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 P-T conditions of 200–1000 MPa and 450–750 °C

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Abstract The relative stabilities of phases within the two systems monazite-(Ce) – fluorapatite – allanite-(Ce) and xenotime-(Y) – (Y,HREE)-rich fluorapatite – (Y,HREE)-rich epidote have been tested experimentally as a function of pressure and temperature in systems roughly replicating granitic to pelitic composition with high and moderate bulk CaO/Na2O ratios over a wide range of P-T conditions from 200 to 1000 MPa and 450 to 750 °C via four sets of experiments. These included (1) monazite-(Ce), labradorite, sanidine, biotite, muscovite, SiO2, CaF2, and 2M Ca(OH)2; (2) monazite-(Ce), albite, sanidine, biotite, muscovite, SiO2, CaF2, Na2Si2O5, and H2O; (3) xenotime-(Y), labradorite, sanidine, biotite, muscovite, garnet, SiO2, CaF2, and 2M Ca(OH)2; and (4) xenotime-(Y), albite, sanidine, biotite, muscovite, garnet, SiO2, CaF2, Na2Si2O5, and H2O. Monazite-(Ce) breakdown was documented in experimental sets (1) and (2). In experimental set (1), the Ca high activity (estimated bulk CaO/Na2O ratio of 13.3) promoted the formation of REE-rich epidote, allanite-(Ce), REE-rich fluorapatite, and fluorcalciobritholite at the expense of monazite-(Ce). In contrast, a bulk CaO/Na2O ratio of ~1.0 in runs in set (2) prevented the formation of REE-rich epidote and allanite-(Ce). The reacted monazite-(Ce) was partially replaced by REE-rich fluorapatite-fluorcalciobritholite in all runs, REE-rich steacyite in experiments at 450 °C, 200–1000 MPa, and 550 °C, 200–600 MPa, and minor cheralite in runs at 650–750 °C, 200–1000 MPa. The experimental results support previous natural observations and thermodynamic modeling of phase equilibria, which demonstrate that an increased CaO bulk content expands the stability field of allanite-(Ce) relative to monazite-(Ce) at higher temperatures indicating that the relative stabilities of monazite-(Ce) and allanite-(Ce) depend on the bulk CaO/Na2O ratio. The experiments also provide new insights into the re-equilibration of monazite-(Ce) via fluid-aided coupled dissolution-reprecipitation, which affects the Th-U-Pb system in runs at 450 °C, 200–1000 MPa, and 550 °C, 200–600 MPa. A lack of compositional alteration in the Th, U, and Pb in monazite-(Ce) at 550 °C, 800–1000 MPa, and in experiments at 650–750 °C, 200–1000 MPa indicates the limited influence of fluid-mediated alteration on volume diffusion under high P-T conditions. Experimental sets (3) and (4) resulted in xenotime-(Y) breakdown and partial replacement by (Y,HREE)-rich fluorapatite to Y-rich fluorcalciobritholite. Additionally, (Y,HREE)-rich epidote formed at the expense of xenotime-(Y) in three runs with 2 M Ca(OH)2 fluid, at 550 °C, 800 MPa; 650 °C, 800 MPa; and 650 °C, 1000 MPa similar to the experiments involving monazite-(Ce). These results confirm that replacement of xenotime-(Y) by (Y,HREE)-

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rich epidote is induced by a high Ca bulk content with a high CaO/Na₂O ratio. These experiments demonstrate also that the relative stabilities of xenotime-(Y) and (Y,HREE)-rich epidote are strongly controlled by pressure.

**Keywords** Monazite-(Ce) · Xenotime-(Y) · Allanite-(Ce) · Epidote · Fluorapatite · Fluorcalciobritholite · Rare earth elements · Experimental petrology

**Introduction**

Monazite [(LREE, Th, U)PO₄], xenotime-(Y) [(Y, HREE)PO₄], fluorapatite [(Ca, LREE, Si, Na)₅(PO₄)₃F], and allanite [(Ca, REE)(Al₂, Fe²⁺)(Si₂O₇)(SiO₄)O(OH)] are common accessory minerals in various types of igneous, metamorphic, and sedimentary rocks and represent the principal hosts of rare earth elements (REEs) in the Earth’s crust. They are widely used as geochronometers, including U-Pb and Th-U-Pb dating of monazite (Williams et al. 2007) and xenotime-(Y) (Hetherington et al. 2008), Lu-Hf, U-Pb, fission track and (U-Th)/He dating of apatite (Chew and Spikings 2015), and Lu-Hf, U-Pb, fission track and (U-Th)/He dating of monazite (Williams et al. 2007) and xenotime-(Y) (Gregory et al. 2007; Darling et al. 2012). Distribution of Y between co-existing monazite and xenotime-(Y) (Gratz and Heinrich 1997; Heinrich et al. 1997; Andrehs and Heinrich 1998) or monazite and garnet (Pyle et al. 2001) can be utilized as geothermometers. In addition to these important applications, monazite, xenotime-(Y), apatite, and allanite can also be used for studying metasomatic processes; the nature of the fluids responsible for these processes (Putnis 2009; Budzyń et al. 2011; Harlov et al. 2011; Harlov 2015); and to constrain timing of mineral-fluid interactions (Williams et al. 2011; Villa and Williams 2013).

The relative stabilities of monazite, allanite, and fluorapatite are of particular interest in studies of igneous and metamorphic processes. For example, in metamorphosed rocks of granitic or pelitic composition, monazite-(Ce) alteration and breakdown involve formation of complex textures involving fluorapatite, allanite-(Ce), epidote [Ca₂(Al₂, Fe³⁺)(Si₂O₇)(SiO₄)O(OH)], and ThSiO₄ or ThO₂, mediated by a fluid with high Ca and F activities (Broska and Siman 1998; Finger et al. 1998; Broska et al. 2005; Petrik et al. 2006; Janots et al. 2008; Ondrejka et al. 2012). More rarely, monazite-(Ce) can be replaced by secondary fluorapatite and monazite, but not allanite-(Ce) (Rasmussen and Muhling 2007; Budzyń et al. 2010). The diversity of products is strictly related to the P-T conditions, bulk rock composition, and composition of the fluid. Several experimental studies have determined the stabilities of monazite-(Ce), allanite-(Ce), and fluorapatite relative to each other. Experiments at 450–500 °C and 450–610 MPa utilizing silicate mineral assemblages and various fluids, including H₂O, 2 M NaOH, 2 M KOH, 1 M/2 M Ca(OH)₂, 1 M HCl, NaCl + H₂O, KCl + H₂O, CaCl₂ + H₂O, CaCO₃ + H₂O, and Na₂Si₂O₅ + H₂O, tested the stability of monazite-(Ce) relative to allanite-(Ce) and fluorapatite as a function of P-T-X conditions (Budzyń et al. 2011). Monazite-(Ce) partially broke down to fluorapatite and/or britholite in most of the experiments. In the presence of Ca-bearing fluids, allanite-(Ce) and REE-rich epidote also formed. In the experiment at 450 °C and 450 MPa with Na₂Si₂O₅ + H₂O, alteration of monazite-(Ce) via fluid-mediated coupled dissolution-reprecipitation resulted in the resetting of monazite Th-U-Pb clock far below the diffusional closure temperature (Williams et al. 2011). Recently, the stability of monazite-(Ce) was tested in the presence of silicate mineral assemblages under conditions of 250–350 °C and 200–400 MPa (Budzyń et al. 2015). Monazite-(Ce) was stable in the presence of 2 M Ca(OH)₂, where some fluorapatite to fluorcalciobritholite [(Ca,REE)₅(SiO₄,PO₄)₃F] formed, but no allanite. The presence of Na₂Si₂O₅ + H₂O promoted the strong alteration of the monazite-(Ce) and the formation of steacyite [(K,□)(Na, Ca)₂(Th, U)Si₈O₂₀] enriched in REE, and fluorcalciobritholite. Furthermore, fluid induced monazite-(Ce) alteration promoted mass transfer with partial removal of Th, U, and Pb via fluid-mediated coupled dissolution-reprecipitation resulting in significant disturbance of the original ages without resetting in contrast to 450 °C and 450 MPa experiment in Williams et al. (2011).

These experiments were based on available data from monazite-allanite relations in metamorphosed granites and pelites (Broska and Siman 1998; Finger et al. 1998; Janots et al. 2006), and the thermodynamic modeling of the relative stabilities of monazite-(La) and dissakisite-(La), Mg-equivalent of allanite (Janots et al. 2007). Later thermodynamic modeling by Spear (2010), which utilized the average whole rock metapelite data of Shaw (1956), showed that increasing the CaO content from 2.17 to 4.34 wt.% shifts the transition of allanite-(Ce) to monazite-(Ce) from ~400–550 °C, depending on a pressure, to ~480 °C at 200 MPa and ~750 °C at 1000 MPa, thereby expanding the allanite-(Ce) stability field. Fluorapatite was stable over the entire calculated P-T range (100–1100 MPa and 350–800 °C) considered. In the experiments of Budzyń et al. (2011), those with a significantly increased bulk CaO content (~11.3–17.7 wt.%) resulted in allanite-(Ce) and fluorapatite-britholite formation at 450–500 °C and 400–610 MPa in agreement with Spear’s (2010) thermodynamic modeling.

Xenotime-(Y) is recognized as a robust geochronometer, which is resistant to alteration (Rasmussen 2005). In addition, volume diffusion of Pb has been experimentally demonstrated to be slower than in zircon or monazite (Cherniak 2006). Similar to monazite-(Ce), fluid-mediated alteration has also led to the replacement of xenotime-(Y) by corona-like textures including (Y,HREE)-rich fluorapatite and (Y,HREE)-rich...
epidote in granitic rocks (Broska et al. 2005; Broska and Petrik 2015) or fluorapatite and hingganite-(Y) in pegmatite (Majka et al. 2011). The P-T conditions for such alterations are not well constrained. During progressive metamorphism of pelites, xenotime-(Y) breaks down before the growth of garnet. This is then followed by the breakdown of HREE-rich clinzoisite to xenotime-(Y) at 560–610 °C, depending on bulk composition of rock, particularly the bulk CaO/Na2O ratio (Janots et al. 2008). Because xenotime-(Y) is less abundant than monazite in nature, our knowledge about its stability during metamorphism, particularly in relation to (Y,HREE)-rich epidote and (Y,HREE)-rich fluorapatite, is still limited.

In this work, the relative stabilities of monazite-(Ce), allanite-(Ce), and fluorapatite are explored in a series of experiments which expand on the previous experiments of Budzyn et al. (2011) to a broader range of P-T conditions at 200 to 1000 MPa and 450 to 750 °C. The study aims to determine (i) if allanite-(Ce) and/or fluorapatite will form at the expense of monazite-(Ce) in experiments utilizing monazite-(Ce) plus a silicate mineral assemblage and a 2 M Ca(OH)2 fluid or a Na2Si2O5 + H2O fluid over the above P-T range; and (ii) the impact of fluid-mediated alteration on the remobilization of Th, U, and Pb in the monazite-(Ce) structure in the presence of a Na2Si2O5 + H2O, with regards to its impact on geochronology. Starting mixes with both fluids had an elevated bulk Ca content that should promote fluorapatite and allanite-(Ce) formation. A simultaneous set of parallel experiments for xenotime-(Y) were aimed at determining the P-T stability relations between xenotime-(Y), (Y,HREE)-rich epidote, and (Y,HREE)-rich fluorapatite. This study also aims to estimate to what degree Y + REE incorporation into epidote-group minerals is a function of fluid composition or P-T conditions or both in a REE-dominated system.

**Experimental and analytical methods**

**Experiments**

Experiments were performed utilizing cold-seal autoclaves on a hydrothermal line and the piston-cylinder apparatus. Pressures and temperatures ranged from 200 to 1000 MPa and from 450 to 750 °C. Each run involved four sets of experiments, two for monazite-(Ce) and two for xenotime-(Y), each one corresponding to two different fluids, 2 M Ca(OH)2 or Na2Si2O5 + H2O (Table 1). In each set of experiments, coarse grains (50–250 μm) of monazite-(Ce) and xenotime-(Y) were used to explore reactions, primarily focused on the partial replacement of monazite-(Ce) and xenotime-(Y) by (Y,REE)-enriched epidote and fluorapatite. In order to effect these reactions in an approximation of a metapelitic, geochemical environment, quartz, albite, biotite, garnet, labradorite, muscovite, K-feldspar, and CaF2 from diverse sources were added to the system. These provided the materials necessary for the reactions: monazite-(Ce) + annite + quartz + Ca + F (in fluid-I) = fluorapatite + allanite-(Ce) + fluid-II (Broska and Siman 1998), and xenotime-(Y) + annite + anorthite + fluid = (Y,HREE)-rich apatite + (Y,HREE)-rich epidote + muscovite (Broska et al. 2005). These experiments were not aimed at achieving thermobarometric equilibria between a group of silicate minerals from a diverse set of sources. Rather, these coarse grains of monazite-(Ce) and xenotime-(Y) were used to induce (Y,REE)-bearing epidote and apatite reaction textures to form, which is the chief focus of this study.

