

# An apatite for progress: Inclusions in zircon and titanite constrain petrogenesis and provenance

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## ABSTRACT

**Apatite has recently gained considerable attention as a mineral with many uses within the Earth and planetary sciences. Apatite chemistry has recently given new insight into a wide range of geological processes and tools, for example, magmatism, metasomatism, planetary geochemistry, and geochronology. We expand the utility of apatite here by presenting a novel way to fingerprint magma chemistry and petrogenesis using apatite inclusions within robust titanite and zircon. We present trace element data from apatite mineral inclusions shielded within magmatic zircon and titanite. Importantly, apatite inclusion and host titanite chemistries detailed in this study allow estimation of the whole-rock Sr and SiO<sub>2</sub>. We show how these data can be used to assess the degree of fractionation of the host magma and to calculate key trace element abundances and ratios. We demonstrate that the inclusions can be linked to discrete periods in the crystallization history of the host phases, thus providing insight into petrogenesis. The results highlight that apatite compositions might discriminate modern granitoids (younger than 2.5 Ga) from Archean–Proterozoic transitional granitoid compositions (sanukitoid signatures). Development of such a petrological tool has important potential for interpretation of provenance and a better understanding of the secular evolution of the continental crust, including that of early Earth.**

## INTRODUCTION

Detrital zircons have revolutionized how we study the evolution of the continental crust, through in situ analysis of U–Pb, Hf, and O isotopes (e.g., Kemp et al., 2009). The robust nature of detrital zircon in sediments means that we can access global records of the continental crust through most of Earth's history with confidence that the data are meaningful and relate to the parental magmas from which the zircons crystallized. However, while these data can provide excellent constraints on the longer scale differentiation of the crust and mantle, plus intracrustal reworking of previously formed crust (e.g., Kemp et al., 2009; Collins et al., 2011), they have not proved promising at giving insights into magma petrogenesis (Hoskin and Ireland, 2000; Coogan and Hinton, 2006; Bruand et al., 2014). Another widespread mineral is required, and apatite is an ideal candidate.

Apatite has recently been the focus of several reviews describing its importance for a better understanding of Earth and moon geological processes (e.g., Webster and Piccoli, 2015; McCubbin and Jones, 2015). Apatite is ubiquitous in magmatic rocks and is able to incorporate more than half of the periodic table, including rare earth elements (REEs) and other important trace elements (e.g., vanadium and strontium). Apatite and other accessory minerals (e.g., zircon, titanite, allanite) represent a low modal proportion of igneous rocks but often dominate the REE budget, and are therefore important in petrogenetic studies. Apatite and titanite are minerals for which trace element partition coefficients have been better characterized and have been shown to be sensitive to changes in magma composition (Prowatke and Klemme, 2005, 2006). Therefore, trace element work on these minerals can be particularly informative (e.g., Hoskin et al., 2000; Belousova et al., 2002; Chu et al., 2009; Jennings et al., 2011; Bruand et al., 2014). Accessory minerals are also used widely to discriminate and record sandstone provenance (e.g., Mange and Maurer, 1992). Recently, detrital apatite has been successfully dated using U–Pb geochro-

nology (e.g., Chew and Donelick, 2012); unfortunately, acidic groundwater, weathering, and limited mechanical stability during sediment transport can adversely affect its preservation in the sediment record, and the lack of a comprehensive database of apatite and titanite chemistries to date limits useful provenance interpretation (Morton and Hallsworth, 2007). A novel way to look at apatite in the sedimentary record would be to analyze apatite inclusions armored in zircon. Indeed, apatite inclusions within zircon have recently been shown to give insight into some elements of the whole-rock chemistry of a granite (Darling et al., 2009; Jennings et al., 2011). This study builds on such work by showing that trace element analysis of apatite inclusions within zircon and titanite can give access to (1) useful constraints on magmatic history, and (2) the whole-rock chemistry of their host magmas. Associated with recent methods of zircon analysis (e.g., Kemp et al., 2009; Collins et al., 2011; Cawood et al., 2012), this provides a novel way to elucidate the tectonic environment within which the magmas were formed, to be preserved after erosion as accumulations of detrital sediments. As the host minerals can be dated and their isotopic compositions analyzed (Hf + O for zircon or Nd + O for titanite), the combined petrogenetic and provenance approach from this study using trace elements will offer the opportunity to investigate magmatic processes in areas where the parental rocks are not exposed for study or have been entirely eroded or reworked by later processes. In turn, this could contribute to a better understanding of the tectonic evolution of Earth's continental crust, and particularly into the vexing issue of early Earth via the sparse Paleoproterozoic to Hadean detrital zircon record.

