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Low-temperature alteration of monazite: Fluid mediated coupled dissolution–precipitation, irradiation damage, and disturbance of the U–Pb and Th–Pb chronometers

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Low-temperature alteration of monazite is documented in three centimeter-sized monazite crystals from Norway (Arendal), Madagascar (Ambato), and Sri Lanka. The three crystals have different chemical compositions, especially in their U, Th, Y and Pb contents and have $^{208}\text{Pb}/^{232}\text{Th}$ ages ranging from 491 to 900 Ma. Optical microscope (OM), Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM) images and electron microprobe analyses (EPMA) show that all three preserve a similar patchy texture. This texture is interpreted as resulting from an alteration reaction in which unaltered monazite (Mnz1) reacts to form a secondary, Th–U(Y)-depleted, high-Th/U, monazite (Mnz2) accompanied by thorite/huttonite (ThSiO_4), thorianite (ThO_2) and xenotime (YPO_4), the proportions of which are dependent upon the initial composition of the monazite (Mnz1). Images reveal variably intense internal fracturing, with cracks filled with Th-rich \pm Fe-rich phases. Monazite-xenotime thermometry demonstrates that the pristine monazites (Mnz1) interacted with a low-temperature fluid. The alteration process is interpreted to follow a mechanism of fluid-mediated coupled dissolution–precipitation. Chemical dating with the electron microprobe shows no Th–U–Pb age differences between primary and secondary monazites, except in the case of the Ambato monazite, in which altered domains yield older (750 Ma) apparent ages than the pristine Mnz1 domains. U–Pb and Th–Pb isotope dating using LA-ICP-MS yields ages consistent with electron probe dates for pristine Mnz1 zones. However, disturbance of these systems in the altered monazite domains leads to variable age results for these, depending on sample. In the case of Sri Lanka and Arendal, only $^{208}\text{Pb}/^{232}\text{Th}$ dates provide a reasonable estimate of the age of alteration, which are constrained to be 450 and 864 Ma, respectively. U/Pb systems are disturbed due to common Pb contamination (up to 40%) and U fractionation relative to Th during alteration, responsible for depletion of U in altered monazites (and increase of Th/U). In contrast, for the Ambato monazite, both the U–Pb and Th–Pb systems were affected and yield inconsistent older dates for altered zones. This is attributed to significant common Pb contamination (up to 80%), which affects all Pb isotopes and explains why electron probe ages are erroneous. Th–U-silicate contamination during measurement, resulting from the presence of a numerous nano-phases and nano-fractures filled with Th–U-silicates that are visible only under TEM, also contributes to the anomalously old ages for these disturbed (Mnz2) domains. These results demonstrate the important role of radiation damage effects, in particular swelling-induced fracturing, and the essential role of porosity and cracks, which allow fluid (charged with elements) migration through monazite during low-temperature alteration.

1. Introduction

The Light Rare Earth Element (LREE) orthophosphate monazite is a common accessory mineral in both metamorphic (see review in Spear

and Pyle, 2002) and magmatic rocks. Because of its high Th content and to a lesser extent U and low content of common Pb, monazite plays an important role as a U–Th–Pb geochronometer (Parrish, 1990; Harrison et al., 2002).

Monazite is highly resistant to alteration, as shown by its widespread occurrence as detrital mineral in sands and sandstones (Van Emden et al., 1997; Roy, 1999). However, some highly aggressive fluids may

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partially or totally alter monazite in rocks, even at moderate temperature. For example, Poitrasson et al. (1996, 2000) show that monazite is significantly altered in granitic rocks at 200–300 °C during sericitization, greisenization or chloritization. Cuney and Mathieu (2000), Hecht and Cuney (2000) and Mathieu et al. (2001) have shown that monazite is destroyed by low-T, highly saline brines in the vicinity of uranium deposits. Other studies have shown that monazite can be altered or broken down by fluorine or CO₂-rich fluids, producing allanite, apatite, rhabdophane, thorianite, thorite/huttonite, bastnäesite, or synchysite (Finger et al., 1998; Berger et al., 2008; Bosse et al., 2009; Budzyn et al., 2010; Didier et al., 2011; Janots et al., 2011; Janots et al., 2012).

The stability of monazite in fluids has been also investigated experimentally. The solubility and kinetics of dissolution of natural monazite (Oelkers and Poitrasson, 2002; Schmidt et al., 2007) or synthetic end-members (LaPO₄—Schmidt et al., 2007, NdPO₄—Devidal et al., 1998; Poitrasson et al., 2004; Pourtier et al., 2010; CePO₄—Tropper et al., 2011) have been determined in H₂O–NaCl–HCl fluids. These studies indicate both low solubility and kinetics in pure water, and enhanced solubility and kinetics in highly acidic or alkaline solutions such as brines. A second type of experiment has addressed the resetting mechanism(s) of geochronological systems (U–Pb and Th–Pb) in monazite in the presence of fluids (Teufel and Heinrich, 1997; Seydoux-Guillaume et al., 2002a; Williams et al., 2011). These studies demonstrate that coupled dissolution–precipitation is more effective than solid-state volume diffusion (Cherniak et al., 2004; Gardés et al., 2006, 2007; Cherniak, 2010) in the resetting of geochronological systems in monazite, especially in the presence of fluids enriched in alkalis. Finally, various experiments have considered the alteration mechanism of natural monazite (mineral stability and element mobility) in the presence of fluid of various compositions and at various temperature conditions (Seydoux-Guillaume et al., 2002a; Hetherington et al., 2010; Harlov et al., 2011). All these experiments confirm that monazite is indeed altered by alkaline fluids through a coupled dissolution–precipitation mechanism.

However, up to now, no experimental work has been able to reproduce the classic internal textures observed in many monazites in pegmatites (Brazil—Bilal et al., 1998; Norway—Seydoux-Guillaume et al., 2007; xenotime and monazite from Norway—Hetherington and Harlov, 2008; Norway—Nasdala et al., 2010). The chemical and isotopic characterization and analysis of these textures will form the focus of the present study. Despite originating from different localities, and having different ages and chemical compositions, all the selected monazite samples present similar textural relationships characterized by close co-occurrence of monazite, partially (Bilal et al., 1998; Seydoux-Guillaume et al., 2007; Hetherington and Harlov, 2008) or completely (Nasdala et al., 2010) altered, with a Th-rich phase such as thorianite (ThO₂; Thn) or thorite/huttonite (ThSiO₄; Thr/Htn). To our knowledge, the only experimental work that has successfully produced a Th-rich phase as the result of monazite alteration is that of Seydoux-Guillaume et al. (2002a). In those experiments, thorianite crystallized between 800 and 1200 °C in the presence of pure H₂O.

The present study investigates large (cm) monazite single crystals from three distinct pegmatite localities in Norway, Madagascar, and Sri Lanka. The crystals share a microtexture characterized by the presence of pristine monazite (Mnz1) partly altered into secondary monazite (Mnz2) accompanied by a Th-rich phase (Th-silicate or Th-oxide), and locally xenotime (Xnt). The samples are characterized using optical microscopy, back scattered electron imaging (BSE), electron probe microanalysis (EPMA) and transmission electron microscope (TEM). The preserved age characteristics have been investigated by chemical dating using EPMA and isotopic dating using laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS). Comparison of the results obtained by these very different techniques is highly illuminating because they are complementary: high spatial resolution (max. 5 μm³ for the volume analyzed) but lower precision total Pb chemical dating with EPMA, as against higher accuracy but lower spatial resolution

(50 μm³ for the volume analyzed) for isotopic dating using LA-ICP-MS. The Arendal sample was previously studied by Seydoux-Guillaume et al. (2007). Here we focus on the chemical and mineralogical changes, during fluid–rock interactions and on its geochronological effects.

2. Analytical methods

2.1. Scanning Electron Microscope (SEM), Electron Microprobe Analysis (EPMA) and chemical dating

Qualitative analysis and mapping using Electron Dispersive X-ray Spectroscopy (EDX) and Back Scattered Electron (BSE) images were performed using the JEOL 6360 equipped with a Sahara detector from PGT at the GET (Géosciences Environnement Toulouse) in Toulouse (France) (Janots et al., 2009).

Quantitative analysis was performed at GET using a CAMECA SX50 EPMA operating with the SAM-X system. Major and minor elements were measured with 20 nA probe current and 15 kV accelerating voltage using following standards: periclase (Mg), wollastonite (Ca and Si), pyrophanite (Mn and Ti), corundum (Al), haematite (Fe), baryte (Ba), albite (Na), sanidine (K), chromite (Cr), zircon (Hf and Zr), graftonite (P), UO₂ (U), ThO₂ (Th), and experimentally synthesised Pb₂P₂O₇ (Pb), REEPO₄ and YPO₄.

All EMPA dating was carried out at GET in Toulouse using a CAMECA SX50 EPMA operating with the SAM-X system. Pb and REE standards are in-house synthetic phosphates. U, Th, and Pb were measured with 300 nA probe current and 15 kV accelerating voltage. With these conditions, the analyzed area is about 1.5 μm diameter according to the equation of Castaing (1960). Thorium was measured using the Mα line, with ThO₂ as a standard, and 30 s count time on peak and background. Uranium was measured on the Mβ line, with synthetic UO₂ as standard, 90 s count time on peak and 60 s on background. Pb was measured using the Mβ line, with Pb₂P₂O₇ as a standard, 150 s count time on peak and 100 s on background. The three elements were counted using PET crystals, U and Th being counted on one spectrometer while Pb was counted simultaneously on another spectrometer. Other analytical details addressing the issues described in Jerčinović and Williams (1999) can be found in Montel et al. (2011). With these operating conditions, typical uncertainties are due to counting statistics (Ancy et al., 1978) and are ± 350 ppm, ± 250 ppm, ± 900 ppm for Pb, U, and Th respectively. Uncertainties on Pb, U, and Th are estimated individually for each analysis, then ages are calculated for each measurement (Montel et al., 1996) and the 2σ standard deviation (95% confidence interval) is calculated by propagation of errors using Monte-Carlo simulation.

2.2. Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS): instrumentation and analytical method

U–Th–Pb isotopic analysis of monazite was conducted by laser ablation inductively coupled plasma spectrometry (LA-ICP-MS) at the Laboratoire Magmas et Volcans, Clermont-Ferrand (France). Analysis involved ablation with a Resonetics Resolution M-50 powered by an ultra short pulse (<4 ns) ATL Atlex Excimer laser system operating at a wavelength of 193 nm (detailed description in Müller et al., 2009). A spot diameter of 7 μm associated with repetition rates of 1 Hz and laser energy of 6 mJ producing a fluence of 12 J/cm² was used for monazite dating. The ablated material is carried into a helium stream, and then mixed with nitrogen and argon, before injection into the plasma source of an Agilent 7500 cs ICP-MS equipped with a dual pumping system to enhance the sensitivity.

Alignment of the instrument and mass calibration were performed before every analytical session using the NIST SRM 612 reference glass, through inspection of the ²³⁸U signal and minimizing the ThO⁺/Th⁺ ratio (<<1%). The mean sensitivity for ²³⁸U using a spot size of 44 μm is about 15,000–20,000 cps/ppm. The analytical method for isotope dating of monazite with laser ablation ICPMS is similar to that

developed for zircon and monazite as reported in Tiepolo (2003) and Paquette and Tiepolo (2007). The signals for $^{204}\text{Pb} + \text{Hg}$, ^{206}Pb , ^{207}Pb , ^{208}Pb , ^{232}Th and ^{238}U masses were acquired. The occurrence of common Pb in the sample can be monitored by the evolution of the $^{204}\text{Pb} + \text{Hg}$ signal intensity, but no common Pb correction was applied owing to the large isobaric interference from Hg. The ^{235}U signal is calculated from ^{238}U on the basis of the ratio $^{238}\text{U}/^{235}\text{U} = 137.88$. Single analyses consisted of 30 s of background integration with laser-off followed by 1 min integration with the laser firing and a 30 seconds delay to wash out the previous sample (approximately 10 s for 6 orders of magnitude) and prepare for the analysis.

Data were corrected for U–Pb fractionation occurring during laser sampling and for instrumental mass discrimination (mass bias) by standard bracketing with repeated measurements of the Moacyr monazite standard (Gasquet et al., 2010). At the beginning and end of every run, repeated analyses of the Manangotry monazite (Paquette and Tiepolo, 2007), treated as an unknown, were used to independently control the reproducibility and accuracy of the corrections applied. Data reduction was carried out with the software package GLITTER® (Macquarie Research Ltd., 2001–van Achterbergh et al., 2001; Jackson et al., 2004). For each analysis, the time-resolved signals of single isotopes and isotope ratios were monitored and carefully inspected to monitor the presence of perturbations related to inclusions, fractures, mixing of different age domains or common Pb. Calculated ratios were exported from GLITTER® and Concordia ages and diagrams generated using the Isoplot/Ex v. 2.49 software package (Ludwig, 2001). The concentrations of U–Th–Pb were calibrated relative to the certified contents of Moacyr monazite standard (Seydoux-Guillaume et al., 2002b, 2004).

2.3. Transmission Electron Microscope (TEM) coupled with Focused-Ion-Beam (FIB) preparation

This technique was used in order to characterize the structural state of monazite in contact with thorite. The Arendal monazite was previously studied by Seydoux-Guillaume et al. (2007) and new TEM foils were prepared from the Ambato monazite to complete these observations. The Focused-Ion-Beam (FIB) method (Overwijk et al., 1993; Young, 1997; Roberts et al., 2001; Seydoux-Guillaume et al., 2003; Wirth, 2004, 2009) allows cutting site-specific TEM foils, ~15–20 μm by 10–15 μm , and ~100 nm thick. Milling was done using gallium ions accelerated to 30 keV. The TEM foil was cut perpendicular to the surface of the sample, and so provided information with respect to the depth from the surface of the specimen. The site-specific specimens were prepared with the FEI FIB200 instrument at the GeoForschungsZentrum (GFZ)—Potsdam. Transmission Electron Microscope (TEM) studies were carried out with the Philips CM200 TEM at the GFZ—Potsdam, operating at 200 keV, and equipped with an energy-dispersive X-ray analyzer (EDX) with ultra-thin window, and a LaB₆ filament.

3. Sample descriptions: hand specimen and transmitted light

Three large (several centimeters in diameter) monazite monocrystals were used. A piece of each was prepared for microscopic studies (optical, SEM and EPMA, \pm TEM). The first crystal is from an unknown locality in Sri Lanka and was donated by T. Geisler (Univ. Bonn). It is the least altered of the three monazites studied. It shows a relatively homogeneous yellow color, and cracks traverse the entire crystal but are more concentrated in some parts of the grain (Fig. 1a). The two other crystals were provided by Benjamin Rondot, from Muséum National d'Histoire Naturelle. The sample named “Ambato” is from Ambatofotsikely in Madagascar. This crystal is mostly yellow in color but has several areas preserving a reddish color, generally associated with alteration. In thin section (Fig. 1b) a large part of the Ambato crystal is dark in color, corresponding to the altered zones, with cracks sometimes filled with reddish inclusions (iron oxides).

