Understanding preservation of primary signatures in apatite by comparing matrix and zircon-hosted crystals from the Eoarchean Acasta Gneiss Complex (Canada)

C. Antoine, Emilie Bruand, Martin Guitreau, Jean-Luc Devidal

To cite this version:
C. Antoine, Emilie Bruand, Martin Guitreau, Jean-Luc Devidal. Understanding preservation of primary signatures in apatite by comparing matrix and zircon-hosted crystals from the Eoarchean Acasta Gneiss Complex (Canada). Geochemistry, Geophysics, Geosystems, AGU and the Geochemical Society, 2020, 10.1029/2020GC008923. hal-02561884

HAL Id: hal-02561884
https://hal.archives-ouvertes.fr/hal-02561884
Submitted on 6 May 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Understanding preservation of primary signatures in apatite by comparing matrix and zircon-hosted crystals from the Eoarchean Acasta Gneiss Complex (Canada)

C. Antoine a,1, E. Bruand a, M. Guitreau a, J-L Devidal a

a Université Clermont Auvergne, CNRS, IRD, OPGC, Laboratoire Magmas et Volcans, F-63000 Clermont-Ferrand, France

Keywords: Acasta; apatite; zircon; Archean; primary composition

Abstract
A novel way to investigate the petrogenesis of ancient poly-metamorphosed terranes is to study zircon-hosted mineral inclusions, which are sensitive to melt evolution such as apatite. Recent contributions on such inclusions in unmetamorphosed granitoids can provide valuable petrogenetic information and, in turn, represent a way to circumvent effects of metamorphism. Yet, the impact of metamorphism on apatite inclusion has never been studied in detail. To address the issue of chemical and isotopic preservation of primary signals in apatite crystals both in the matrix and armored within zircons, we have studied apatite crystals from four 3.6-4.0 Ga TTG granitoids from Acasta Gneiss Complex (Canada).
the Acasta Gneiss Complex (Canada). Our results demonstrate that U-Th-Pb isotope systematics
in matrix apatite crystals were reset at 1.8-1.7 Ga (Wopmay orogen) whereas primary REE
signatures were preserved in many crystals. In contrast, zircon-hosted apatite inclusions all
preserved primary REE signatures despite variable ages between 1.7 and 4.0 Ga. We interpret reset
ages to be a consequence of metamorphism that managed to affect U-Th-Pb systematics because
of advanced radiation damage accumulation in host-zircon lattices. Only the most pristine zircon
crystal has an apatite inclusion with a concordant age consistent with the magmatic age of the
zircon (4.0 Ga). In addition, our results show that apatite crystals from TTG have distinct REE
composition from post-Archean granitoids apatites, that is preserved even in some apatites with
reset ages. This capacity to retain primary information and discriminate granitoid types makes
apatite a very valuable tool for reconstructing the nature and evolution of ancient crustal rocks
through the use of detrital minerals.

1. Introduction

Rare-Earth bearing minerals such as apatite (Ca$_5$(PO$_4$)$_3$(OH, Cl, F)), have proven to be extremely
valuable in retrieving the nature of their host magmas and the crystallization history of granitoids
(Chu et al., 2009; Jennings et al., 2011; Bruand et al., 2016). Hence, they can be very useful
complements to zircon in crustal evolution studies (e.g., Iizuka and Hirata, 2005; Belousova et al.,
2010; Dhuime et al., 2012). Apatite is ubiquitous in different rock types, and contains measurable
amounts of a large variety of trace elements (e.g., LREE-MREE, Sr, Pb, Mn, halogens; e.g.,
Prowatke and Klemme, 2006; Gregory et al., 2009; Miles et al., 2014). The concentration of trace
elements in apatite is sensitive to melt evolution (in-situ crystal fractionation, mixing, SiO$_2$ and
ASI contents; e.g., Sha and Chappell, 1999; Belousova et al., 2001; Prowatke and Klemme, 2006;
Furthermore, apatite is also datable via U-Pb geochronology although prone to resetting during metamorphism, which makes it problematic to recover meaningful information about the magmatic history of old crustal segments. One way to overcome this limitation is to study apatite inclusions armored within zircon and, thus, combine the potential of apatite in retrieving magmatic information with the resilience of zircon to metamorphic processes. Previous workers have shown that zircon-hosted apatite inclusions can indeed retain important information about its host-rock (Jennings et al., 2011; Bruand et al., 2016; Emo et al., 2018). For instance, Bruand et al. (2016) have studied an unmetamorphosed suite of granitoids and showed that zircon-hosted inclusions shared the same trace element signatures as cogenetic apatite crystals within the matrix. They have also shown that Sr/Sm ratio in apatite can discriminate felsic magmas from mafic ones and, as previously suggested by Belousova et al. (2001), that Sr content in apatite inclusions can be used as a proxy for the degree of differentiation of their parental magma (evaluation of the SiO₂ and Sr contents).

Very recently, Emo et al. (2018) demonstrated that zircon-hosted and matrix apatite crystals in two 3.6-3.7 Ga orthogneisses from the Acasta Gneiss Complex (AGC, Canada) exhibit a general discrepancy in their Sr isotope signatures. The authors interpreted the Sr isotopic signature in apatite inclusions as the first direct estimate of initial ⁸⁷Sr/⁸⁶Sr for these ancient rocks whereas Sr isotope signatures in matrix apatite were reset during later metamorphic event. This interpretation is in line with recent findings of Fisher et al. (2019) who demonstrated that Sm-Nd isotope systematics in matrix apatite from Acasta gneisses were reset during the Wopmay orogen at about 1.85 Ga. However, it is presently unclear to which extent zircon-hosted apatite inclusions can resist metamorphic resetting, especially in ancient zircon crystals that experienced significant radiation damage such as those in the AGC (e.g. Guitreau et al., 2018). Consequently, the aim of
this paper is to study the preservation potential of trace element and U-Th-Pb isotope signatures in zircon-hosted inclusions and, hence, better constrain the extent to which such approach can allow retrieval of information about the formation of Earth’s first crusts. For this purpose, we carefully and systematically measured trace element contents and U-Th-Pb isotope systematics in zircon-hosted apatite as well as in matrix apatite crystals in well-characterized 3.6-3.96 Ga samples from the Acasta Gneiss Complex (Guitreau et al., 2012, 2014, 2018; Mojzsis et al., 2014).

2. Geological background and sample description

The Acasta Gneiss Complex (AGC) is located on the western edge of the Slave craton (Northwest Territories, Canada; Fig.1; e.g. Bowring et al., 1989). It is bordered to the west by the Wopmay orogen (1900-1700 Ma; Bleeker and Hall, 2007). The key outcrop locality of the AGC covers an area of ~30 km² although its true extent is presently unknown (e.g. Iizuka et al., 2007). This latter is divided into a western and an eastern domain by a major northeast-trending shear-zone with the western part being highly-strained and the eastern part being less deformed (Iizuka et al., 2007; Reimink et al., 2016a, 2016b, 2018). The AGC is mostly made of orthogneisses of dioritic to granitic affinity but some mafic-ultramafic gneisses are also present. (Bowring et al., 1989; Iizuka et al., 2007; Guitreau et al., 2014; Mojzsis et al., 2014; Koshida et al., 2016; Reimink et al., 2016b). The earliest magmatic events that occurred in the AGC had been dated between 3962 ± 3 (Bowring et al., 1989) and 4031 ± 3 Ma (Bowring and Williams, 1999), and recently revised to 4019.6 ± 1.8 Ma by (Reimink et al., 2016b) The AGC, therefore, hosts Earth’s oldest rocks but also exhibits evidence for a crustal pre-history as argued by the presence of a 4200 Ma inherited zircon core (Iizuka et al., 2006) and by signatures of both short- and long-lived isotope systematics (e.g., Bowring and Housh 1995; Iizuka and Hirata 2005; Iizuka et al., 2009; Guitreau et al., 2014;
The AGC evolution was marked by several geological events that started out with the formation of the Idiwhaa unit at 4020 Ma (Reimink et al., 2016b) and ended around 1700-1800 Ma with a pervasive metamorphic event related to the Wopmay orogen (Hoffman et al., 2011; St-Onge and Davis, 2017; Table A.1). The igneous activity of the AGC essentially consists in several granitic pulses that occurred between 4020 and 2900 Ma, with a major event at 3600 Ma that involved both juvenile addition and crustal anatexis (Table A.1). The metamorphic history of the AGC is less constrained and mostly derived from U-Pb dating of zircon, apatite and titanite (e.g., Hodges and Bowring, 1995; Bleeker and Stern, 1997; Sano et al., 1999; Iizuka et al., 2007; Mojzsis et al., 2014; Guitreau et al., 2018; Fisher et al., 2019; Kirkland et al., 2020). However, with the available dataset, it clearly appears that during the AGC geological history, most metamorphic events are closely linked to the magmatic activity (e.g., Bleeker and Stern, 1997). Major identified metamorphic events occurred at 3750-3700 Ma, 3400-3300 Ma, 3200-2900 Ma, and the latest important metamorphic event identified is linked to the Wopmay orogeny (1800-1700 Ma) with Wopmay associated P-T estimates ranging from 3.3-9 kbar and 575-745 °C (Sano et al., 1999; St-Onge and Davis, 2017). Some more discrete events also likely occurred afterwards (e.g. Hodges and Bowring, 1995; Guitreau et al., 2018).