The Burnet monazite-(Ce) used in experiments originates from a pegmatite from Burnet County, Texas, USA. This monazite-(Ce) (10.18–12.54 wt.% ThO2; 0.28–0.40 wt.% UO2; 0.51–0.65 wt.% PbO; see supplementary Table S1 for average composition) was selected to test the relative mobility of Y, REE, Th, U, and Pb. A fragment of the Burnet monazite-(Ce) was crushed and sieved to a 50–250 μm fraction. Optically clear to slightly foggy, reddish-brown grains were hand picked out under a binocular microscope. The separated grains were washed in ethanol in an ultrasonic bath. Under high-contrast back-scattered electrons (BSE) imaging, the monazite-(Ce) grains show faint zonation and patchiness in cross section, which is related to slight variations in the ThO2 content.

The xenotime-(Y) used for experiments is a part of a gem quality, euhedral crystal from a pegmatite in the North-West Frontier Province (NWFP), Pakistan. A fragment of the xenotime-(Y) crystal was crushed and sieved to obtain a 50–250 μm grain size fraction. Optically clear grains with no inclusions of foreign mineral phases were hand picked out using a binocular microscope. The xenotime-(Y) separate was then washed in ethanol in an ultrasonic bath.

Four mineral starting mixes were prepared, two for monazite-(Ce) and two for xenotime-(Y) in the presence of silicate minerals. The silicate starting mixes roughly replicate the composition of granitic to pelitic rocks in which the altered monazite-(Ce) and xenotime-(Y) are most commonly found. Each set of experiments have a high bulk CaO content with respect to natural granites and pelites, i.e. estimated 10.08 wt.% in set (1), 5.91 wt.% in set (2), 9.21 wt.% in set (3) and 5.56 wt.% in set (4) (Table 2). The two silicate starting mixes were prepared for the monazite-(Ce) and xenotime-(Y) experiments (Table 1). These included (1) monazite-(Ce), labradorite (Ab37An60Kfs3; Chihuahua, Mexico), sanidine (Eifel region, Germany), biotite (migmatitic gneiss, Sikkim Himalaya, India), muscovite (pegmatite, Siedlimowice, Sudety Mts., Poland), SiO2, CaF2, and 2 M Ca(OH)2; (2) monazite-(Ce), hydrothermal albite (Ab100; Rožňava, Slovak Republic), sanidine, biotite, muscovite, SiO2, CaF2, Na2Si2O5, and doubly distilled H2O; (3) xenotime-(Y),
| Exp.     | T (°C) | P (MPa) | Duration (days) | Mnz | Xtm | Ab | Lbr | Kfs | Bt | Ms | Grt | SiO₂ | CaF₂ | Ca(OH)₂ | Na₂Si₂O₅ | H₂O | Total charge | Solids added | Real charge | pH | Mineral products |
|---------|-------|---------|-----------------|-----|-----|----|-----|-----|-----|-----|-----|-------|-------|--------|-----------|------|---------------|--------------|-------------|----|-----------------|
| M12C-01 | 450   | 200     | 16              |     |     |    |     |     |     |     |      |       |       |        |           |      |              |              |             |    | REE-Ap, Brt, Wo, REE-Ep |
| M12C-10 | 450   | 400     | 18              |     |     |    |     |     |     |     |      |       |       |        |           |      |              |              |             |    | Brt, REE-Ep, Aln |
| M12C-23 | 450   | 600     | 16              |     |     |    |     |     |     |     |      |       |       |        |           |      |              |              |             |    | Brt, Aln |
| M12C-16 | 450   | 800     | 16              |     |     |    |     |     |     |     |      |       |       |        |           |      |              |              |             |    | Brt, Aln |
| M12C-17 | 450   | 1000    | 16              |     |     |    |     |     |     |     |      |       |       |        |           |      |              |              |             |    | Brt, Aln |
| M12C-06 | 550   | 200     | 12              |     |     |    |     |     |     |     |      |       |       |        |           |      |              |              |             |    | Brt, REE-Ep, Aln |
| M12C-02 | 550   | 400     | 6               |     |     |    |     |     |     |     |      |       |       |        |           |      |              |              |             |    | Brt, REE-Ep, Aln |
| M12C-14 | 550   | 600     | 8               |     |     |    |     |     |     |     |      |       |       |        |           |      |              |              |             |    | Brt, REE-Ep, Aln |
| M12C-13 | 550   | 800     | 8               |     |     |    |     |     |     |     |      |       |       |        |           |      |              |              |             |    | Brt, REE-Ep, Aln |
| M12C-07 | 550   | 1000    | 8               |     |     |    |     |     |     |     |      |       |       |        |           |      |              |              |             |    | Brt, REE-Ep, Aln |
| M12C-09 | 650   | 200     | 6               |     |     |    |     |     |     |     |      |       |       |        |           |      |              |              |             |    | Brt, REE-Ep, Aln |
| M12C-03 | 650   | 400     | 6               |     |     |    |     |     |     |     |      |       |       |        |           |      |              |              |             |    | Brt, REE-Ep, Aln |
| M12C-12 | 650   | 600     | 6               |     |     |    |     |     |     |     |      |       |       |        |           |      |              |              |             |    | Brt, REE-Ep, Aln, melt |
| M12C-11 | 650   | 800     | 6               |     |     |    |     |     |     |     |      |       |       |        |           |      |              |              |             |    | Brt, REE-Ep, Aln, melt |
| M12C-08 | 650   | 1000    | 6               |     |     |    |     |     |     |     |      |       |       |        |           |      |              |              |             |    | Brt, REE-Ep, Aln, melt |
| M12C-18 | 750   | 200     | 4               |     |     |    |     |     |     |     |      |       |       |        |           |      |              |              |             |    | Brt, REE-Ep, Aln, melt |
| M12C-19 | 750   | 400     | 4               |     |     |    |     |     |     |     |      |       |       |        |           |      |              |              |             |    | Brt, REE-Ep, Aln, melt |
| M12C-22 | 750   | 600     | 4               |     |     |    |     |     |     |     |      |       |       |        |           |      |              |              |             |    | Brt, REE-Ep, Aln, melt |
| M12C-21 | 750   | 800     | 4               |     |     |    |     |     |     |     |      |       |       |        |           |      |              |              |             |    | Brt, REE-Ep, Aln, melt |
| M12C-20 | 750   | 1000    | 4               |     |     |    |     |     |     |     |      |       |       |        |           |      |              |              |             |    | Brt, REE-Ep, Aln, melt |
| M12N-01 | 450   | 200     | 16              |     |     |    |     |     |     |     |      |       |       |        |           |      |              |              |             |    | rq-Mnz, Brt, REE-Stc, Amph |
| M12N-10 | 450   | 400     | 18              |     |     |    |     |     |     |     |      |       |       |        |           |      |              |              |             |    | rq-Mnz, Brt, REE-Stc, Amph |
| M12N-23 | 450   | 600     | 16              |     |     |    |     |     |     |     |      |       |       |        |           |      |              |              |             |    | rq-Mnz, Brt, REE-Stc, Amph |
| M12N-16 | 450   | 800     | 16              |     |     |    |     |     |     |     |      |       |       |        |           |      |              |              |             |    | rq-Mnz, REE-Ap, Brt, REE-Stc, Amph |
| M12N-17 | 450   | 1000    | 16              |     |     |    |     |     |     |     |      |       |       |        |           |      |              |              |             |    | rq-Mnz, REE-Ap, Brt, REE-Stc, Amph |
| M12N-06 | 550   | 200     | 12              |     |     |    |     |     |     |     |      |       |       |        |           |      |              |              |             |    | rq-Mnz, REE-Ap, Brt, REE-Stc, ThSiO₄, Amph |
| M12N-02 | 550   | 400     | 6               |     |     |    |     |     |     |     |      |       |       |        |           |      |              |              |             |    | rq-Mnz, REE-Ap, Brt, REE-Stc, ThSiO₄, Amph |
| M12N-14 | 550   | 600     | 8               |     |     |    |     |     |     |     |      |       |       |        |           |      |              |              |             |    | rq-Mnz, REE-Ap, Brt, REE-Stc, Amph |

