allows investigation

of the extent to which magma affects the extent of Ce anomalies in apatite. Comparison is
 made here between reported Ce^{4+}/Ce^{3+} ratios in zircon, calculated from zircon and whole rock data
 Ballard et al. (2002) and . Eu_N/Eu^* data for zircon is compared to .
 Figure 10A demonstrates that Ce^{4+}/Ce^{3+}_{zircon} and Ce_N/Ce^* in apatite are inversely related. This is
 expected based on contrasting compatibility of Ce^{4+} in zircon and apatite. High Ce^{4+}/Ce^{3+}_{zircon} (>400)
 are consistent with Ce_N/Ce^* apatite of 0.98 to 1.0. There is weak linear correlation in data at high
 Ce^{4+}/Ce^{3+}_{zircon} which may imply that small apatite Ce anomalies are only due to scatter about
 zero. Higher $Ce^{Ap}_{anom} > 0.2$, correlate with samples which have low $Ce^{4+}/Ce^{3+}_{zircon} < 200$. There is
 obvious scatter in the data, and magmatic trends recorded by two phases may not strictly be
 comparable as apatite is typically an earlier crystallising phase. Both phases might also record
 progressive changes in fO₂ and both phases do not directly coexist in all samples. Horizontal trends
 in Figure 10A, for example in Xie et al. (2018b) data, probably mask progressive changes in Ce
 anomalies as a function of fO₂ or some other control. Despite this, the observed correlation
 between the datasets is notable. A similar, although weaker, correlation is observed when
 comparing zircon data to Ce anomalies calculated from apatite REE data normalised to whole rock
 REE compositions. This implies that systematic changes in the extent of Ce anomalies in apatite are
 not simply inherited from the magma, but reflect a change in partitioning behaviour. However,
 greater scatter limits use of apatite/whole rock ratios.
 In contrast, Figure 10B demonstrates that there is no relationship between Eu anomalies
 in apatite and zircon. Eu^{2+} incorporation in zircon is unfavourable (Taheri et al., 2012). Therefore,
 under reducing conditions, an increase in the proportion of Eu^{2+} should result in large negative
 Eu anomalies in both zircon and apatite normalized REE data. Again, limitations in this,
 although the clear lack of any correlation, especially considering the relative magnitude of Eu
 anomalies, suggests that other factors control Eu concentrations in apatite. Most likely
 this again emphasises the influence of fO₂ on magmatic crystallisation. This is demonstrated in plots of

Eu_N/Eu_N^{*} (apatite) and Ce_N/Ce_N^{*} (apatite) is a function of whole rock SiO₂ (Figure 11). There is a broad trend in apatite data where increasingly negative Eu anomalies are noted with increasing whole rock SiO₂ above a value of 25.05%. Similar trends are noted if other measures of magmatic fractionation are used, such as A_{St}, as noted by Chu et al. (2009). This is consistent with enhanced feldspar crystallisation and Eu²⁺ depletion in more evolved magmatic systems. In contrast, Ce_N/Ce_N^{*} in apatite shows no dependence on whole rock SiO₂ or other measures of magmatic evolution. Importantly, this suggests that melt structure also has little discernible control on apatite.

6.4. Dependence of the extent of Ce and Eu anomalies in apatite on magmatic fO₂

Eu and Ce anomalies in apatite should be coupled, with reducing conditions resulting in large, negative Eu anomalies which progressively decrease with increasing fO₂. Oxidising conditions resulting in negative Ce anomalies. Valence changes in both Eu and Ce will depend on system in question, and there is a lack of data to show Eu²⁺/Eu³⁺ and Ce³⁺/Ce⁴⁺ vary in apatite as a function of fO₂. Figure 12 gives approximate ranges of valence changes in magmatic systems illustrating that Eu valence changes occur under reducing conditions, and that Ce valence changes occur under oxidising conditions atypical for terrestrial magmas. Negative Eu anomalies for apatite are expected for more reduced magmas, as will dominate in most conditions in terrestrial magmas, so the presence of notable anomalies in most apatite data implies that a small proportion of Eu exists to higher, fO₂ and/or that incorporation of Eu in feldspar is able to drive Eu depletion in magmas over a wide range of magmatic fO₂. Positive Eu anomalies in apatite must reflect magmatic sources rather than any control of apatite on Eu partitioning. Ce is predicted to be stabilised only under very oxidising conditions, as absorption data demonstrate that very small proportions of Ce⁴⁺ in various silicate melts are stabilised above the QFM buffer (Burnham and Berry, 2014; Smythe and Brenan, 2015). The presence of large Ce anomalies in zircon