The samples studied in this contribution (AG09009, AG09014, AG09015, and AG09016) are orthogneisses located in the eastern domain of the AGC (Fig. 1) and have been already described and characterized in Guitreau et al. (2012) and Mojzsis et al. (2014). Samples AG09014, AG09015, and AG09016 have major and trace element compositions that are similar to typical TTG series (e.g., low K₂O/Na₂O, high La/Yb, and strong depletion in heavy REE; e.g. Moyen and Martin, 2012) and they fall within the field of tonalite and trondhjemite in a normative An-Ab-Or
Sample AG09009 is more potassic (K$_2$O= 3.64 wt %; K$_2$O/ Na$_2$O ~ 1) despite high La/Yb, and strong depletion in HREE, and therefore falls within the field of granite in a normative An-Ab-Or plot. Samples AG09009, AG09014, and AG09015 were dated by zircon U-Pb geochronology at 3600 Ma (Guitreau et al., 2012), whereas AG09016 was dated at 3947 Ma (Guitreau et al., 2012, 2018).

3. Analytical Methods

3.1. Sample preparation

Samples were crushed with a jaw crusher and sieved to recover the fraction < 400 µm. This fraction was subsequently run on a Wilfley table and heavy mineral further sorted using heavy liquids. Recovered zircon crystals were handpicked, mounted in epoxy resin, and polished to their approximate center. Zircons and apatites in mounts and thick sections were imaged for back-scattered electrons (BSE) and cathodoluminescence (CL) using a scanning electron microscope (SEM) JEOL JSM-5910 LV at Laboratoire Magmas et Volcans (LMV; Clermont-Ferrand, France). The accelerating voltage was set to 15 kV during image acquisition.

3.2. Electron probe microanalysis (EPMA)

Apatite crystals occurring as zircon-hosted inclusions and matrix grains were analyzed for major and minor elements with an EPMA CAMECA SX100 at LMV. Analyses were made with an accelerating voltage of 20kV and a 10 nA beam current. The crystals used for analysis were PET for Ca, Ce and S, TAP for Si, Na and Y, LPET for P, Cl, La and Sr, and PC0 for F and O. Apatite analysis was done with a defocused beam of 5 µm to minimize potential halogen migration (Pyle et al., 2002). Durango apatite reference material was used as a secondary standard for quality.
control during analysis (Marks et al., 2012).

3.3. Trace element analysis by LA-ICP-MS

Trace element analysis of zircon-hosted apatite inclusions was done by laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS) using the Resonetics Resolution M-50E 193nm excimer laser coupled to the Thermo Element XR at LMV. The spot sizes used ranged between 4 and 12 μm (depending on the phases analyzed) with a repetition rate of 1 Hz and a fluence of 2.88 J/cm². We purposely set a low frequency to avoid drilling through apatite too quickly. Each run lasted 2 minutes with 20 seconds of background acquisition. Each sequence was bracketed by two analyses of GSE-1G standards (9 μm spot size) at the beginning and at the end of the sequence, and one GSC-1G in the middle of the sequence (Jochum et al., 2005). Hf content was monitored during analysis of apatite inclusions in order to identify potential concurrent sampling of the host zircon. All analyses with Hf content above the background values were discarded.

Matrix apatites were analyzed by LA-ICP-MS using the same laser as for inclusions but coupled to an Agilent 7500 ICP-MS with a spot size of 40 μm, a frequency of 4 Hz, and a fluence of 4.5 J/cm². The same amount of time as for inclusion apatites was used for data acquisition and each run started and finished with two measurements of NIST 610 standard (Pearce et al., 1997). For all runs (matrix and inclusions), Durango apatite (Marks et al., 2012) was regularly analyzed throughout the analytical session to monitor data quality at the same spot size as the analyzed unknowns to account for downhole fractionation (Table A.2). Internal normalization for LA-ICP-MS data was done using ⁴³Ca and data processing was conducted using the GLITTER software (Griffin, 2008).
3.4. U-Th-Pb geochronology by LA-ICP-MS

Apatite crystals were dated by LA-ICP-MS at LMV using a Resonetics Resolution M-50E laser-ablation system coupled to a Thermo Element XR ICP-MS. During U-Th-Pb measurements, the laser frequency was set to 2 Hz, the fluence to 2.5 J.cm\(^{-2}\) and the spot size between 40 and 9 μm so as to adapt to the size of the crystals targeted for analysis. Analyses consisted in ~20s background counting followed by 60s of signal acquisition in peak-jumping mode (5 ms dwell time and 20 μs settling time). Bahia and Xuxa apatite were analyzed for quality check (Rosa et al., 2017; Schuch, 2018). The apatite standard MAD (Thomson et al., 2012) was used for external normalization. Unknowns were analyzed as batches of 6 and were bracketed by analyses of MAD apatite. Data were processed using in-house spreadsheets based on the \(t_0\) intercept method (Chew et al., 2011, 2014). Because we do not know the true \(^{207}\text{Pb}/^{206}\text{Pb}\) of MAD apatite, which is a combination of radiogenic Pb and common Pb, and that it is not reported in Thomson et al. (2012), one cannot determine the mass bias for \(^{207}\text{Pb}/^{206}\text{Pb}\) during LA-ICP-MS analyses. Consequently, we derived the Pb isotope mass bias by using the \(^{208}\text{Pb}/^{206}\text{Pb}\) expected from the “true” \(^{232}\text{Th}/^{238}\text{U}\) and the age of MAD apatite. Similarly, we estimated the amount of common Pb within analyzed apatite crystals using the difference between the mass-bias corrected \(^{208}\text{Pb}/^{206}\text{Pb}\) and that expected from the mass-bias corrected \(^{232}\text{Th}/^{238}\text{U}\) in a way akin to that of Chew et al. (2011). Common Pb corrections were further done using the Pb evolution model of Stacey and Kramers (1975) and a convergence method similar to that of Thomson et al. (2012) except that we monitored \(^{206}\text{Pb}/^{238}\text{U}\) and \(^{208}\text{Pb}/^{232}\text{Th}\) for convergence. U-Th-Pb age calculations were done using a present-day \(^{238}\text{U}/^{235}\text{U}\) of 137.818 (Hiess et al., 2012) and decay constants for \(^{238}\text{U},^{235}\text{U}\) and \(^{232}\text{Th}\) of 1.55125.10\(^{-10}\), 9.8485.10\(^{-10}\), and 4.9475.10\(^{-11}\), respectively (Jaffey et al., 1971; Le Roux and Glendenin, 1963). The Isoplot software (Ludwig 2008) was used to build Tera-Wasserburg plots.
The 2056 ± 3 Ma Bahia (Rosa et al., 2017) and 573.0 ± 0.8 Ma Xuxa (Schuch, 2018) apatite standards were analyzed using 40, 20, 15, and 9 μm spot sizes. The results for apatite standards are detailed in Table A.3 and Fig. A.1. With all spot sizes combined, we obtained U-Pb Concordia intercept and weighted average $^{206}$Pb/$^{238}$U and $^{208}$Pb/$^{232}$Th ages of 2048 ± 31 (2σ; MSWD = 2.7; n = 30), 2086 ± 34 (2σ; MSWD = 1.5; n = 13), and 2127 ± 40 Ma (2σ; MSWD = 2.7; n = 13), respectively, for Bahia, and 569.4 ± 2.9 (2σ; MSWD = 1.1; n = 20), 574.9 ± 4.4 (2σ; MSWD = 0.39; n = 17), and 575.1 ± 3.2 Ma (2σ; MSWD = 0.97; n = 17), respectively, for Xuxa. Therefore, our measurements are in good agreement with previously reported ages.

As illustrated in Fig. A.1, common Pb correction results in migration of data points towards the Concordia curve but not complete converge to a concordant age, especially for Bahia apatite data. This can be explained by our correction method, which is well suited for minerals with low Th/U but becomes less precise and less accurate as Th/U increases as a result of radiogenic $^{208}$Pb/$^{206}$Pb getting closer to that of common Pb (Ireland and Williams, 2003). Consequently, the influence of common Pb becomes less detectable in high Th/U mineral. As an illustration, a 10% contamination of a 2056 Ma Bahia apatite (Th/U = 15), a 573 Ma Xuxa apatite (Th/U = 30), and a 1700 Ma Acasta apatite (Th/U = 0.5) decreases determined $^{208}$Pb/$^{206}$Pb ratios by 5 and 7 % in Bahia and Xuxa apatites, respectively, while increasing the $^{208}$Pb/$^{206}$Pb by almost 150% in the Acasta apatite. This observation can explain why, later in the manuscript, the common Pb corrections work much better for Acasta apatites, which commonly have low Th/U, as most data points become concordant once corrected for common Pb.