Table 1: Experimental conditions, starting materials (mg), pH of the remaining fluid after runs and highlighted products.
| Exp.  | T (°C) | P (MPa) | Duration (days) | Mnz | Xtm | Ab | Lbr | Kfs | Ms | Grt | SiO₂ | CaF₂ | Ca(OH)₂ | Na₂Si₂O₅ | H₂O | Total charge | Solids added | Real charge | pH | Mineral products |
|-------|--------|---------|----------------|-----|-----|----|-----|-----|-----|-----|-------|-------|---------|----------|------|---------------|-------------|-------------|----|----------------|
| M12N-13 | 550   | 800    | 8              | 4.89 –   | 4.36 – | 2.91 | 4.14 | 2.20 – | 4.28 | 3.16 – | 5.08 | 5.40 | 36.42 | 29.17 | 34.57 | n.m. | REE-Ap, Bt, Amph |
| M12N-07 | 550   | 1000   | 8              | 5.12 –   | 4.38 – | 2.92 | 4.07 | 2.03 – | 4.03 | 2.96 – | 4.73 | 5.23 | 35.47 | 29.91 | 35.14 | 10-11 | REE-Ap, Bt, Amph |
| M12N-09 | 650   | 200    | 6              | 5.43 –   | 4.38 – | 2.94 | 4.16 | 2.14 – | 3.98 | 2.96 – | 5.07 | 5.60 | 36.66 | 30.65 | 36.25 | 12 | REE-Ap, Bt, Cher, Ttn, Amph, melt |
| M12N-03 | 650   | 400    | 6              | 5.12 –   | 4.16 – | 3.18 | 3.90 | 2.06 – | 3.83 | 3.00 – | 4.98 | 5.41 | 35.64 | 29.88 | 35.29 | >10 | REE-Ap, Bt, Cher, Amph, melt |
| M12N-12 | 650   | 600    | 6              | 5.43 –   | 4.38 – | 3.49 | 3.98 | 2.32 – | 3.96 | 3.10 – | 4.80 | 5.60 | 36.70 | 29.26 | 34.86 | 10-11 | REE-Ap, Bt, Cher, Ttn, Amph, melt |
| M12N-08 | 650   | 700    | 6              | 5.25 –   | 3.80 – | 3.13 | 3.87 | 1.85 – | 4.25 | 2.80 – | 4.90 | 5.53 | 35.38 | 29.24 | 34.77 | 10-11 | REE-Ap, Bt, Cher, Ttn, Amph, melt |
| X12C-01 | 450   | 200    | 16             | 5.70 –   | 3.95 | 3.17 | 4.18 | 2.10 | 4.14 | 4.06 | 3.13 | 0.90 | 5.46 | 36.79 | 29.89 | 35.35 | 7 | YBrt |
| X12C-10 | 450   | 400    | 18             | 5.12 –   | 3.99 | 3.15 | 4.40 | 1.82 | 3.73 | 4.04 | 3.14 | 0.70 | 5.69 | 35.78 | 29.18 | 34.87 | n.m. | YBrt |
| X12C-23 | 450   | 600    | 16             | 5.67 –   | 3.81 | 3.29 | 4.15 | 2.10 | 4.08 | 4.09 | 3.12 | 0.74 | 4.78 | 31.05 | 30.58 | 35.36 | n.m. | YBrt |
| X12C-16 | 450   | 800    | 16             | 5.15 –   | 3.91 | 2.86 | 3.86 | 1.92 | 4.16 | 4.01 | 2.92 | 0.75 | 5.37 | 29.54 | 28.87 | 34.24 | 10 | YBrt |
| X12C-17 | 450   | 1000   | 16             | 5.18 –   | 4.36 | 3.28 | 3.73 | 1.78 | 4.00 | 4.05 | 3.21 | 0.70 | 5.26 | 30.29 | 29.57 | 34.83 | 10 | YBrt |
| X12C-06 | 550   | 200    | 12             | 4.85 –   | 4.31 | 3.17 | 3.93 | 2.09 | 4.03 | 3.92 | 2.93 | 0.89 | 5.18 | 35.30 | 29.01 | 34.19 | 7 | YBrt |
| X12C-02 | 550   | 400    | 6              | 5.00 –   | 4.05 | 3.07 | 3.96 | 2.09 | 4.05 | 4.00 | 3.05 | 0.74 | 5.07 | 35.08 | 29.41 | 34.48 | 7-8 | YBrt |
| X12C-14 | 550   | 600    | 8              | 4.95 –   | 3.88 | 3.04 | 4.03 | 2.00 | 4.10 | 3.89 | 2.87 | 0.89 | 5.45 | 35.10 | 28.62 | 34.07 | n.m. | YBrt |
| X12C-13 | 550   | 800    | 8              | 5.09 –   | 4.32 | 2.86 | 3.88 | 2.03 | 3.75 | 3.96 | 2.88 | 0.87 | 5.45 | 35.09 | 28.67 | 34.12 | n.m. | YBrt, (YHREE)-Ep |
| X12C-07 | 550   | 1000   | 8              | 5.01 –   | 4.32 | 3.17 | 4.43 | 1.82 | 4.59 | 3.91 | 2.96 | 0.75 | 5.50 | 36.46 | 29.58 | 35.08 | 8 | YBrt |
| X12C-09 | 650   | 200    | 6              | 5.26 –   | 3.87 | 2.89 | 3.99 | 2.03 | 3.78 | 3.70 | 2.97 | 0.77 | 5.57 | 34.83 | 28.81 | 34.38 | 7 | YBrt, melt |
| Exp.  | T (°C) | P (MPa) | Duration (days) | Mnz | Xtm | Ab | Lbr | Kfs | Bt | Ms | Grt | SiO₂ | CaF₂ | Ca(OH)₂ | Na₂Si₂O₅ | H₂O | Total charge | Solids added | Real charge | pH | Mineral products |
|-------|--------|---------|-----------------|-----|-----|----|-----|-----|----|----|-----|-------|-------|-------|-----------|-------|------------|-------------|-------------|----|----------------|------------|
| X12C-03 | 650   | 400    | 6              | –   | –   | –  | –   | –   | –  | –  | –   | –     | –     | –     | –         | –     | –          | 4.99        | 34.90      | 28.53 | 33.52         | YBrt       |
| X12C-12 | 650   | 600    | 6              | –   | –   | –  | –   | –   | –  | –  | –   | –     | –     | –     | –         | –     | –          | 4.99        | 34.90      | 28.53 | 33.52         | YBrt, melt |
| X12C-11 | 650   | 800    | 6              | –   | –   | –  | –   | –   | –  | –  | –   | –     | –     | –     | –         | –     | –          | 5.46        | 36.88      | 30.58 | 36.04         | 8          |
| X12C-08 | 650   | 1000   | 6              | –   | –   | –  | –   | –   | –  | –  | –   | –     | –     | –     | –         | –     | –          | 5.41        | 36.28      | 29.21 | 34.62         | 10–11       |
| X12C-18 | 750   | 200    | 4              | –   | –   | –  | –   | –   | –  | –  | –   | –     | –     | –     | –         | –     | –          | 5.40        | 30.25      | 29.30 | 34.70         | 7          |
| X12C-19 | 750   | 400    | 4              | –   | –   | –  | –   | –   | –  | –  | –   | –     | –     | –     | –         | –     | –          | 4.92        | 31.48      | 31.32 | 36.24         | 7          |
| X12C-22 | 750   | 600    | 4              | –   | –   | –  | –   | –   | –  | –  | –   | –     | –     | –     | –         | –     | –          | 4.96        | 30.54      | 30.11 | 35.07         | 7          |
| X12C-21 | 750   | 800    | 4              | –   | –   | –  | –   | –   | –  | –  | –   | –     | –     | –     | –         | –     | –          | 5.12        | 39.42      | 33.56 | 38.63         | 7–8        |
| X12C-20 | 750   | 1000   | 4              | –   | –   | –  | –   | –   | –  | –  | –   | –     | –     | –     | –         | –     | –          | 4.90        | 39.14      | 31.34 | 36.66         | 10         |
| X12N-01 | 450   | 200    | 16             | –   | –   | –  | –   | –   | –  | –  | –   | –     | –     | –     | –         | –     | –          | 5.12        | 39.42      | 33.56 | 38.63         | 7          |
| X12N-10 | 450   | 400    | 18             | –   | –   | –  | –   | –   | –  | –  | –   | –     | –     | –     | –         | –     | –          | 4.90        | 39.14      | 31.34 | 36.66         | 10         |
| X12N-23 | 450   | 600    | 16             | –   | –   | –  | –   | –   | –  | –  | –   | –     | –     | –     | –         | –     | –          | 5.28        | 36.78      | 36.23 | 41.39         | n.m.       |
| X12N-16 | 450   | 800    | 16             | –   | –   | –  | –   | –   | –  | –  | –   | –     | –     | –     | –         | –     | –          | 5.16        | 34.35      | 33.42 | 38.71         | 10         |
| X12N-17 | 450   | 1000   | 16             | –   | –   | –  | –   | –   | –  | –  | –   | –     | –     | –     | –         | –     | –          | 4.87        | 33.76      | 32.88 | 38.13         | 10         |
| X12N-06 | 550   | 200    | 12             | –   | –   | –  | –   | –   | –  | –  | –   | –     | –     | –     | –         | –     | –          | 5.13        | 39.31      | 30.75 | 36.24         | n.m.       |
| X12N-02 | 550   | 400    | 6              | –   | –   | –  | –   | –   | –  | –  | –   | –     | –     | –     | –         | –     | –          | 5.15        | 39.31      | 30.75 | 36.24         | n.m.       |
| X12N-14 | 550   | 600    | 8              | –   | –   | –  | –   | –   | –  | –  | –   | –     | –     | –     | –         | –     | –          | 5.13        | 39.31      | 30.75 | 36.24         | n.m.       |
| X12N-13 | 550   | 800    | 8              | –   | –   | –  | –   | –   | –  | –  | –   | –     | –     | –     | –         | –     | –          | 5.10        | 40.35      | 34.53 | 40.02         | n.m.       |
| X12N-07 | 550   | 1000   | 8              | –   | –   | –  | –   | –   | –  | –  | –   | –     | –     | –     | –         | –     | –          | 5.35        | 40.48      | 33.12 | 38.54         | 10–11      |
| X12N-09 | 650   | 200    | 6              | –   | –   | –  | –   | –   | –  | –  | –   | –     | –     | –     | –         | –     | –          | 4.92        | 39.73      | 32.26 | 37.58         | 10–11      |
| X12N-08 | 650   | 400    | 6              | –   | –   | –  | –   | –   | –  | –  | –   | –     | –     | –     | –         | –     | –          | 5.21        | 39.96      | 33.21 | 38.81         | 10–11      |
| X12N-12 | 650   | 600    | 6              | –   | –   | –  | –   | –   | –  | –  | –   | –     | –     | –     | –         | –     | –          | 4.99        | 40.36      | 33.27 | 39.07         | 10–11      |
| X12N-11 | 650   | 800    | 6              | –   | –   | –  | –   | –   | –  | –  | –   | –     | –     | –     | –         | –     | –          | 5.16        | 40.81      | 33.48 | 39.14         | 10–11      |
Table 1  (continued)

| Exp. | T (°C) | P (MPa) | Duration (days) | Mnz Xtm Ab Lbr Kfs Bt Ms Grt SiO$_2$ CaF$_2$ Ca(OH)$_2$ Na$_2$Si$_2$O$_5$ H$_2$O Total charge | Solids added | Real charge | pH | Mineral products |
|------|--------|---------|-----------------|-------------------------------------------------|-------------|--------------|----|-----------------|
| X12N-18 | 750 | 200 | 4 | – | 4.86 | 4.05 | – | 3.54 | 4.45 | 1.84 | 4.42 | 4.06 | 3.45 | – | 4.74 | 5.45 | 35.41 | 34.29 | 39.74 | 10 | YBrt, Amph, Ttn, Bt$_2$, melt |
| X12N-19 | 750 | 400 | 4 | – | 5.24 | 3.80 | – | 3.27 | 3.86 | 2.20 | 4.26 | 3.84 | 3.12 | – | 4.99 | 5.05 | 34.58 | 34.11 | 39.16 | 10 | YBrt, Amph, Bt$_2$, Melt |
| X12N-22 | 750 | 600 | 4 | – | 5.65 | 4.62 | – | 3.41 | 4.18 | 2.87 | 4.05 | 3.83 | 3.18 | – | 5.02 | 4.88 | 36.81 | 36.31 | 41.19 | 10 | YBrt, Amph, Bt$_2$, Melt |
| X12N-21 | 750 | 800 | 4 | – | 5.24 | 4.12 | – | 3.16 | 3.83 | 2.34 | 3.83 | 2.91 | – | 5.01 | 5.01 | 34.23 | 33.77 | 38.78 | 10 | YBrt, Px, Amph, Melt |
| X12N-20 | 750 | 1000 | 4 | – | 5.00 | 4.17 | – | 2.64 | 3.92 | 1.96 | 3.92 | 4.28 | 3.05 | – | 5.08 | 4.90 | 34.06 | 33.37 | 38.27 | 10 | YBrt, Amph, Bt$_2$, Ttn, Melt |

n.m. not measured

Table 2  Estimated average bulk compositions of the capsule charges calculated from the average EPMA analysis results of the starting minerals

| Bulk compositions of mixed silicates (in wt.%) | FeO | MnO | NiO | BaO | SrO | Na$_2$O | K$_2$O | F | H$_2$O | Total |
|------------------------------------------------|-----|-----|-----|-----|-----|--------|------|---|-------|-------|
| Set (1) Mn - Ca runs: Lbr + Kfs + Bt + Ms + SiO$_2$ | 61.69 | 60.96 | 15.93 | 15.93 | 1.86 | 0.53 | 0.06 | 0.06 | 0.06 | 99.89 |
| Set (2) Mn - Ca-Na runs: Ab + Kfs + Bt + Ms + SiO$_2$ | 65.56 | 65.56 | 18.15 | 18.15 | 0.96 | 0.96 | 0.06 | 0.06 | 0.06 | 99.94 |
| Set (3) Xtm - Ca runs: Lbr + Kfs + Bt + Ms + SiO$_2$ + Grt | 57.37 | 60.50 | 17.17 | 17.17 | 0.78 | 0.78 | 0.06 | 0.06 | 0.06 | 99.76 |
| Set (4) Xtm - Ca-Na runs: Ab + Kfs + Bt + Ms + SiO$_2$ + Grt | 60.50 | 60.50 | 17.17 | 17.17 | 0.78 | 0.78 | 0.06 | 0.06 | 0.06 | 99.81 |