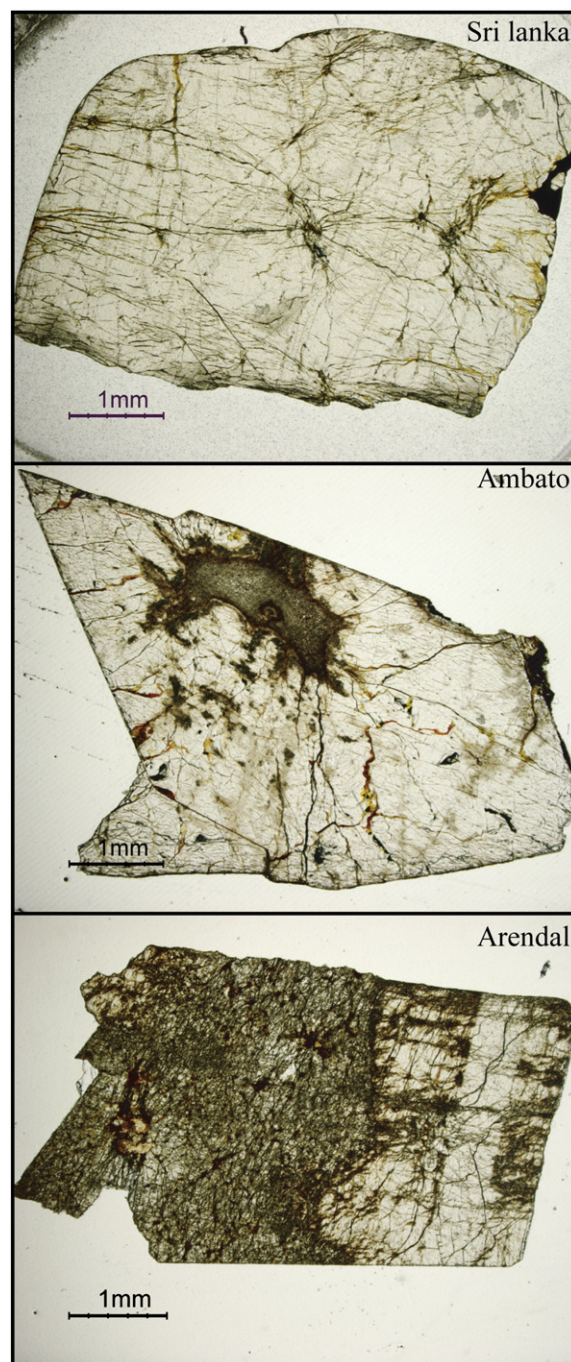


Fig. 1. Transmitted light binocular microscope photo of three thin sections of large monazite single crystals from three localities in Sri Lanka, Madagascar and south-Norway. The alteration features are more penetratively developed from Sri Lanka to the Ambato and the Arendal samples.

The third monazite crystal, is denoted as “Arendal”, as it comes from this pegmatite district and was previously studied in detail by Seydoux-Guillaume et al. (2007). Geochronological data obtained in this study suggests that the sample is from Iveland-Evje pegmatite field in Agder. It is a reddish-brown, dull and opaque crystal. Optical observations (Fig. 1c) show that the crystal is pervaded by cracks that are always filled with orange to red inclusions (iron oxides).

4. Sample descriptions: from micrometer to nanometer

Back scattered electron (BSE) images coupled with energy dispersive X-ray (EDX) mapping (Figs. 2 to 4) show that the crystals contain

thorianite or thorite (we will use thorite to denote the thorium silicate, although it could be huttonite) and sometimes xenotime inclusions.

4.1. Sri Lanka monazite (Fig. 2)

For the most part, the crystal appears uniformly gray in BSE, suggesting that it is chemically homogeneous (Mnz1). Some parts of the crystal are traversed by an interconnected network of fractures, several mm-long (Fig. 2c). A monazite that is darker in BSE (Mnz2—Fig. 2d) is systematically developed as zones or halos that are concentric around thorite or thorianite inclusions. Chemical mapping (Fig. 2a) demonstrates that this darker monazite is depleted in Th and Si and enriched in Ce and P. Cracks around thorianite are radial and intersect both Mnz2 and Mnz1 (Fig. 2b), suggesting that fracturing is directly related to the presence of this Th-rich phase and took place after the formation of both Mnz1 and Mnz2. Some porosity occurs in the vicinity of thorianite (e.g. black zones in Fig. 2b and d). The preliminary interpretation from this textural evidence is that the initial higher-Th Mnz1 transformed to the assemblage Mnz2 + thorite/thorianite + quartz (Fig. 2—Si map), and that the formation of the Th-rich minerals during this transformation is responsible for later fracturing.

4.2. Ambato monazite (Fig. 3)

The Ambato crystal contains larger areas affected by fracturing and the alteration of Mnz1 to Mnz2 and Th-phases (several mm in Fig. 3c). Xenotime (Xnt, Fig. 3a) is observed together with Mnz2 and thorite. Th-rich phases occur both as isolated large crystals (up

to 100 μm), and dispersed smaller grains (Figure 3a, b and d). Porosity and intense fracturing are observed in all altered domains (e.g. Fig. 3d). There are two varieties of fractures: radial fractures around Th-rich phases, which propagate through the Mnz2 phase (Fig. 3b), and extended fractures that traverse across the entire crystal (Fig. 1b). Segments of the latter fractures affect only the unaltered parts of the crystal and terminate in the vicinity of the altered zones (e.g. see the fractures stopping just before the large Th-rich inclusion Fig. 3a or Fig. 3c).

4.3. Arendal monazite (Fig. 4)

Only a small amount of the initial monazite Mnz1 is preserved in this crystal (right zone in Fig. 1c and middle zone in Fig. 4b). Thorite (up to 100 μm in size) and xenotime crystals larger than 100 μm (Fig. 4b, c and d) can be observed in the altered zones (Fig. 4a). Two kinds of fractures dominate the crystal: radial cracks around thorites, as seen in Fig. 4c and d, and a dense network of fractures that occur throughout the entire crystal without apparent preferential orientation (Fig. 4b). Fractures are in filled by a Th-rich phase (Fig. 4a and d).

4.4. Observations at nanometer scale using Transmission Electron Microscope (TEM) (Fig. 5)

Two TEM foils were prepared, across the contact between the thorite (Thr) and altered monazite (Mnz2) in both the Arendal and Ambato crystals. Detailed results concerning the structural state of the Arendal crystal have been reported previously (Seydoux-Guillaume et al., 2007). However a new bright field (BF) image is presented in Fig. 5a

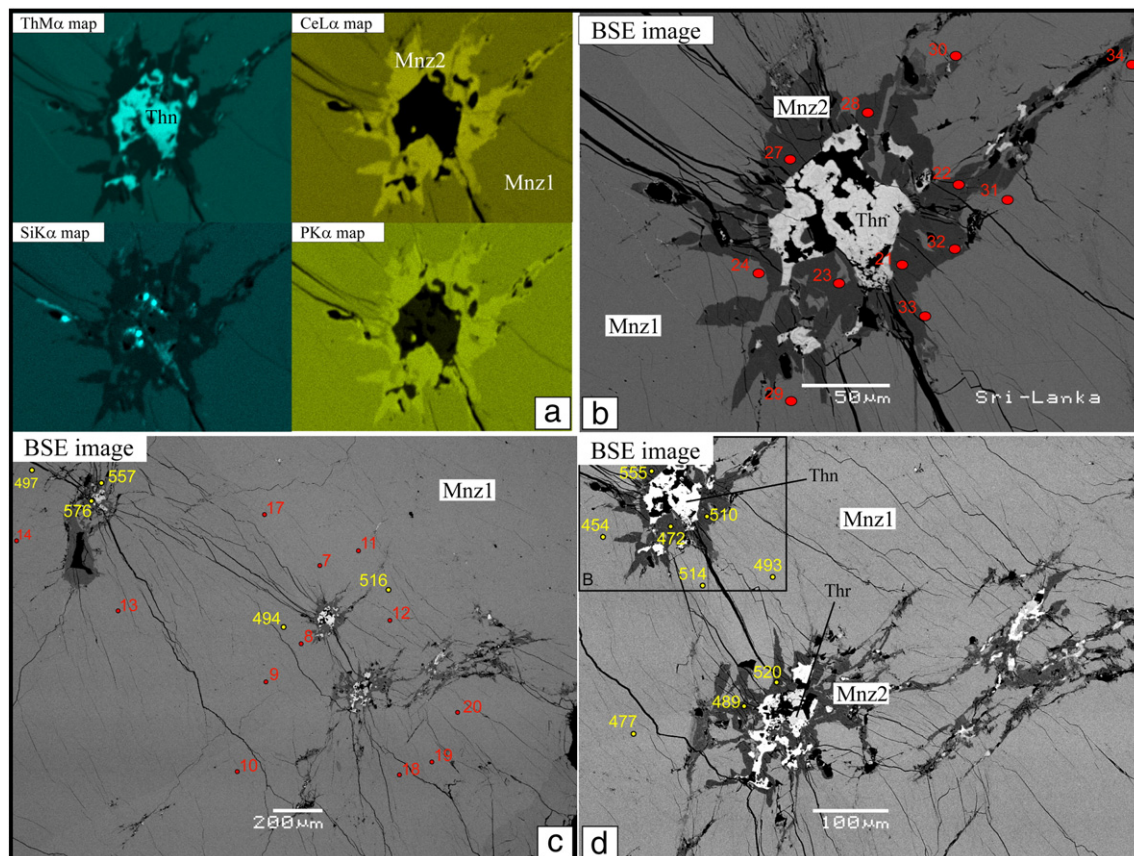


Fig. 2. Th, Si, Ce, P-chemical composition maps (a) and Back Scattered Electron (BSE) images (b–d) of a selected area of the Sri-Lanka monazite sample. The large monazite single crystal is composed of pristine monazite (Mnz1) and localized alteration zones, consisting of Th-depleted monazite (Mnz2) associated with Th-rich phase thorianite and/or thorite (Thn/Thr). Altered zones are connected to each other by a dense fracturing network across the entire crystal. Red ellipses correspond to location of LA-ICP-MS analyses with # numbers and yellow ellipses to EPMA chemical ages.

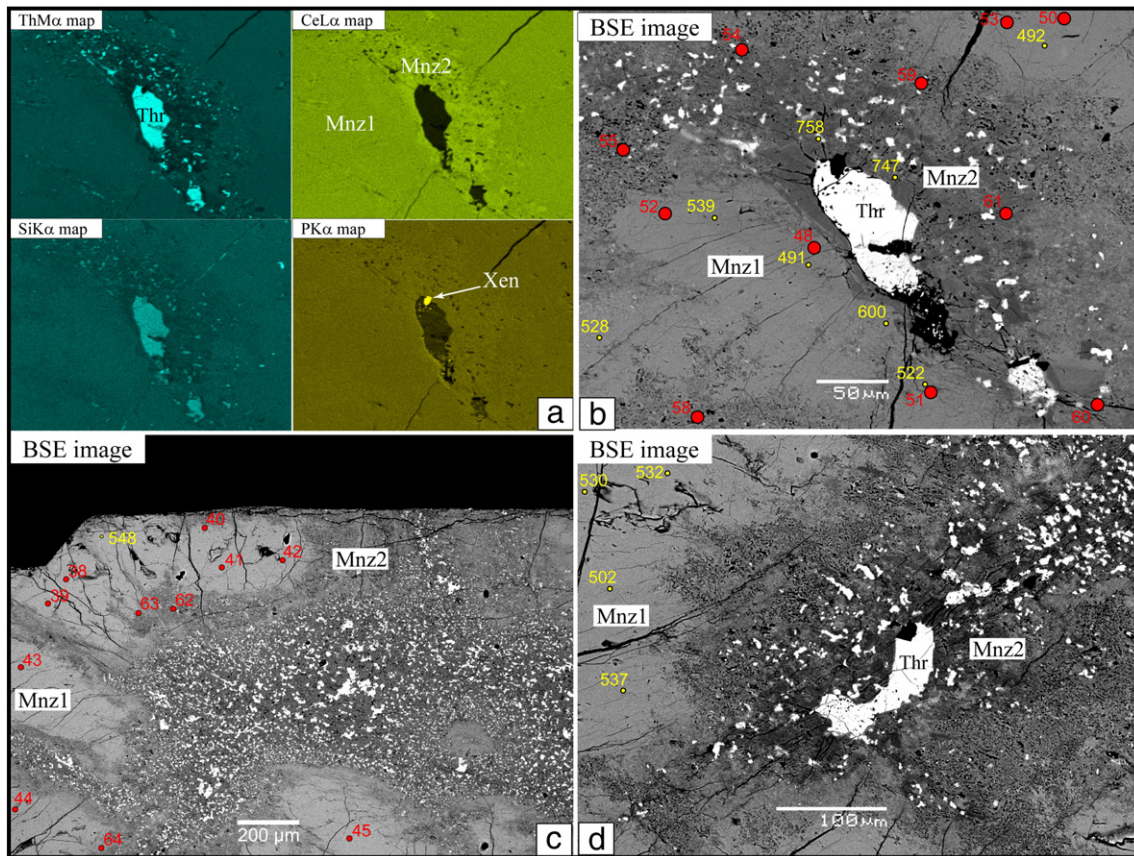


Fig. 3. Th, Si, Ce, P-chemical composition maps (a) and BSE images (b–d) of the Ambato monazite sample. The same features as in Fig. 2 are shown.

to provide a comparison with the Ambato monazite. Both altered monazites (Mnz2, Fig. 5a and b) show the characteristic mottled diffraction contrasts, indicating limited lattice distortion and radiation damage (Seydoux-Guillaume et al., 2002c, 2003, 2004, 2007), even along the thorite–monazite interface (Fig. 5c and e; Seydoux-Guillaume et al., 2007). In contrast, the thorite is totally amorphous (absence of diffraction contrasts for Thr—Fig. 5e). In accordance with the observations based on SEM images (Fig. 3), the TEM images show that the Ambato monazite is traversed by cracks originating along the thorite–monazite interface, propagating through Mnz2 and filled with amorphous thorite (Thr in Fig. 5e). Even when in direct contact with these cracks, monazite is crystalline and has the same mottled diffraction contrasts that can be seen in Fig. 5b. Mnz2 contains inclusions of polycrystalline hematite (Hmt—Fig. 5d) infilling large pockets (2–3 μm in diameter) completely included in Mnz2 or infilling cracks (Fig. 5c and e).

5. Chemical composition: EPMA

The average compositions of the different phases (Mnz1 and 2, Xnt, and Thr) are given in Tables 1 and 2. Fig. 6 presents element composition spectra for Mnz2 normalized against Mnz1 in order to show the chemical changes associated with alteration. These chemical changes are also visualized in the binary plot of Fig. 7.