demonstrates that small changes in proportions of $\text{Ce}^{4+}/\text{Ce}^{3+}$ have a significant effect on zircon REE compositions due to large differences in the compatibility of species to zircon. As an extension of this argument, Ce anomalies in apatite might also be expected over a similar range of $f\text{O}_2$ to zircon. This would reduce the range of magmatic $f\text{O}_2$ for which either Eu and/or Ce anomalies in apatite are predicted based on observations of redox couples in magmas shown in Figure 1. However, the extent of fO₂ driven changes in apatite Ce content will depend on differences in compatibility of Ce^{3+} and Ce^{4+} . As noted by Ballard et al. (2002) there is a large order of magnitude difference in Ce^{3+} and Ce^{4+} partitioning in zircon. The extent of differences in Ce partitioning in apatite can be estimated by comparing experimental partitioning data from Prowatke and Klemme (2006). Capsule design used by Prowatke and Klemme (2006) constrained log $f\text{O}_2$ approximately FMQ log units, corresponding to a $\text{Ce}^{4+}/\text{Ce}^{3+}$ ratio of approximately 0.004, according to melt speciation data of Smythe and Brenan (2015). Apatite/melt Ce partition coefficients from the Prowatke and Klemme (2006) data set are consistent with $D_{\text{apatite/melt}}$ of approximately 10. Their partitioning data for 4+ elements suggests that $D_{\text{apatite/melt}}$ is likely to range from 0.01 to 0.1. As such, although there is a large difference in Ce and Ce⁴⁺ compatibility in apatite, this difference is much smaller than in zircon. Correspondingly, Ce anomalies in apatite are probably smaller and much harder to detect, especially given the low proportions of Ce in terrestrial systems.

Comparison of calculated Ce and Eu anomalies across the entire dataset also demonstrates that simple site and ionic radius arguments fail to explain trends in normalised REE data for apatite (Figure 1). Aside from a few exceptionally metamorphosed Archaean samples, apatites display negative Eu anomalies, likely due to a combination of the effects of magnetite crystallisation of feldspar. This implies that at least a proportion of Fe²⁺ is stable in magmas over a large range of $f\text{O}_2$. The extent of Ce anomalies is significantly less, ranging from 0.8 to 1.2, as opposed to 0.1 for Eu. Despite predictions of negative Ce anomalies, a significant majority of apatites display weak, positive anomalies. Scatter in data at zero cannot be used to simply explain this as an artefact in

the data. Even if all Ce anomalies from 0.92 to 1.08 are discounted there is a clear dominance of small, positive Ce anomalies and absence or larger negative Ce anomalies in oxidised systems. Large, positive Ce anomalies in samples with no Eu anomaly in Figure 13 are from carbonatite hosted apatites, for which Ce anomalies are generally assumed to reflect enrichment in host magmas (Mao et al., 2016). In general, contrary to expectations, apatites simultaneously display negative Eu anomalies and small positive Ce anomalies. In part this may reflect a strong control of magmatic composition on normalised Eu concentrations in apatite. However, predicted negative Ce anomalies in normalised apatite REE data are, generally, not observed.

Contrasting Eu and Ce anomalies in apatite have been documented previously. Puchelt and Emmermann (1976) observed coupled Eu and Ce depletion in apatite, which they assigned to an effect of f_{O₂} and the occurrence of REE-rich phases such as monazite and allanite. The presence of such phases should also result in overall depletion in REE in apatite, coupled to Ce anomalies. However, Ce/Ce* appears to be independent of overall REE concentrations in apatite, suggesting that any effect due to crystallisation of REE-rich phases is of limited importance. Similarly, no correlation between Ce/Ce* and either whole rock or apatite Zr is observed, as might be expected if apatite Ce trends were assigned to crystallisation of preferential Ce depletion from magma. It is more likely that negative Ce anomalies reflect relatively oxidised magmatic systems, and that contradictory Eu anomalies are simply due to preferential incorporation of Eu in plagioclase.