Apatite crystals from Acasta gneisses were analyzed in three different contexts: (1) as separate grains within an epoxy mounts (40, 20, and 9 μm spots on the same apatite crystals), (2) as grains within polished sections (matrix apatite), and (3) as inclusions within zircon crystals.
mounted in epoxy. All results are available in Table A.4.

4. Petrography

4.1. Sample AG09009

Sample AG09009 is mainly made of quartz, alkali feldspar, plagioclase, biotite, muscovite, chlorite and accessory phases such as zircon, apatite, monazite, allanite, thorite, ilmenite and rutile (Fig. 2A). Locally, chlorite partly replaces micas and can occur as small veins. Felspars are slightly sericitized. In this sample, apatite is the main accessory phase and most commonly occurs as euhedral crystals (<150 microns in length) either directly in contact with biotite or as inclusions in quartz and feldspar. Apatite can be zoned from light gray (core) to dark gray (rim) in cathodoluminescence (Fig. 2D) and can contain zircon inclusions. Apatite occasionally appears as secondary mineral associated with allanite and monazite. In these rare cases, a monazite grain is surrounded by a corona of apatite, itself surrounded by a corona of fibrous allanite (Fig. 2B). Numerous small inclusions of monazite are persistent inside the apatite corona.

Biotite, alkali feldspar, plagioclase, chlorite, apatite, chromite and chalcopyrite have been identified as inclusions in zircon (Fig. 2C) and are usually < 20 microns. Most zircon crystals are metamict (damaged by radioactivity), which leads to the formation of fractures that can be filled by several minerals (e.g. biotite, chlorite, plagioclase) thereby forming polymineralic inclusions. Most apatite inclusions are monomineralic and euhedral except for one case where apatite is surrounded by chlorite (Fig. 2C).

4.2. Sample AG09014

Sample AG09014 is made of quartz, biotite, plagioclase and accessory phases. These latter
are zircon, apatite, pyrite, monazite and rutile crystals. In this sample, apatite is the main accessory phase (Fig. 2I-J), it is euhedral, small (< 100 microns) and can contain zircon inclusions. Apatite can be found either as inclusion in quartz and plagioclase or in contact with biotite. Apatite is usually unzoned (Fig. 2I-J). In this sample, inclusions in zircon are monomineralic and small (< 10 microns). They are mostly apatite (Table 1), quartz, chlorite and monazite crystals.

4.3. Sample AG09015

In sample AG09015, the main rock forming minerals are quartz, biotite, plagioclase and oxides (rutile, ilmenite; Table 1). Accessory phases are zircon, apatite, sulfides (pyrite, chalcopyrite), titanite and allanite. As for samples AG09014, AG09015 is only slightly altered. Apatite is the main accessory phase; it is euhedral and < 200 microns. It is either in direct contact with biotite or as inclusion within quartz and feldspar. Most crystals are zoned with a light gray core and a dark gray rim in CL (Fig. 2H). They can also be found as clusters where zonation is oscillatory with a dark gray core (Fig. 2G).

In this sample, inclusions found in zircon are apatite, biotite, plagioclase and chlorite. These inclusions are small (< 5 microns) and monomineralic.

4.4. Sample AG09016

Sample AG09016 is made of quartz, plagioclase, biotite and muscovite. Accessory phases are zircon, apatite, rutile and titanite. This sample shows limited alteration. Apatite is ubiquitous, euhedral and < 250 microns in size and occurs in contact with biotite or in inclusions in quartz and plagioclase. Apatite crystals have two types of zonation: (i) a light gray core with a dark rim or (ii) an oscillatory zoning with a dark core (Fig. 2F). Some apatite grains are occasionally fractured with biotite filling these cracks.
In this sample, inclusions in zircon can be either mono- or polymineralic with grain sizes < 20 microns. The identified inclusions are apatite (Fig. 2E), chlorite, biotite, plagioclase, quartz and thorite. For this sample, apatite inclusions are always monomineralic.

5. Results

5.1. Apatite chemistry

Apatite crystals from the studied samples are all fluorapatites (Table A.5). Based on EPMA data, apatite chemistries define two groups: a first group (samples AG09009 and AG09016) with high $Y_2O_3$ (0.04 to 0.6 wt %) and low Cl (Cl <0.045 wt %) and a second group (AG09014 and AG0915) with lower $Y_2O_3$ (<0.2 wt %) and higher Cl (0.048-0.2 wt%; Table A.5).

Contrary to samples AG09009 and AG09016, only matrix apatite has been analyzed in AG09014 and AG09015 samples because inclusions were too small (< 10 µm in size).

Sample AG09009. Chondrite-normalized REE patterns ofapatites from the matrix define two groups: group 1 shows depleted LREE compared to HREE and a negative Eu anomaly ($Eu/Eu^* = Eu_N/\sqrt{(Sm_N)(Gd_N)} < 0.5$; Fig. 3A, Table 2) whereas group 2 patterns are sub-parallel to group 1 but with lower REE content and no Eu anomaly. Apatite inclusions have the same REE patterns as group 1 with some grains having a higher REE concentration (Fig. 3A, 4A). Overall, apatites from AG09009 have the highest concentrations in La (~166 ppm) and Yb (~353 ppm, Table A.4) among all samples analyzed in this study (Fig. 4A). These highest values are systematically associated with analyses done within crystal cores whereas lower concentrations are linked to analyses done within rims (Fig. 4B-C). On the other hand, group 2 apatite compositions have only been found in the outer-part of grains that had core compositions belonging to group 1 apatites (Fig. 2D) and have the lowest REE concentrations (Fig. 4A).
Sample AG09014. Chondrite-normalized REE patterns for apatite from sample AG09014 show similar LREE depletion compared to HREE. In this sample, two groups of apatite can be distinguished. The first group (Group 1) is similar to group 1 identified in other samples from this study (Fig. 3C). The second group is depleted in all REE compared to group 1 and has a distinctive impoverishment in LREE.

Sample AG09015. Contrary to previous samples, apatite from AG09015 displays multiple and strongly distinguishable compositions. Five groups can be defined based on chondrite-normalized patterns (Fig. 3D). Group 1 REE pattern is comparable to group 1 from the other samples with a depletion in LREE compared to HREE (Fig.4A) and a negative Eu anomaly (0.4 < Eu/Eu* < 0.6). All other groups have a strong depletion in LREE, which distinguishes them from group 1. In Fig. 4A, it can be seen that the other groups (2-5) have low La and Yb contents and are undistinguishable from each other (gray dots in Fig. 4D). These groups have highly depleted LREE chondrite-normalized patterns (LaN < 100) compared to HREE (YbN < 1000). The best chemical criterion that allows these groups to be discriminated is their respective Eu anomaly (Fig.3D). Group 2 has no Eu anomaly (0.9 < Eu/Eu* < 1.3), Group 3 a slightly negative Eu anomaly (Eu/Eu* ≈ 0.5) and Group 4 a positive Eu anomaly (Eu/Eu* > 1.2). Group 5 apatite has slightly higher LREE chondrite-normalized values compared to group 4, and a small negative Eu anomaly (Eu/Eu* ≈ 0.75). Group 2, 3 and 5 are always neoformed (no zonation, low REE content) or recrystallized grains, while group 4 can be found as new generation grains or as an overgrowth surrounding group 2 apatites.

Sample AG09016. Much as for sample AG09009, chondrite-normalized REE patterns of matrix apatites from AG09016 define two groups. Group 1 is depleted in LREE compared to HREE (mean (La/Yb)N = 0.14) with a consistent negative Eu anomaly (~0.3; Fig. 3B, Table A.4.).
Group 2 defines a sub-parallel pattern to group 1, with lower REE content, a stronger depletion in LREE compared to HREE (c.a. \((\text{La/Yb})_N=0.03\)) and small Eu anomalies \((0.6 < \text{Eu/Eu}^* < 0.7)\).

Chondrite-normalized REE patterns of zircon-hosted apatite inclusions have strong similarities with group 1 apatite, although the LREE content in the former is more variable (Fig. 3B).

### 5.2. Apatite U-Th-Pb geochronology

#### 5.2.1. Matrix apatite

Most of matrix apatite crystals in AG09009 define a major trend that intersects the Concordia curve in a Tera-Wasserburg plot (Fig. 5A) at 1797 ± 27 Ma (MSWD = 3.6; n = 27). Once corrected for common Pb (red ellipses in Fig. 5A), most data points plot onto the Concordia curve with a weighted average \(^{206}\text{Pb}/^{238}\text{U} \) age of 1794 ± 24 Ma (MSWD = 1.4). One data point lingers outside the major trend and has a Concordia age of 3197 ± 82 Ma (MSWD = 0.09) and 3184 ± 120 Ma (MSWD = 0.11; Fig. 5A) before and after common Pb correction, respectively.