| Bulk compositions of starting mixes (in wt.%) | P$_2$O$_5$ | SiO$_2$ | TiO$_2$ | ThO$_2$ | UO$_2$ | Al$_2$O$_3$ | Cr$_2$O$_3$ | MgO | CaO | FeO | MnO | NiO | BaO | SrO | PbO | Na$_2$O | K$_2$O | F | H$_2$O | YO$_2$ | La$_2$O$_3$ | Ce$_2$O$_3$ | Pr$_2$O$_3$ | Nd$_2$O$_3$ | Sm$_2$O$_3$ | Eu$_2$O$_3$ | Gd$_2$O$_3$ | Tb$_2$O$_3$ | Dy$_2$O$_3$ | Ho$_2$O$_3$ | Er$_2$O$_3$ | Tm$_2$O$_3$ | Yb$_2$O$_3$ | Lu$_2$O$_3$ | Total | CaO / Na$_2$O | Y(O + REE)O$_3$ |
|-------------------------------------------------|--------|--------|--------|--------|--------|--------|--------|-----|-----|-----|-----|-----|-----|-----|-----|-----|---|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Set (1) Mn - Ca runs: Mnz + Lbr + Kfs + Bt + Ms + SiO$_2$ + CaF$_2$ + 2 M Ca(OH)$_2$ | 4.46 | 34.39 | 0.53 | 1.86 | 0.06 | 10.04 | 0.01 | 1.17 | 10.08 | 2.45 | 0.01 | 0.01 | 0.09 | 0.01 | 0.10 | 0.76 | 3.14 | 3.31 | 18.16 | 0.13 | 1.40 | 4.66 | 0.54 | 1.43 | 0.58 | 0.03 | 0.28 | 0.02 | 0.15 | 0.00 | 0.00 | 0.06 | 0.00 | 0.00 | 99.89 | 13.3 | 9.3 |
| Set (2) Mn - Ca-Na runs: Mnz + Ab + Kfs + Bt + Ms + SiO$_2$ + CaF$_2$ + 2 M Na$_2$Si$_2$O$_5$ + H$_2$O | 3.92 | 41.51 | 0.46 | 1.63 | 0.05 | 7.74 | 0.00 | 1.01 | 5.91 | 2.12 | 0.01 | 0.01 | 0.07 | 0.00 | 0.08 | 6.17 | 2.73 | 2.91 | 15.43 | 0.11 | 1.23 | 4.10 | 0.47 | 1.26 | 0.51 | 0.02 | 0.25 | 0.08 | 0.13 | 0.00 | 0.00 | 0.05 | 0.00 | 0.00 | 99.93 | 1.0 | 8.2 |
| Set (3) Xtm - Ca runs: Xtm + Lbr + Kfs + Bt + Ms + SiO$_2$ + Grt + CaF$_2$ + 2 M Ca(OH)$_2$ | 5.02 | 34.68 | 0.47 | 0.00 | 0.02 | 11.47 | 0.01 | 2.28 | 9.21 | 4.75 | 0.07 | 0.00 | 0.03 | 0.00 | 0.06 | 6.78 | 2.78 | 2.93 | 16.06 | 5.60 | 0.00 | 0.00 | 0.02 | 0.05 | 0.05 | 0.73 | 0.24 | 1.20 | 0.22 | 0.62 | 0.08 | 0.48 | 0.07 | 99.86 | 13.7 | 9.4 |
| Set (4) Xtm - Ca-Na runs: Xtm + Ab + Kfs + Bt + Ms + SiO$_2$ + Grt + CaF$_2$ + 2 M Na$_2$Si$_2$O$_5$ + H$_2$O | 4.47 | 41.04 | 0.42 | 0.00 | 0.01 | 9.25 | 0.01 | 2.02 | 5.56 | 4.20 | 0.06 | 0.01 | 0.07 | 0.00 | 0.06 | 5.54 | 2.45 | 2.61 | 13.85 | 4.99 | 0.00 | 0.00 | 0.02 | 0.04 | 0.04 | 0.65 | 0.21 | 1.07 | 0.20 | 0.55 | 0.07 | 0.43 | 0.06 | 99.90 | 1.0 | 8.3 |
labradorite, sanidine, biotite, muscovite, garnet (Gore Mt., USA), SiO$_2$, CaF$_2$, and 2 M Ca(OH)$_2$ fluid; and (4) xenotime-(Y), albite, sanidine, biotite, muscovite, garnet, SiO$_2$, CaF$_2$, Na$_2$Si$_2$O$_5$, and doubly distilled H$_2$O (Table 1). The 2 M Ca(OH)$_2$ solution was prepared using a CatOH$_2$ chemical reagent (Merck) and doubly distilled H$_2$O. Synthetic amorphous SiO$_2$ was used instead of quartz to increase the reaction rates. CaF$_2$ (suprapur; Merck 2842) was used as a source of Ca and F to form fluorapatite. Labradorite was used in experiments with 2 M Ca(OH)$_2$ as an additional source of Ca, whereas albite was used in experiments with Na$_2$Si$_2$O$_5$ + H$_2$O to increase the Na bulk content. Experiments with xenotime-(Y) included garnet to test Y partitioning between xenotime-(Y) and garnet. The estimated average bulk composition of the silicate mixes and all other components used in each capsule charge, calculated based on the average composition of each starting phase, are presented in Table 2. High amounts of monazite-(Ce) and xenotime-(Y) in the starting mixes were used in order that these phases might be easily found in the grain mounts. This, however, significantly increased the bulk REE and P contents in the experiments compared to their actual relative abundances in natural rocks.

The minerals in the silicate mixes were crushed and sieved to obtain a 50 to 250 μm fraction. Foreign and cloudy mineral grains were hand picked out under the binocular microscope. The Au capsules, 15 mm long and 3 mm wide (outer diameter 3.0 mm, inner diameter 2.6 mm), were loaded with ~5 mg of doubly distilled H$_2$O, 20–36 mg of mixed solids (Table 1), and arc-welded shut using a Lampert PUK-04 precision welding device. The Au capsules were checked for leaks by weighing, heating in a 105 °C oven overnight, and then weighed again.

Experiments at 200 to 400 MPa and 450 to 750 °C (Table 1) were performed in standard cold-seal, 6 mm bore, René metal autoclaves with H$_2$O as the pressure medium. Four gently flattened Au capsules, two with monazite-(Ce) [experimental sets (1) and (2)] and two with xenotime-(Y) [experimental sets (3) and (4)], were placed in each autoclave. During the run, the experiments were buffered at approximately the Ni-NiO oxygen buffer due to the presence of Ni metal filler rods, which occupied the bore of the autoclave not occupied by the Au capsules. Temperatures were measured externally by a thermocouple tip inserted into the end of autoclave near the Au capsules. Thermocouples are accurate to within ±3 °C. No variation in temperature was observed during each run. The maximum temperature gradient along the length of a capsule was approximately 5 °C at 750 °C. The temperature gradient was measured in a sealed autoclave on a hydrothermal line at 400 MPa by placing two thermocouples in contact with both ends of a 1 cm long Au capsule and placing a third thermocouple in contact with the center of the capsule. For the case of 750 °C, as measured by the central thermocouple, the thermal gradient was then determined by the difference between this temperature and the two temperatures measured at either end of the capsule. Pressure on the hydrothermal line was calibrated against a pressure transducer calibrated against a Heise gauge manometer for which the quoted pressure is accurate to ±5 MPa. The autoclaves were quenched after the run using compressed air, reaching temperatures of ~100 °C within 1 min.

Experiments at 600 to 1000 MPa and 450 to 750 °C (Table 1) were performed using the piston-cylinder apparatus (Johannes et al. 1971; Johannes 1973). An NaCl assembly with a graphite oven was used in the 450, 500, and 650 °C runs, and a CaF$_2$ assembly with a graphite oven was used in the 750 °C runs. In the case of the CaF$_2$ assembly, the actual pressure during the experimental run was corrected for friction (cf. Harlov and Milke 2002). Four gently flattened Au capsules [two for the monazite-(Ce) and two for the xenotime-(Y) experiments] were positioned vertically with the Ni-Cr thermocouple tip placed approximately halfway up alongside of one of the capsules (Fig. 1). Biotite sheets were used to separate the capsules. Estimated maximum thermal gradients along the length of the capsule are ±20 °C and were estimated in the same manner as described above for the hydrothermal autoclave experiments. Estimated uncertainty in pressure is ±50 MPa (cf. Harlov and Milke 2002). At the start of a run, the pressure was taken up to approximately 10–15 % below run conditions, and then the temperature was brought up to the desired value. Thermal expansion caused the pressure to increase to the approximate target value. The pressure was then adjusted to the desired value, and automatically maintained within a preset range during the course of the experiment.

![Fig. 1 Sketch of the assembly used in experiments with piston-cylinder apparatus](image-url)
During the run, the presence of the graphite oven buffered the experiment to the C-CO-CO$_2$ oxygen buffer. Quench was achieved by turning off the current, such that H$_2$O-cooling jacket cooled down the NaCl or CaF$_2$ assembly to below 50 °C within about 15 s.

After each run, the capsules were carefully examined, cleaned, weighed, and opened. The pH of the fluid within the capsule was measured using litmus paper. The capsules were then dried at 105 °C overnight. A portion of the extracted experiment was mounted in epoxy and polished for back scattered electron (BSE) imaging and electron probe micro analysis. A second part of the extracted experimental products was sprinkled on an adhesive carbon mount and carbon coated for BSE imaging. Product phase dimensions were measured in cross section in polished grain mounts. Because the exposures strongly depend dimensionally on the cross cut of the minerals during grinding down and polishing, particularly in the replacement textures, image analysis was not applied in order to avoid misleading volumetric data.

Analytical methods

The BSE imaging, and preliminary chemical analyses of the starting minerals and the experimental products were performed using a Hitachi S-4700 field emission scanning electron microscope equipped with energy dispersive spectrometer (EDS). Chemical analyses of the mixes and experimental products were performed using a JEOL JXA-8530F HyperProbe Field Emission Electron Probe Microanalyzer (EPMA) equipped with four wavelength spectrometers. Monazite-(Ce) and xenotime-(Y) analyses were collected using a 20 kV accelerating voltage, 100 nA beam current, 100 ms dwell time, 0.33 μm step size, and a focused beam.

Experimental constraints on the relative stabilities of Mnz - Aln - Ap and Xtm - (Y ,HREE)-Ep - Ap 191

and xenotime-(Y) were collected using a 15 kV accelerating voltage, 100 nA beam current, 100 ms dwell time, 0.33 μm step size, and a focused beam.

Abbreviations

The abbreviations of mineral names are used according to those proposed by Whitney and Evans (2010). Ab – albite, Aln – allanite-(Ce), Amph – amphibole, Brt – fluorcalciobritholite, Bt – biotite, Bt$_2$ – secondary low-Ti biotite, Btw – bytownite, Cher – cheralite, Chl – chlorite, Crn – corundum, Grt – garnet, Kfs – K-feldspar, Lbr – labradorite, Mnz – monazite-(Ce), rq-Mnz – re-equilibrated monazite-(Ce) with patchy zoning, Ms – muscovite, Ms$_2$ – secondary muscovite, Or – orthoclase, Px – pyroxene, Qz – quartz, REE-Ap – REE-rich fluorapatite, REE-Ep – REE-rich epidote, Ste – REE-rich steacyite, Tm – titanite, Wo – wollastonite, Xtm – xenotime-(Y), (Y,REE)-Ap – (Y,REE)-rich fluorapatite, YBr – Y-rich fluorcalciobritholite, (Y,HREE)-Ep – (Y,HREE)-rich epidote.

Experimental results

Experiments with monazite-(Ce) and 2 M Ca(OH)$_2$

Monazite-(Ce) breakdown, including various degrees of dissolution on the surface and formation of new phases, were documented in all runs (Fig. 2a, Table 3). The remaining fluid had a neutral pH in most products, except in runs at 450 °C, 800–1000 MPa; and 550 °C, 1000 MPa, which tended to have a moderately high pH (Table 1). Monazite-(Ce) grains from runs at 450–550 °C and 200–400 MPa are altered mostly along the rims, showing partial dissolution and overgrowth by other mineral phases (Fig. 3b, d and e). In the higher P-T experiments, most of the monazite-(Ce) grains were partially dissolved in the same way, with occasional almost complete replacement by REE-rich epidote-allanite-(Ce) (Fig. 3i). The composition of the monazite-(Ce) in the experimental products is the same as the original Burnet monazite-(Ce), indicating that the remaining monazite-(Ce) was not affected by compositional alteration (Fig. 4a and b; supplementary Table S1). High Th content, in both the altered and original monazite-(Ce), is related to the huttonitic and cheralitic substitutions (Fig. 5a and b).

Chemical analyses of feldspars, micas, garnets, and titanite from experiments with xenotime-(Y) [sets (3) and (4)], analyses of melt, and compositional X-ray maps of monazite-(Ce) and xenotime-(Y), were performed using a JEOL JXA-8230 SuperProbe Electron Probe Microanalyzer. Measurement conditions can be found in supplementary Table S2. Compositional WDS X-ray maps of altered monazite-(Ce) and xenotime-(Y) were collected using a 15 kV accelerating voltage, 100 nA beam current, 100 ms dwell time, 0.33 μm step size, and a focused beam.
(Fig. 3j). The fluorcalciobritholite is characterized by high Y + REE and Th concentrations of 24.7–45.3 wt.% (Y + REE)2O3 and 3.1–10.3 wt.% ThO2 (supplementary Table S3). The U content is relatively low and ranges between 0.1 and 0.3 wt.% UO2. The fluorcalciobritholite phase represents a solid solution between fluorapatite – calciobritholite – fluorbritholite, due to coupled heterovalent substitutions on the M and T sites (cf. Pasero et al. 2010).

REE-rich epidote-allanite-(Ce) formed in all the runs. The grain size ranges from several to ~50 μm in low P-T runs, to large ~130 μm grains formed at the highest P-T conditions. From the BSE images, it is evident that the degree of monazite-(Ce) replacement by allanite-(Ce) increases with increasing P-T conditions. It should be noted that occasionally fluorcalciobritholite is present in the near vicinity of the monazite-(Ce) grain surface, while the allanite-(Ce) crystals form outer rims around the monazite-(Ce) grains (Fig. 3m). Allanite-(Ce) is characterized by an REE content reaching 19.7 wt.% REE2O3, and a Th concentration of 1.2 wt.% ThO2 on average (supplementary Table S4). The Al vs. Y + REE diagram (after Petrík et al. 1995) shows that the epidote-group minerals are compositionally solid solutions of epidote, clinozoisite, and allanite (Fig. 6). The REE-rich epidote-allanite-(Ce) from these experiments commonly demonstrate REE enrichment in the cores as relatively small areas that, when analyzed, may be contaminated with analyses from neighboring, lower REE content domains.