It is feasible that positive Ce anomalies in apatite reflect Ce enrichment in host magmas. To test this, the same polynomial fitting method can be used to quantify the extent of Ce and Eu anomalies in whole rock data. Comparison of apatite and whole rock Ce/Ce* and Eu/Eu* is shown in figure 14 for a subset of data for which corresponding whole rock data is available. For the available dataset, whole rock Ce/Ce* scatter about 1, with some displaying small positive and negative anomalies. This contrasts with apatite data, and there is no clear dependence of apatite Ce on whole rock

composition. Apatite and whole rock Eu by contrast, show a reasonable correlation. Both typically show negative Eu anomalies, consistent with a control of feldspar fractionation on magmatic composition, although Eu depletion in apatite is typically larger. While large rock data only gives an approximate measure of magma composition at the point of 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 $\text{Ce}^{4+}/\text{Ce}^{3+}$ and that high zircon $\text{Ce}^{4+}/\text{Ce}^{3+}$ results in negligible Ce anomalies in apatite. Examination of the data 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 currently is used to assess magmatic fO₂.

609

610 7. Mn, Ce and Eu in apatite as an indicator of magmatic fO₂

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 apatite Mn on melt structure, and the proposed oxybarometer of Miles et al. (2014) is unreliable. Experimental studies, and analysis of compositional data from large numbers of sample suites, fail to demonstrate any systematic change in apatite Mn content, or in apatite partitioning, which support an oxybarometer. This is consistent with absorption data from Stokes et al. (2019) and with experimental data on forsterite 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
621 apatite chemistry to determine magma fO₂. 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 felsic
624 systems. This most likely arises due to ready substitution of Eu for Ca, 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 (Coil et al., 2012) if the effects of feldspar crystallisation can be
627 discounted, for example in systems where apatite is a primary crystallising phase, Eu anomalies
628 provide a means of estimating relative changes in fO₂. 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 fO₂.

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 Ce⁴⁺ 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 Ce³⁺ and Ce⁴⁺, while large, is significantly smaller than is that of
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 large 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

644 zircon Ce data does suggest that there is some control of f_O on apatite Ce content. However,
645 the limited extent of Ce anomalies in natural apatite largely limits application as a
646 oxybarometer, and the control of REE behaviour in apatite remains unexplained. Although
647 apatite composition provides a useful record of the chemical characteristics of the magma from which it
648 crystallised it provides, at best, an unreliable indicator of the oxidation state of magmas.

649

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653

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	Arcadia-related granitoids, New Brunswick, Canada
Belousova et al., 2002	Metastudy: granite, larvikite, dolerite, carbonatite, Iron ore deposits, Iherzolite	Metastudy: various
Birski et al., 2019a	Nakhlite meteorites (Martian)	NWA 10153 and NWA 10645 Martian meteorites
Birski et al., 2019b	Phosphates: cherts, BIFs, silicified felsic volcanoclastics, igneous derived detrital apatites	Barberton greenstone belt, Kapvaal Craton, S. Africa.
Bruand et al., 2014	Granites; apatite, granodiorite	Rogart and Strontian plutons, N Highlands, Scotland.
Bruand et al., 2020	Various granitoids	Various Archaean granitoids, plus comparative Phanerozoic granitoids
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 porphyry, S. Gangdese Belt, S. Tibet
Chu et al., 2009	Suite of rocks, categorised as type granite type granites and adakites	Trashimalayan igneous plutonic suite, Tibet
Duan et al., 2019	Granodiorites	Wushan granitoid, Middle Yangtze Metallogenic Belt, and Zhuxiling granitoids, Dabangnan Orogenic Belt, E. China.
Fabrizio et al., 2019	Volcanic despoits: granular, leucocratic, lithic breccia (ital)	Colli Albani Volcanic District, Central Italy
Hoskin et al., 2000	Zoned pluton: adamellite, granodiorite, diorite, quartz monzodiorite and aplite	Boggy Plain pluton, E. Australia
Kogarko, 2018	Ijoliteurtite; peralkaline intrusions	Khibina alkaline complex, Kola Peninsula, Russia
Miles et al., 2013	Granodiorites, granite	Criffell pluton, S. Scotland
Qu et al., 2019, 2020	Metastudy: various (igneous and metamorphosed igneous derived apatite only)	Metastudy: various
Qian et al., 2019	Mineralised granodiorite	S. Anhui Province, China
Qu et al., 2019	I-type granite	#8, China
Richards et al., 2017	Broad range of igneous intrusions associated with IOCG and porphyry deposits (Cu mineralisation)	Mesozoic Coastal Cordillera, N. Chile
Sha and Chappell, 1999	I-type and S-type granites	Lachlan Fold Belt, SE Australia