Data for AG09014 apatite crystals form a robust trend with a lower intercept at 1700 ± 15 Ma (MSWD = 1.6; n = 12; Fig. 5B). Once corrected for common Pb, most data points plot on the Concordia curve and exhibit a weighted average \(^{206}\text{Pb}/^{238}\text{U} \) age of 1710 ± 20 Ma (MSWD = 0.92).

With the exception of one data point, all analyses from AG09015, show a trend that gives a lower-intercept age of 1713 ± 21 Ma (MSWD = 4.1; n = 35; Fig. 5C). Once corrected for common Pb, all data points plot on or very near the Concordia curve and give a weighted average \(^{206}\text{Pb}/^{238}\text{U} \) age of 1723 ± 20 Ma (MSWD = 1.9). One data point plots on the Concordia and gives an age of 2721 ± 63 Ma.

All data points for apatites from AG09016 plot along a linear trend towards a lower-intercept of 1746 ± 46 Ma (MSWD = 3.7; n = 37; Fig. 5D). Once corrected for common Pb, most
data points are concordant and have a weighted average $^{206}\text{Pb}/^{238}\text{U}$ age of 1721 ± 23 Ma (MSWD = 2.2).

5.2.2. Zircon-hosted apatite

Over the large quantity of zircons mounted in epoxy and examined within thin sections (~200), only a few apatite inclusions larger than 10 μm were found. One apatite was analyzed in sample AG09009 whereas eight were analyzed in sample AG09016. Most zircon crystals in which we found apatite inclusions have non-pristine internal textures, except for zircon AG09016-88 which exhibits fine-oscillatory zoning. Ages for 6 of the 9 host-zircons are reported in Figure 6. The 3 remaining zircon crystals were not dated because of their disturbed internal zoning which would have resulted in meaningless discordant ages. Apatite ages mentioned in this section correspond to data corrected for common Pb unless specified otherwise. Overall, U-Pb isotope systematics in apatite inclusions exhibit contrasting behavior compared to matrix apatite. The former essentially distribute along the Concordia curve between 1700 and 4000 Ma whereas the latter forms a robust trend between 1700-1800 Ma and common Pb (Fig. 7). In detail, zircon-hosted apatite inclusions display three distribution behaviors: (i) on or close to the Concordia curve, (ii) on the matrix apatite trend, and (iii) inverse discordance.

The oldest inclusion (AG09016-88) has a concordant age of 4003 ± 89 Ma ($^{207}\text{Pb}/^{206}\text{Pb}$ age corrected for common Pb; 2 SE; 0.7% discordance; Fig. 7) which is consistent with data obtained on the pristine-looking host-zircon (3967 ± 49 My, Guitreau et al., 2018). A second analysis in the rim of the same inclusion shows a reversely discordant age, though consistent with the first one (4111 ± 90 Ma). Two other data points from apatites AG09016-100 and 108 plot on the left of the Concordia curve at $^{207}\text{Pb}/^{206}\text{Pb}$ ages corresponding to ~4000 Ma. Apatites AG09016-24 and 37...
show concordant ages between 3200 and 4000 Ma. Apatite AG09016-15 is the biggest inclusion and is not fully enclosed within the host-zircon (Fig. 6). The zircon exhibits a dark patchy zoning indicative of advanced radiation damage accumulation. In this apatite inclusion, 3 analyses from core to rim were done. Obtained U-Th-Pb ages decrease progressively from core (~3200 My) to rim (~1800 My old; Fig. 7). Apatite AG09016-62 displays two ages consistent with the oldest domains of apatite AG09016-15 (i.e., 3200 Ma and 2400 Ma). The single data point for AG09009 (08) corresponds to an age of 1867 ± 143 Ma (207Pb/206Pb age; 2 SE) and comply well with the major trend defined by matrix apatites, much as inclusion AG09016-11 (Fig. 7). It is important to note that inclusion AG09009-08 is surrounded by chlorite and chlorite-filled cracks, suggesting later fluid circulation within the zircon crystal (Fig. 6). Similarly, apatite AG09016-11 is traversed by a major crack that runs through the zircon.

6. Discussion

6.1. Preservation of magmatic chemical signature

In all studied TTG samples, apatite exhibits at least two chemical groups of which Group 1 has the same characteristics across the entire range of samples. Group 1 apatites are characterized by chondrite-normalized REE patterns depleted in LREE compare to HREE and a negative Eu anomaly (Fig. 3). In a Nd vs Eu/Eu* diagram, group 1 apatites (both matrix and inclusions) have systematically lower Eu/Eu* values and higher Nd content than that of other apatite groups (Fig. 8). Texturally, this group corresponds to core composition when a core to rim systematic is present (Fig. 4B, C). Moreover, all zircon-hosted inclusions have group 1 chemical characteristics. Finally, recent data on apatite from adakite (TTG-like signature; Bruand et al., 2020 and TTGs from two other cratons (Kaapvaal, South Africa and Karelia, Finland) show comparable chemistry to group
1 apatite. All these results indicate that group 1 apatite composition represents primary (magmatic) apatite REE signature.

6.1.1. Matrix apatite

Our new U-Th-Pb ages on matrix apatite indicate that the vast majority of analyzed crystals exhibit ages that are consistent with the latest pervasive metamorphic event recorded by Acasta gneisses, i.e., the 1800-1700 Ma Wopmay orogen (Fig. 5). This is in line with apatite ages obtained by Sano et al., 1999) and Fisher et al. (2019) and indicate that metamorphic conditions associated with the Wopmay orogen exceeded the closure temperature of apatite (> 350-600°C e.g. Cherniak et al., 1991; Chamberlain and Bowring, 2001; Cochrane et al., 2014). We can, therefore, assume that any previously recorded metamorphic events had been overprinted by that related to the Wopmay orogen (Table A.1). Rare concordant matrix apatite ages at 3197 ± 82 and 2721 ± 63 Ma can point to possible local preservation of older ages, in line with titanite geochronology (Davidek et al., 1997; Fisher et al., 2019; Fig. 5), but overall magmatic ages are not preserved in matrix apatites despite the local preservation of primary REE signature in the same apatites (group 1). The dichotomy between the primary chemical signature of group 1 matrix apatite and the secondary record of its U-Th-Pb data is consistent with diffusion work done on REE by Cherniak (2000) who showed that REE in apatite can diffuse relatively slowly even in the case of high temperature metamorphic events. This study demonstrates that two different types of substitution are responsible for diffusion in apatite; simple substitution (REE$^{3+}$<->REE$^{3+}$) and coupled substitutions (i.e. REE$^{3+}$ + Si$^{4+}$ <-> Ca$^{2+}$ + P$^{5+}$). In diffusion experiments, Cherniak (2000) showed that Sr, Pb and O are more readily reset in apatite but can keep their primary signature in the core of the crystal (10 μm zoning) for metamorphic episodes below 750°C and for a duration of $1.05 \times 10^4$
years. On the other hand, apatite grains (100μm in size) keep their primary REE signature for metamorphic episodes of less than $10^5$ years in simple substitutions and $10^7$ years in coupled substitutions for the same temperature.

6.1.2. Apatite inclusions

Zircon-hosted apatite inclusions within AG09016, all exhibit primary REE signatures and, contrary to matrix apatites, essentially distribute along the Concordia curve with ages ranging between ~1700 and 4000 Ma (Fig. 7; Table A.6). This demonstrates that apatite inclusions have not been completely overprinted by the Wopmay orogen but, on the contrary, kept the memory of older metamorphic events and even original igneous U-Pb ages in some cases. This is precisely the case for apatite AG09016-88 which displays a concordant age of $4003 \pm 89$ Ma ($^{207}\text{Pb} / ^{206}\text{Pb}$ age, 0.7% discordant) that is very consistent with that obtained on the host-zircon (3967 ± 49 Ma; Guitreau et al., 2018). The large range of ages exhibited by apatite inclusions is consistent with the fact that the AGC recorded several tectono-thermal events from 3750 to 1700 Ma, although it is difficult to associate all ages to specific events (Table 2). Yet, three data points correspond to an age of ~3200 Ma consistent with that of titanite and garnet within Acasta samples (Maneiro, 2016; Fisher et al., 2019). We interpret the general distribution to represent punctual thermally activated resetting during metamorphic events (e.g., Cochrane et al., 2014). Three other data points are consistent with the matrix apatite trend, which suggest that the U-Pb system in these crystals were reset in a similar way as matrix apatite, despite encapsulation within zircon. Therefore, apatite inclusions have been either reset within zircon without any influence from the external media, or in connection with this latter via cracks and porous zircon domains.