5.1. Sri Lanka monazite

Mnz1 is very rich in Th (~23 wt.% ThO₂) and has associated high SiO₂ contents (~5 wt.%); Pb, Ca, Y, MREE (Dy) and U oxides are less than 1 wt.%, LREE (La–Gd) concentrations are ~48 wt.% and P₂O₅ ~22 wt.% (Table 1). Mnz2 is strongly depleted in Th (~5 wt.% ThO₂), SiO₂ (~0.65 wt.%) and UO₂ (~0.09 wt.%, Fig. 6). As a result, Mnz2 is enriched in LREE₂O₃ (~63 wt.%) and P₂O₅ (28 wt.%). The Th/U ratio

increases from 30 for Mnz1 to 64 for Mnz2. Thr and Thn display low EPMA totals (~90 wt.%), and contain few measurable cations other than (Th, U) and Si. Only the Fe concentration is occasionally high (up to 7 wt.% in Thr), but it is difficult to be certain that the Fe is actually incorporated into the Thr structure rather than present as a mineral inclusion in Thr. UO₂ is higher in Thr (~2 wt.% UO₂) than in thorianite (ca 0.7 wt.% UO₂).

The distribution of the data is visible in the binary compositional diagram (REE + Y + P) vs (Th + U + Si) of Fig. 7a; Mnz1 analyses plot along a line between Mnz2, which lies near an end member depleted in Th and a Th-rich phase depleted in REE and P.

5.2. Ambato monazite

Ambato Mnz1 is characterized by high ThO₂ (~14 wt.%) associated with relatively high SiO₂ (~3 wt.%); Pb, Ca, MREE (Dy) and UO₂ are less than 1 wt.%, and Y₂O₃ is near 1 wt.%. In comparison with Mnz1, Mnz2 is depleted in ThO₂ (~6 wt.%), SiO₂ (~1.15 wt.%), Y₂O₃ (0.61 wt.%) and UO₂ (~0.08 wt.%, Fig. 6). The Th/U ratio increases from 25 for Mnz1 to 71 for Mnz2. Thorite, which has a low EPMA total, is composed essentially of ThO₂ (72 wt.%), SiO₂ (~9 wt.%) and UO₂ (~2.6 wt.%), resulting in a Th/U ratio of 28. Xenotime has high Y₂O₃ (50 wt.%), P₂O₅ (~37 wt.%), Gd₂O₃ (~6 wt.%) and HREE₂O₃ (8 wt.%), but contains only very low amounts of ThO₂ (~0.22 wt.%), and PbO (~0.08 wt.%). U is below the detection limit (Table 2). Both monazite types (Mnz1 and Mnz2) plot along a straight line in the compositional diagram (REE + Y + P) vs (Th + U + Si), with xenotime and thorite at the ends of that line (Fig. 7b).

5.3. Arendal monazite

Mnz1 is initially heterogeneous in composition, with the variations interpreted as reflecting relict magmatic zoning (Mnz1 vs Mnz1'—sharp

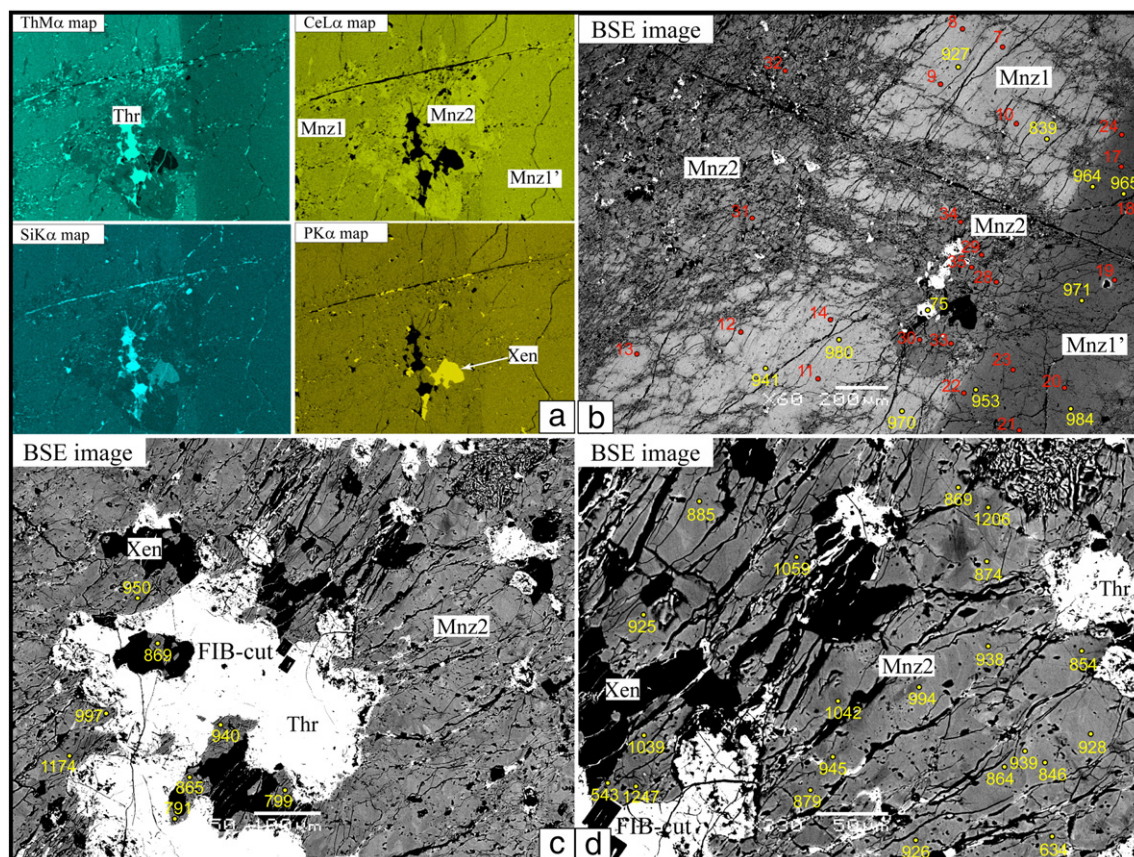


Fig. 4. Th, Si, Ce, P-chemical composition maps (a) and BSE images (b-d) of the Arendal monazite sample. The same features as in Fig. 2 are shown. Note that the pristine monazite can be divided into two magmatic zones Mnz1 and Mnz1'. Dense fracturing network crosscuts the entire crystal and originates at the Th-silicate boundary.

interface Fig. 4B): the main variation is in the Th content (12 % ThO₂ to 7 % ThO₂; Table 1). Mnz2 is depleted in ThO₂ (~6 wt.%), SiO₂ (~0.66 wt.%), Y₂O₃ (0.48 wt.%) and UO₂ (~0.13 wt.%, Table 2) with respect to both Mnz1 and Mnz1'. These changes are illustrated using the plot of Mnz2 normalized against Mnz1 and Mnz1' for the main elements (Fig. 6). The Th/U ratio increases from 18 (Mnz1) and 11 (Mnz1') for unaltered monazite, to 48 for altered monazite (Mnz2). Thorite, which has low EPMA totals, is composed essentially of ThO₂ (63 wt.%), SiO₂ (~16 wt.%) and UO₂ (~7 wt.%), resulting in a Th/U ratio of 9. Xenotime has high Y₂O₃ (45 wt.%) with P₂O₅ (~35 wt.%), Gd₂O₃ (~6 wt.%) and HREE₂O₃ (8 wt.%), but contains very low ThO₂ (~0.87 wt.%), PbO (~0.08 wt.%), and UO₂ (~0.29 wt.%, Table 2).

These compositional variations result in a distribution of monazite analyses (1, 1' and 2) along a straight line in the compositional diagram (REE + Y + P) vs (Th + U + Si) (Fig. 7c), with Xnt and Thr at the extremities of the line.

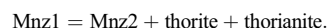
5.4. Estimation of the temperature of alteration

Making the assumption that Mnz2 formed in equilibrium with Xnt and Thr, which appears to be the case for the Ambato and Arendal monazites based on the occurrence of the latter phases in Mnz2 domains, it is possible to estimate the temperature of alteration to form this assemblage (Gratz and Heinrich, 1997; Seydoux-Guillaume et al., 2002b) (Table 1). For the Ambato monazite, these calculations yield temperatures ranging from 210 °C (using Th content of monazite; after Seydoux-Guillaume et al., 2002b) to 319 °C (using Y content of monazite; after Gratz and Heinrich, 1997). For Arendal, the crystallization temperature of the Mnz2-Xnt-Thr assemblage (Table 1) is even lower and ranges from 43 °C (using the Th content of monazite; after Seydoux-Guillaume et al., 2002b) to 136 °C (using Y content of monazite; after Gratz and Heinrich, 1997). Nevertheless, it must be emphasized that the very

large standard deviation obtained for Y in Mnz2 (Table 1), related to high relative variations in Y at low Y-concentrations (e.g. 0.34 to 0.87 wt.% and 0 to 1.2 wt.% for Ambato and Arendal monazite samples respectively) in monazite samples, leads to large temperature uncertainties, and hence the calculated temperatures should be used with caution. Although disequilibrium between these grains cannot be excluded, the Mnz-Xnt thermometry indicates that alteration took place at low temperatures (<320 °C).

5.5. Mass balance calculations

The chemical compositions reported in Tables 1 and 2 were used to perform some elementary mass balance calculations for the proposed reactions, based on the most immobile elements. For Sri Lanka monazite the proposed reaction is:



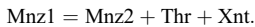
In this case the amount of Mnz2 produced is initially calculated from Ce + La + Nd, Thr from SiO₂, and Thn from ThO₂. This calculation, however, does not produce satisfactory results, because after Thr is formed using the available SiO₂, no Th is left to form Thn. This suggests that the appearance of Thn is due to a local deficit of SiO₂, so that the consumption of SiO₂ by Thr leaves an excess of Th that must be incorporated in Thn. With the simpler reaction:



and based on balancing for La, Ce and Nd in the Sri Lanka monazite, we calculate that 1 g of Mnz1 can produce 0.76 g of Mnz2. The remaining Th allows 0.27 g of Thr to be made. This reaction produces an excess of Si, P and U but requires some Ca to balance the reaction. Assuming that density of monazite is 5.3 g/cm³ and that of thorite 6.8 g/cm³, we

can estimate that 0.189 cm^3 of Mnz1 produces 0.143 cm^3 of Mnz2 and 0.039 cm^3 of Thr, yielding a 3.6:1 volume ratio. The volumetric proportion of the two phases can also be estimated by analyzing SEM images, using the assumption that the area proportions are approximately equivalent to the volume proportions for the random distribution of Thr in Mnz2. Processing of the image in Fig. 2b yielded a Mnz2/Thr area ratio of 4.1, in reasonable agreement with the simplified mass balance calculations described above.

For the Arendal and Ambato samples, xenotime, estimated from Y, must be added as reaction product; the proposed reaction becomes:



Using the same method and assuming that the density of xenotime is 4.3 g/cm^3 we calculate that, for Ambato, 0.88 g of Mnz2, 0.12 g of Thr and 0.10 g of Xnt are produced for each gram of Mnz1 consumed, or 0.166 cm^3 , 0.018 cm^3 , 0.023 cm^3 for each cm^3 of Mnz1 transformed. With these phase proportions, some excess SiO_2 and U remain. For Arendal we obtained 0.87 g Mnz2, 0.10 g Thr, and 0.04 g Xnt forming from Mnz1, and 0.92 g Mnz2, 0.03 g Thr, 0.05 g Xnt from Mnz1'. With those phase proportions U is only liberated by the alteration of Mnz1'. Unfortunately, the microtextures of these two samples are too complex

for reliable image analysis to be performed in order to compare the predictions of the mass balance modeling with observed modal proportions.

6. Geochronology

6.1. Chemical Th-U-total Pb ages with EMPA

Results of EMPA dating are reported in Tables 3 to 6. The ages were calculated following the approach of Montel et al. (1996). The data are plotted using the isochron-like diagram of Suzuki and Adachi (1991) in Fig. 8. This representation requires the transformation of the U content into "fictive Th" content, i.e. the amount of Th that would give the same amount of Pb as U for a given age. The sum of the "fictive Th" and the real Th corresponds to the "equivalent Th" value, Th^* . The plot of Pb vs Th^* should give a straight line, the slope of which yields the age and the intercept at the origin the initial Pb content (assuming that is constant). More details about these methods can be found in Harrison et al. (2002).

For the Sri-Lanka monazite sample, Mnz1 yielded ages from 454 ± 37 to 517 ± 42 Ma and Mnz2 from 472 ± 152 to 576 ± 135 Ma. From a statistical point of view, all ages must be considered to belong to

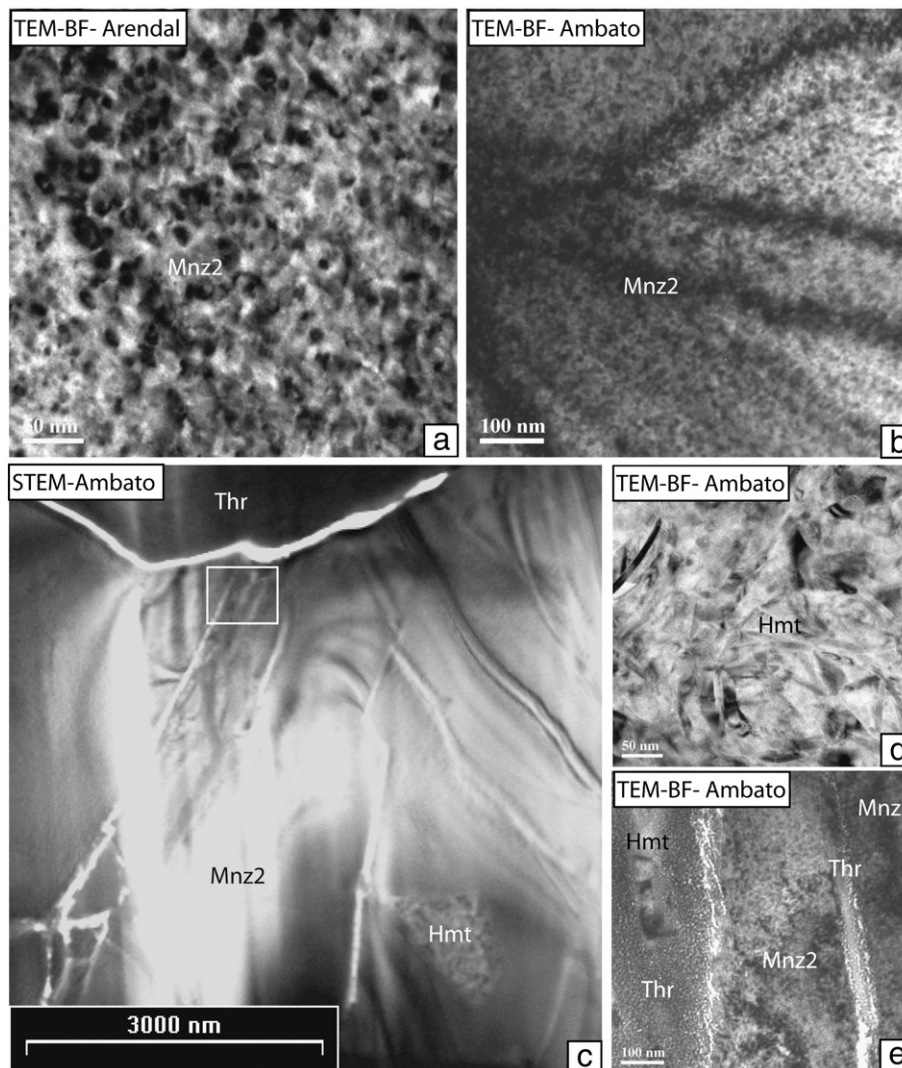


Fig. 5. Transmission Electron Microscope (TEM) images of Arendal (a) and Ambato (b–e) monazites. TEM bright field (BF) images of the Arendal (a) and the Ambato (b) monazite samples showing mottled diffraction contrasts reflecting radiation damage. c—Scanning TEM image of the Ambato monazite with many cracks, filled with thorite (Thr), passing through monazite. d—TEM BF image of a hematite (Hmt) pocket (detail from panel c). e—TEM BF image of the Ambato monazite—the enlargement from panel c shows cracks filled with Thr and Hmt inclusions in altered monazite (Mnz2).