The starting labradorite grains preserved in all runs occasionally show compositional alterations (Table 3; supplementary Table S5). These include albite rims formed at 450 °C, 800 MPa, and K-feldspar rims formed at 550 °C, 200 MPa; and 650 °C, 200, 400, 1000 MPa. In runs at 750 °C and 400, 800, 1000 MPa, the altered labradorite grain rims achieved a composition of An79.94Ab6.17Kfs1.9 with the porosity filled by melt (Fig. 3n; supplementary Table S5). The starting K-feldspar is present in the products, except runs at
Table 3 Overview of the products from runs with monazite-(Ce)

| Run Code | Temperature °C | Pressure MPa | Duration Days | Description |
|----------|----------------|--------------|---------------|-------------|
| M12C-01  | 450            | 200          | 16            | Monazite-(Ce) shows partial dissolution with REE-rich fluorapatite-fluorcalciobritholite formed on the surface. Small amounts of REE-rich epidote and wollastontite formed. Labradorite, K-feldspar and biotite are preserved. Muscovite is gone. |
| M12C-02  | 450            | 400          | 18            | Monazite-(Ce) shows partial dissolution with small amounts of fluorcalciobritholite and REE-rich epidote-allanite-(Ce) formed on the surface. Labradorite, K-feldspar, biotite and muscovite are preserved. |
| M12C-03  | 450            | 600          | 16            | Monazite-(Ce) shows partial dissolution with numerous fluorcalciobritholite and allanite-(Ce) formed. K-feldspar, labradorite, muscovite and biotite are preserved. |
| M12C-04  | 450            | 800          | 16            | Monazite-(Ce) shows partial dissolution with numerous fluorcalciobritholite formed. Some labradorite grains achieved K-feldspar rims. K-feldspar, muscovite and biotite are preserved. |
| M12C-05  | 550            | 200          | 16            | Monazite-(Ce) shows partial dissolution with numerous allanite-(Ce) and fluorcalciobritholite formed. K-feldspar, labradorite, muscovite and biotite are preserved. |
| M12C-06  | 550            | 400          | 12            | Monazite-(Ce) shows partial dissolution with small amounts of fluorcalciobritholite and REE-rich epidote-allanite-(Ce) formed. Labradorite achieved K-feldspar rims. K-feldspar and biotite are preserved. Muscovite is gone. |
| M12C-07  | 550            | 600          | 8             | Monazite-(Ce) shows partial dissolution with fluorcalciobritholite and numerous REE-rich epidote-allanite-(Ce) formed. Labradorite, K-feldspar, biotite and muscovite are present. Muscovite is gone. |
| M12C-08  | 550            | 800          | 8             | Monazite-(Ce) shows partial dissolution with fluorcalciobritholite and numerous REE-rich epidote-allanite-(Ce) formed. Labradorite, K-feldspar, biotite and muscovite are preserved. |
| M12C-09  | 550            | 1000         | 8             | Monazite-(Ce) shows partial dissolution with fluorcalciobritholite and numerous REE-rich epidote-allanite-(Ce) formed. Labradorite, K-feldspar, biotite and muscovite are present. Muscovite is gone. |
| M12C-10  | 550            | 1200         | 6             | Monazite-(Ce) shows partial dissolution with small amounts of REE-rich epidote formed on the surface. Delicate crystals of fluorcalciobritholite are present on the monazite-(Ce) surface. K-feldspar achieved albite rims. Large grains of REE-rich steacyite formed. Delicate needle-like crystals of Na-(Fe-Mg)-amphibole are present. Albite and biotite are preserved. Muscovite is gone. |

Table 3 (continued)

| Run Code | Temperature °C | Pressure MPa | Duration Days | Description |
|----------|----------------|--------------|---------------|-------------|
| M12C-12  | 600            | 200          | 6             | Monazite-(Ce) shows partial dissolution with numerous REE-rich epidote-allanite-(Ce) formed on the surface. Delicate crystals of fluorcalciobritholite formed on the monazite-(Ce) surface. Labradorite, K-feldspar and biotite are preserved. Melt formed. Muscovite is gone. |
| M12C-13  | 600            | 400          | 6             | Monazite-(Ce) shows partial dissolution with numerous REE-rich epidote-allanite-(Ce) formed on the surface. REE-rich epidote is also dispersed in formed melt. |
| M12C-14  | 600            | 600          | 8             | Monazite-(Ce) shows partial dissolution with fluorcalciobritholite and numerous REE-rich epidote-allanite-(Ce) formed. Labradorite, K-feldspar, biotite and muscovite are preserved. |
| M12C-15  | 600            | 800          | 8             | Monazite-(Ce) shows partial dissolution with small grains of fluorcalciobritholite formed on the surface. Melt formed. Some REE-rich epidote-allanite-(Ce) are dispersed in melt. Feldspar with composition of bytownite forming porous grains filled with melt is present. Biotite preserved. K-feldspar, labradorite and muscovite are gone. |
| M12C-16  | 600            | 1000         | 8             | Monazite-(Ce) shows strong dissolution with fluorcalciobritholite formed on the surface. Large REE-rich epidote-allanite-(Ce) grains are present on monazite-(Ce) surface and are dispersed in melt. Some biotite flakes are preserved. Melt formed. Feldspar with composition of bytownite forming porous grains filled with melt is present. Labradorite, K-feldspar and muscovite are gone. |
| M12C-17  | 750            | 200          | 6             | Monazite-(Ce) shows strong dissolution with fluorcalciobritholite and REE-rich epidote-allanite-(Ce) formed on the surface. REE-epidote-allanite-(Ce) grains are present also as separate aggregates. Some K-feldspar, labradorite and biotite grains are preserved. Melt formed. Muscovite is gone. |
| M12C-18  | 750            | 1000         | 6             | Monazite-(Ce) shows strong dissolution with small grains of fluorcalciobritholite and large grains of REE-rich epidote-allanite-(Ce) formed on the surface. Melt formed. REE-rich epidote-allanite-(Ce) is also dispersed in melt. Some biotite preserved. Feldspar with composition of bytownite forming porous grains filled with melt is present. K-feldspar, labradorite and muscovite are gone. |
| M12C-19  | 750            | 400          | 4             | Monazite-(Ce) shows strong dissolution with fluorcalciobritholite formed on the surface. Large REE-rich epidote-allanite-(Ce) grains are present on monazite-(Ce) surface. REE-rich steacyite formed grains attached to albite rims. Large grains of REE-rich steacyite formed. Delicate needle-like crystals of Na-(Fe-Mg)-amphibole are present. Albite and biotite are preserved. Muscovite is gone. |
| M12C-20  | 750            | 1000         | 4             | Monazite-(Ce) shows partial dissolution on the surface. Melt formed. Large grains of REE-rich epidote-allanite-(Ce) are present in melt. Some starting biotite flakes are preserved. Feldspar with composition of bytownite forming porous grains filled with melt is present. Labradorite, K-feldspar and muscovite are gone. |
| M12C-21  | 750            | 800          | 4             | Monazite-(Ce) shows strong dissolution with small grains of fluorcalciobritholite and large grains of REE-rich epidote-allanite-(Ce) formed on the surface. Melt formed. REE-rich epidote-allanite-(Ce) is also dispersed in melt. Some biotite preserved. Feldspar with composition of bytownite forming porous grains filled with melt is present. K-feldspar, labradorite and muscovite are gone. |
| M12C-22  | 750            | 600          | 4             | Monazite-(Ce) shows strong dissolution with fluorcalciobritholite and REE-rich epidote-allanite-(Ce) formed on the surface. REE-epidote-allanite-(Ce) grains are present also as separate aggregates. Some K-feldspar, labradorite and biotite grains are preserved. Melt formed. Muscovite is gone. |
| M12C-23  | 750            | 400          | 4             | Monazite-(Ce) shows strong dissolution with small grains of fluorcalciobritholite and large grains of REE-rich epidote-allanite-(Ce) formed on the surface. Melt formed. REE-rich epidote-allanite-(Ce) is also dispersed in melt. Some biotite preserved. Feldspar with composition of bytownite forming porous grains filled with melt is present. K-feldspar, labradorite and muscovite are gone. |

Set (2) monazite-(Ce) + albite + sanidine + biotite + muscovite + SiO₂ + CaF₂ + Na₂Si₂O₅ + H₂O

M12N-01, 450 °C, 200 MPa, 16 days. Monazite-(Ce) shows partial dissolution with developed porosity along the rims and shows patchy zoning related to compositional alteration. Delicate fluorcalciobritholite grains are present on the monazite-(Ce) surface. K-feldspar achieved albite rims. Large grains of REE-rich steacyite formed. Delicate needle-like crystals of Na-(Fe-Mg)-amphibole are present. Albite and biotite are preserved. Muscovite is gone. |
| M12N-10, 450 °C, 400 MPa, 18 days. Monazite-(Ce) shows strong dissolution with developed porosity along the rims or across the whole grains, and displays patchy zoning. REE-rich steacyite formed grains attached to- partially replacing monazite-(Ce) and as large individual grains. Large fluorcalciobritholite grains formed. Delicate needle-like crystals of Na-(Fe-Mg)-amphibole are present. Albite achieved K-feldspar rims, and K-feldspar achieved albite rims. Biotite and muscovite are preserved. |
| M12N-21, 450 °C, 400 MPa, 8 days. Monazite-(Ce) shows strong dissolution with developed porosity across the grains and displays patchy zoning. REE-rich steacyite formed grains attached to- partially replacing monazite-(Ce) and as large individual grains. Large fluorcalciobritholite grains formed. Delicate needle-like crystals of Na-(Fe-Mg)-amphibole are present. Albite and biotite are preserved. Muscovite is gone. |
crystals of Na-(Fe-Mg)-amphibole are present. K-feldspar is partially replaced by albite. Albite achieved K-feldspar rims. Muscovite and biotite are preserved.

**M12N-16, 450 °C, 800 MPa, 16 days.** Monazite-(Ce) shows patchy zoning and strong dissolution with developed porosity partially filled with REE-rich steatite. REE-rich steatite forms also large grains attached to monazite-(Ce). Large grains of fluorapatite to fluorocalciobritholite formed. K-feldspar achieved albite rims. Albite achieved K-feldspar rims. Delicate needle-like crystals of Na-(Fe-Mg)-amphibole are present. Muscovite and biotite are gone.

**M12N-17, 450 °C, 1000 MPa, 16 days.** Monazite-(Ce) shows strong dissolution with developed porosity partially filled with REE-rich steatite, and displays internal patchy zoning. REE-rich steatite forms also large grains attached to monazite-(Ce). Large grains of fluorapatite-fluorocalciobritholite formed. K-feldspar achieved albite rims. Albite achieved K-feldspar rims. Delicate needle-like crystals of Na-(Fe-Mg)-amphibole are present. Rare muscovite and biotite are present.

**M12N-06, 550 °C, 200 MPa, 12 days.** Monazite-(Ce) shows strong dissolution with porosity along the rims and displays internal patchy zoning. ThSiO₄ and fluorapatite-fluorocalciobritholite inclusions formed in monazite-(Ce). Delicate fluorapatite-fluorocalciobritholite grains are also present on the monazite-(Ce) surface. REE-rich steatite formed on the monazite-(Ce) surface and as individual grains. K-feldspar achieved albite rims. Delicate needle-like crystals of Na-(Fe-Mg)-amphibole are present. Aggregates of newly-formed small grains of albite are present. Muscovite and biotite are gone.

**M12N-02, 550 °C, 400 MPa, 6 days.** Monazite-(Ce) shows dissolution with fluorapatite-fluorocalciobritholite formed on the surface, and displays internal patchy zoning. Small grains of REE-rich steatite formed. K-feldspar achieved albite rims. Albite achieved K-feldspar rims. Delicate needle-like crystals of Na-(Fe-Mg)-amphibole are present. Biotite and muscovite are gone.

**M12N-14, 550 °C, 600 MPa, 8 days.** Monazite-(Ce) shows strong dissolution with fluorocalciobritholite present on the surface, and displays internal patchy zoning. Fluorocalciobritholite forms also single grains and shows sector zoning with two compositions:—fluorapatite-fluorocalciobritholite in the cores and fluorocalciobritholite in the rims. Delicate needle-like crystals of Na-(Fe-Mg)-amphibole are present. Large grains of REE-rich steatite formed. Albite shows porosity developed along the rims or achieved K-feldspar rims. K-feldspar achieved albite rims. Muscovite and biotite are gone.