Reversely discordant data can be seen as either analytical artifacts or evidence for Pb
contamination, which would significantly lower the measured U/Pb ratio. An analytical artifact would mean odd fractionation between U and Pb, which is inconsistent with the relatively good agreement between U, Th, and Pb concentrations determined during trace element analyses and U-Th-Pb isotope measurements. In addition, such extreme displacement from the Concordia curve would mean an instrumental fractionation much too large compared to the rest of our U/Pb data. Therefore, we think that the U-Pb isotope signatures of these inclusions are real and come from Pb contamination of apatite inclusions. Common Pb cannot be responsible for this contamination because the $^{208}\text{Pb}/^{206}\text{Pb}$ of reversely discordant apatite inclusions is too low. Figure 9 shows that matrix apatite Pb isotope composition is controlled to a large extent by common Pb contamination because data points form a positive correlation towards the common Pb end-member. In contrast, apatite inclusions have a horizontal distribution and, hence, no visible influence from common Pb, except for a few apatites that exhibited U-Pb data distribution consistent with the matrix apatite trend in Figure 7. Therefore, we conclude that common Pb contamination cannot account for the reversely discordant apatite data. Instead, we propose that reversely discordant apatite inclusions were contaminated by radiogenic Pb coming from the host zircon during a thermal event such as the Wopmay orogen. Radiogenic Pb migration has already been described in Archean zircons, notably from the Napier Complex, Antarctica (Williams et al., 1984; Kusiak et al., 2013; Lyon et al., 2019). The evolution of the Pb isotope composition of a zircon with a Th/U of 0.5 is presented in Figure 9 and it is clearly visible that contamination by such radiogenic Pb would result in horizontal spread of data in a $^{208}\text{Pb}/^{206}\text{Pb}$ versus $^{207}\text{Pb}/^{206}\text{Pb}$ plot.

The zircons that host apatite inclusions analyzed in this study are often not pristine-looking (Fig. 6). Instead, they show advanced signs of radiation damage, a common feature in Archean zircon, have variably discordant ages, and some of them even display metamorphic ages (See BSE
images in Fig. 6). Because zircons underwent disturbances in their U-Pb isotope systematics by thermal events (Guitreau et al., 2018), one can easily expect that apatite inclusions might also be affected. This would be consistent with our geochronological results. An important conclusion from our apatite dating is that compared to matrix apatite, no common Pb seems to influence the data distribution in AG09016 (Table A.6. and Fig. 9). This means that host-zircons satisfactorily isolated apatite inclusions from external fluids possibly bringing common Pb, which accounts for both the resetting of U-Pb ages, the existence of reversely discordant U-Pb data and the fact that Sr isotope data for apatite inclusions from Emo et al. (2018) are less radiogenic than those in the matrix despite zircons showing advanced radiation damage in CL images. If external fluids were to penetrate within zircon, apatite Sr isotope composition should be influenced by the fluids, which are more radiogenic. In summary, our results highlight that U-Th-Pb ages can be compromised in apatite inclusions hosted in zircons with advanced radiation damage but this is not the case for REE concentrations.

6.2. Secondary apatite signatures

The secondary groups of apatites are chemically distinct from the primary group described above. All of them show a strong decrease in REE compared to group 1 apatites (or magmatic apatites), with HREE depleted to a lesser extent than LREE. All apatites from groups 2 and more (except AG09014), display no or more rarely a positive Eu anomaly (Fig.3D). These groups texturally appear as new or recrystallized grains or are rimming group 1 cores. Their growth are related to secondary processes such as metamorphism and/or metasomatism which in the light of current literature on those phases are sometimes difficult to distinguish (Bau, 1991; Henrichs et al., 2018).

In the studied samples, we identified different late apatite generations:
In one sample (AG09009), a core (group 1) to rim (group 2) systematic has been identified (Fig. 4B). The depletion in LREE and the absence of Eu anomaly characterizing the rim is interpreted as metamorphic (Fig. 3A). This type of overgrowth is also observed in metamorphosed post-Archean apatites and has similar low REE+Y, U+Th rims around igneous apatite cores (Henrichs et al., 2018).

For the three other samples, second generation of apatite crystals (Fig. 3 group 2 to 5 depending on samples have been observed. In samples AG09015 and AG09016, these groups are interpreted as metamorphic and/or metasomatic. On the other hand, group 2 from sample AG09014 is the only second generation displaying a strong negative Eu anomaly and rather magmatic characteristics. This could be related to a late magmatic interaction with a different magma or the consequence of the crystallization of another LREE-mineral during the crystallization of the granitoid (Hoskin et al., 2000; Bruand et al., 2014; Table 2). Here it probably points to a lower grade of metamorphism (than for AG09015) because of its higher content in Cl and lower content in Y (Table A.5.).

Apatites derived from primary monazite. These secondary apatites have only been identified in sample AG09009 (Fig. 2B). In this case, primary monazite is destabilized in a metamorphic corona of apatite and fibrous allanite. This type of secondary textures has been described occasionally in natural samples (Gasser et al., 2012 in metapelite under amphibolite facies; Finger et al., 1998 metamorphosed I and S-type granites under amphibolite facies) and in experimental studies (Budzyń et al., 2017), and is characteristic of amphibolite facies metamorphic conditions.

All secondary apatite compositions have U-Th-Pb ages corresponding to the Wopmay orogen 1800-1700 Ma and have nucleated or were reset during this event (Fig. 5). Again, this is
consistent with young ages obtained by Sano et al. (1999) and Fisher et al. (2019).

6.3. Apatite chemistry and identification of host-granitoid

Archean TTGs are known for their specific geochemical signature, notably their high (La/Yb)$_N$ and low HREE concentrations (Fig. 10C; e.g., Moyen and Martin, 2012). They can be easily discriminated from post-Archean granitoids in (La/Yb)$_N$ vs Yb$_N$ diagrams. In this study, we found that the same diagram discriminates very well TTG apatite from Post-Archean granitoid apatite (Fig. 10A) alike in Bruand et al. 2020. However, the chemical characteristics define an opposite trend when compared to the whole rock data. Indeed, apatites from TTGs have systematically low (La/Yb)$_N$ ratios, high HREE contents and notably high Y concentrations, whereas apatites from post-Archean granitoids commonly show the opposite. Interestingly, apatite chemistry from peraluminous post-Archean granitoids are marginally overlapping with the apatite from TTG (Fig 10a-d). Their (La/Yb)$_N$ are nonetheless systematically higher than apatite TTG from Archean cratons (Fig. 10D). Yet, a very important conclusion of our study is that we observed distinct generations of apatite that we attribute to magmatic, late-stage, metamorphic and/or metasomatic processes. The late events affecting the AGC have an impact on the LREE chemistry of apatite whereas the HREE signature is similar. The consequence of this, is that the (La/Yb)$_N$ ratio of secondary apatite in TTG will be even lower than the magmatic one (Fig. 10B). However, no matter which generation analyzed apatites belong to, they all show the peculiar chemistry of TTG apatite in a (La/Yb)$_N$ vs Yb$_N$ diagram, hence, allowing identification of their source rock (Fig. 10). This signature is not specific to Acasta samples as shown by Bruand et al. (2020). Apatites analyzed in TTG from Kaapvaal and Karelia cratons (South-Africa and Finland respectively) have the same chemical characteristics.
Sr/Y vs Y diagram is another well-known discriminating diagram for TTG whole-rock. However, this diagram only moderately discriminates the TTG from other granitoids when using apatite chemistry. Indeed, Sr and Y contents in apatite have been shown to be strongly influenced by SiO₂, Sr and the ASI of the melt (Bea and Montero, 1999; Sha and Chappell, 1999; Belousova et al., 2002; Jennings et al., 2011; Bruand et al., 2014). Consequently, in a Sr/Y vs Y diagram, apatite from peraluminous and TTG granitoid are undistinguishably defining the same field. REE partitioning in apatite are intimately linked to the host rock ASI, substitutions and co-crystallizing phases. To explain the dichotomy between the LREE depleted and enriched HREE characters of TTG apatite and the LREE-enriched and HREE-depleted characters of TTG (whole rock; Fig. 10 A-C), we need to invoke the presence of other LREE-bearing phases. Recently, Bruand et al. 2020 have highlighted that the presence of monazite is not rare in TTG granitoids. In the studied samples, only few occurrences of monazite interpreted as primary have been identified. The occurrences of monazite in one of the samples suggest that the presence of monazite could be partially responsible for the specific chemistry of TTG apatite. In post Archean granitoids co-crystallizing monazite would mean a reduced host magma with ASI >1 and relatively low Ca content (Hsieh et al., 2008). Trace elements allow making the distinction between mafic I-type granitoids and I/S-type granitoids (Sha and Chappell, 1999) but the different types of granites can only be discriminated by using Sr and Th. The concentrations in both elements are rather different from the ones from post-Archean apatite, which shows that the composition of apatite in TTG are most likely due to different melt composition and probably fO₂ during crystallization of the apatite in the Archean granitoid. However, the competition between REE-bearing phases in TTG are not well known and the absence of partition coefficient for those REE-bearing phases in such granitoid preclude further interpretation of the data but highlight that more work is needed on this subject.
6.4. Implications