Table 1
Representative electron microprobe analyses of monazites.

Sample	Sri Lanka monazite				Ambato monazite				Arendal monazite					
	Unaltered		Altered		Unaltered		Altered		Unaltered 1		Unaltered 1'		Altered	
wt.%	av. 22 anal.	$\pm 2\sigma$	av. 5 anal.	$\pm 2\sigma$	av. 15 anal.	$\pm 2\sigma$	av. 7 anal.	$\pm 2\sigma$	av. 10 anal.	$\pm 2\sigma$	av. 8 anal.	$\pm 2\sigma$	av. 28 anal.	$\pm 2\sigma$
SiO ₂	4.7	0.4	0.6	0.1	3.1	0.5	1.2	0.3	2.1	0.2	1.1	0.1	0.7	0.3
P ₂ O ₅	21.8	0.6	28.4	0.6	24.3	0.7	27.4	0.6	26.6	0.3	28.2	0.3	28.7	0.5
CaO	0.6	0.1	0.7	0.2	0.2	0.1	0.2	0.1	0.9	0.1	0.9	0.0	0.8	0.2
Y ₂ O ₃	0.6	0.0	0.5	0.2	1.0	0.1	0.6	0.2	2.2	0.2	2.8	0.1	0.5	0.3
La ₂ O ₃	12.0	0.6	15.9	0.4	6.6	0.3	7.4	0.3	11.1	0.4	12.0	0.2	12.2	0.6
Ce ₂ O ₃	23.4	0.1	30.8	0.6	23.9	0.9	27.3	0.8	25.5	0.5	27.0	0.3	29.0	1.3
Pr ₂ O ₃	2.5	0.4	3.2	0.2	3.7	0.4	4.5	0.5	3.1	0.4	3.2	0.4	3.6	0.4
Nd ₂ O ₃	8.1	0.6	10.6	0.5	14.7	0.6	17.0	0.8	10.6	0.4	11.2	0.3	13.1	0.8
Sm ₂ O ₃	1.0	0.3	1.4	0.4	4.4	0.3	5.0	0.4	2.1	0.4	2.2	0.4	2.6	0.4
Gd ₂ O ₃	0.5	0.5	0.9	0.2	1.9	0.4	2.3	0.2	1.5	0.2	1.8	0.3	1.6	0.4
Dy ₂ O ₃	0.2	0.2	0.1	0.1	0.2	0.1	0.1	0.1	0.7	0.3	0.7	0.1	0.3	0.2
PbO	0.6	0.3	0.1	0.1	0.4	0.2	0.2	0.2	0.6	0.2	0.4	0.2	0.2	0.2
ThO ₂	22.9	0.1	5.5	0.6	14.1	2.1	5.8	1.6	12.0	1.2	7.3	0.5	6.2	2.0
UO ₂	0.8	0.2	0.1	0.1	0.6	0.2	0.1	0.1	0.7	0.1	0.7	0.1	0.1	0.2
Total	99.7		98.7		99.0		99.0		99.7		99.4		99.6	
Th/U	29.9		63.9		25.4		70.9		17.9		10.7		48.1	
Cations/40														
Si	0.20		0.03		0.13		0.05		0.08		0.04		0.03	
P	0.79		0.97		0.86		0.95		0.91		0.95		0.97	
Ca	0.03		0.03		0.01		0.01		0.04		0.04		0.04	
Y	0.01		0.01		0.02		0.01		0.05		0.06		0.01	
La	0.19		0.24		0.10		0.11		0.17		0.18		0.18	
Ce	0.37		0.45		0.37		0.41		0.38		0.39		0.42	
Pr	0.04		0.05		0.06		0.07		0.05		0.05		0.05	
Nd	0.12		0.15		0.22		0.25		0.15		0.16		0.19	
Sm	0.01		0.02		0.06		0.07		0.03		0.03		0.04	
Gd	0.01		0.01		0.03		0.03		0.02		0.02		0.02	
Dy	0.00		0.00		0.00		0.00		0.01		0.01		0.00	
Pb	0.01		0.00		0.00		0.00		0.01		0.00		0.00	
Th	0.22		0.05		0.13		0.05		0.11		0.07		0.06	
U	0.01		0.00		0.01		0.00		0.01		0.01		0.00	
Total	2.01		2.01		2.01		2.01		2.01		2.01		2.01	
U + Th + Pb + Si	0.44		0.08		0.27		0.10		0.21		0.12		0.09	
\sum REE + Y + P	1.54		1.90		1.72		1.89		1.76		1.85		1.88	
X _Y ^a							0.03	0.01					0.02	0.02
T (°C) ^a							319	± 120					136	± 240
T (°C) ^b							210	± 140					43	± 220

^a Calculated after Gratz and Heinrich (1997) –X_Y is the mole fraction Y in monazite assuming a total occupancy of 1 in a Ce–Y system and considering that monazite crystallized in equilibrium with xenotime.

^b Calculated after Seydoux-Guillaume et al. (2002b) –X_Y is the mole fraction Y in monazite assuming a total occupancy of 1 in a Ce–Y–Th system (and X_{Th} = 0.09) and assuming that monazite crystallized in equilibrium with xenotime and thorium silicate.

one single population, the best estimate of which is 491 ± 9 Ma, with MSWD = 0.74 (n = 24).

For the Ambato monazite sample, Mnz1 yielded ages from 495 ± 75 to 604 ± 104 Ma. Due to the high density of inclusions and fractures, only two measurements can be considered to unambiguously belong to Mnz2; one of these two measurements is chemically similar to Mnz1 (#18 in Table 4), but the other one is significantly lower in Th and U. Mnz1 defines a homogeneous population with a best age estimate at 537 ± 16 Ma. The two measurements in Mnz2 yielded a significantly older age, at 750 ± 33 Ma. The global MSWD is 0.83 (n = 19).

The Arendal monazite sample displays more variable U and Th contents. The Th contents in pristine areas define two groups of analyses: a Th-rich one (about 10 wt.% Th–Mnz1) and a Th-poor one (about 6 wt.% Th–Mnz1'). The Th content in the Mnz2 areas ranges from 2.7 wt.% to 8.4 wt.%, but most values are in the 3–5 wt.% Th range. Resulting ages are of 840 ± 76 to 984 ± 107 Ma for pristine zones (Mnz1 and 1'), and 791 ± 144 to 1247 ± 277 Ma for Mnz2. The whole set of data can be fitted to a single-aged population with a best age estimate at 934 ± 21 Ma (n = 37; MSWD = 1.17).

6.2. U/Pb and Th/Pb ages with LA-ICP-MS (Tables 6–8; Figs. 9 and 10)

U–Th–Pb isotopic analysis was carried out on the three monazite crystals. Analytical points were chosen both in the unaltered and altered

zones of monazite grains; the locations of analyses are shown in Figs. 2–4. Results are listed in Tables 6–8 and presented graphically in ²⁰⁶Pb/²³⁸U vs ²⁰⁸Pb/²³²Th modified concordia and in Tera Wasserburg (TW–²⁰⁷Pb/²⁰⁶Pb vs ²³⁸U/²⁰⁶Pb) diagrams in Fig. 9.

Twenty-four analyses were obtained on the Sri Lanka monazite (Table 6, Fig. 2), 18 in Mnz1 and 6 in Mnz2. The results from Mnz1 (18 measurements) yield a weighted ²⁰⁶Pb/²³⁸U mean (WM) age of 500 ± 5 Ma [MSWD = 3.1] and a WM ²⁰⁸Pb/²³²Th age of 491 ± 4 Ma [MSWD = 2.4] (Fig. 9a and b). The latter age is indistinguishable from the EPMA age (491 ± 9 Ma). ²⁰⁷Pb/²⁰⁶Pb and ²⁰⁶Pb/²³⁸U ages for Mnz2 are widely scattered (from 698 ± 127 to 4105 ± 88 Ma and from 483 ± 23 to 1737 ± 67 Ma, respectively), and are interpreted to reflect the incorporation of common Pb. A regression through data from Mnz2 analyses defines an intercept age of 484 ± 39 Ma (Fig. 9a). Corresponding ²⁰⁸Pb/²³²Th ages are less scattered (from 435 ± 10 to 483 ± 11 Ma), showing younger ages compared to Mnz1 with WM ²⁰⁸Pb/²³²Th apparent ages of 450 ± 18 Ma [MSWD = 11.7].

Twenty one analyses were obtained from the Ambato monazite (Table 7, Fig. 3): thirteen in Mnz1 and eight in Mnz2. In the case of Mnz1 two analyses (#48 and 49) display higher ²⁰⁷Pb/²⁰⁶Pb ratios and demonstrate common Pb contamination, probably due to their proximity to both cracks and (Th,U)-silicate inclusions (Fig. 3); these analyses were not considered in the calculation of WM ages for Mnz1. The remaining analyses yield a WM ²⁰⁶Pb/²³⁸U age of 514 ± 6 Ma

Table 2
Representative electron microprobe analyses of Th-rich phases (thorianite and ThSiO₄) and xenotime.

Sample	Sri Lanka monazite				Ambato monazite				Arendal monazite			
	Thorianite		ThSiO ₄		ThSiO ₄		Xenotime		ThSiO ₄		Xenotime	
Characteristics	Thorianite		ThSiO ₄		ThSiO ₄		Xenotime		ThSiO ₄		Xenotime	
wt.%	av. 6 anal.	±2σ	av. 5 anal.	±2σ	av. 2 anal.	±2σ	av. 8 anal.	±2σ	av. 6 anal.	±2σ	av. 10 anal.	±2σ
SiO ₂	0.34	0.20	12.99	1.42	8.91	0.73	0.01	0.02	16.39	0.65	0.00	
P ₂ O ₅	–	–	–	–	–	–	35.20	0.41	0.56	0.24	34.51	0.43
V ₂ O ₅	0.05	0.05	0.25	0.14	0.17	0.07	–	–	–	–	–	–
As ₂ O ₅	0.01	0.02	0.00	–	0.06	0.06	–	–	–	–	–	–
SO ₂	0.30	0.09	0.12	0.09	0.03	0.02	–	–	–	–	–	–
CaO	0.72	0.26	1.10	0.12	0.17	0.14	0.01	0.01	2.01	0.38	0.01	0.01
FeO	0.55	0.55	1.30	2.95	0.09	0.10	0.00	–	–	–	0.00	–
MnO	0.02	0.04	0.03	0.05	–	–	0.02	0.02	–	–	0.01	0.02
Y ₂ O ₃	0.03	0.01	0.89	0.36	–	–	48.33	0.59	0.51	0.37	44.32	0.61
La ₂ O ₃	–	–	–	–	–	–	0.07	0.06	0.00	0.01	0.05	0.05
Ce ₂ O ₃	–	–	–	–	–	–	0.12	0.06	0.00	0.01	0.05	0.06
Pr ₂ O ₃	–	–	–	–	–	–	–	–	0.09	0.19	–	–
Nd ₂ O ₃	–	–	–	–	–	–	0.15	0.10	0.10	0.16	0.22	0.15
Sm ₂ O ₃	–	–	–	–	–	–	1.16	0.14	0.04	0.04	0.46	0.21
Gd ₂ O ₃	–	–	–	–	–	–	5.74	0.55	0.09	0.14	4.95	0.42
Tb ₂ O ₃	–	–	–	–	–	–	1.00	0.16	–	–	1.03	0.16
Dy ₂ O ₃	0.07	0.10	0.13	0.19	–	–	5.35	0.18	0.30	0.35	7.98	0.60
Ho ₂ O ₃	–	–	–	–	–	–	0.24	0.27	–	–	1.12	0.39
Er ₂ O ₃	0.06	0.10	0.15	0.08	–	–	0.81	0.17	–	–	3.27	0.25
Tm ₂ O ₃	–	–	–	–	–	–	0.00	–	–	–	0.16	0.12
Yb ₂ O ₃	–	–	–	–	–	–	0.08	0.10	–	–	1.28	0.27
Lu ₂ O ₃	–	–	–	–	–	–	0.20	0.32	–	–	0.15	0.25
PbO	0.05	0.08	0.17	0.16	0.15	0.08	0.03	0.05	0.11	0.10	0.05	0.07
ThO ₂	88.53	3.00	72.65	4.61	72.22	1.22	0.51	0.56	62.90	0.61	0.34	0.34
UO ₂	0.71	0.18	1.91	0.50	2.57	0.58	0.13	0.13	6.99	0.48	0.11	0.11
Total	91.45		91.69		84.37		99.12		90.08		100.06	
Th/U	125		38		28		4		9		3	
Cations/40												
U + Th + Pb + Si			1.90		1.97		0.01		1.88		0.00	
Σ REE + Y + P			0.02		0.03		2.00		0.06		2.01	
Total			1.92		2.00		2.01		1.94		2.01	

[MSWD = 9; n = 11]. In the modified Concordia diagram, data are concordant and yield a WM ²⁰⁸Pb/²³²Th age (Fig. 9d) of 507 ± 7 Ma [MSWD = 13; n = 11], younger than but close to the EPMA age (537 ± 16 Ma for Mnz1—see above). Mnz2 data show considerable scatter, along with data high degree of discordance (Fig. 9c and d: 3261 to 4908 Ma for ²⁰⁷Pb/²⁰⁶Pb ages, 611 to 5565 Ma for ²⁰⁶Pb/²³⁸U ages, and 294 to 1022 Ma for ²⁰⁸Pb/²³²Th ages). In this sample most of the Mnz2 analytical points plotting along a discordia line (Fig. 9c) at a position corresponding to ~80% contribution from common Pb (²⁰⁷Pb/²⁰⁶Pb ~ 0.7), and it is therefore not possible to define an intercept age for Mnz2. Except for one analysis (#59—see below), all ²⁰⁸Pb/²³²Th apparent ages measured in Mnz2 are significantly older than the ²⁰⁸Pb/²³²Th ages determined for Mnz1 (Table 7, Figs. 9d and 10b). This is

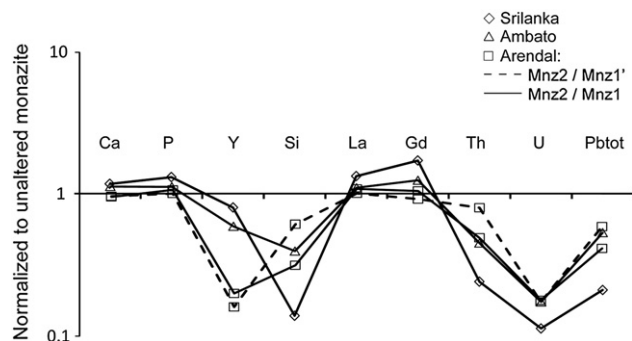


Fig. 6. Electron Probe Micro Analyser (EPMA) analyses showing the chemical effects of alteration in the Sri Lanka, Arendal and Ambato monazite samples. The mean value of altered monazite (Mnz2) is normalized to the mean of unaltered analyses (Mnz1). All three monazites have the same pattern reflecting loss of Th, Si, Y, U, and Pb with a preferential loss of U relative to Th leading to an increase of the Th/U ratio.

consistent with the “old” chemical U–Th–Pb apparent ages obtained by EPMA in the altered areas (750 ± 33 Ma). One analysis (#59) differs strongly from the other Mnz2 data in having very high Th and U contents (22.3 wt.% Th and 8375 ppm U) and lower ²⁰⁶Pb/²³⁸U and ²⁰⁸Pb/²³²Th ages of 611 ± 7 and 294 ± 3 Ma respectively. These unique features are considered to reflect the incorporation of high (Th,U)-silicate inclusions (see Table 2) in this analysis, an interpretation supported by the similarity between the measured Th/U ratio (= 27) of Mnz2 and that of Th-silicate (= 28—Table 2).