## SAMPLES AND METHODS

The samples studied were selected from a suite of late Caledonian plutons from the northern Highlands of Scotland (Fowler et al., 2008). Specifically, samples were collected from the Strontian and Rogart plutons, which are thought to derive from variably enriched subcontinental lithospheric mantle, and range in composition from granodiorite to granite; the whole-rock chemistry as well as their O, Sr, and Nd isotopic characteristics were described by Fowler et al. (2001, 2008). The subject plutons are high Ba–Sr granites, chosen for their similarity to sanukitoids (Fowler and Rollinson, 2012), the sudden appearance of which at the Archean–Proterozoic transition reflects major changes in early Earth geodynamics (Martin et al., 2005).

Images of apatite inclusions within titanite and zircon were generated by backscattered electron and cathodoluminescence techniques using a scanning electron microscope (Fig. DR1 in the GSA Data Repository<sup>1</sup>; discussed in the following) and trace elements of these inclusions were analyzed using a Cameca IMS 4f ion microprobe at the University of Edinburgh, Scotland. Additional apatite inclusions in zircons from sanukitoids in the Karelian province (Heilimo et al., 2013) were analyzed using a Cameca SX100 electron microprobe at the University of Bristol, UK (Tables

<sup>1</sup>GSA Data Repository item 2016023, Item DR1 (sample coordinates and analytical techniques description), Figure DR1 (pictures of apatite inclusions and host minerals), Figure DR2 (inclusions in zircon–titanite versus rock matrix), Figure DR3 (correlations between matrix apatite and apatite inclusions from Rogart and Strontian localities), Table DR1 (analyses of apatite inclusions compositions), Table DR2 (analyses of host titanite compositions obtained by LA–ICP–MS), and Table DR3 (statistical values for Figure 1 regression lines), is available online at [www.geosociety.org/pubs/ft2016.htm](http://www.geosociety.org/pubs/ft2016.htm), or on request from [editing@geosociety.org](mailto:editing@geosociety.org) or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

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DR1–DR3 in the Data Repository). Trace elements of titanite, zircon, and apatite from the rock matrix were analyzed by laser ablation–inductively coupled plasma–mass spectrometry at the University of Portsmouth, UK and the data set is available in Bruand et al. (2014) and in Table DR2. (Full details of the analytical techniques are provided in Item DR1.)

## RESULTS

### Apatite Inclusions versus Apatite in Matrix and Whole-Rock Compositions

Strontium is homogeneously distributed in all apatites studied herein; no zoning has been detected. The strontium content in apatite ( $Sr_{ap}$ ) has been shown to be a function of plagioclase fractionation during magmatic differentiation (Belousova et al., 2002). Jennings et al. (2011) suggested, based on a set of granitoids from Dronning Maud Land (Antarctica), that (1) the Sr content and Ce/Y of apatite inclusions within zircon seemed to correlate with that of apatite in the matrix, and (2) Sr concentrations in apatite matrix or apatite inclusions correlate with Sr in the whole rock. In Figure 1A, we demonstrate that not only are apatite inclusions in zircon consistent with the latter, but so are apatite inclusions within titanite (Fig. 1A; Fig. DR2). One whole-rock sample that plots significantly off the correlation line has been heavily altered (RHG1), and this is discussed further in the following.