Sun et al., 2020	Monzonitic mafic enclaves and host granites	Qianjia pluton, Hainan Island, China
Wang et al., 2019	Carbonatite veins associated with aegirine syenite	Weishan carbonatite, Shandong province, E. China
F. Xie et al., 2018a	Quartz diorite porphyries	Xiongcuo district, southern Gangdese porphyry Cu belt, Tibet
F. Xie et al., 2018b	Granite porphyry, granodiorite, granodiorite porphyry, monzonite	S. Lhasa subterranean, Tibet
J. Xie et al., 2018	Monzodiorite, granodiorite	Tongling region, E. China
Xie et al., 2019	Granodiorites (porphyries) (peraluminous 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 orogenic belt, NW China
Zirner et al., 2015	Granodiorite, augite syenites, monzonites, phonolites, pulaskite, apatite	Ilímaussaq complex, S. Greenland
Zhang et al., 2020	Granite, monzodiorite; quartz diorite, granodiorite and diorite; minor mafic intrusions	Yunmengshan, Fangshan, Tiantangzhai, Dabie, and Shicheng intrusions, North China Craton
Apatite-melt Mn partitioning data: experimental studies		
Danni et al., 2001	Analogue Shergotty (Martian) meteorite system (water-free, halogen-free)	Phase equilibria (high melt fraction, fixed pressure/temperature/ fO_2)
Stokes et al., 2019	Basaltic andesite to rhyolitic melt compositions saturated with apatite	Apatite-melt Mn partitioning at fixed pressure/temperature/ fO_2
Vander Auwera et al., 1998	natural jotunite starting composition: accessory apatite with low fraction melt	Phase equilibria at fixed pressure/temperature, some fO_2 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 total Fe as Fe²⁺ and Fe as Fe³⁺
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.
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
879 data, or melt compositions for experimental studies), and B. whole rock (or melt for experimental
880 studies) SiO₂ 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 of
884 whole rock or melt A. ASI, B. SiO₂ content (by weight), and C. NBO/T.

885

886 Figure 4. Dependence of apatite Mn content on: A. degree of iron reduction (defined from chemistry of other
887 phases (see references for detail) or as constrained in experiments; larger data points are those
888 by Miles et al. (2013) to constrain their oxybarometer (solid line) in B. (Eu/Eu*) zircon,
889 i.e. calculated Eu anomaly compared to general REE trend in chondritised data, defined as
890 $(Eu/Eu^*) = \frac{Eu}{Eu^*}$, where Eu^* is the chondrite normalised concentration of Eu; C.

891 Calculated $\text{Ce}^{3+}/\text{Ce}^{4+}$ 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 (normalised) of key
895 REE as a function of NBO/T (A,D), whole rock (B,E) and ASI (C,F).

896

897 Figure 6. Variations in concentrations of various trace elements in apatite with NBO/T (from whole
898 rock data) and whole rock (SiO₂ 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 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. Branch et al. (2020)
905 is data from Th-hosted apatite showing reverse pattern of LREE depletion relative to HREE, MREE
906 and data from Xie et al. (2019) 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 granodiorite-hosted apatite showing a
909 flat REE pattern with negative Eu anomaly and small positive Ce anomaly. Borski et al. (2019)
910 data is from apatite in altered volcaniclastic sediment from the Barbeton Greenstone belt,
911 showing MREE enrichment and no negative Eu anomaly.

912

913 Figure 8. Procedure for normalising 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. Figure 8 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 [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
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 f (Srnreiber, 1987) relative to the IW-F(Fe) 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

938