Twenty-two analyses were obtained from the Arendal monazite (Table 8, Fig. 4), sixteen in the pristine zones (8 for Mnz1 + 8 for Mnz1') and 6 in Mnz2. The Mnz1 and Mnz1' data fall slightly below the concordia curve (Fig. 9e). The WM ²⁰⁶Pb/²³⁸U age for Mnz1 is 917 ± 14 Ma [MSWD = 10.1; n = 8] and for Mnz1' is 896 ± 9 Ma [MSWD = 4.7; n = 8]. The results for these two magmatic zones statistically overlap and so warrant the pooling of all the data for the pristine monazite. This produces a poorly fitting WM ²⁰⁶Pb/²³⁸U age of 906 ± 9 Ma [MSWD = 11.6; n = 16]. The corresponding WM ²⁰⁸Pb/²³²Th ages (Fig. 9f) are 909 ± 18 Ma [MSWD = 19; n = 8] for Mnz1 and 892 ± 12 Ma [MSWD = 8.9; n = 8] for Mnz1', and the pooled WM ²⁰⁸Pb/²³²Th age for both is 900 ± 11 Ma [MSWD = 16; n = 16]. For comparison, the chemical U–Th–Pb age obtained by EPMA (see above) is arguably older (934 ± 21 Ma), but as indicated by the MSWD for Mnz1 and Mnz1' there is considerable scatter in the isotopic data that preclude a simple interpretation of them as representing a single, geologically-meaningful age. Since Mnz2 ²⁰⁶Pb/²³⁸U and ²⁰⁷Pb/²³⁵U ratios are higher than those of Mnz1 these result in Pb–U data with poor precisions (large ellipses in Fig. 9) scattered along the concordia curve, as well as apparent ages equivalent to or older than those of Mnz1 (²⁰⁶Pb/²³⁸U ages between 902 ± 15 and 1203 ± 21 Ma). In contrast, ²⁰⁸Pb/²³²Th ages for Mnz2 are on average younger than in

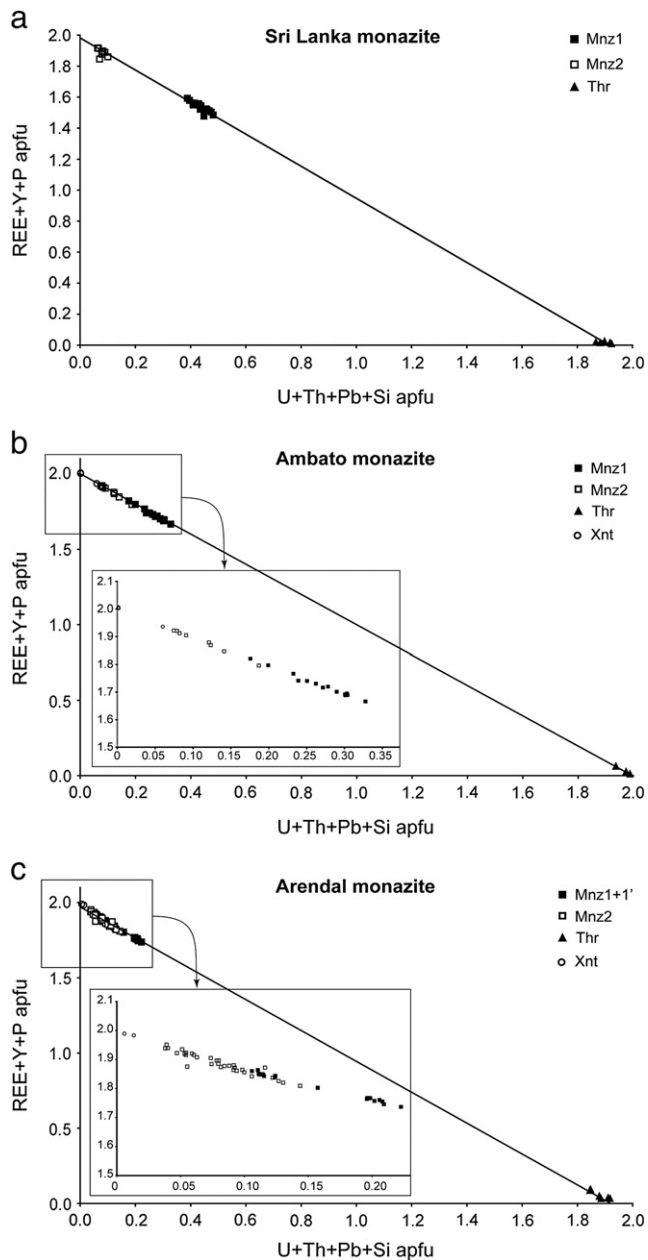


Fig. 7. Compositional variation diagrams (REE + Y + P) vs (Th + U + Si + Pb) in atoms per formula unit, for 4 oxygens (apfu) for unaltered (Mnz1 and Mnz1'), altered monazite (Mnz2) and other recrystallized phases, such as Th-rich thorite (Thr) and Y-rich xenotime (Xnt), for the Sri Lanka (a), Ambato (b) and Arendal (c) monazite samples. In all samples, unaltered and altered monazites (Mnz1-1' and Mnz2) plot along a straight line in the compositional diagram, with xenotime and thorite on both ends of the line.

Mnz1, and are less scattered (from 837 ± 9 to 929 ± 10 Ma) than the $^{206}\text{Pb}/^{238}\text{U}$ ages (Fig. 9f). Exclusion of analysis #31 (929 ± 10 Ma), which shows considerably higher Th (8.7 wt.%) and U (3266 ppm) concentrations than those typical of Mnz2 (EPMA: 5.8 wt.% Th and 800 ppm U), possibly produced by mixing of Mnz2 and Mnz1' volumes in the analysis, yields a poorly fitted WM $^{208}\text{Pb}/^{232}\text{Th}$ age of 864 ± 21 Ma [MSWD = 12; n = 5] for Mnz2.

7. Discussion

Large crystals of monazite are unusual mineralogical samples which are difficult to find and collect. The crystals studied here were sourced

from mineralogical collections for which location data and geologic context are absent. Therefore, discussion of the nature of the alteration processes is limited, especially concerning the fluids which caused monazite alteration. Despite this we consider that useful data on how monazite reacts with geological fluids at the micro- and nano-scale can still be obtained from these samples.

7.1. Alteration conditions and consequences for element mobility

The data presented here confirm the results of a recent study on alteration of xenotime and monazite from granitic pegmatites hosted in an orthosite, SW Norway (Hetherington and Harlov, 2008). Th and U are incorporated in the three monazite grains studied here (Sri Lanka, Ambato and Arendal) via a substitution mechanism involving both crystallographic sites $[(\text{Th}, \text{U})^{4+} + \text{Si}^{4+} = (\text{REE}, \text{Y})^{3+} + \text{P}^{5+}]$ of the monazite lattice (9-fold coordinated REE-site and tetrahedral P-site; Ni et al., 1995). The other well-known substitution that occurs in monazite (Friedrich et al., 1987; Franz et al., 1996; Förster, 1998) involving Ca on one crystallographic site $[(\text{Th}, \text{U})^{4+} + \text{Ca}^{2+} = 2(\text{REE}, \text{Y})^{3+}]$ is negligible in these samples, consistent with a low concentration or availability of Ca in the environment of monazite growth in these samples. For all monazite samples, the composition of the unaltered monazites (Mnz1) plots along a straight line between the two product phases, a Th-rich phase (thorite) on one side and one corresponding to secondary monazite (Mnz2) on the other (Fig. 7). In the case of the Ambato and Arendal monazites, in which the Y content is higher in the unaltered monazite, newly-formed xenotime plots at one end of the compositional line (Fig. 7b and c). An interesting point concerns the increase of Th/U ratio in monazites during hydrothermal alteration (Table 1); from 30 to 64 in the case of Sri Lanka monazite, 25 to 71 for the Ambato and 18 to 48 for the Arendal monazite samples. Such a difference has previously been observed in some hydrothermally altered monazites by Poitrasson et al. (2000) in the Skiddaw granite, in hydrothermal monazite by Janots et al. (2012) and in monazite from granitic pegmatites from Norway by Hetherington and Harlov (2008). This trend is the consequence of a chemical fractionation between U and Th during alteration (greater loss of U than of Th). Furthermore, while some U is incorporated in the Th-rich phase (Table 2) no U-rich phase such as coffinite or uraninite formed. The mass balance calculations show that some uranium is liberated from the system during the reaction, which could have important consequences, as far as the formation of uranium deposits is concerned.

The temperature estimates obtained here for Ambato and Arendal monazite grains (<320 °C), are consistent with previous examples in which monazite is altered by moderate-temperature fluids (Poitrasson et al., 2000; Mathieu et al., 2001). However, none of the experimental studies so far have been able to reproduce the specific alteration textures as described in the three samples of this study, i.e. secondary monazite associated with thorite and xenotime. To our knowledge, the only experimental evidence for a Th-rich phase forming as the result of monazite alteration via dissolution in the presence of fluid is thorianite that crystallized during the experiments of Seydoux-Guillaume et al. (2002a) in the presence of pure H_2O fluid over the temperature range of 800–1200 °C. It is also known from the experiments that at high temperatures above 600 °C large amounts of ThSiO_4 can be entirely substituted into the monazite lattice (Seydoux-Guillaume et al., 2002b; Hetherington et al., 2010; Harlov et al., 2011). Under such conditions (i.e. alkaline fluids–high temperatures; see Introduction), Th-rich monazite forms at the reaction front between unaltered and altered monazites (Figs. 2–4 in Seydoux-Guillaume et al., 2002b; Figs. 6–7 in Harlov et al., 2011). These results demonstrate the need for experimental studies and modeling of monazite alteration at low temperature (<320 °C).

Considering now the alteration mechanism, two possible processes can be distinguished: solid state exsolution (= volume diffusion) and coupled dissolution–precipitation in the presence of fluid. Although as noted above monazite is able to incorporate high amounts

Table 3
Analytical data for the Sri Lanka monazite (EPMA).

#	U (ppm)	± (2σ)	Th (ppm)	± (2σ)	Pb (ppm)	± (2σ)	Th*	Age (Ma)	± (2σ)
1	6531	274	212,496	1840	4772	338	233,935	454	37
2	6346	273	192,181	1737	4728	341	213,078	494	41
3	6420	272	190,708	1725	4545	340	211,820	477	41
4	6841	275	203,082	1791	5003	343	225,607	493	39
5	7040	276	207,873	1816	5365	341	231,095	516	38
6	7102	275	206,837	1808	5331	343	230,260	514	39
7	612	232	49,317	915	1091	318	51,329	472	152
8	561	230	44,885	884	1168	314	46,741	555	167
9	688	229	41,275	856	1000	317	43,543	510	179
10	495	231	43,104	875	1048	317	44,737	520	175
11	1026	233	53,263	943	1246	315	56,640	489	137
12	915	234	55,601	953	1523	316	58,634	576	135
13	630	231	46,492	900	1218	314	48,577	557	161
14	6441	272	189,583	1721	4709	339	210,798	497	41
15	6644	273	192,683	1740	4580	341	214,527	474	41
16	6800	273	197,739	1761	4915	340	220,136	497	40
17	6961	275	208,764	1820	4980	343	231,657	478	38
18	7359	276	212,668	1838	5339	343	236,912	500	37
19	7298	277	215,401	1852	5188	345	239,410	482	37
20	7038	276	208,371	1820	4834	345	231,494	465	38
21	6691	273	196,501	1758	4939	341	218,548	502	40
22	6747	274	195,130	1750	4856	342	217,353	497	41
23	6204	270	185,983	1701	4800	338	206,449	517	42
24	6549	273	194,869	1749	4774	339	216,429	491	40

Th* corresponds to Th+the equivalent of U (after Suzuki and Adachi, 1991).
Cells in gray correspond to Mnz2.

of ThSiO₄ and YPO₄ at high temperatures, at lower temperature a miscibility gap exists (Gratz and Heinrich, 1997; Heinrich et al., 1997; Seydoux-Guillaume et al., 2002b). As a result, Th and Y should be excluded from monazite lattice at low temperatures ($\ll 600$ °C). Solid state exsolution of thorite and xenotime at low temperature is highly unlikely because of the very slow diffusion kinetics in monazite (Cherniak and Pyle, 2008). The sharp interfaces between different phases, the presence of cracks and porosity (Figs. 2–5), and the sharp boundaries between thorite and monazite on the TEM images (Fig. 5c) instead are supportive of a dissolution–precipitation mechanism facilitated by a fluid medium (see review in Putnis, 2009). The key observation about the alteration mechanism of these monazite samples is that it does not correspond to pseudomorphic replacement (i.e. dissolution–precipitation coupled at the interface of the parent and product phases with preservation of the external morphology of the parents), as is commonly observed in nature and experiments (see review in Putnis, 2009). In the present study dissolution, and associated precipitation, began and progressed via a pre-existing fracture network, allowing access and pathways for fluid. In contact with a reactive low temperature fluid (<320 °C), the Th-(±Y)-rich magmatic monazite (Mnz1) became unstable and dissolved. The interfacial fluid became supersaturated, leading to the precipitation of new

mineral phases, i.e. Th–Y-depleted monazite (Mnz2), thorite, ± xenotime, less soluble in the fluid than the original Mnz1 (see also Bilal et al., 1998; Seydoux-Guillaume et al., 2007; Hetherington and Harlov, 2008; Putnis, 2009). Although the composition of the fluid in this study is unknown, it must have been Fe-bearing, because hematite precipitated within Mnz2 and along cracks (Figs. 1 and 5). It is important to emphasize the essential role of porosity and cracks, which allow fluid migration through the samples during this process. In the next section the role and origin of fracturing (hydration, radiation damage induced swelling, volume change due to phase transformation) will be discussed.