### Apatite Inclusions and Host Titanite

As with apatite, Sr content in titanite is homogeneously distributed, with  $Sr_{ap}$  being ~10 /times higher than host titanites (Fig. 1B). Significantly, matrix compositions of apatite and titanite plot on the same correlation (Fig. 1B). Therefore, following the correlation in Figure 1A, Sr in titanite increases with whole-rock content and can also be used to monitor whole-rock Sr content.

The Sr content of whole-rock sample RHG1 is considerably lower than that of the general trend (Fig. 1A). Significant alteration of feldspar in this

sample suggests that whole-rock Sr concentrations have been disturbed. Importantly, both minerals (titanite and apatite) plot on the single correlation in Figure 1B, confirming that these accessory minerals preserve the original whole-rock Sr signature even after the whole rock has undergone alteration.

### Apatite Inclusions versus Zonation in Matrix Apatite and Titanite

New results presented here (Fig. DR2; Tables DR1 and DR2) confirm that average Sr and Ce/Y ratios of apatite in inclusions correlate with apatites in the rock matrix (Jennings et al., 2011). However, systematic variability of REE content from core to rim is also preserved, and may retain useful petrogenetic information. To better understand such variation in apatite chemistry, the following description is organized by sample locality. It is notable that, at both localities, the homogeneous composition of zircon does not permit similar interpretation and confirms that zircon trace element chemistry is not sensitive enough to evolving magmatic conditions in most cases (e.g., Hoskin and Ireland, 2000; Bruand et al., 2014), at least within the resolution of the techniques used in this study.

### Strontian, Southwest Northern Highlands

In the matrix apatites of samples SR1, SR3, and SR4, two groups of REE analyses can be distinguished: one corresponds to core compositions and the other represents rims (see Fig. 2; Fig. DR3; Bruand et al., 2014). The  $\Sigma$ REE content decreases abruptly between core and rim. Apatite inclusions in zircon and titanite cores have a core composition signature, and apatite inclusions with a rim composition signature are found in titanite rims and (more rarely) in zircons (Fig. 2B).

Host titanites from Strontian also reveal two groups of apatite data, corresponding to cores and rims (Fig. 2; Fig. DR3). The rims imply a significant late change in the chemistry of the crystallizing minerals, previously interpreted as the result of mixing with the local mafic component in the area (Fig. 2A; Bruand et al., 2014). At Strontian, mixing and mingling features are preserved at the outcrop scale between the granitoids