**M12N-13, 550 °C, 800 MPa, 8 days.** Monazite-(Ce) shows strong dissolution with parallelly oriented porosity across the grains. Grains of fluorocalciobritholite grains formed on the monazite-(Ce) surface and as individual grains. Fluorocalciobritholite shows sector zoning with two compositions of fluorapatite-fluorocalciobritholite in the cores and fluorocalciobritholite in the rims. Delicate needle-like crystals of Na-(Fe-Mg)-amphibole are present. Albite shows porosity developed along the rims or achieved K-feldspar rims. K-feldspar is preserved. Muscovite and biotite are gone.

**M12N-07, 550 °C, 1000 MPa, 8 days.** Monazite-(Ce) shows partial dissolution on the surface and some porosity developed. Delicate fluorapatite-fluorocalciobritholite grains formed on the monazite-(Ce) surface. Albite achieved K-feldspar rims. Delicate needle-like crystals of Na-(Fe-Mg)-amphibole are present. K-feldspar, muscovite and biotite are preserved.

**M12N-09, 650 °C, 200 MPa, 6 days.** Monazite-(Ce) shows strong dissolution with porosity channels across the grains filled with fluorocalciobritholite and cheralite. Fluorocalciobritholite shows sector zoning with compositions of fluorapatite-fluorocalciobritholite in the cores, and fluorocalciobritholite in the rims. Delicate needle-like crystals of Na-(Fe-Mg)-amphibole are present. Melt and single grains of titanite formed. Some K-feldspar and albite are preserved. Albite achieved K-feldspar rims. K-feldspar is partially replaced by albite. Muscovite and biotite are gone.

**M12N-03, 650 °C, 400 MPa, 6 days.** Monazite-(Ce) shows strong dissolution with fluorocalciobritholite and cheralite formed on the surface. Fluorocalciobritholite shows sector zoning with composition of fluorapatite-fluorocalciobritholite in the cores, and fluorocalciobritholite in the rims. Delicate needle-like crystals of Na-(Fe-Mg)-amphibole are present. Melt formed. Some K-feldspar and albite are preserved. Albite achieved K-feldspar rims. Muscovite and biotite are gone.

**M12N-12, 650 °C, 600 MPa, 6 days.** Monazite-(Ce) shows strong dissolution with porosity channels along the rims filled with fluorocalciobritholite and cheralite. Fluorocalciobritholite shows sector zoning with composition of fluorapatite-fluorocalciobritholite in the cores and fluorocalciobritholite in the rims. Delicate needle-like crystals of Na-(Fe-Mg)-amphibole are present. Melt formed. Some albite and K-feldspar are preserved. Muscovite and biotite are gone.

**M12N-11, 650 °C, 800 MPa, 6 days.** Monazite-(Ce) shows strong dissolution with fluorocalciobritholite and cheralite formed on the surface. Fluorocalciobritholite shows sector zoning with composition of fluorapatite-fluorocalciobritholite in the cores and fluorocalciobritholite in the rims. Delicate needle-like crystals of Na-(Fe-Mg)-amphibole are present. Melt formed. Some albite and K-feldspar are preserved. Muscovite and biotite are gone.

**M12N-08, 650 °C, 1000 MPa, 6 days.** Monazite-(Ce) shows strong dissolution with porosity channels across the grains filled with fluorocalciobritholite and cheralite. Fluorocalciobritholite shows sector zoning with composition of fluorapatite-fluorocalciobritholite in the cores and fluorocalciobritholite in the rims. Delicate needle-like crystals of Na-(Fe-Mg)-amphibole are present. Some albitite and K-feldspar are preserved. Some albite and K-feldspar are preserved. Muscovite and biotite are gone.

**M12N-18, 750 °C, 200 MPa, 4 days.** Monazite-(Ce) shows strong dissolution with fluorocalciobritholite and cheralite formed on the surface. Fluorocalciobritholite shows sector zoning with composition of fluorapatite-fluorocalciobritholite in the cores and fluorocalciobritholite in the rims. Delicate needle-like crystals of Na-(Fe-Mg)-amphibole are present. Melt formed. Some albite and K-feldspar are preserved. Muscovite and biotite are gone.

**M12N-19, 750 °C, 400 MPa, 4 days.** Monazite-(Ce) shows strong dissolution with fluorocalciobritholite and cheralite formed on the surface. Fluorocalciobritholite shows sector zoning with composition of fluorapatite-fluorocalciobritholite in the cores and fluorocalciobritholite in the rims. Delicate needle-like crystals of Na-(Fe-Mg)-amphibole are present. Melt formed. Albite, K-feldspar, muscovite and biotite are gone.

**M12N-22, 750 °C, 600 MPa, 4 days.** Monazite-(Ce) shows strong dissolution with fluorocalciobritholite and cheralite formed on the surface. Fluorocalciobritholite shows sector zoning with composition of fluorapatite-fluorocalciobritholite in the cores and fluorocalciobritholite in the rims. Delicate needle-like crystals with composition close to ferri-taramite are present. Titanite and melt formed. Albite, K-feldspar, muscovite and biotite are gone.

**M12N-21, 750 °C, 800 MPa, 4 days.** Monazite-(Ce) shows strong dissolution with fluorocalciobritholite and cheralite formed on the surface. Fluorocalciobritholite shows sector zoning with composition of fluorapatite-fluorocalciobritholite in the cores and fluorocalciobritholite in the rims. Delicate needle-like crystals with composition close to ferri-taramite are present.
750 °C, 200, 400, and 1000 MPa. The K-feldspar grains are partially to completely compositionally altered in most runs, with the altered domains depleted in Na and Ba relative to the starting Eifel sanidine (supplementary Table S5).

Muscovite was found in run products from the 450 °C, 400–1000 MPa, and the 550 °C, 400, 800, and 1000 MPa experiments (supplementary Table S6). Muscovite was not observed in the products of the remaining experiments. The biotite was observed to be unaltered in all the runs (supplementary Table S6).

Melt formed in experimental runs at 650 °C, 600–1000 MPa; and 750 °C, 200–1000 MPa (Figs. 1a and 3l–p; Table 3). The melt contains 63.56–69.84 wt.% SiO₂, and is enriched in 0.81–1.28 wt.% F (supplementary Table S7). Concentrations of 12.91–14.99 wt.% Al₂O₃, 2.21–4.69 wt.% CaO, 1.33–1.80 wt.% K₂O, and 0.14–0.70 wt.% Na₂O define a peraluminous composition with an alumina saturation index (ASI) of 2.4–3.5. The CIPW Qz-Ab-Or diagram (supplementary Fig. S1) shows that the melt is dominated by quartz, which places the normative composition of the melt outside that of a granite.

**Experiments with monazite-(Ce) and Na₂Si₂O₅ + H₂O**

All experiments with Na₂Si₂O₅ + H₂O resulted in monazite-(Ce) breakdown (Figs. 7, 8 and 9; Table 3). At the end of each experiment, the remaining fluid in the capsule had a high pH (Table 1). Monazite-(Ce) in the 450 °C, 200–1000 MPa; and 550 °C, 200–600 MPa experiments developed dissolution pits on the surface and porosity within altered areas of the grains (Figs. 7a and 8). Some monazite-(Ce) grains are partially replaced by REE-rich steacyite (Figs. 7c and 9). In cross section, the monazite-(Ce) shows patchy zoning with irregular boundaries between bright and dark patches under high contrast BSE imaging. The bright domains have a composition similar to the starting Burnet monazite-(Ce), while the dark domains are depleted in Th, U, and Y (Fig. 8b–d), with almost complete removal of Pb (Fig. 4c and d), and subsequent enrichment in REE, particularly LREE (supplementary Table S1).

Monazite-(Ce), from the runs at P-T conditions of 550 °C, 800 and 1000 MPa, and 650–750 °C, 200–1000 MPa, was strongly reacted, showing large dissolution pits on the surface (Fig. 7f and h), and an oriented porosity across the grains, filled with other minerals. The monazite-(Ce) is overgrown by REE-rich fluorapatite-fluorcalciobritholite (Fig. 7g, h, n and o; supplementary Table S3). Occasionally, most of the monazite-(Ce) is replaced by REE-rich fluorapatite-fluorcalciobritholite formed in pores oriented parallel to each other along grain rims (Fig. 7g) or across whole grains (Fig. 7k and l). Minute, euhedral to anhedral, anhedral grains of cheralite are also present as inclusions at the boundary between the REE-rich fluorapatite-fluorcalciobritholite and host monazite-(Ce) (Fig. 7l).

REE-rich fluorapatite-fluorcalciobritholite formed in all the experiments. Beside partially replacing and/or overgrowing monazite-(Ce), the REE-rich fluorapatite-fluorcalciobritholite also formed individual grains or grain aggregates. These individual grains are elongated hexagonal crystals, which range in size from several microns (lowest P-T runs), up to 100 μm long and ~8 μm across (in the moderate to highest P-T runs). Some grains are sector zoned with a fluorcalciobritholite composition in the center, and a REE-rich fluorapatite in triangular sectors expanding from the center of the grain towards the rim (Fig. 7m). The sector zoning is related to trace element incorporation as controlled by the crystal surface structure during growth of the apatite crystals, and subsequent enrichment of selected sectors in REE (Rakovan and Reeder 1996; Rakovan 2002). The crystals in cross section commonly have cores with a REE-rich fluorapatite-fluorcalciobritholite composition, and a fluorcalciobritholite rim (Fig. 7n).

REE-rich steacyite is present only in products from runs at 450 °C, 200–1000 MPa; and 550 °C, 200–600 MPa. It forms subhedral to euhedral tetragonal grains varying in size from 10 μm in the lower P-T runs up to ~100 μm in the 550 °C, 600 MPa run (Fig. 7a, d and e). REE-rich steacyite also partially replaces altered monazite-(Ce), irregularly filling the inner regions or, occasionally, filling roughly oriented, parallel channels (Figs. 7c and d and 9). The composition of REE-rich steacyite is variable, ranging from 10.24 to 27.06 wt.% ThO₂, 0.72–2.14 wt.% UO₂, and 1.93–9.64 wt.% (Y + REE)₂O₃ (supplementary Table S8).

Starting albite and K-feldspar are present in products of all runs at 450–650 °C and 200–1000 MPa, whereas none was preserved in the 750 °C experiments (Table 3). Secondary albite rims formed on K-feldspar grains in runs at 450 °C, 200–1000 MPa; 550 °C, 200–600 MPa; and 650 °C, 200 MPa (Fig. 7b; supplementary Table S5). Albite developed on K-feldspar rims in runs at 450–550 °C, 200–1000 MPa; and 650 °C, 200 and 600 MPa (Fig. 7j; supplementary Table S5).
Starting biotite and muscovite are found only in products from runs at 450 °C, 400, 600, and 1000 MPa; and 550 °C, 1000 MPa. The composition of the micas remained unaltered with respect to the starting composition (supplementary Table S6).

Fig. 3 BSE images showing the results from experiments with monazite-(Ce) and 2 M Ca(OH)₂: a small crystals of REE-rich epidote formed in the run at 450 °C, 200 MPa, and 16 days; b altered monazite-(Ce) overgrown by secondary fluorcalciobritholite and allanite-(Ce) at 450 °C, 400 MPa, and 18 days; c allanite-(Ce) overgrowing altered monazite-(Ce) from the run at 450 °C, 1000 MPa and 16 days; d–e REE-rich fluorapatite-fluorcalciobritholite and allanite-(Ce) overgrowing altered monazite-(Ce) in experiments at 550 °C, 200 MPa, and 12 days (d) and 550 °C, 400 MPa, and 6 days (e); f altered monazite-(Ce) overgrown by numerous tabular crystals of allanite-(Ce) at 550 °C, 800 MPa, and 8 days; g hexagonal prisms of fluorcalciobritholite formed on the altered monazite-(Ce) surface (650 °C, 200 MPa, 6 days); h tabular crystals of allanite-(Ce) and minute hexagonal prisms of fluorcalciobritholite on the altered surface of the monazite-(Ce) (650 °C, 200 MPa, 6 days); i labradorite with developed K-feldspar rim (650 °C, 200 MPa, 6 days); j monazite-(Ce) partially replaced by an aggregate of REE-rich fluorapatite and fluorcalciobritholite (650 °C, 400 MPa, 6 days); k altered monazite-(Ce) grains overgrown by large crystals of allanite-(Ce) (650 °C, 600 MPa, 6 days); l remnants of altered monazite-(Ce) replaced by allanite-(Ce) (650 °C, 800 MPa, 6 days); m overgrowths of fluorcalciobritholite, allanite-(Ce), and REE-rich epidote grains on altered monazite-(Ce), showing a decreasing distribution of REE in the products as a function of the distance from the monazite-(Ce) going outwards (650 °C, 1000 MPa, 6 days); n bytownite formed at the expense of labradorite, showing a melt-filled porosity (750 °C, 400 MPa, 4 days); o monazite-(Ce) grains overgrown by fluorcalciobritholite and allanite-(Ce) (750 °C, 600 MPa, 4 days); p large crystals of allanite-(Ce) formed at the expense of monazite-(Ce) (750 °C, 1000 MPa, 4 days)
Amphibole formed in all runs with $\text{Na}_2\text{Si}_2\text{O}_5 + \text{H}_2\text{O}$. In experiments at 450, 550, and 650 °C, needle-like crystals of amphibole were too small for EPMA measurements (Fig. 7a, b, d–g, j, and k). SEM-EDS analyses indicate that these are Na-(Fe-Mg) amphiboles, suggesting that $\text{Na}_2\text{Si}_2\text{O}_5 + \text{H}_2\text{O}$ and the micas were the main sources of elements for the amphibole. The highest P-T runs, at 750 °C, 600–1000 MPa, promoted the formation of amphibole crystals up to 20 μm long and several microns across with a composition similar to ferritaramite (Leake et al. 1997; Fig. 7o; supplementary Table S9).