7.2. Effects of radiation damage

Over geological time, U- and Th-rich minerals, like monazite and thorite, accumulate radiation damage, mainly from α -decay. Radiation destroys the host crystal lattice to a variable extent, in some cases leading to an amorphous structure, called the metamict state (see summary in Ewing, 1994). Collision cascades due to the alpha-recoil nuclei (= daughter nuclei) are the main cause of amorphization of the crystal lattice. Although daughter nuclei are less energetic (100–400 keV) and less penetrative (20–50 nm) than α -particles emitted during α -decay,

Table 4
Analytical data for the Ambato monazite (EPMA).

#	U (ppm)	± (2σ)	Th (ppm)	± (2σ)	Pb (ppm)	± (2σ)	Th*	Age (Ma)	± (2σ)
1	3379	253	106,460	1283	2599	354	117,584	491	75
2	5802	264	127,523	1402	3247	361	146,626	492	62
3	6015	265	134,659	1442	3491	361	154,478	502	59
4	5751	262	118,379	1356	3227	357	137,358	522	65
5	5881	264	131,370	1427	3582	362	150,787	528	60
6	6080	265	135,108	1448	3705	358	155,186	530	58
7	5913	265	134,262	1446	3683	362	153,791	532	59
8	5913	266	132,201	1432	3665	358	151,738	537	60
9	5145	260	122,998	1380	3399	356	140,000	539	64
10	4120	254	87,831	1176	2482	353	101,450	543	87
11	3465	247	69,118	1062	1982	349	80,575	546	107
12	5519	264	148,250	1516	4105	363	166,501	548	55
13	4283	253	89,639	1190	2594	352	103,810	555	85
14	4045	254	102,449	1260	2948	352	115,844	565	77
15	5428	259	109,981	1311	3262	355	127,957	566	70
16	6036	263	119,891	1367	3786	356	139,934	600	65
17	3516	248	73,524	1089	2321	353	85,203	604	104
18	2327	244	110,085	1301	3986	357	117,905	747	79
19	1326	237	68,560	1055	2503	347	73,020	758	122

Th* corresponds to Th+the equivalent of U (after Suzuki and Adachi, 1991).
Cells in gray correspond to Mnz2.

they are heavier, and thus more destructive (800–2000 displacement/particle) than α -particles (e.g. Ewing et al., 1995; Nasdala et al., 1996; Weber et al., 1998; Ewing et al., 2000). The balance between damage accumulation and annealing controls the metamictization, i.e. the amorphization of the host mineral. Annealing may be due to temperature, or to other more complex processes, such as healing by alpha particles (Ouchani et al., 1997). Monazite is well known to remain in a crystalline state, because its lattice repairs faster than it is destroyed, even at low temperatures (60–200 °C depending on its composition—Meldrum et al., 1997). In natural monazite, clear evidence of radiation damage has been shown to be limited to isolated nm-sized domains within the crystal (Black et al., 1984; Meldrum et al., 1998; Seydoux-Guillaume et al., 2002c, 2003, 2004, 2007; Nasdala et al., 2010). This study confirms these results as the TEM observations demonstrate the same brightness contrasts in both Arendal and Ambato monazites (Fig. 5a–b), characteristics that result from the presence of very little lattice distortion and corresponding to moderate degrees of accumulated radiation damage, as observed in previous studies (Black et al., 1984; Meldrum et al., 1998; Seydoux-Guillaume et al., 2002c, 2003, 2004, 2007; Nasdala et al., 2010). In contrast, thorite has been found mostly in a metamict (i.e. amorphous) state (Pabst, 1952; Lumpkin and Chakoumakos, 1988; Farges and Calas, 1991). Observations using TEM on the inclusions in the Arendal monazite (Seydoux-Guillaume et al., 2007) and the Ambato monazite (Fig. 5c) also point to an amorphous state for the secondary (i.e. within altered monazite) thorite.

The most important consequence for rocks containing radioactive minerals is that the long-time scale integration of these atomic-scale interactions (amorphization) will dramatically change the physical properties of the radioactive host minerals (e.g. Weber et al., 1998).

The present study shows that swelling can trigger intense fracturing within and around secondary radioactive minerals (see also Lee and Tromp, 1995; Nasdala et al., 2010; Seydoux-Guillaume et al., 2007, 2009). These fractures can be interconnected to form a network, and so constitute an efficient way for fluids to pass through the monazite host crystals.

In the Sri Lanka sample, the large cracks that traverse through the entire crystal (Fig. 1a) originate at the Th-rich inclusions and secondary monazite (Mnz2) (Fig. 2c) interface, and propagate through the Mnz2 domains (Fig. 2b). These cracks are therefore interpreted to form as a consequence of the swelling of the Th-rich inclusions. Even though these features are more complicated for the two other monazite samples, because their fracture networks are very dense, it again appears that the cracks originate from the thorite inclusions. On smaller scales (Fig. 5) the cracks initiate at the thorite–Mnz2 interface in the Ambato crystal. An interesting observation from some images (Figs. 3, 4 and 5) is that some cracks are partially to completely filled with a Th-rich phase and a Fe-rich phase (hematite; Figs. 1 and 5), providing evidence that late fluid circulation can transport Fe^{3+} and Th over several microns to millimeter scales. This suggests that fluid was continually passing through the monazite for some time after the recrystallization event. This could lead to complications with inferring the “timing” of a specific geological event, because ages could be disturbed for some period after the main event as a consequence of continued fluid ingress and reaction.

Macroscopic swelling due to metamictization can reach 16 vol.%, for Pu-doped zircon (Weber et al., 1994), or 8 vol.%, for externally irradiated LaPO_4 monazites (Picot et al., 2008). No data exist for thorite, but it is expected to be similar to zircon, with which it is isostructural. Thorianite, like uraninite, remains crystalline even for high irradiation

Table 5
Analytical data for the Arendal monazite (EPMA).

#	U (ppm)	± (2σ)	Th (ppm)	± (2σ)	Pb (ppm)	± (2σ)	Th*	Age (Ma)	± (2σ)
1	6226	259	101,259	1254	5411	362	122,582	970	79
2	5959	261	102,749	1259	5491	363	123,175	980	79
3	6569	263	110,904	1307	5701	367	133,345	941	74
4	5823	259	103,745	1265	5210	365	123,613	927	79
5	6306	261	104,626	1271	4792	363	125,981	839	76
6	6486	256	64,085	1025	3779	352	86,287	964	106
7	6245	255	57,771	978	3470	350	79,150	965	115
8	6060	253	57,912	985	3474	349	78,668	971	115
9	5974	255	66,040	1036	3876	353	86,525	984	107
10	6631	257	62,728	1014	3701	354	85,404	953	108
11	364	230	32,592	802	1333	337	33,828	869	255
12	740	231	40,228	861	1828	344	42,756	940	208
13	344	230	29,304	772	1102	341	30,465	799	283
14	389	228	27,583	761	1135	345	28,903	865	302
15	1400	234	56,451	973	2191	344	61,173	791	144
16	527	231	44,065	876	1981	346	45,867	950	196
17	577	231	32,925	803	1584	342	34,906	997	254
18	434	228	29,910	780	1685	344	31,424	1174	289
19	519	227	30,970	775	1871	341	32,793	1247	277
20	1081	233	37,966	841	1974	345	41,691	1039	216
21	485	231	39,387	850	1949	346	41,059	1042	221
22	665	231	45,338	888	2044	346	47,611	945	189
23	968	233	57,884	980	2569	346	61,186	925	148
24	742	234	59,382	987	2489	347	61,905	885	146
25	951	232	38,386	838	2010	346	41,669	1059	217
26	1375	238	77,821	1111	3253	351	82,489	869	111
27	520	231	41,422	865	2385	345	43,241	1206	214
28	1010	237	72,690	1079	3017	355	76,121	874	122
29	1152	233	67,026	1037	3023	347	70,960	938	129
30	644	231	45,009	891	1827	346	47,193	854	188
31	1481	238	76,710	1102	3448	352	81,764	928	114
32	961	235	62,401	1009	2573	349	65,662	864	138
33	1108	235	67,624	1042	2736	348	71,378	846	127
34	2054	240	84,310	1145	3900	352	91,326	939	102
35	838	233	49,064	920	2350	346	51,940	994	175
36	564	233	50,913	938	2221	348	52,837	926	171
37	586	231	43,914	882	1830	348	45,905	879	195

Th* corresponds to Th+the equivalent of U (after Suzuki and Adachi, 1991).

Cells in gray correspond to Mnz2.

Mnz1: #1 to 5 and Mnz1': #6 to 10.

doses (Evron et al., 1994; Seydoux-Guillaume et al., 2009). Therefore, swelling is not caused by amorphization of thorianite. Another possible process is hydration, as shown by Seydoux-Guillaume et al. (2007). EPMA totals (Table 2) for all the Th-rich phases are low (~90 wt.%), a feature which can be attributed to presence of water. Nasdala et al. (2009) demonstrated that deficient EPMA totals in zircon can be also assigned to the presence of nano-pores; this nanoporous texture is explained by the replacement via a fluid driven reaction of radiation-damaged zircon by a crystalline nanoporous (with smaller volume) zircon (see also Hay and Dempster, 2009). Furthermore, the presence of nanopores allows incorporation of water (or other non-formula elements). The final possible cause of swelling is volume change due to reaction. From the proportions obtained by mass balance (c.f. above), assuming densities of 5.3 g/cm³, 6.7 g/cm³ and 4.3 g/cm³ for monazite, thorite and xenotime respectively, we calculated a volume change of about -3% (decrease in volume) in the Sri Lanka, +10% in the Ambato, and 0 (Mnz1) to +1% (Mnz1') in the Arendal monazite samples. The volume change due to mineral reaction may create porosity or swelling, depending on the precise reaction.

Based on the measured U and Th contents (Table 1) and the corresponding ²⁰⁸Pb-²³²Th ages (Fig. 9—mean weight averages calculated only on unaltered monazites: 491, 507 and 909 (Mnz1) and 892 (Mnz1') Ma for Sri Lanka, Ambato and Arendal respectively) it is possible to estimate the theoretical self-irradiation doses (Ewing et al., 2000;

Nasdala et al., 2001) received by the monazite grains in this study. These doses, for unaltered monazites, are: 10.1 × 10¹⁹ α-decay/g (i.e. 8.5 dpa, displacements per atom), 6.6 × 10¹⁹ α-decay/g (5.5 dpa) and 10.7 × 10¹⁹ α-decay/g (9 dpa) and 7.35 × 10¹⁹ α-decay/g (6.2 dpa) for Sri Lanka, Ambato and Arendal (1-1') monazites respectively. These values are quite high relative to several other monazites reported in the literature. As a comparison, the self-irradiation dose received by the well-studied Moacyr monazite (474 Ma) is 2.8 × 10¹⁹ α-decay/g (2.3 dpa), 6.12 × 10¹⁹ α-decay/g (5.13 dpa) for the Manangotry monazite from Madagascar (545 Ma) and 17 × 10¹⁹ α-decay/g (14 dpa) for the old (1.9 Ga) monazite DIG19 from Devon Island (Seydoux-Guillaume et al., 2002c, 2004). Another monazite (1 Ga, 6 wt.% ThO₂ and 0.1 wt.% UO₂) from Norway (Nasdala et al., 2010) received a dose of 4.5 × 10¹⁹ α-decay/g and is still crystalline. Such high doses must have been sufficient to totally amorphize all these monazites, because a dose of ca. 10¹⁹ α-decay/g is generally sufficient to completely amorphize solids (Weber et al., 1994). Since this is not the case for the monazites described herein, it must be concluded that they all have experienced annealing. As monazite is well-known to heal its radiation damage even at low temperature (Meldrum et al., 1997), thermal annealing provides an appropriate mechanism for the self-healing of the crystal structure contemporaneously with amorphization.

Since observations using TEM were also performed on altered monazites (Mnz2 from Ambato and Arendal), maximum self-irradiation

Table 6

U/Pb and Th/Pb data from LA-ICP-MS analyses of Sri Lanka monazite (altered monazite-Mnz2—in gray).

#	Isotopic ratios								Apparent ages (Ma)								Concentration (ppm)		
	²⁰⁷ Pb/ ²⁰⁶ Pb	2σ %	²⁰⁷ Pb/ ²³⁵ U	2σ %	²⁰⁶ Pb/ ²³⁸ U	2σ %	²⁰⁸ Pb/ ²³² Th	2σ %	²⁰⁷ Pb/ ²⁰⁶ Pb	2σ	²⁰⁷ Pb/ ²³⁵ U	2σ	²⁰⁶ Pb/ ²³⁸ U	2σ	²⁰⁸ Pb/ ²³² Th	2σ	Th	U	Th/U
7	0.053	3.0	0.58	3.1	0.079	2.3	0.025	2.2	337	68	463	11	489	11	492	11	271,991	6696	41
8	0.055	3.1	0.61	3.2	0.080	2.3	0.024	2.1	414	69	483	12	498	11	485	10	248,251	6172	40
9	0.060	3.1	0.67	3.2	0.080	2.3	0.024	2.2	619	67	518	13	496	11	482	10	245,230	6099	40
10	0.054	3.1	0.60	3.2	0.080	2.3	0.024	2.2	360	70	475	12	499	11	489	10	243,913	6029	40
11	0.054	3.3	0.60	3.3	0.081	2.3	0.025	2.2	360	74	479	13	504	11	498	11	262,698	6398	41
12	0.054	3.1	0.59	3.2	0.079	2.3	0.025	2.2	357	69	469	12	492	11	492	11	259,164	6404	40
13	0.055	3.2	0.61	3.2	0.080	2.3	0.024	2.2	421	69	485	12	499	11	488	11	234,114	5878	40
14	0.054	3.1	0.61	3.2	0.082	2.3	0.025	2.2	369	69	484	12	509	11	497	11	229,442	5772	40
17	0.054	3.1	0.59	3.2	0.081	2.3	0.025	2.2	351	70	474	12	499	11	494	11	247,856	5980	41
18	0.055	3.3	0.61	3.3	0.080	2.3	0.025	2.2	398	71	481	13	499	11	490	11	222,658	5526	40
19	0.057	3.1	0.64	3.2	0.082	2.3	0.025	2.2	482	69	501	13	506	11	496	11	235,465	5780	41
20	0.057	3.3	0.63	3.3	0.080	2.3	0.025	2.2	486	73	495	13	497	11	496	11	233,714	5756	41
24	0.059	3.6	0.65	3.6	0.080	2.4	0.024	2.2	555	78	509	15	499	11	488	11	178,521	4180	43
29	0.063	3.4	0.70	3.4	0.081	2.4	0.025	2.2	710	71	540	15	500	11	493	11	215,482	5438	40
30	0.060	3.4	0.72	3.5	0.086	2.4	0.026	2.2	616	74	550	14	534	12	516	11	218,898	5230	42
31	0.060	3.6	0.65	3.7	0.079	2.4	0.024	2.2	594	78	510	24	492	11	475	10	261,113	6297	41
33	0.056	3.6	0.61	3.7	0.079	2.4	0.024	2.2	449	79	482	15	489	11	487	11	219,193	5261	42
34	0.061	3.5	0.70	3.5	0.082	2.4	0.025	2.2	645	74	536	51	511	12	489	11	245,670	5956	41
21	0.409	5.8	12.12	5.1	0.215	4.0	0.023	2.2	3943	86	2614	26	1255	46	455	10	54,801	50	1087
22	0.147	4.2	1.83	4.1	0.090	2.7	0.023	2.2	2316	71	1055	48	555	14	451	10	98,300	1394	71
23	0.063	6.1	0.74	5.9	0.085	2.8	0.024	2.2	698	127	561	14	528	14	483	11	80,546	983	82
27	0.456	6.1	19.43	1.0	0.309	4.4	0.022	2.2	4105	88	3064	59	1737	67	439	10	54,352	47	1145
28	0.087	12.6	0.93	0.1	0.078	4.9	0.022	2.3	1359	234	669	27	483	23	443	10	87,595	838	105
32*	0.086	5.1	0.94	4.9	0.079	2.7	0.022	2.2	1329	97	671	15	492	13	435	10	153,383	2643	58

Location of analytical points (#) is in Fig. 2 (in red).