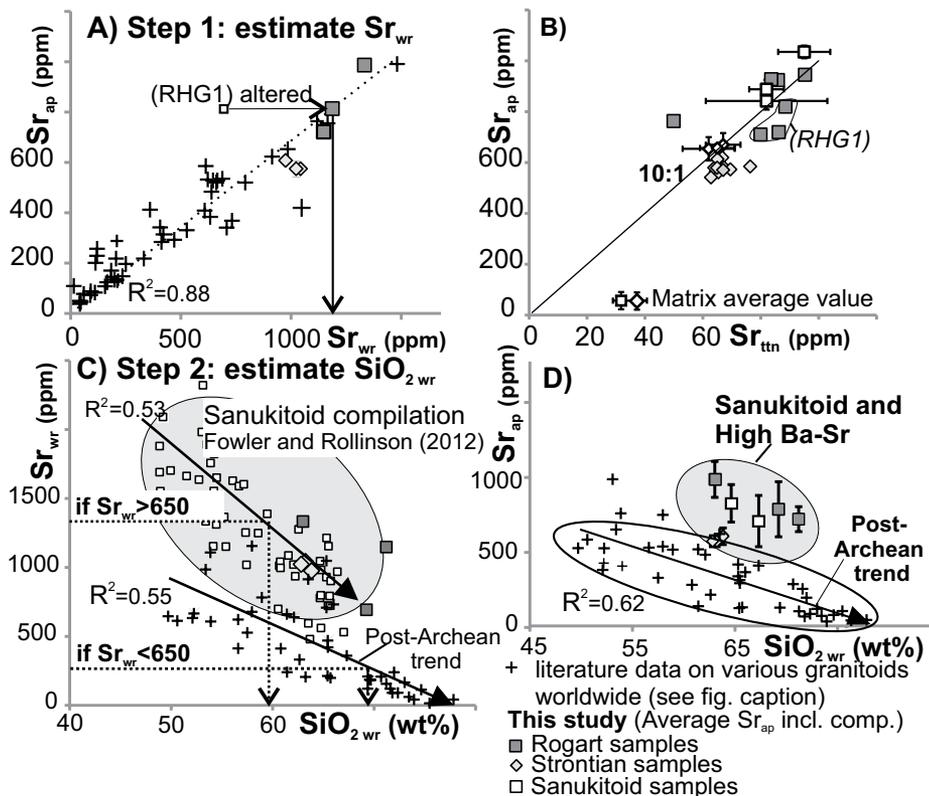
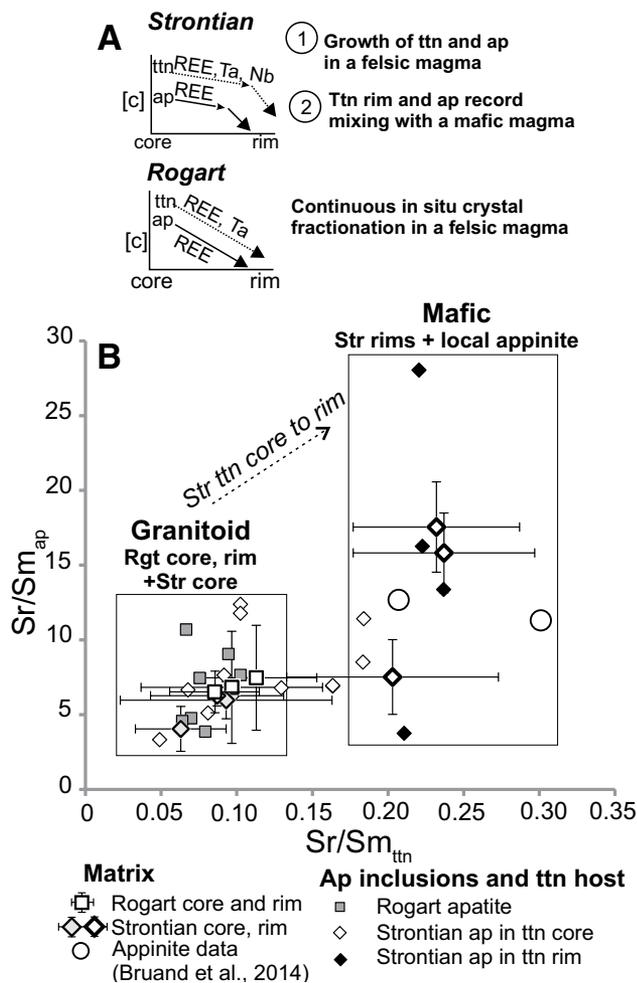


Figure 1. A: Strontium content in apatite ( $Sr_{ap}$ ) inclusions (incl. average compositions (comp.) versus  $Sr_{wr}$  (wr—whole rock; error bars are  $2\sigma$ ). Available data set on various post-Archean granitoids (crosses; Jennings et al., 2011; Belousova et al., 2002; Chu et al., 2009; Hoskin et al., 2000) has been added to this figure. B:  $Sr_{ap}$ – $Sr_{ttn}$  diagram for Strontian and Rogart apatite (ap) inclusions and titanite (ttn) host compositions. Ap and ttn average compositions from the matrix are also reported ( $2\sigma$  error bars; Bruand et al., 2014; Table DR2 [see footnote 1]). C:  $Sr_{wr}$  versus  $SiO_{2wr}$  with the sanukitoid compilation (Fowler and Rollinson, 2012;  $SiO_{2wr} > 46\%$ ), the studied high Ba-Sr granites (Fowler et al., 2001, 2008), and the post-Archean data set. D:  $Sr_{ap}$  versus  $SiO_{2wr}$  with apatite inclusions in the gray field of the studied high Ba-Sr samples (sanukitoid like,  $2\sigma$  error bars) and two sanukitoids from the Karelian province analyzed by microprobe (Table DR1), and post-Archean apatite data set in the white field. Additional p-values for regression lines (A, C–E) proving their statistical significance can be found in Table DR3.