The results of the present study demonstrate that matrix apatites in polymetamorphosed Acasta gneisses can preserve primary REE signatures, whereas U-Th-Pb isotope systematics have been fully reset. On the contrary, zircon-hosted apatite inclusions can both preserve primary REE signatures and U-Th-Pb isotope systematics provided that the host-zircon experienced limited radiation damage and remained isolated from the external medium. Interestingly, apatite can be used as a discriminating tool for different granitoid types (This study; Jennings et al., 2011; Bruand et al., 2014, 2016, 2020). Therefore, our results strongly suggest that the geochemistry and geochronology of detrital apatite and/or detrital zircon-hosted apatite inclusions can be used as a new tool to unravel the origin, nature and evolution of complex multistage Archean cratons as well as the type of granitoid Hadean detrital zircons crystallized from. However, one needs to be aware of the limitations of this approach that essentially pertain to metamorphic resetting of isotope systematics. This limits the use of detrital apatite but also suggests that when one focuses on zircon-hosted inclusions, the host-zircon should be well characterized for, at least, internal textures and U-Pb ages so as to understand the pristineness of the information encapsulated in the apatite inclusion. This is because all inclusions within zircon are not systematically primary but could grow within old radiation-damaged detrital zircons (e.g. Rasmussen et al., 2011). Consequently, analyzed inclusions should be monomineralic to avoid perturbation from later events and should be contained within a zircon with limited radiation-damage.

7. Conclusions

The aim of this study was to decipher whether or not, matrix apatites and apatite inclusions in
zircons from Archean TTGs from the Acasta Gneiss Complex (Canada) preserved primary compositions. Here, we were able to demonstrate that primary REE composition of apatite in the matrix can be preserved for large crystals (in this study mostly over 40 µm), whereas their U-Th-Pb isotope systematics were fully reset by HT metamorphism around 1.8-1.7 Ga (Wopmay Orogen). Our study also shows that apatites from TTGs have geochemical signatures \((\text{La/Yb})_N\) vs \(\text{Yb}_N\) that are very distinct from those of apatite from other granitoid type, regardless of their primary or secondary origin. In addition, our results show that Archean apatites trapped within zircon that have withstood multiple HT metamorphic events were effectively protected and kept their primary isotopic and geochemical signature, provided that zircon lattice underwent moderate radiation damage. Altogether, these new results have important implications for studies of Archean and Hadean crustal evolution because this tool can be applied to detrital apatites, knowing the limitations of such an approach, but more importantly to detrital zircon-hosted apatites. In the latter case, it is important to target the most pristine-looking zircon crystals, to characterize them for, at least, U-Pb ages, and look for monomineralic apatite inclusions in priority.

Acknowledgements

We are grateful to Claire Fonquernie for mineral separation and to Jean-Marc Hénot for technical help during SEM sessions. The authors acknowledge financial support from LabEx ClerVolc (ANR-10-LABX-0006), Région Auvergne (Auvergne Fellowship program), and the French Agence Nationale de la Recherche (ANR) through the funded project Zircontinents (PI: M. Guitreau; ANR-17-CE31-0021). This is a Laboratory of Excellence ClerVolc contribution number 404.. We thank Steve Mozjsis and The John Templeton Foundation– FfAME Origins program in the support of CRiO. Finally, we deeply thank the editor W. Behr, T. Iizuka and an anonymous reviewer for their input.

Figure Captions
Figure 1: Map of the AGC with the location of the samples for this study (red dot). Map modified from Guitreau et al., 2018).

Figure 2: BSE and CL images of the studied samples A) Representative picture of AG09009 mineral assemblage typical for TTG compositions. B) Destabilization of monazite in apatite+allanite linked to metamorphism in AG09009. C) Apatite inclusion in a zircon from AG09009 (BSE). D) CL image of apatite zoning in the matrix from sample AG09009 E) Apatite inclusions in zircons (BSE) from sample AG09016 F) Apatite from the matrix (CL) from sample AG09016 G) Apatite aggregate from the matrix (CL) from sample AG09015. H) Apatite from the matrix (CL) from sample AG09014. I-J) Apatite from the matrix (CL) from sample AG09014.

Figure 3: Chondrite-normalized REE patterns (normalization factor : Sun and McDonough, 1989) from LA-ICP-MS analysis of apatites from all samples. A) Sample AG09009 groups 1 and 2 are matrix apatites; last group is inclusions in zircons. B) Sample AG09016 groups 1 and 2 are matrix apatites; last group is inclusions in zircons. C) Sample AG09014, all groups are matrix apatites. D) Sample AG09015, all groups are matrix apatites.

Figure 4: A) La vs Yb diagram for all samples with first and secondary groups of matrix apatites. B) La vs Yb diagram for samples AG09009/14 showing the decrease in REE from core to rim. C) CL image of a matrix apatite with LA-ICP-MS laser spots location. The La and Yb composition of each points match the bold circles in Fig.4B.

Figure 5: Tera-Wasserburg diagrams presenting U-Pb results for matrix apatites from AG09009
(A), AG09014 (B), AG09015 (C), and AG09016 (D).

Figure 6: Cathodoluminescence (CL) and back-scattered-electron (BSE) images for zircons containing apatite inclusions analyzed in this study. Also reported are locations and labels of U-Th-Pb isotope measurements together with zircon ages, when available (Guitreau et al., 2012, 2018).

Figure 7: Tera-Wasserburg diagram for apatite inclusions in AG09009 and AG09016 corrected for common Pb. Also reported are matrix apatite data with (black dashed-circles) and without common Pb correction (grey dashed-circles). Numbers next to colored ellipses correspond to analysis numbers as reported in Table A.6., and in Figure 7.

Figure 8: Discriminating Nd vs Eu/Eu* diagram for all samples, matrix and inclusions.

Figure 9: $^{208}\text{Pb}/^{206}\text{Pb}$ versus $^{207}\text{Pb}/^{206}\text{Pb}$ plot for apatite data from this study. Also reported are the evolution of the terrestrial lead, as given in Stacey and Kramers (1975), and the Pb isotope evolution of a 4 Ga zircon that has a present-day Th/U of 0.5. Matrix and zircon-hosted apatites exhibit a clear dichotomy with the former defining a positive trend towards common Pb whereas the latter distribute horizontally, except for a few data points that have U-Pb ages consistent with those of matrix apatite (see Fig. 6). Note that apatite $^{207}\text{Pb}/^{206}\text{Pb}$ ratios vary between values that correspond to the age of the Wopmay orogen and that of the oldest Acasta gneisses, except for three data points that we surmise incorporated zircon-derived radiogenic Pb during metamorphism related to Wopmay orogen (see text for details).
Figure 10: A) (La/Yb)$_N$ vs Yb$_N$ discriminating diagram for apatites from Archean granitoids (TTG) and post-Archean granitoids. Literature data from (Hoskin et al., 2000; Belousova et al., 2001; Dempster et al., 2003; Chu et al., 2009; Jennings et al., 2011; Bruand et al., 2014, 2020). B) Details on the distinction between magmatic and metamorphic apatites from this study. C) (La/Yb)$_N$ vs Yb$_N$ discriminating diagram between TTG and post-archean rocks modified from Hansen et al., 2002. D) Log(La/Yb)$_N$ vs Yb$_N$ discriminating diagram between TTG and post-archean granitoids.

Table Captions

Table 1: Recapitulative table of the sample characteristics.

Table 2: Representative LA-ICP-MS analysis for all apatite samples from the matrix and inclusions within zircons.

References

Barker, F. (1979) Trondhjemite: definition, environment and hypotheses of origin, Developments in petrology. Elsevier, pp. 1-12.

Bau, M. (1991) Rare-earth element mobility during hydrothermal and metamorphic fluid-rock interaction and the significance of the oxidation state of europium. Chemical Geology 93, 219-230.

Bauer, A.M., C.M. Fisher, J.D. Vervoort, and S.A. Bowring (2017), Coupled zircon Lu-Hf and U-Pb isotopic analyses of the oldest terrestrial crust, the >4.03 Ga Acasta Gneiss Complex. Earth Planet. Sci. Lett. 458, 37-48.
Bea, F., & Montero, P. (1999). Behavior of accessory phases and redistribution of Zr, REE, Y, Th, and U during metamorphism and partial melting of metapelites in the lower crust: an example from the Kinzigite Formation of Ivrea-Verbano, NW Italy. Geochimica et Cosmochimica Acta, 63(7-8), 1133-1153.

Belousova, E., Kostitsyn, Y., Griffin, W.L., Begg, G.C., O'Reilly, S.Y. and Pearson, N.J. (2010) The growth of the continental crust: constraints from zircon Hf-isotope data. Lithos 119, 457-466.

Belousova, E.A., Walters, S., Griffin, W.L. and O'Reilly, S.Y. (2001) Trace-element signatures of apatites in granitoids from the Mt Isa Inlier, northwestern Queensland. Australian Journal of Earth Sciences 48, 603-619.

