Accessory mineral constraints on crustal evolution: elemental fingerprints for magma discrimination

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Abstract

Somewhat less explored accessory minerals such as titanite and apatite have the potential to give insights into the petrogenesis of their host rock. Their trace element and REE-rich chemistries carry a record of crystallisation history and chemical characteristics of their source. The robust nature of these phases make them ideal candidates to extract such information from Archean rocks that have usually been affected by secondary processes (metamorphism, deformation, hydrothermal activity). Moreover, they are resistant to erosion during multiple sedimentary cycles which makes them ideal to reconstruct the history of long-eroded continental landmasses. Here we report new trace element data on apatite and titanite from granitoids of different Archean cratons and comparative granitoids from the Phanerozoic. Trace elements signatures of both minerals reveal chemical systematics in Y, LREE and Sr contents related to the nature of the host magma, which are used to construct discrimination diagrams delineating Archean TTGs from sanukitoids, and modern adakites from S/I-type granites.

1. Introduction

Rare earth element (REE) bearing minerals have been used widely to date geological events and to understand magmatic petrogenesis. Their ability also to incorporate a range of trace elements in addition to REE make them extremely useful to track geological processes. In the last decade, most studies on accessory minerals have focused on zircon (e.g. U-Pb, Hf isotopes, O isotopes, trace elements), but the development of in-situ techniques has allowed other phases to be dated (e.g. monazite, Parrish 1990, apatite, Chew et al. 2011), thus providing additional chronological constraints on host rock history. However, despite the impressive number of studies on accessory minerals available today (see Nasdala et al. 2017), knowledge of the behaviour of trace elements within accessory minerals in rocks that make up the continental crust is still limited. The few contributions focusing on less-studied REE-bearing minerals (e.g. apatite and titanite) have shown that trace element concentrations retain considerable information relevant to petrogenesis and provenance. In experimental work focusing on metaluminous compositions, Protwake and Klemme (2005, 2006) have
suggested that REE and other trace elements are sensitive to melt evolution. Others (e.g. Belousova et al. 2002; Chu et al. 2009; Jennings et al. 2011; Bruand et al. 2014) have shown that accessory mineral chemistry provides useful information about petrogenetic process and can closely reflect parent magma composition. Recent publications based on a small number of samples (Bruand et al. 2016; 2017; 2019) have shown that apatite and titanite trace element chemistry and isotope systematics have the potential to discriminate different granite trace element types relevant to the ongoing debate about secular evolution of the early Earth and the onset of modern plate tectonics. For this contribution, we have studied the chemical signatures of accessory minerals in a range of granitoids through time, from a relatively hot Archaean Earth producing «tonalites-trondjhemites-granodiorites» (TTG) toward a cooler modern Earth producing plutonic equivalents of the calc-alkaline series (basalt-andesite-dacite-rhyolite – BADR), via the Neoarchean – Palaeoproterozoic transition to modern tectonics signalled by sanukitoids and related rocks. We demonstrate that their trace element signatures can be used to discriminate between critical magma types and can be robust with respect to metamorphism. We then discuss the causes of consistent differences in accessory mineral chemistry and implications of their robust discrimination for studies of historical evolution of continental crust, for example quantitative source apportionment within mixed-provenance samples provided by the sedimentary cycle (in the manner of detrital zircons).