**Figure 2. Diagram showing petrogenetic processes and discriminating the nature of the magma (felsic versus mafic) using Sr/Sm ratios in apatite (ap) inclusions and host titanites (ttn). For comparison, apatite and titanite average compositions from the matrix have also been reported (error bars are 1 $\sigma$ ; Bruand et al., 2014; Table DR2; see footnote 1). REE—rare earth element; Rgt—Rogart pluton; Str—Strontian pluton.**

and mafic components (so called appinite and synplutonic microdiorite dikes), but these were not recognized using whole-rock chemistry (Fowler et al., 2008).

### Rogart, Northeast Northern Highlands

Such mixing and mingling features are not present at the Rogart localities. REE contents within cores and rims of matrix apatites and titanites overlap and are characterized by a general decrease of REE content toward the edge of the crystal (Fig. 2A; Fig. DR3; Bruand et al., 2014). Data from the inclusions are within the appropriate fields of data for the matrix apatite analyses (Fig. DR3). There is no evidence of distinctive rim compositions.

## DISCUSSION

This new study on apatite inclusions provides a novel and innovative application for provenance studies and the interrogation of the crustal evolution record. These are discussed in the following.

### Petrogenetic Snapshots from Single Grain Analysis

The direct link between apatite inclusion chemistry and different zones of host accessory minerals highlights the potential to reveal significant

petrogenetic detail from analysis of a single grain. Recent constraints of melt compositional influence on mineral-melt partition coefficients (Prowatke and Klemme, 2005, 2006) suggest that the abrupt decrease in REE concentration evident in apatite and titanite rims at Strontian can be interpreted as a consequence of mixing of the granitoid with a mafic component (here appinite or microdiorite) late in the crystallization of Strontian magmas (Fig. 2; Bruand et al., 2014). However, the continuous REE decline in Rogart samples suggests simple in situ crystal fractionation with no late mixing event. These interpretations are illustrated in Figure 2B, using Sr/Sm ratios in both minerals (Sr is homogeneously distributed in the crystals, but Sm shows significantly different partition behavior between mafic and felsic melts for both minerals). The average compositions of matrix apatite and titanite (symbols with standard deviation) plot in the same areas as the coupled apatite inclusion-titanite host data. Results for all Rogart samples (matrix and inclusions) and the apatite inclusions in cores of titanite at Strontian plot in a limited, low Sr/Sm region (granitoid field in Fig. 2). However, the matrix apatite and titanite rims from Strontian plus apatite inclusions found in titanite rims (black diamonds) plot at consistently higher values of Sr/Sm<sub>titanite</sub>, with Sr/Sm<sub>apatite</sub> being considerably more variable. Reported values for appinite matrix grains (white dots) plot in the same area and support the late mafic mixing interpretation for Strontian granitoids (Fig. 2B). Thus, a significant snapshot of crystallization history can be observed with analyses of a single grain of titanite and associated apatite inclusions.