Bleeker, W. and Hall, B. (2007) The Slave Craton: geology and metallogenic evolution. Mineral deposits of Canada: a synthesis of major deposit-types, district metallogeny, the evolution of geological provinces, and exploration methods. Edited by WD Goodfellow. Geological Association of Canada, Mineral Deposits Division, Special Publication 5, 849-879.

Bleeker, W. and Stern, R. (1997) The Acasta gneisses: an imperfect sample of Earth’s oldest crust, in: (Ed.)^c(Eds.), Slave-Northern Cordillera lithospheric evolution (SNORCLE) transect and cordilleran tectonics workshop meeting, ed., p.^cpp. 32-35.

Bowring, S.A. and Housh, T. (1995) The Earth's early evolution. Science 269, 1535-1540.

Bowring, S.A. and Williams, I.S. (1999) Priscoan (4.00–4.03 Ga) orthogneisses from northwestern Canada. Contributions to Mineralogy and Petrology 134, 3-16.

Bowring, S.A., Williams, I.S. and Compston, W. (1989) 3.96 Ga gneisses from the Slave province, Northwest Territories, Canada. Geology 17, 971-975.
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 55, 1619-1651.

Bruand, E., Storey, C. and Fowler, M. (2016) An apatite for progress: Inclusions in zircon and titanite constrain petrogenesis and provenance. Geology 44, 91-94.

Budzyń, B., Harlov, D.E., Kozub-Budzyń, G.A. and Majka, J. (2017) Experimental constraints on the relative stabilities of the two systems monazite-(Ce)–allanite-(Ce)–fluorapatite and xenotime-(Y)–(Y, HREE)-rich epidote–(Y, HREE)-rich fluorapatite, in high Ca and Na-Ca environments under PT conditions of 200–1000 MPa and 450–750 C. Mineralogy and Petrology 111, 183-217.

Chamberlain, K.R. and Bowring, S.A. (2001) Apatite–feldspar U–Pb thermochronometer: a reliable, mid-range (~450°C), diffusion-controlled system. Chemical Geology 172, 173-200.

Cherniak, D. (2000) Rare earth element diffusion in apatite. Geochimica et Cosmochimica Acta 64, 3871-3885.

Cherniak, D.J., Lanford, W.A. and Ryerson, F.J. (1991) Lead diffusion in apatite and zircon using ion implantation and Rutherford Backscattering techniques. Geochimica et Cosmochimica Acta 55, 1663-1673.

Chew, D.M., Sylvester, P.J. and Tubrett, M.N. (2011) U–Pb and Th–Pb dating of apatite by LA-ICPMS. Chemical Geology 280, 200-216.

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 50, 1829-1855.
Cochrane, R., Spikings, R.A., Chew, D., Wotzlaw, J.-F., Chiaradia, M., Tyrrell, S., Schaltegger, U. and Van der Lelij, R. (2014) High temperature (> 350 C) thermochronology and mechanisms of Pb loss in apatite. Geochimica et Cosmochimica Acta 127, 39-56.

Davidek K. L., Martin M. W., Bowring S. A., and Williams I. S. (1997). Conventional U-Pb geochronology of the Acasta gneisses using single crystal fragmentation techniques. Abstract of GAC/MAC Annual Meeting, Ottawa, pp. A-75.

Dempster, T., Jolivet, M., Tubrett, M. and Braithwaite, C. (2003) Magmatic zoning in apatite: a monitor of porosity and permeability change in granites. Contributions to Mineralogy and Petrology 145, 568-577.

Dhuime, B., Hawkesworth, C.J., Cawood, P.A. and Storey, C.D. (2012) A change in the geodynamics of continental growth 3 billion years ago. Science 335, 1334-1336.

Emo, R.B. (2018) Archean crustal evolution constrained by strontium isotopes in apatite and uranium-lead geochronology and trace element geochemistry of zircon, in: (Ed.)^(Eds.), ed. University of British Columbia, p.^pp.

Emo, R.B., Smit, M.A., Schmitt, M., Kooijman, E., Scherer, E.E., Sprung, P., Bleeker, W. and Mezger, K. (2018) Evidence for evolved Hadean crust from Sr isotopes in apatite within Eoarchean zircon from the Acasta Gneiss Complex. Geochimica et Cosmochimica Acta.

Finger, F., Broska, I., Roberts, M.P. and Schermaier, A. (1998) Replacement of primary monazite by apatite-allanite-epidote coronas in an amphibolite facies granite gneiss from the eastern Alps. American Mineralogist 83, 248-258.

Fisher, C.M., Bauer, A.M. and Vervoort, J.D. (2019) Disturbances in the Sm–Nd isotope system of the Acasta Gneiss Complex—Implications for the Nd isotope record of the early Earth. Earth and Planetary Science Letters, 115900.
Gasser, D., Bruand, E., Rubatto, D. and Stüwe, K. (2012) The behaviour of monazite from greenschist facies phyllites to anatectic gneisses: An example from the Chugach Metamorphic Complex, southern Alaska. Lithos 134, 108-122.

Gregory, C.J., McFarlane, C.R., Hermann, J. and Rubatto, D. (2009) Tracing the evolution of calc-alkaline magmas: in-situ Sm–Nd isotope studies of accessory minerals in the Bergell Igneous Complex, Italy. Chemical Geology 260, 73-86.

Griffin, W. (2008) GLITTER: data reduction software for laser ablation ICP-MS. Laser Ablation ICP-MS in the Earth Sciences: Current practices and outstanding issues, 308-311.

Guitreau, M., Blichert-Toft, J., Martin, H., Mojzsis, S.J. and Albarède, F. (2012) Hafnium isotope evidence from Archean granitic rocks for deep-mantle origin of continental crust. Earth and Planetary Science Letters 337, 211-223.

Guitreau, M., Blichert-Toft, J., Mojzsis, S.J., Roth, A.S., Bourdon, B., Cates, N.L. and Bleeker, W. (2014) Lu–Hf isotope systematics of the hadean–Eoarchean Acasta gneiss complex (northwest territories, Canada). Geochimica et Cosmochimica Acta 135, 251-269.

Guitreau, M., Mora, N. and Paquette, J.L. (2018) Crystallization and Disturbance Histories of Single Zircon Crystals From Hadean-Eoarchean Acasta Gneisses Examined by LA-ICP-MS U-Pb Traverses. Geochemistry, Geophysics, Geosystems.

Hansen, J., Skjerlie, K.P., Pedersen, R.B. and De La Rosa, J. (2002) Crustal melting in the lower parts of island arcs: an example from the Bremanger Granitoid Complex, west Norwegian Caledonides. Contributions to Mineralogy and Petrology 143, 316-335.

Henrichs, I.A., O'Sullivan, G., Chew, D.M., Mark, C., Babechuk, M.G., McKenna, C. and Emo, R. (2018) The trace element and U-Pb systematics of metamorphic apatite. Chemical Geology 483, 218-238.
Hiess, J., Condon, D.J., McLean, N. and Noble, S.R. (2012) $^{238}\text{U}/^{235}\text{U}$ Systematics in Terrestrial Uranium-Bearing Minerals. Science 335, 1610-1614.

Hodges, K. and Bowring, S. (1995) $^{40}\text{Ar}^{39}\text{Ar}$ thermochronology of isotopically zoned micas: Insights from the southwestern USA proterozoic orogen. Geochimica et Cosmochimica Acta 59, 3205-3220.

Hoffman, P.F., Bowring, S.A., Buchwaldt, R. and Hildebrand, R.S. (2011) Birthdate for the Coronation paleocean: age of initial rifting in Wopmay orogen, Canada. Canadian Journal of Earth Sciences 48, 281-293.

Hoskin, P.W., 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 41, 1365-1396.

Hsieh, P.-S., Chen, C.-H., Yang, H.-J. and Lee, C.-Y. (2008) Petrogenesis of the Nanling Mountains granites from South China: Constraints from systematic apatite geochemistry and whole-rock geochemical and Sr–Nd isotope compositions. Journal of Asian Earth Sciences 33, 428-451.

Iizuka, T. and Hirata, T. (2005) Improvements of precision and accuracy in in situ Hf isotope microanalysis of zircon using the laser ablation-MC-ICPMS technique. Chemical Geology 220, 121-137.

Iizuka, T., Horie, K., Komiya, T., Maruyama, S., Hirata, T., Hidaka, H. and Windley, B.F. (2006) 4.2 Ga zircon xenocryst in an Acasta gneiss from northwestern Canada: Evidence for early continental crust. Geology 34, 245-248.
Iizuka, T., Komiya, T., Johnson, S.P., Kon, Y., Maruyama, S. and Hirata, T. (2009) Reworking of Hadean crust in the Acasta gneisses, northwestern Canada: evidence from in-situ Lu–Hf isotope analysis of zircon. Chemical Geology 259, 230-239.