2. Granite samples and their crustal evolution context

The granitoid record (Fig. 1) has evolved from TTGs throughout the Archean, the products of partial melting of basaltic composition mafic crust, via sanukitoids and related rocks in the Neoarchean and Palaeoproterozoic that carry the signature of a nascent mantle wedge, towards granodiorites and granites with arc magma compositions (the plutonic equivalents of BADR) plus the typical products of crustal differentiation (S-type granites). Many fundamental questions remain regarding the geodynamics of the early Earth, the growth of the continental crust and the transition to subduction-driven tectonics, some of which may be addressed with a more complete understanding of timings and proportions of granitoid magma genesis. Here we present new geochemical data on titanite and apatite from granitoids selected from this overall temporal progression (i) Archean TTG from three different cratons (Slave Province, Karelia and Kaapvaal), (ii) sanukitoids from the Karelia and Kaapvaal cratons, (iii) Neoproterozoic calc-alkaline granitoids from Guernsey (UK Channel Islands) in the Armorican terrane. In addition to these, we have included likely Phanerozoic equivalents to test the impact of metamorphism on their older counterparts: TTG-like (adakites from Antarctica) and sanukitoid-like (high Ba-Sr granites from Caledonian Scotland). Detailed sample descriptions, geological settings and whole-rock compositions can be found in Supplementary Information.
3. Results

LA-ICPMS chemical data and related analytical protocols obtained are described in Supplementary Information. After initial data interrogation using principal component analysis (PCA), REEs, Y and Sr were found to be most effective for discriminating magma type, so these results are presented and discussed below.

3.1. Apatite chemistry

Chondrite-normalized REE patterns of apatite from all studied samples are plotted on Figure 2A-E. TTG samples (Fig. 2A) are characterized by a systematic depletion in light REE (LREE) relative to heavy REE (HREE) usually with a significant negative Eu anomaly. The most depleted patterns tend to have a less pronounced to absent Eu anomaly and significant middle REE (MREE) fractionation from HREE. Adakite (TTG-like) apatites (Fig. 2B) have a relatively flat LREE pattern with slightly lower HREE and a significant Eu anomaly. Typical BADR REE patterns (Fig. 2C) show higher LREE content with strong enrichment compared to the HREE, with moderate negative Eu anomalies. Similarly, sanukitoids and high Ba-Sr granite REE patterns (Fig. 2 D-E) reveal a general enrichment in LREE relative to HREE usually with moderate negative Eu anomalies. In the high Ba-Sr group, the most mafic samples often lack Eu anomalies.

Following the PCA procedure, a 10*Sr-LREE-10*Y discrimination diagram was constructed (Fig. 3A). Apatite from TTG and TTG-like granitoids are clearly distinguishable from other granite types, defining a distinct cluster towards the 10*Y corner. On the other hand, sanukitoids, sanukitoid-like and BADR samples are characterized by higher LREE and Sr contents and thus form a separate field towards that baseline. Similarly, a LaN/SmN versus Y diagram (Fig. 4A) highlights a strong compositional difference. TTG and TTG-like apatites are Y rich (up to 4566 ppm) with low LaN/SmN (< 3), while sanukitoid, high Ba-Sr granite and BADR apatites define a field poor in Y (<1000 ppm) and with (La/Sm)N up to 19.

3.2. Titanite chemistry

REE patterns of titanite from the studied samples are presented in figure 2G-J, although titanite is not present in all studied samples (see supplementary information). There are many similarities with those for apatite (Fig. 2A-E). Titanites from one TTG sample (Fig. 2G) are characterized by pronounced LREE depletion relative to HREE. In contrast with apatite, the patterns have variable, usually large Eu anomalies, generally negative for those with higher
total REE, positive for lower total REE. Titanite from sanukitoids and high Ba-Sr granites (Fig.
2H-I) show strong enrichment of LREE relative to HREE, usually with a convex-upward LREE
section and a significant negative Eu anomaly. A few sanukitoid titanites in each of the samples
studied have steep downward LREE slopes and/or a positive Eu anomaly (Fig. 2H). The BADR
REE patterns (Fig. 2J) are closely comparable with the high Ba-Sr samples, but can be
separated into two groups that are sample specific. Sample EG-07 titanites have convex-
upward LREE and a negative Eu anomaly while one from sample BD-02 has continually
decreasing LREE with no Eu anomaly (Fig. 2J, Appendix A.1).

Using a similar trivariate diagram to apatite (Fig. 3B, but note the different Sr multiplier),
TTG titanite compositions may be discriminated from all other samples, which themselves
overlap – as for apatite. Titanite from TTG define an end member with high Y and low Sr and
LREE contents relative to sanukitoids and BADR samples.