Th and U concentrations were calculated using Moacyr monazite standard.

#*: mixing with Mnz1.

doses were calculated for both crystals using the same ages as those of the unaltered monazites. Calculated doses are 2.4×10^{19} α-decay/g (2.1 dpa) for Ambato and 4.7×10^{19} α-decay/g (3.9 dpa) for Arendal. Both monazites (Arendal—Fig. 5a and Ambato—Fig. 5b) display very similar contrasts in TEM bright field images and have also very similar contrasts to previously studied monazites from Moss (Nasdala et al., 2010), Manangotry (Seydoux-Guillaume et al., 2004) and Moacyr (Seydoux-Guillaume et al., 2002c), which received similar doses (4.5×10^{19} α-decay/g, 2.8×10^{19} α-decay/g, and 6.12×10^{19} α-decay/g respectively). These results are in agreement with recrystallization occurring during the late stage of magma crystallization, but following Mnz1 growth (e.g. only few million years after).

7.3. Fluid-induced disturbance of U–Pb and Th–Pb geochronological systems

Poitrasson et al. (2000) have already emphasized the possibility of giving “a reasonable estimate of the age of the mineral–fluid interaction using the altered parts of the monazites”. However in their case studies, except for one sample (M0111bis-Skiddaw granite), the compositions of the altered phases and alteration products were very different to that documented here (e.g. Th/U lower in altered monazites; Al and Ca involved). The present study has highlighted some important information related to the behavior of the U–Pb and Th–Pb geochronological systems with respect to low temperature (<320 °C—see above) hydrothermal alteration. The first one concerns the evolution of the Th/U ratio during alteration of monazite. Excluding the analyses clearly disturbed by thorite or Mnz1 contamination (i.e. #48, 49 and 59 for Ambato; #31 for Arendal or #32 for Sri Lanka), correlations between ²⁰⁸Pb/²³²Th ages and Th/U ratios (Fig. 10) during alteration of monazite (Mnz1 => Mnz2) demonstrate that Th/U ratios systematically increase with alteration. This is attributed to the higher solubility of U (as uranyl ions) in oxidized geological fluids (Mathieu et al., 2001). The observation that U is lost during the

reaction, when mass balance is calculated for other elements, is in agreement with this interpretation. Th/U fractionation during monazite alteration has crucial consequences for the U–Pb and Th–Pb geochronological systems, as shown in Th–Pb Concordia diagrams in the cases of the Sri Lanka and the Arendal monazite samples (Fig. 9b and f). For both monazite samples, the U–Pb systems are affected by alteration (Tables 6 and 8). In the case of the Sri Lanka monazite (Fig. 9a) the Tera Wasserburg diagram demonstrates considerable common-Pb contamination (up to ~40% common-Pb). Combination of ²⁰⁶Pb/²³⁸U ratios with Th/U ratios indicates preferential loss of U. In the Arendal monazite, ages of the altered domains are scattered, but plot on the concordia curve of the TW diagram. These U–Pb ages are older than the age of the pristine domains, and hence are meaningless. Disturbance in U–Pb results is interpreted to arise from contamination by inherited Pb, but this is not clear in the TW diagram (certainly due to the analytical uncertainties). This shows that possible U–Pb disturbances cannot be ruled out even in cases in which the U–Pb data are concordant. In the case of geochronological studies based on large U–Pb datasets with no petrological control (as, for example, in provenance studies; e.g. Hietpas et al., 2010), similar U–Pb disturbances caused by later-stage low-grade hydrothermal alteration will be therefore hard to identify. In contrast, the ²⁰⁸Pb/²³²Th system in the altered domains gives ages (450 ± 18 Ma for Sri Lanka and 864 ± 21 Ma for Arendal) that appear to be reasonable and are consistent with the alteration occurring soon after the magmatic crystallization of the Sri Lanka (491 ± 4 Ma) and Arendal (900 ± 11 Ma) monazites. Moreover, combination of Th/U ratios with these ²⁰⁸Pb/²³²Th ages (Fig. 10) helps to trace alteration events and increase the confidence in these alteration ages.

The behavior of the geochronological systems in the Ambato monazite in response to alteration contrasts with that of the other monazites. In this case both Th–Pb and U–Pb systems were affected. First, analyses within altered monazites exhibit strong common-Pb contamination (²⁰⁷Pb/²⁰⁶Pb ratios enhanced; up to ~80% common-Pb in altered zones—Fig. 9c) leading to the disturbance of both U–Pb systems

Table 7

U/Pb and Th/Pb data from LA-ICP-MS analyses of Ambato monazite (altered monazite-Mnz2—in gray).

#	Isotopic ratios								Apparent ages (Ma)								Concentration (ppm)		
	²⁰⁷ Pb/ ²⁰⁶ Pb	2σ %	²⁰⁷ Pb/ ²³⁵ U	2σ %	²⁰⁶ Pb/ ²³⁸ U	2σ %	²⁰⁸ Pb/ ²³² Th	2σ %	²⁰⁷ Pb/ ²⁰⁶ Pb	2σ	²⁰⁷ Pb/ ²³⁵ U	2σ	²⁰⁶ Pb/ ²³⁸ U	2σ	²⁰⁸ Pb/ ²³² Th	2σ	Th	U	Th/U
38	0.054	3.6	0.63	3.6	0.084	2.4	0.026	2.2	371	40	495	7	522	6	521	6	169,768	4953	34
39	0.054	3.6	0.63	3.6	0.084	2.4	0.025	2.3	389	39	497	7	520	6	508	6	170,436	4987	34
40	0.053	3.9	0.59	3.9	0.080	2.5	0.024	2.2	346	43	472	7	498	6	482	5	184,878	5704	32
41	0.055	3.6	0.63	3.7	0.084	2.4	0.026	2.3	394	40	499	7	522	6	512	6	170,013	5233	32
43	0.054	3.6	0.62	3.6	0.084	2.4	0.026	2.2	353	40	489	7	519	6	515	6	161,171	5899	27
44	0.055	3.6	0.63	3.7	0.083	2.4	0.026	2.3	404	40	496	7	517	6	510	6	145,147	5619	26
45	0.053	3.6	0.62	3.7	0.084	2.5	0.025	2.3	346	41	488	7	519	6	508	6	160,315	5967	27
48*	0.085	4.1	0.96	4.1	0.082	2.6	0.025	2.3	1306	39	681	10	508	6	493	5	134,111	2851	47
49*	0.083	3.6	0.99	3.6	0.086	2.5	0.026	2.2	1275	35	700	9	535	6	517	6	152,581	96228	2
50	0.054	3.8	0.63	3.8	0.084	2.5	0.025	2.3	381	42	495	7	519	6	508	6	144,983	5674	26
51	0.054	4.0	0.62	4.0	0.084	2.5	0.025	2.3	370	44	492	8	518	6	508	6	139,235	5057	28
52	0.054	4.0	0.60	4.0	0.080	2.5	0.025	2.3	374	44	476	8	498	6	507	6	140,609	4089	34
53	0.054	3.9	0.61	4.0	0.082	2.5	0.025	2.2	352	44	481	8	509	6	500	6	145,882	5616	26
58	0.696	3.6	49.50	3.6	0.516	2.5	0.046	2.2	4722	25	3982	18	2683	27	903	10	142,294	3952	36
59	0.703	3.7	9.64	3.7	0.099	2.5	0.015	2.3	4737	26	2401	17	611	7	294	3	223,407	8375	27
60	0.771	3.6	80.39	3.7	0.757	2.5	0.042	2.2	4869	26	4467	18	3632	35	828	9	101,930	1879	54
61	0.262	3.9	6.88	3.9	0.190	2.6	0.027	2.3	3261	31	2096	17	1123	13	540	6	87,778	1265	69
62	0.793	3.7	149.76	3.7	1.371	2.5	0.047	2.2	4908	26	5093	19	5565	46	920	10	183,144	2035	90
63	0.767	3.7	84.73	3.8	0.801	2.5	0.052	2.2	4862	26	4520	19	3794	35	1022	11	162,464	3247	50
64	0.696	3.7	54.70	3.8	0.571	2.5	0.047	2.2	4722	27	4082	19	2910	29	935	10	147,973	3864	38
65	0.719	3.8	62.06	3.8	0.626	2.5	0.047	2.3	4770	27	4208	19	3133	31	923	10	153,133	3215	48

Location of analytical points (#) is in Fig. 3 (in red). #*: analytical points in unaltered monazite but close to a crack.

Th and U concentrations were calculated using Moacyr monazite standard.

59: near thorium silicate inclusion.

(increases in ²⁰⁶Pb/²³⁸U and ²⁰⁷Pb/²³⁵U ratios and corresponding ages: Table 7 and Figs. 9c and 10b), and the Th–Pb system (increases in ²⁰⁸Pb/²³²Th ratios and corresponding ages: Table 7 and Figs. 9d and 10b), due to ²⁰⁸Pb enhancement (Table 7 and Fig. 9d). Furthermore, in addition to common Pb contamination, evidence of (Th, U)-silicate contamination is provided by comparing the Th and U concentrations obtained by LA-ICP-MS (Table 7) with the concentrations obtained by EPMA analyses (Table 1). Both Th and U concentrations (LA-ICP-MS) are higher than the concentrations measured with EPMA (Table 1). This can be easily explained, firstly by the presence of many nano-fractures filled with Th–U-silicate (e.g. like analyses in Table 2) that may not be visible

with SEM because of their size and their position under the surface (Fig. 5). Secondly, because the volumes analyzed by LA-ICP-MS (~50 μm³) are at least 10 times larger than those measured by EPMA (max. 5 μm³); the probability of producing mixed analyses (monazite + Th, U-silicate) through incorporation of high proportions of “unexpected” phases in the measured volume, is significantly higher in the case of LA-ICP-MS analyses.

The possibility of common-Pb contamination and chemical fractionation between Th and U has consequences for the interpretation or choice of analytical method used for dating. In the case of the Sri Lanka or the Arendal monazite samples, the common-Pb contaminations are relatively

Table 8

U/Pb and Th/Pb data from LA-ICP-MS analyses of Arendal monazite (altered monazite-Mnz2—in gray).

#	Isotopic ratios								Apparent ages (Ma)								Concentration (ppm)		
	²⁰⁷ Pb/ ²⁰⁶ Pb	2σ %	²⁰⁷ Pb/ ²³⁵ U	2σ %	²⁰⁶ Pb/ ²³⁸ U	2σ %	²⁰⁸ Pb/ ²³² Th	2σ %	²⁰⁷ Pb/ ²⁰⁶ Pb	2σ	²⁰⁷ Pb/ ²³⁵ U	2σ	²⁰⁶ Pb/ ²³⁸ U	2σ	²⁰⁸ Pb/ ²³² Th	2σ	Th	U	Th/U
7	0.065	2.9	1.38	3.0	0.153	2.4	0.047	2.3	775	30	879	9	920	10	928	10	108,793	6093	18
8	0.065	2.8	1.39	3.0	0.154	2.4	0.046	2.3	789	30	883	9	922	10	913	10	113,231	6264	18
9	0.065	2.9	1.38	3.0	0.153	2.4	0.047	2.2	786	30	882	9	920	10	922	10	109,113	5961	18
10	0.066	2.9	1.35	3.0	0.149	2.4	0.046	2.2	797	30	866	9	894	10	905	10	108,089	6224	17
11	0.066	3.0	1.38	3.1	0.152	2.4	0.046	2.2	800	32	880	9	912	10	918	10	88,006	4819	18
12	0.066	2.9	1.38	3.0	0.153	2.4	0.046	2.2	790	30	881	9	917	10	918	10	105,997	6120	17
13	0.066	3.0	1.37	3.1	0.150	2.4	0.046	2.3	804	31	875	9	904	10	911	10	108,499	6304	17
14	0.068	3.2	1.49	3.3	0.159	2.4	0.044	2.3	866	33	925	10	950	11	861	9	103,658	5179	20
17	0.066	2.9	1.35	3.1	0.149	2.4	0.045	2.2	805	31	870	9	895	10	899	10	58,119	6507	9
18	0.066	3.0	1.35	3.1	0.148	2.4	0.045	2.3	810	31	868	9	890	10	895	10	64,163	5971	11
19	0.065	3.0	1.34	3.1	0.149	2.4	0.045	2.2	790	32	864	9	893	10	883	10	57,555	5950	10
20	0.065	3.1	1.33	3.2	0.149	2.4	0.044	2.2	758	32	858	9	897	10	866	10	60,001	5598	11
21	0.065	3.1	1.34	3.2	0.148	2.4	0.045	2.2	785	32	861	9	891	10	883	10	56,738	5731	10
22	0.066	3.0	1.34	3.1	0.147	2.4	0.045	2.2	811	31	862	9	882	10	898	10	62,638	6662	9
23	0.065	3.1	1.35	3.1	0.150	2.4	0.045	2.2	788	32	867	9	898	10	898	10	54,275	6035	9
24	0.066	3.0	1.39	3.1	0.153	2.4	0.046	2.2	801	31	886	9	920	10	915	10	59,178	6569	9
28	0.070	8.2	1.55	8.0	0.161	3.4	0.044	2.3	929	82	951	25	960	15	871	10	57,422	185	311
29	0.070	9.3	1.45	9.0	0.150	3.6	0.044	2.2	930	92	910	27	902	15	866	10	61,608	169	365
30	0.073	7.8	1.73	7.6	0.173	3.3	0.044	2.2	1000	77	1018	24	1027	16	871	10	59,815	157	380
31*	0.067	3.5	1.43	3.6	0.154	2.5	0.047	2.3	851	36	903	11	924	11	929	10	86,696	3266	27
33	0.075	11.9	1.792	11.5	0.173	4.3	0.044	2.3	1076	115	1043	38	1027	21	879	10	50,132	83	603
34	0.081	9.5	2.29	9.2	0.205	3.9	0.042	2.3	1218	90	1208	32	1203	21	837	9	63,898	133	479

Location of analytical points (#) is in Fig. 4 (in red). Mnz1 from 7 to 14; Mnz1' from 17 to 24 and Mnz2 from 28 to 34.