Iizuka, T., Komiya, T., Ueno, Y., Katayama, I., Uehara, Y., Maruyama, S., Hirata, T., Johnson, S.P. and Dunkley, D.J. (2007) Geology and zircon geochronology of the Acasta Gneiss Complex, northwestern Canada: new constraints on its tectonothermal history. Precambrian Research 153, 179-208.

Jaffey, A., Flynn, K., Glendenin, L., Bentley, W.t. and Essling, A. (1971) Precision measurement of half-lives and specific activities of U 235 and U 238. Physical Review C 4, 1889.

Jennings, E.S., Marschall, H., Hawkesworth, C. and Storey, C. (2011) Characterization of magma from inclusions in zircon: Apatite and biotite work well, feldspar less so. Geology 39, 863-866.

Jochum, K.P., Willbold, M., Raczek, I., Stoll, B. and Herwig, K. (2005) Chemical Characterisation of the USGS Reference Glasses GSA-1G, GSC-1G, GSD-1G, GSE-1G, BCR-2G, BHVO-2G and BIR-1G Using EPMA, ID-TIMS, ID-ICP-MS and LA-ICP-MS. Geostandards and Geoanalytical Research 29, 285-302.

Kirkland, C., Johnson, T., Kinny, P. and Kapitany, T. (2020) Modelling U-Pb discordance in the Acasta Gneiss: Implications for fluid–rock interaction in Earth's oldest dated crust. Gondwana Research 77, 223-237.

Koshida, K., Ishikawa, A., Iwamori, H. and Komiya, T. (2016) Petrology and geochemistry of mafic rocks in the Acasta Gneiss Complex: Implications for the oldest mafic rocks and their origin. Precambrian Research 283, 190-207.
Kusiak, M.A., M.J. Whitehouse, S.A. Wilde, A.A. Nemchin, and C. Clark (2013), Mobilization of radiogenic Pb in zircon revealed by ion imaging: implications for early Earth geochronology. Geology 41, 291–294.

Le Roux, L.a. and Glendenin, L. (1963) Half-life of 232Th, in: (Ed.)^(Eds.), Proceedings of the National Meeting on Nuclear Energy, Pretoria, South Africa, ed., p.^pp. 94.

Ludwig, K. (2008) User’s manual for Isoplot 3.6: A geochronological toolkit for Microsoft Excel: Berkeley Geochronology Center Special Publication 4, 77 p. 6: A geochronological toolkit for Microsoft Excel. Berkeley Geochronology Center, 77.

Lyon, I.C., Kusiak, M.A., Wirth, R., Whitehouse, M.J., Dunkley, D.J., Wilde, S.A., Schaumlöffel, D., Malherbe, J., and Moore, K.L. (2019) Pb nanospheres in ancient zircon yield model ages for zircon formation and Pb mobilization. Scientific Reports 9, 13702.

Maneiro, K.A. (2016) Development of a detrital garnet geochronometer and the search for Earth's oldest garnet, in: (Ed.)^(Eds.), ed., p.^pp.

Marks, M.A., Wenzel, T., Whitehouse, M.J., Loose, M., Zack, T., Barth, M., Worgard, L., Krasz, V., Eby, G.N. and Stosnach, H. (2012) The volatile inventory (F, Cl, Br, S, C) of magmatic apatite: An integrated analytical approach. Chemical Geology 291, 241-255.

Miles, A., Graham, C., Hawkesworth, C., Gillespie, M., Hinton, R. and Bromiley, G. (2014) Apatite: A new redox proxy for silicic magmas? Geochimica et Cosmochimica Acta 132, 101-119.

Mojzsis, S.J., Cates, N.L., Caro, G., Trail, D., Abramov, O., Guitreau, M., Blichert-Toft, J., Hopkins, M.D. and Bleeker, W. (2014) Component geochronology in the polyphase ca. 3920 Ma Acasta Gneiss. Geochimica et Cosmochimica Acta 133, 68-96.
Moyen, J.-F. and Martin, H. (2012) Forty years of TTG research. Lithos 148, 312-336.

Pearce, N.J., Perkins, W.T., Westgate, J.A., Gorton, M.P., Jackson, S.E., Neal, C.R. and Chenery, S.P. (1997) A compilation of new and published major and trace element data for NIST SRM 610 and NIST SRM 612 glass reference materials. Geostandards and Geoanalytical Research 21, 115-144.

Prowatke, S. and Klemme, S. (2006) Trace element partitioning between apatite and silicate melts. Geochimica et Cosmochimica Acta 70, 4513-4527.

Pyle, J.M., Spear, F.S. and Wark, D.A. (2002) Electron microprobe analysis of REE in apatite, monazite and xenotime: protocols and pitfalls. Reviews in Mineralogy and Geochemistry 48, 337-362.

Rasmussen, B., Fletcher, I.R., Muhling, J.R., Gregory, C.J. and Wilde, S.A. (2011) Metamorphic replacement of mineral inclusions in detrital zircon from Jack Hills, Australia: Implications for the Hadean Earth. Geology 39, 1143-1146.

Reimink, J., Davies, J., Chacko, T., Stern, R., Heaman, L., Sarkar, C., Schaltegger, U., Creaser, R. and Pearson, D. (2016a) No evidence for Hadean continental crust within Earth’s oldest evolved rock unit. Nature Geoscience 9, 777.

Reimink, J.R., Chacko, T., Carlson, R.W., Shirey, S.B., Liu, J., Stern, R.A., Bauer, A.M., Pearson, D.G. and Heaman, L.M. (2018) Petrogenesis and tectonics of the Acasta Gneiss Complex derived from integrated petrology and 142Nd and 182W extinct nuclide-geochemistry. Earth and Planetary Science Letters 494, 12-22.

Reimink, J.R., Chacko, T., Stern, R.A. and Heaman, L.M. (2016b) The birth of a cratonic nucleus: lithogeochemical evolution of the 4.02–2.94 Ga Acasta Gneiss Complex. Precambrian Research 281, 453-472.
Rosa, M.d.L.d.S., Conceicao, H., Oberli, F., Meier, M., Martin, H., Macambira, M.J.B., dos Santos, E.B., Paim, M.M., LEAHY, G.A.D.S. and Leal, L.R.B. (2017) Geochronology (U-Pb/Pb-Pb) and isotopic signature (Rb-Sr/Sm-Nd) of the Paleoproterozoic Guanambi batholith, southwest Bahia State (NE Brazil). Revista Brasileira de Geociências 30, 062-065.

Roth, A.S., Bourdon, B., Mojzsis, S.J., Rudge, J.F., Guitreau, M. and Blichert-Toft, J. (2014) Combined \(^{147, 146}\)Sm-\(^{143, 142}\)Nd constraints on the longevity and residence time of early terrestrial crust. Geochemistry, Geophysics, Geosystems 15, 2329-2345.

Sano, Y., Terada, K., Hidaka, H., Yokoyama, K. and Nutman, A.P. (1999) Palaeoproterozoic thermal events recorded in the~ 4.0 Ga Acasta gneiss, Canada: Evidence from SHRIMP U-Pb dating of apatite and zircon. Geochimica et Cosmochimica Acta 63, 899-905.

Schuch, C.S. (2018) Caracterização de apatitas da Província Borborema, NE do Brasil, como materiais de referência para geocronologia U-Pb via LA-ICP-MS.

Sha, L.-K. and Chappell, B.W. (1999) Apatite chemical composition, determined by electron microprobe and laser-ablation inductively coupled plasma mass spectrometry, as a probe into granite petrogenesis. Geochimica et Cosmochimica Acta 63, 3861-3881.

St-Onge, M.R. and Davis, W.J. (2017) Wopmay orogen revisited: Phase equilibria modeling, detrital zircon geochronology, and U-Pb monazite dating of a regional Buchan-type metamorphic sequence. Bulletin 130, 678-704.

Stacey, J.t. and Kramers, J. (1975) Approximation of terrestrial lead isotope evolution by a two-stage model. Earth and planetary science letters 26, 207-221.
Sun, S.-S. and McDonough, W.-s. (1989) Chemical and isotopic systematics of oceanic basalts: implications for mantle composition and processes. Geological Society, London, Special Publications 42, 313-345.

Thomson, S.N., Gehrels, G.E., Ruiz, J. and Buchwaldt, R. (2012) Routine low-damage apatite U-Pb dating using laser ablation–multicollector–ICPMS. Geochemistry, Geophysics, Geosystems 13.

Williams, I.S., W. Compston, L.P. Black, T.R. Ireland, and J.J. Foster (1984), Unsupported radiogenic Pb in zircon: a cause of anomalously high Pb-Pb, U-Pb and Th-Pb ages. Contrib. Mineral. Petrol. 88, 322-327.

Zirner, A.L., Marks, M.A., Wenzel, T., Jacob, D.E. and Markl, G. (2015) Rare earth elements in apatite as a monitor of magmatic and metasomatic processes: The Ilímaussaq complex, South Greenland. Lithos 228, 12-22.