Melt formed in runs at 650 °C, 200 and 600–1000 MPa (Fig. 7g–i, k, and m), and 750 °C, 200–1000 MPa (Fig. 7o and p). It dominates the experimental products from runs at 750 °C, in which the feldspars have totally disappeared. The melt contains 66.17–70.56 wt.% SiO$_2$ and is characterized by a peraluminous composition ($\text{ASI} = 3.1–5.9$) defined by 13.40–15.65 wt.% Al$_2$O$_3$, 0.18–0.59 wt.% CaO, 0.88–2.18 wt.% Na$_2$O, and 1.16–2.16 wt.% K$_2$O (supplementary Table S7). The F content is 0.71–1.61 wt.%. The Qtz-Ab-Or diagram (supplementary Fig. S1) demonstrates that the non-granitic melt is dominated by normative quartz with small amounts of normative albite and orthoclase.

Titanite also formed in most runs with melt (Table 3). Their small size did not allow for accurate EPMA measurements.
Experiments with xenotime-(Y) and 2 M Ca(OH)₂

Xenotime-(Y) reacted in all runs with 2 M Ca(OH)₂ (Table 4; Figs. 2c and 10). The remaining fluid in the capsule had a pH of 7 except in runs at 450 °C, 800–1000 MPa; and 650 °C, 1000 MPa, where the pH was high (Table 1). Xenotime-(Y) grains from the 450 °C, 200 MPa run show dissolution pits. A few, delicate, micron-sized crystals of Y-rich fluorcalciobritholite formed on the surface (Fig. 10a and b). Unreacted xenotime-(Y) surfaces are relatively common. In all other runs, the xenotime-(Y) is moderately to strongly reacted, with etching on the surface and overgrowth by numerous crystals of Y-rich fluorcalciobritholite (Fig. 10f and g). Strong dissolution occasionally resulted in the replacement of most of the xenotime-(Y) grain along grain fractures, by aggregates of secondary, Y-rich fluorcalciobritholite with only a few remnants of xenotime-(Y) remaining (Fig. 10d). Although experiments at 450 °C and 200 MPa resulted in the lowest degree of alteration, a few xenotime-(Y) grains occasionally remained unreacted even at 750 °C (Fig. 10p). Remnant xenotime-(Y) after the experiment showed no compositional alterations and preserved the composition of the original NWFP xenotime-(Y) (supplementary Table S10)

Yttrium-rich fluorcalciobritholite formed on the xenotime-(Y) grain surface in all the runs and commonly grew along fractures in the xenotime-(Y) grains. The elongated crystals of Y-rich fluorcalciobritholite, up to 20 μm long and a few microns thick, show zoning with (Y,REE)-rich fluorapatite cores and Y-rich fluorcalciobritholite rims (Fig. 10g). Due to the small size of the Y-rich...
fluorcalciobritholite crystals, EPMA measurements provide a mixed composition consisting of the cores and the rims (supplementary Table S11).

(Y,HREE)-rich epidote formed in three runs with 2 M Ca(OH)$_2$, i.e. at 550 °C, 800 MPa; 650 °C, 800 MPa; and 650 °C, 1000 MPa. The (Y,HREE)-rich epidote forms elongated crystals, up to ~120 μm long and 20 μm thick, and is present as individual grains or grain aggregates not associated with xenotime-(Y) (Fig. 10h, k and l). The average Y and total REE contents in the (Y,HREE)-rich epidote are 4.06 wt.% Y$_2$O$_3$ and 1.71 wt.% REE$_2$O$_3$ in the 650 °C, 1000 MPa run; and 1.77 wt.% Y$_2$O$_3$ and 0.54 wt.% REE$_2$O$_3$ in the 650 °C, 800 MPa run (supplementary Table S12). According to the Al versus Y + REE plot in Fig. 11, the (Y,HREE)-rich epidote represents a solid solution between allanite, epidote, and clinzoisite.

Labradorite is present in the products of all runs at 450, 550, 650 °C; and in the products of the 750 °C, 200, 600 MPa runs. Labradorite was rimmed by albite in two runs at 550 °C, 800 and 1000 MPa (supplementary Table S13). Secondary K-feldspar rims formed at 550 °C, 200 and 400 MPa; and 550 °C, 200 and 1000 MPa. The starting labradorite was not found in the experimental products at 750 °C, 400, 800, and 1000 MPa, where the feldspar has a bytownite composition and melt-filled porosity. Remnants of the starting K-feldspar were preserved in all the runs at 450, 550, and 650 °C. K-feldspar was not found in the experimental products from the 750 °C runs.

Biotite is present in products from all runs at 450, 550, and 650 °C. In runs at 750 °C, secondary biotite formed (Fig. 10p), which is characterized by low Ti concentrations (0.09–0.45 wt.% TiO$_2$) compared to the 4.09 wt.% TiO$_2$ content in the starting biotite (supplementary Table S14). Muscovite is preserved in all runs at 450 °C, three runs at 550 °C, 600–1000 MPa, and two runs at 650 °C, 600 and 800 MPa. Small, 10–50 μm flakes of secondary muscovite formed at 650 °C, 1000 MPa. In the remaining experimental products, i.e.
550 °C, 200 and 400 MPa; 650 °C, 200 and 400 MPa; and 750 °C, 200–1000 MPa, muscovite disappeared. Garnet was preserved unreacted in all runs at 450, 550, and 650 °C (supplementary Table S15). All experiments at 750 °C, 200–1000 MPa resulted in the breakdown of the garnet rims with partial replacement by low-Ti biotite (Fig. 10p). The remaining garnet cores preserved the original composition. Although the xenotime-(Y) experiments included garnet to test the partitioning of Y between xenotime-(Y) and garnet in terms of geothermometric applications, no change in Y or HREE enrichment in garnet, compared to the original garnet, was found. This indicates that garnet was not a stable phase in the 750 °C experiments since it did not recrystallize and incorporate Y, HREE but rather broke down to biotite. In contrast, it was non-reactive in the lower temperature experiments either because it was a stable phase or more likely due to lower reaction rates such that the garnet was metastable.

Clinopyroxene formed in runs at 750 °C, 200–1000 MPa, where it occurs as euhedral crystals up to $4 \times 20 \mu$m in size (Fig. 10o). Titanite is found only in the high temperature runs with 2 M Ca(OH)$_2$. It incorporates up to 3.91 wt.% Y$_2$O$_3$ and 2.53 wt.% REE$_2$O$_3$ (based on EDS analyses), presumably from the xenotime-(Y).

Melt formed in runs at 650 °C, 200, 800, and 1000 MPa (Fig. 10i and m); and in runs at 750 °C, 200–1000 MPa (Fig. 10o and p). The melt composition consisted of 64.26–71.45 wt.% SiO$_2$, 10.58–14.79 wt.% Al$_2$O$_3$, 0.20–4.66 wt.% CaO, 0.08–1.32 wt.% Na$_2$O, and 0.77–1.94 wt.% K$_2$O, which defines a peraluminous character for the melt with an ASI = 2.6–4.0 (supplementary Table S16). The F content is 0.60–1.31 wt.%. Similar to experiments with monazite-(Ce), the non-granitic melt is dominated by normative quartz (supplementary Fig. S1).

### Experiments with xenotime-(Y) and Na$_2$Si$_2$O$_5$ + H$_2$O

All experiments with Na$_2$Si$_2$O$_5$ + H$_2$O resulted in xenotime-(Y) breakdown and the formation of new phases (Table 3; Figs. 2, 12 and 13). The remaining fluid had a high pH, except two runs in which the fluid had a neutral pH (450 °C, 200 MPa and 550 °C, 400 MPa; Table 1). Xenotime-(Y) shows dissolution pits and some etching on the surface. In all runs numerous crystals of Y-rich fluorcalciobritholite formed on the xenotime-(Y) surface as masses of individual grains, which overgrew and partially replaced the xenotime-(Y) both on the surface and along internal fractures. In most of the 450–550 °C experiments, the xenotime-(Y) is occasionally preserved completely unreacted. In all runs, the remnant xenotime-(Y) reflects the composition of the starting NWFP xenotime-(Y), showing no compositional alteration (supplementary Table S10).

In all the runs, Y-rich fluorcalciobritholite formed euhedral to subhedral, hexagonal crystals whose size varied from a few microns in length to several microns thick and up to 100 μm long. The size of crystals in the reaction rims was independent with respect to temperature conditions, whereas the amount of Y-rich fluorcalciobritholite formed increased with increasing temperature. Beside overgrowth and partial replacement of...
xenotime-(Y), Y-rich fluorcalciobritholite formed aggregates of individual grains commonly dispersed in the melt in the 650–750 °C runs (Fig. 12o). The Y-rich fluorcalciobritholite commonly shows sector zoning, related to crystal surface
structure control of trace element incorporation (cf. Rakovan and Reeder 1996; Rakovan 2002), with (Y,REE)-rich fluorapatite cores and Y-rich fluorcalciobritholite rims (Fig. 12g and h; supplementary Table S11).

Albite was preserved in all the runs at 450, 550, and 650 °C, but not in the 750 °C experiments. K-feldspar rims formed on albite at 450 °C, 200–800 MPa; and at 550 °C, 200, 600, and 800 MPa (supplementary Table S13). K-feldspar was found in the products from all 450, 550, and 650 °C runs, and in one run at 750 °C, 600 MPa. Albite rims developed on K-feldspar in almost all the runs, i.e. 450 °C, 200–800 MPa; 550 °C, 200–800 MPa; 650 °C, 400, 800, and 1000 MPa; and 750 °C, 600 MPa (supplementary Table S13).

Biotite is present unaltered in products from most runs. Only some starting biotite was preserved in the products from the 750 °C temperature experiments (Table 3). Secondary low-Ti biotite formed aggregates of small flakes in runs at 550 °C, 200 MPa; 650 °C, 200–1000 MPa; and 750 °C, 200–1000 MPa (Fig. 12k and p; supplementary Table S14). Muscovite was present only in the products of four runs at 450 °C, 200, 600, 800, and 1000 MPa, whereas it was not found in the products from the remaining experiments.
Garnet is preserved unaltered only in runs at 450 °C, 200–1000 MPa. In runs at 550 °C, the garnet grains reacted along the rims and fractures, with partial replacement by secondary low-Ti biotite, chlorite, and/or Na-K feldspar (Fig. 12c). The remaining garnet preserved the original composition (supplementary Table S15) indicating no recrystallization had occurred during partial alteration to biotite (supplementary Fig. S2). Garnet was not found in the products from runs at 650 and 750 °C. Experiments under these temperature conditions resulted in complete breakdown of garnet judging from the presence of aggregates of secondary, low-Ti biotite and/or secondary albite occasionally forming post-garnet pseudomorphs.

Amphibole formed in all the runs. In runs at 450, 550, and 650 °C, needle-like crystals of Na-(Fe-Mg) amphiboles were identified using EDS analysis (Fig. 12a, b, g, i and l). Experiments at 750 °C promoted the formation of amphibole grains up to 40 μm across, with a composition similar to ferritaramite (Leake et al. 1997; Fig. 12o and p; supplementary Table S17).

Titanite was found in the products from experiments at 650 °C, 200, 600, 800, and 1000 MPa; and 750 °C, 200 and 1000 MPa. Commonly it forms small grains, although occasional grains, up to 150 μm long and 40 μm across, are present (Fig. 12l). The titanite contains 5.07–6.30 wt.% (Y + REE)2O3 (supplementary Table S18).