Th and U concentrations were calculated using Moacyr monazite standard.

#*: mixed with Mnz1.

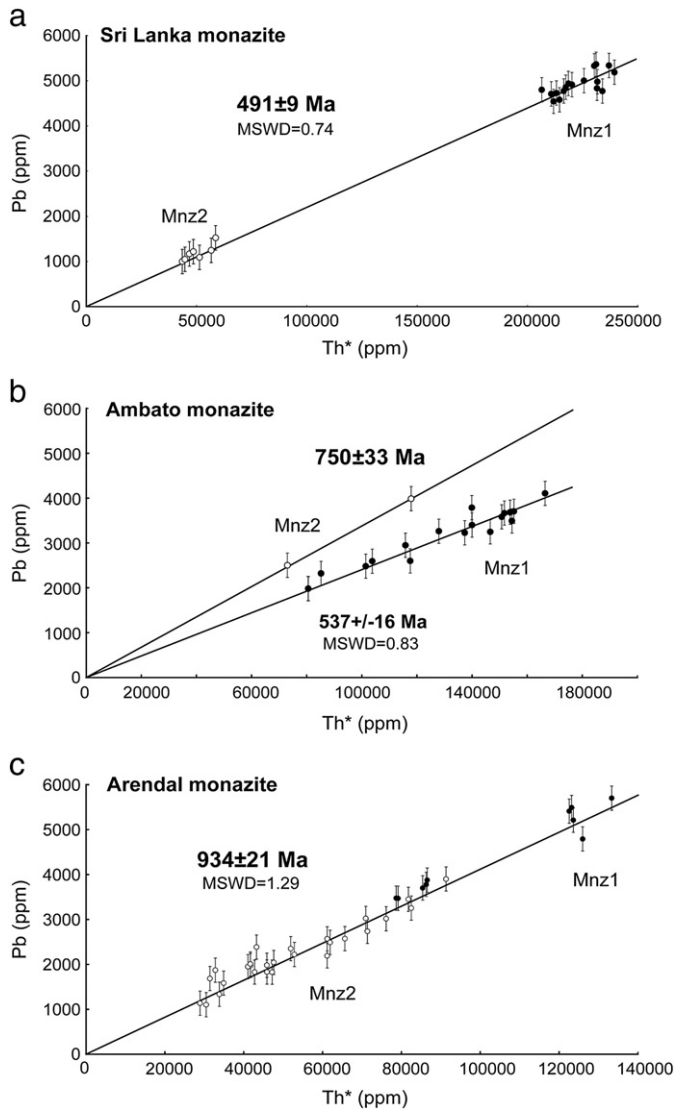


Fig. 8. EPMA chemical Th equivalent–total Pb pseudo-isochron (after Suzuki and Adachi, 1991) for Sri Lanka (a), Arendal (b) and Ambato (c) monazites. In the Sri Lanka and Ambato monazite samples, the ages for both pristine (Mnz1) and altered (Mnz2) zones are statistically similar. For Ambato monazite, ages from the altered zones are significantly older (750 Ma): see discussion in text. Ages were calculated following Montel et al. (1996).

low, i.e. only visible on the ^{206}Pb and ^{207}Pb signals, but not in ^{208}Pb . As a result, only the U–Pb systems have been noticeably affected. Chemical dating by EPMA, which uses total Pb for analyses, i.e. essentially ^{208}Pb for monazite, therefore remains unaffected by the common-Pb contamination and yields ages consistent with LA-ICP-MS. LA-ICP-MS dating, on the other hand, allows a consistent estimation of the alteration age to be obtained since it is only a few million years younger than the initial age. EPMA dating cannot distinguish between these ages due to the significantly lower precision of this method (Fig. 8). The combination of Th–Pb dating (LA-ICP-MS) with Th/U ratios, increases in which provide evidence for hydrothermal alteration, gives a powerful tool to estimate the age of alteration, provided the monazites are carefully characterized previously by methods such as SEM and TEM. Finally, if the Th–Pb and U–Pb systems are both disturbed (Ambato monazite), and if common-Pb contamination is so high that even ^{208}Pb is affected, both analytical techniques (LA-ICP-MS and EPMA) do not allow the alteration age to be discriminated and quantified. However, careful analyses with these

methods coupled with meticulous analyses with SEM and TEM allow alteration events to be traced and the disturbance of the geochronological systems applied as well as element mobility to be evaluated.

8. Conclusions

This investigation of large (cm) single monazite crystals from three distinct pegmatite localities allows the following important, more general, conclusions to be drawn.

- 1- The typical alteration of a primary (Mnz1) high-temperature monazite by a fluid at moderate temperature ($<320\text{ }^\circ\text{C}$) results in the formation of Th(Y)-depleted monazite (Mnz2) in association with Th-rich phases (thorium silicate or thorium oxide) \pm Y-xenotime. The resulting Mnz2 monazite always displays a higher Th/U ratio than the primary monazite, due to a fractionation of U relative to Th during the alteration process, which itself could be a good signature to trace the presence of hydrothermal alteration.
- 2- Alteration textures are always associated with radial cracks emanating from highly radioactive microscopic phases (thorium silicate or thorium oxide) present in the altered domains. The networks of fractures, interpreted to be caused by radiation-damage induced swelling of the radioactive phases, may facilitate the circulation of fluids, which can then mobilize and carry dissolved elements (e.g. Fe, Th, Pb, U) away.
- 3- Attempts to date alteration using electron probe chemical dating have not been successful, because the age difference between the original monazite and its alteration products in each case is well within the accuracy of the technique. In one case, the altered monazite (Ambato) is so contaminated by common-Pb that it also affected by the amount of ^{208}Pb , so that the total Pb measured by EPMA is higher than it should be. In this case, dates obtained in the altered zones are anomalously old and meaningless. However, chemical U–Th–Pb ages obtained for primary and pristine monazites are in agreement with LA-ICP-MS dating.
- 4- It is possible to produce indicative ages for alteration using high-resolution ($5\text{ }\mu\text{m}$) U–Pb and Th–Pb dating with the LA-ICP-MS technique. This is only possible when the altered zones are not too contaminated by common-Pb and contain few nano-phases or nano-cracks filled with Th-rich phases (case of Ambato monazite). Under these conditions, the Th–Pb system has been shown to be more reliable than the U–Pb systems, because of the preferential loss of U and the high Th contents (and hence high radiogenic ^{208}Pb) in even the altered monazite.
- 5- The combination of Th–Pb dating (LA-ICP-MS) with Th/U ratios, which can be used as evidence for hydrothermal alteration, provides a powerful tool for discriminating and estimating monazite alteration ages. However, it must be emphasized that even careful microscopic (SEM) characterization of the monazites may be not sufficient to achieve this goal, since nano-phases only observable by TEM (e.g. Ambato monazite), may influence the Th–Pb isotopic system and hence lead to disturbed and meaningless ages.

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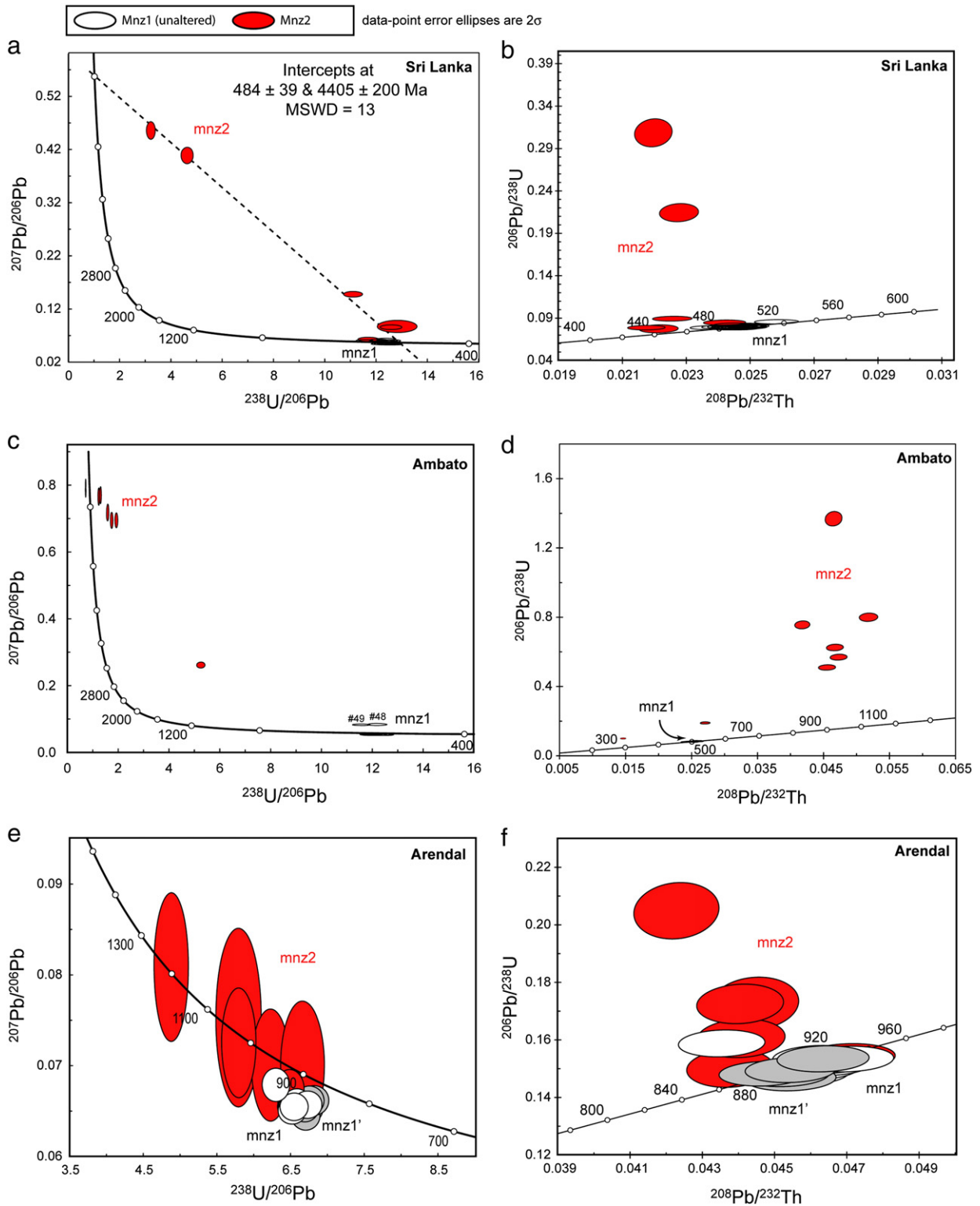


Fig. 9. Tera Wasserburg ($^{207}\text{Pb}/^{206}\text{Pb}$ vs $^{238}\text{U}/^{206}\text{Pb}$) and $^{206}\text{Pb}/^{238}\text{U}$ vs $^{208}\text{Pb}/^{232}\text{Th}$ modified concordia diagrams with analyses obtained by laser ablation inductively coupled plasma spectrometry (LA-ICP-MS) for each monazite: Sri Lanka (a–b), Ambato (c–d) and Arendal (e–f)—see Tables 6–8 and locations in Figs. 2–4. Data-point error ellipses are 2σ , red filled ellipses correspond to altered monazites (Mnz2) and white (Mnz1) or light gray filled ellipses (Mnz1') for pristine zones. For the Sri Lanka-Mnz1, the weighted $^{206}\text{Pb}/^{238}\text{U}$ mean (WM) age is 500 ± 5 Ma [MSWD = 3.1; $n = 18$] and 491 ± 4 Ma [MSWD = 2.4; $n = 18$] for the WM $^{208}\text{Pb}/^{232}\text{Th}$ age. In the case of the Ambato-Mnz1, the WM $^{206}\text{Pb}/^{238}\text{U}$ age is 514 ± 6 Ma [MSWD = 9; $n = 11$] and 507 ± 7 Ma [MSWD = 13; $n = 11$] for WM $^{208}\text{Pb}/^{232}\text{Th}$ age. Finally, for the Arendal-Mnz(1 + 1'), the pooled WM $^{206}\text{Pb}/^{238}\text{U}$ age is 906 ± 9 Ma [MSWD = 11.6; $n = 16$] and the pooled WM $^{208}\text{Pb}/^{232}\text{Th}$ age is 900 ± 11 Ma [MSWD = 16; $n = 16$]. See details in the text.

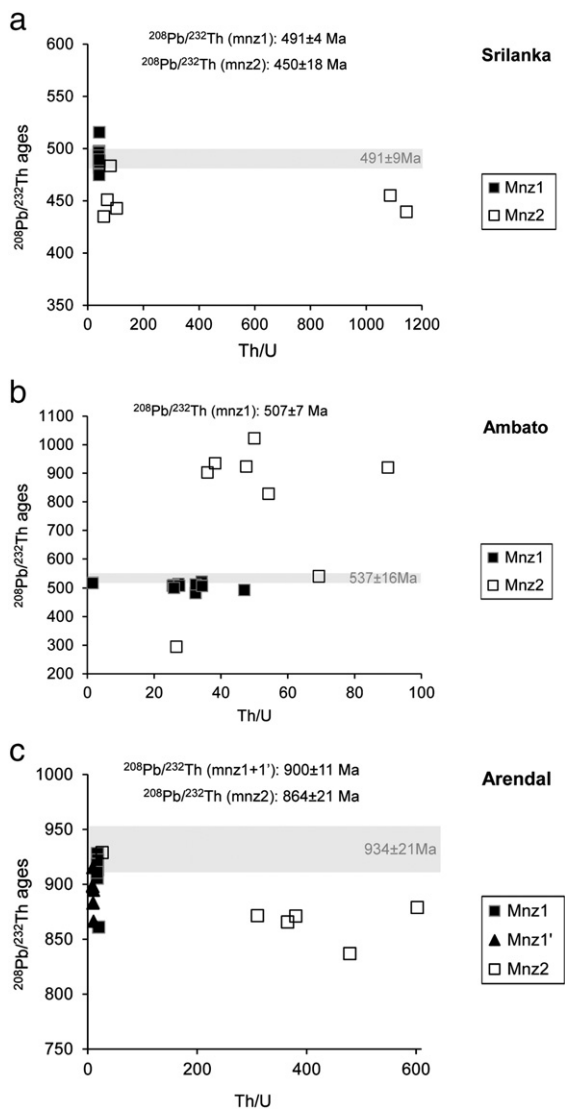


Fig. 10. $^{232}\text{Th}/^{208}\text{Pb}$ ages vs Th/U ratios in pristine and altered zones of the Sri Lanka (a), Ambato (b) and Arendal (c) monazite samples. Data points and errors for ages are in Tables 6 to 8, Th/U ratios are in Table 1.

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