### Accessory Mineral Provenance Signatures

Despite considerable effort and a promising principle with which to work, it has proven difficult to back-calculate magma composition using zircon chemistry (Hoskin and Ireland, 2000). However, the demonstration here, that Sr<sub>ap</sub> and Sr<sub>ttn</sub> allow estimation of Sr<sub>wr</sub> (wr—whole rock; Figs. 1A and 1B), lends optimism that estimates with these minerals might be more successful. The correlation of Sr<sub>ap</sub>-Sr<sub>wr</sub> (Fig. 1A) and their relation to whole-rock SiO<sub>2</sub> (Figs. 1C and 1D), also permits a factor with which to estimate SiO<sub>2</sub> (whole rock) from Sr<sub>ap</sub> (after Belousova et al., 2002; Jennings et al., 2011). It is important, however, that samples analyzed in this contribution plot consistently above the trend previously defined using post-Archean granites from the literature (Fig. 1D). Because high Ba-Sr granites are believed to be Phanerozoic equivalents of sanukitoids, this can be understood with reference to sanukitoid data (Fowler and Rollinson, 2012; Fig. 1C). On the Sr<sub>wr</sub>-SiO<sub>2</sub> diagram (Fig. 1C), for a similar SiO<sub>2</sub> range, sanukitoids define a subparallel but Sr-rich trend appropriate to their general chemistry, into which the high Ba-Sr granites of this study comfortably fit (Fig. 1C). More importantly, additional apatite inclusion analyses obtained by microprobe on two sanukitoids (Table DR1) dated at ca. 2.7 Ga (Heilimo et al., 2013) from the Karelian province (Finland; Koitere and Arola localities) plot consistently within the second trend defined by the high Ba-Sr in Figure 1D, confirming the discrimination potential of apatite.

Here we suggest a two-step protocol for the estimation of SiO<sub>2</sub> and Sr of the whole rock and therefore the selection of the appropriate partition coefficient for magmatic REE content.

1. The Sr<sub>ap</sub> and Sr<sub>ttn</sub> composition permits recovery of the primary Sr<sub>wr</sub> even when samples have been altered (Fig. 1A).

2. Based on the Sr<sub>wr</sub> calculated, SiO<sub>2</sub> is estimated using Figure 1C. If Sr<sub>wr</sub> > 650 ppm, the correlation based on sanukitoid compilation is used and if Sr<sub>wr</sub> < 650 ppm, the correlation based on the post-Archean trend is used. The 650 ppm cutoff is based on the Sr<sub>wr</sub> value of the most mafic end member of the post-Archean trend. The Sr<sub>wr</sub> data for the sanukitoid samples are more scattered and could be explained by some alteration, which seems to affect accessory minerals to a lesser extent (Fig. 1A). Estimation of SiO<sub>2</sub> tends to have a higher uncertainty for mafic compositions. It is important to mention that these correlations rely on a compilation of literature data for which the available apatite compositions are averaged

for each sample. The Y content in apatite is another factor that could help to improve our actual cutoff (<650 ppm) in Sr-SiO<sub>2</sub> compositional space, because it correlates with SiO<sub>2</sub><sub>wr</sub> (e.g., Jennings et al., 2010). However, Y<sub>ap</sub> content can vary significantly within a single grain (see Bruand et al., 2014). Therefore, the improvement of these correlations can be achieved in the future by systematic and detailed petrology, imaging the different zones of the studied apatite, and providing precise locations for microanalysis within the apatites.

The use of this discrimination procedure has potential for future whole-rock REE reconstruction and therefore is a useful tool that should be further developed for provenance studies. Following this procedure and using the apatite composition, the closest partition coefficient can be chosen (e.g., Luhr et al., 1984; Prowatke and Klemme, 2005, 2006) and the REEs of the host rock can be thus modeled, as demonstrated in Bruand et al. (2014). A more comprehensive data set on apatite in various granitoids is now needed to implement this potential technique on detrital grains.

### Secular Crustal/Tectonic Evolution and a Window into the Early Earth?

The retention in apatite inclusions of such important chemical information on bulk chemistry and petrogenesis gives a new opportunity to interrogate at the rock record through geological time. Ultimately, U-Pb dating of detrital zircons coupled with trace element analysis of their apatite inclusions could elucidate evolving magmatic styles and their relative volumetric importance over geological time. We prove that apatite inclusions and especially Sr content from sanukitoids (ca. 2.7 Ga; Heilimo et al., 2013) and sanukitoid-like localities (high Ba-Sr granites) record chemical changes consistent with whole-rock data (Fig. 1D). Sanukitoids are important in the magmatic record as they are Archean magmatic rocks originating in the suprasubduction mantle wedge and have been inferred to reflect major geodynamic changes and possibly the beginnings of modern plate tectonics (e.g., Martin et al., 2009). Our new data suggest that there may be considerable merit in using the apatite inclusions within early Earth zircons to provide robust information on the geochemistry of the host magmas.