4. Discussion

The temporal evolution of granitoids has been well established (Fig. 1, see also Moyen and
Martin 2012 for review). TTGs can be discriminated on the basis of several whole-rock
chemical indicators, the most obvious of which is strong HREE depletion (Fig.2F). The present
study has also shown systematic differences in TTG apatite and TTG titanite compositions
relative to sanukitoids and post-Archean granitoids (Figs 2-3), in particular higher Y and HREE
contents with low La\textsubscript{N}/Sm\textsubscript{N} ratio (Fig. 2, 4A). Intriguingly, this is opposite to the whole-rock
discrimination (Fig. 2F). In the following text, we attempt to rationalise such observations in
terms of possible controls on apatite and titanite chemistry, and in the light of current literature.

4.1 Effects of metamorphism and/or deformation

Most Archean rocks have been affected by metamorphism and deformation, so there is the
obvious possibility that accessory mineral chemistry has been modified, whereby magmatic
crystal-liquid equilibration gives way to metamorphic mineralogical control. The few studies
available (e.g. Bea and Montero 1999; Garber et al. 2017) describe lithologies (metapelites or
orthogneisses) that are very different from our samples. Therefore, in order to test the
robustness of magmatic signatures, we have analysed Phanerozoic equivalents of TTG
(adakite) and sanukitoid (high Ba-Sr granites), unaffected by any metamorphic event. Their
chondrite-normalized REE patterns correspond closely to the Archean equivalents (Fig. 2) and
overlap the relevant fields on the discrimination diagrams above (Fig. 3, Fig. 4A).

A few TTG apatite patterns show extreme depletion in LREE with no Eu anomaly (Fig
2A). Recent work by Antoine et al. (submitted) on apatite inclusions armoured within TTG
zircons have the same signature as our most enriched patterns while matrix apatites can also display strong LREE-depletion. This can be explained petrographically, by the observed association of secondary allanite and apatite. The highly LREE-depleted group is therefore interpreted to result from high grade metamorphism, such that typical metamorphic apatite has reduced La<sub>N</sub>/Sm<sub>N</sub> but retains original HREE signatures.

4.2 Effects of whole-rock composition

The systematic chemical differences between the accessory mineral groups studied here, from different types of granitoid, strongly suggest that bulk rock character exerts strong control.

4.2.1 The influence of whole rock SiO<sub>2</sub>

Partition coefficient studies have shown that the magmatic incorporation of REE in apatite and titanite increases with SiO<sub>2</sub> (Prowatke and Klemme 2006a,b). TTGs studied herein vary between 65 wt% and 74 wt% SiO<sub>2</sub>, the other granitoids range between 53 and 77 wt%. Within the former, apatite and titanite total REE contents do not systematically increase with SiO<sub>2</sub> (Appendix A.1). Furthermore, sanukitoid or BADR samples with similar SiO<sub>2</sub>WR have apatite and titanite characterised by comparatively higher LREE and lower HREE. Such systematic differences are therefore not controlled simply by silica content.

4.2.2 The influence of Alumina Saturation Index (ASI).

The striking dichotomy in the TTG between LREE depletion in the accessory minerals and LREE enrichment in whole rocks suggests that another LREE-bearing phase is required for mass balance. Likely contenders would be allanite and monazite, but since these are also common in many other granitoid types, this is unlikely to be the sole explanation.

Figure 4A includes literature data (Sha and Chappell 1999; Belousova et al. 2001; Miles et al. 2013), and highlights the presence of two distinct groups of apatite that are strongly dependent on ASI. ASI < 1 samples (metaluminous) correspond to our sanukitoids-BADR apatites (Group 1), whereas peraluminous samples (ASI >1) have a comparable chemical signature to TTG apatites (low LREE and high HREE-Y, Group 2). This corroborates previous studies on apatite (Harrison and Watson 1984; Pichavant et al. 1992) and monazite (Montel 1986) solubilities, which suggest that apatite solubility increases with ASI and (to a lesser extent) with SiO<sub>2</sub> in metaluminous magmas. Conversely, Montel (1986) has shown that monazite solubility decreases as ASI increases. Therefore, in peraluminous compositions early monazite will
strongly partition LREE with the remaining melt relatively enriched in HREE and Y, which will
be incorporated by later apatite and titanite.