In turn, this method coupled with isotope data on apatites and the surrounding minerals (U-Pb, Hf, Nd, Sr and O isotopes) could elucidate the tectonic setting of the early Earth crust and test the ongoing debate and models (e.g., Dhuime et al., 2015) on the formation and evolution of the continental crust through time.

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### REFERENCES CITED

Belousova, E.A., Griffin, W.L., O'Reilly, S.Y., and Fisher, N.I., 2002, Apatite as an indicator mineral for mineral exploration: Trace-element compositions and their relationship to host rock type: *Journal of Geochemical Exploration*, v. 76, p. 45–69, doi:10.1016/S0375-6742(02)00204-2.

Bruand, E., Storey, C., and Fowler, M., 2014, Accessory mineral chemistry of high Ba-Sr granites from northern Scotland: Constraints on petrogenesis and records of whole-rock signature: *Journal of Petrology*, v. 55, p. 1619–1651, doi:10.1093/petrology/egu037.

Cawood, P.A., Hawkesworth, C.J., and Dhuime, B., 2012, Detrital zircon and tectonic setting: *Geology*, v. 40, p. 875–878, doi:10.1130/G32945.1.

Chew, D., and Donelick, R., 2012, Combined apatite fission track and U-Pb dating by LA-ICP-MS and its application in apatite provenance analysis, in Sylvester, P., ed., *Quantitative mineralogy and microanalysis of sediments and sedimentary rocks: Mineralogical Association of Canada Short Course 42*, p. 219–247.

Chu, M.F., Wang, K.L., Griffin, W.L., Chung, S.L., O'Reilly, S.Y., Pearson, N.J., and Iizuka, Y., 2009, Apatite composition: Tracing petrogenetic processes in transhimalayan granitoids: *Journal of Petrology*, v. 50, p. 1829–1855, doi:10.1093/petrology/egp054.

Collins, W.J., Belousova, E.A., Kemp, A.I.S., and Murphy, B., 2011, Two contrasting Phanerozoic orogenic systems revealed by hafnium isotope data: *Nature Geoscience*, v. 4, p. 333–337, doi:10.1038/ngeo1127.

Coogan, L.A., and Hinton, R.W., 2006, Do the trace element compositions of detrital zircons require Hadean crust?: *Geology*, v. 34, p. 633–636, doi:10.1130/G22737.1.

Darling, J., Storey, C., and Hawkesworth, C., 2009, Impact melt sheet zircons and their implications for the Hadean crust: *Geology*, v. 37, p. 927–930, doi:10.1130/G30251A.1.

Dhuime, B., Wuestefeld, A., and Hawkesworth, C.J., 2015, Emergence of modern continental crust about 3 billion years ago: *Nature Geoscience*, v. 8, p. 552–555, doi:10.1038/ngeo2466.

Fowler, M., and Rollinson, H., 2012, Phanerozoic sanukitoids from Caledonian Scotland: Implications for Archean subduction: *Geology*, v. 40, p. 1079–1082, doi:10.1130/G33371.1.

Fowler, M.B., Henney, P.J., Darbyshire, D.P.F., and Greenwood, P.B., 2001, Petrogenesis of high Ba-Sr granites: The Rogart pluton, Sutherland: *Journal of the Geological Society [London]*, v. 158, p. 521–534, doi:10.1144/jgs.158.3.521.

Fowler, M.B., Kocks, H., Darbyshire, D.P.F., and Greenwood, P.B., 2008, Petrogenesis of high Ba-Sr plutons from the Northern Highlands terrane of the British Caledonian Province: *Lithos*, v. 105, p. 129–148, doi:10.1016/j.lithos.2008.03.003.