Interestingly, apatites from two metaluminous samples are Y-rich and LREE poor (Fig.
4A), which is inconsistent with the general trend. These exceptions have the highest SiO$_2$
content (>73 wt%), a phenomenon also described by Sha and Chappell (1999). High melt SiO$_2$
content increases apatite solubility (Harrison and Watson 1984) and therefore delays its
saturation. Consequently, apatite may grow late, allowing early LREE phases (monazite and/or
allanite) to incorporate most of the LREE.

4.2.3 Other variables

We have shown above that aluminosity and consequent timing of mineral saturation is a first
order control. However, our TTG apatite compositions have systematically even lower LREE
concentrations than published data for peraluminous rocks (Fig. 4A) so other variables must
also be important. For example, previous authors have inferred that differences in magmatic
apatite composition could be related to magma fO$_2$ (Sha and Chappell 1999; Belousova et al.
2001). It remains unclear whether this is linked to TTG source parameters (e.g. composition,
fO$_2$, temperature, H$_2$O-saturated or undersaturated melting) or is another effect of co-
crystallising accessory phases. Experimental constraints are currently lacking.

4.2.4 The significance of Sr

In this section, we rationalise the utility of Sr concentration in apatite and titanite, in association
with REEs to discriminate magma type. Previous work has distinguished high-pressure TTG,
corresponding to a deep source in equilibrium with garnet and rutile but no plagioclase, from
low-pressure TTG consistent with residual plagioclase. As a direct consequence of residual
mineralogy, HP-TTG have low HREE, Nb and Ta and high Sr while LP-TTG show the opposite
signature for comparable bulk compositions. Previous authors (Belousova et al. 2001;
Jennings et al. 2011; Bruand et al. 2014) have shown a strong correlation between Sr in apatite
and in the corresponding whole-rock. Accordingly, in our apatite dataset, two TTG and our
adakite samples that have typical HP-TTG signature have systematic higher Sr concentrations
than the others that have MP-LP TTG signature (Fig. 4C). Figure 4C also shows that the HP-
TTG apatites have lower Y (and by analogy, HREE). All these observations confirm that apatite
Sr content can allow discrimination between HP and LP TTG.

4.4 Implications for historical evolution of continental crust
The preservation of magmatic trace element signatures in apatite and titanite from metamorphosed terranes provides a new methodology to reconstruct their magmatic history. In addition, the ability to distinguish parent magma type encourages application to the detrital mineral record. Voluminous data exist from zircons, but the results described above promise much tighter constraints on parent rock identity, thus providing vital access to the primary history of old eroded terranes and helping to reconstruct the parameters of the historical evolution of continental crust from the early Earth to the present day.

Figure Captions

Fig. 1 Cartoon of continental crust evolution, from TTG and sanukitoid in the Archean towards typical arc magma in the Phanerozoic, plus samples studied in this contribution.

Fig. 2 Chondrite-normalised REE patterns for apatite (A-E) and titanite (G-J). F is modified after Moyen and Martin (2012).

Fig. 3 Ternary discrimination diagrams; 10*Sr-LREE-10*Y for apatite and 100*Sr-LREE-10*Y for titanite.

Fig. 4 Apatite compositions: A - La vs Y diagram discriminating 2 groups of apatite, B - LaN/SmN vs ASI (nAl/(nCa-3.33*nP)+nNa+nK)), discriminating peraluminous from metaluminous compositions and C - Sr vs Y, discriminating HP- and LP-TTG magmas.

References

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