Heilimo, E., Halla, J., Andersen, T., and Huhma, H., 2013, Neoproterozoic crustal recycling and mantle metasomatism: Hf, Nd, Pb, O isotope evidence from sanukitoids of the Fennoscandian shield: *Precambrian Research*, v. 228, p. 250–266, doi:10.1016/j.precamres.2012.01.015.

Hoskin, P.W.O., and Ireland, T.R., 2000, Rare earth element chemistry of zircon and its use as a provenance indicator: *Geology*, v. 28, p. 627–630, doi:10.1130/0091-7613(2000)28<627:REECOZ>2.0.CO;2.

Hoskin, P.W.O., Kinny, P.D., Wyborn, D., and Chappell, B.W., 2000, Identifying accessory mineral saturation during differentiation in granitoid magmas: An integrated approach: *Journal of Petrology*, v. 41, p. 1365–1396, doi:10.1093/petrology/41.9.1365.

Jennings, E.S., Marschall, H.R., Hawkesworth, C.J., and Storey, C.D., 2011, Characterization of magma from inclusions in zircon: Apatite and biotite work well, feldspar less so: *Geology*, v. 39, p. 863–866, doi:10.1130/G32037.1.

Kemp, A.I.S., Hawkesworth, C.J., Collins, W.J., Gray, C.M., Blevin, P.L., and the EIMF, 2009, Isotopic evidence for rapid growth in extensional accretionary orogen: The Tasmanides, eastern Australia: *Earth and Planetary Science Letters*, v. 284, p. 455–466, doi:10.1016/j.epsl.2009.05.011.

Luhr, J.F., Carmichael, I.S.E., and Varekamp, J.C., 1984, The 1982 eruptions of El-Chichon volcano, Chiapas, Mexico—Mineralogy and petrology of the anhydrite-bearing pumices: *Journal of Volcanology and Geothermal Research*, v. 23, p. 69–108, doi:10.1016/0377-0273(84)90057-X.

Mange, M.A., and Maurer, H.F.W., 1992, Heavy minerals in colour: London, Chapman and Hall, 147 p., doi:10.1007/978-94-011-2308-2.

Martin, H., Smithies, R.H., Rapp, R., Moyen, J.F., and Champion, D., 2005, An overview of adakite, tonalite-trondhjemite-granodiorite (TTG), and sanukitoid: Relationships and some implications for crustal evolution: *Lithos*, v. 79, p. 1–24, doi:10.1016/j.lithos.2004.04.048.

Martin, H., Moyen, J.F., and Rapp, R., 2009, The sanukitoid series: Magmatism at the Archean-Proterozoic transition: *Royal Society of Edinburgh Transactions*, v. 100, p. 15–33, doi:10.1017/S1755691009016120.

McCubbin, F.M., and Jones, R.H., 2015, Extraterrestrial apatite: Planetary geochemistry to astrobiology: *Elements*, v. 11, p. 183–188, doi:10.2113/gselements.11.3.183.

Morton, A., and Hallsworth, C., 2007, Stability of detrital heavy minerals during burial diagenesis, in Mange, M., and Wright, D.K., eds., *Heavy minerals in use: Developments in Sedimentology Volume 58: Amsterdam, Elsevier*, p. 215–245, doi:10.1016/S0070-4571(07)58007-6.

Prowatke, S., and Klemme, S., 2005, Effect of melt composition on the partitioning of trace elements between titanite and silicate melt: *Geochimica et Cosmochimica Acta*, v. 69, p. 695–709, doi:10.1016/j.gca.2004.06.037.

Prowatke, S., and Klemme, S., 2006, Trace element partitioning between apatite and silicate melts: *Geochimica et Cosmochimica Acta*, v. 70, p. 4513–4527, doi:10.1016/j.gca.2006.06.162.

Webster, J.D., and Piccoli, P.M., 2015, Magmatic apatite: A powerful yet deceptive mineral: *Elements*, v. 11, p. 177–182, doi:10.2113/gselements.11.3.177.

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