Melt formed in runs at 650 °C, 200, 600, 800, and 1000 MPa (Fig. 12g, h, k and l), and 750 °C, 200–1000 MPa (Fig. 12m–p). The non-granitic, peraluminous melt (ASI = 1.9–4.7) contains 62.07–70.71 wt.% SiO2, 8.85–16.98 wt.% Al2O3, 0.15–1.96 wt.% CaO, 1.34–3.36 wt.% Na2O, and 1.46–2.07 K2O (supplementary Table S16). The F content is 0.86–2.06 wt.% The non-granitic melt is dominated by normative quartz with minor normative albite and orthoclase according to the Qz-Ab-Or diagram (supplementary Fig. S1).
Discussion

Interpretation of the experimental results: runs with monazite-(Ce)

Similar to what was found in Budzyń et al. (2011), the results from these experiments demonstrate that the two fluids used were highly reactive with respect to both monazite-(Ce) and xenotime-(Y) over the broad P-T range considered. The neutral pH of the fluid in the 2 M Ca(OH)$_2$ runs suggests that all of the Ca(OH)$_2$ was used up as the main source of Ca for the apatites and REE-rich epidote-allanite-(Ce). This was the case except in the high pressure experiments at 450–550 °C, where the remaining fluid still maintained a high pH suggesting slower reaction rates. In contrast, the high pH character of the remaining fluid from runs with Na$_2$Si$_2$O$_5$ + H$_2$O indicates that not all the Na supplied by the Na$_2$Si$_2$O$_5$ was used up.

Conversion of monazite-(Ce) to REE-rich epidote and allanite-(Ce), over the entire P-T range considered for the 2 M Ca(OH)$_2$ experiments, indicates that the significantly increased Ca bulk content (10.08 wt.% CaO; Table 2), compared to natural rocks of metapelitic to granitic composition [e.g. 2.17 wt.% CaO for pelites; Shaw (1956)], was high enough to expand the stability field of allanite-(Ce) to at least 750 °C and 1000 MPa. At the same time, the relative size and abundance of the allanite-(Ce) grains increased with increasing temperature, though this was less dependent on pressure.

Here, monazite-(Ce) served as the source of REE for the REE-epidote and allanite-(Ce). The chemical variability in either product phase is related to the coupled substitutions REE$^{3+}$ + Fe$^{2+}$ = Ca$^{2+}$ + Fe$^{3+}$ and REE$^{3+}$ + Fe$^{2+}$ = Ca$^{2+}$ + Al$^{3+}$ (Petrik et al. 1995). The data indicate high variations in the allanite-(Ce) REE content (Fig. 6), with significant enrichment in the 750 °C, 200 MPa run.

REE-rich fluorapatite-fluorcalciobritholite also formed in most of the experiments due to the presence of monazite-(Ce) and CaF$_2$. Differences in the apatite mineral chemistry and abundances in the experimental products are mainly related to the degree of monazite-(Ce) breakdown and the growth ratio of these phases, which are themselves related to increasing reaction kinetics with increasing temperature and pressure. Monazite-(Ce) breakdown to REE-rich fluorapatite-fluorcalciobritholite, and REE-epidote-allanite-(Ce), most likely occurred via the reaction monazite-(Ce) + annite + quartz + Ca + F (in fluid-I) = fluorapatite + allanite-(Ce) + fluid-II (Broska and Siman 1998). Although in most of the runs biotite appears unaltered, some biotite, apart from the muscovite and feldspars, must have reacted as the primary source of Fe for the REE-epidote and allanite-(Ce).

The unaltered monazite-(Ce) cores demonstrate that the interior of the grains was shielded from fluid-aided alteration, except for partial dissolution near the surface, which occasionally progressed towards the cores of some of the
Table 4 Overview of the products from runs with xenotime-(Y)

| Experiment | Temperature (°C) | Pressure (MPa) | Duration (days) | Description |
|------------|-----------------|----------------|----------------|-------------|
| X12C-01   | 450             | 200            | 16             | Xenotime-(Y) shows partial dissolution, with small amounts of small crystals of Y-rich fluoroalcibiortholite formed on the surface. Labradorite achieved K-feldspar rims. Melt formed. High amounts of Y-rich fluoroalcibiortholite formed on xenotime-(Y) surface, partially replacing xenotime-(Y). Large grains of (Y,HREE)-rich epidote formed. Melt formed. Aggregate of Y-rich fluorcalciobritholite grains. Labradorite, K-feldspar, muscovite and garnet are preserved. |
| X12C-10   | 450             | 400            | 18             | Xenotime-(Y) shows partial dissolution, with numerous small grains of Y-rich fluoroalcibiortholite formed on the surface and in xenotime-(Y) fractures. Labradorite, K-feldspar, biotite, muscovite and garnet are preserved. |
| X12C-23   | 450             | 600            | 16             | Xenotime-(Y) shows partial dissolution, with small amounts of small crystals of Y-rich fluoroalcibiortholite formed on the surface. Labradorite, K-feldspar, biotite, muscovite and garnet are preserved. |
| X12C-16   | 450             | 800            | 16             | Xenotime-(Y) shows partial dissolution with small crystals of Y-rich fluoroalcibiortholite formed on the surface. Occasionally most of the xenotime-(Y) is replaced by aggregate of Y-rich fluoroalcibiortholite grains. Labradorite, K-feldspar, biotite, muscovite and garnet are preserved. |
| X12C-06   | 550             | 200            | 12             | Xenotime-(Y) shows partial dissolution with Y-rich fluoroalcibiortholite formed on the surface, partially replacing the xenotime-(Y). Labradorite achieved K-feldspar rims. Starting biotite, K-feldspar and garnet are preserved. Muscovite is gone. |
| X12C-02   | 550             | 400            | 6              | Xenotime-(Y) shows partial dissolution with Y-rich fluoroalcibiortholite formed on the surface, partially replacing the xenotime-(Y). Labradorite achieved K-feldspar rims. Starting biotite, K-feldspar and garnet are preserved. Muscovite is gone. |
| X12C-14   | 550             | 600            | 8              | Xenotime-(Y) shows partial dissolution on the surface. High amounts of Y-rich fluoroalcibiortholite formed on xenotime-(Y) surface, partially replacing the xenotime-(Y). Occasionally xenotime-(Y) is almost completely replaced by Y-rich fluoroalcibiortholite. Starting labradorite, K-feldspar, biotite and garnet are preserved. Muscovite is gone. |
| X12C-13   | 550             | 800            | 8              | Xenotime-(Y) shows partial dissolution on the surface. High amounts of Y-rich fluoroalcibiortholite formed on xenotime-(Y) surface, partially replacing xenotime-(Y) along fractures. Several small grains of (Y,HREE)-rich epidote formed. Starting labradorite, K-feldspar, biotite, muscovite and garnet are preserved. Occasionally labradorite achieved albitic rims. |
| X12C-07   | 550             | 1000           | 8              | Xenotime-(Y) shows partial dissolution on the surface. High amounts of Y-rich fluoroalcibiortholite formed on xenotime-(Y) surface, partially replacing the xenotime-(Y). Starting labradorite, K-feldspar, biotite, muscovite and garnet are preserved. Occasionally labradorite achieved albitic rims. |
| X12C-09   | 650             | 200            | 6              | Xenotime-(Y) shows partial dissolution with high amounts of Y-rich fluoroalcibiortholite formed on the surface, partially replacing the xenotime-(Y). Melt formed. Labradorite achieved K-feldspar rims. Garnet, biotite and K-feldspar are preserved. Muscovite is gone. |
| X12C-03   | 650             | 400            | 6              | Xenotime-(Y) shows partial dissolution with high amounts of Y-rich fluoroalcibiortholite formed on the surface, partially replacing the xenotime-(Y). Labradorite, K-feldspar, biotite and garnet are preserved. Muscovite is gone. |

Table 4 (continued)

| Experiment | Temperature (°C) | Pressure (MPa) | Duration (days) | Description |
|------------|-----------------|----------------|----------------|-------------|
| X12C-12   | 650             | 600            | 6              | Xenotime-(Y) shows partial dissolution on the surface. High amounts of Y-rich fluoroalcibiortholite formed on xenotime-(Y) surface, partially replacing the xenotime-(Y). Labradorite, K-feldspar, biotite, muscovite and garnet are preserved. |
| X12C-19   | 750             | 400            | 4              | Xenotime-(Y) shows partial dissolution on the surface. High amounts of Y-rich fluoroalcibiortholite formed on xenotime-(Y) surface, partially replacing the xenotime-(Y). Melt formed. Feldspar with composition of bytownite forming porous grains filled with melt is present. Single grains of pyroxene are present. Some starting biotite preserved. Garnet rims display partial alteration and replacement by secondary low-Ti biotite and Fe oxides. Some labradorite preserved. K-feldspar and muscovite are gone. |
| X12C-22   | 750             | 600            | 4              | Xenotime-(Y) shows partial dissolution on the surface. High amounts of Y-rich fluoroalcibiortholite formed on xenotime-(Y) surface, partially replacing the xenotime-(Y). Melt formed. Feldspar with composition of bytownite forming porous grains filled with melt is present. Garnet rims display partial alteration and replacement by secondary low-Ti biotite. Altered labradorite developed porosity filled with melt. Labradorite, K-feldspar and muscovite are gone. |
| X12C-21   | 750             | 800            | 4              | Xenotime-(Y) shows partial dissolution on the surface. High amounts of Y-rich fluoroalcibiortholite formed on xenotime-(Y) surface, partially replacing the xenotime-(Y). Single grains of pyroxene are present. Some starting labradorite, biotite and garnet are preserved. Garnet rims display partial alteration and replacement by secondary low-Ti biotite/chlorite. K-feldspar and muscovite are gone. |
| X12C-20   | 750             | 1000           | 4              | Xenotime-(Y) shows partial dissolution on the surface. High amounts of Y-rich fluoroalcibiortholite formed on xenotime-(Y) surface, partially replacing the xenotime-(Y). Melt formed. Feldspar with composition of bytownite forming porous grains filled with melt is present. Some biotite preserved. Garnet is partially altered, surrounded by secondary mica. Pyroxene and secondary low-Ti biotite formed. Labradorite, K-feldspar and muscovite are gone. |
| X12N-01   | 450             | 200            | 16             | Xenotime-(Y) shows partial dissolution on the surface. Small amounts of Y-rich fluoroalcibiortholite formed on xenotime-(Y) surface. K-feldspar, garnet, biotite and muscovite are preserved. Albite achieved K-feldspar rims. Small grains of secondary feldspars with albite cores and K-feldspar rims formed. Delicate needle-like crystals of Na-(Fe-Mg)-amphibole are present. Garnet is not found. |
| X12N-10   | 450             | 400            | 18             | Xenotime-(Y) shows partial dissolution on the surface. Grains of (Y,HREE)-rich fluorapatite and Y-rich fluoroalcibiortholite formed, some on the surface of xenotime-(Y). Y-rich fluoroalcibiortholite grains show sector
Table 4 (continued)

| Reaction Conditions | Sample Composition | Notes |
|---------------------|--------------------|-------|
| X12N-11, 650 °C, 800 MPa, 6 days. Xenotime-(Y) shows partial dissolution on the surface. High amounts of Y-rich fluorocalciobritholite formed on xenotime-(Y) surface, partially replacing the xenotime-(Y). Melt formed. Some starting albite, K-feldspar and biotite are preserved. Aggregates of secondary low-Ti biotite are present in melt. Titanite formed. Delicate needle-like crystals of Na-(Fe-Mg)-amphibole are present. Garnet and muscovite are gone. |
| X12N-12, 650 °C, 800 MPa, 6 days. Xenotime-(Y) shows partial dissolution on the surface. Y-rich fluorocalciobritholite formed on xenotime-(Y) surface, partially replacing the xenotime-(Y). Biotite is preserved. Albite achieved K-feldspar rims. K-feldspar achieved albite rims. Aggregates of secondary low-Ti biotite and secondary albite form post-garnet pseudomorphs. Delicate needle-like crystals of Na-(Fe-Mg)-amphibole are present. Garnet and muscovite are gone. |
| X12N-09, 650 °C, 200 MPa, 6 days. Xenotime-(Y) shows partial dissolution on the surface. High amounts of Y-rich fluorocalciobritholite formed on xenotime-(Y) surface, partially replacing the xenotime-(Y). Garnet and muscovite are not found. Y-rich fluorocalciobritholite grains show sector zoning with (Y,REE)-rich fluorapatite cores and Y-rich fluorocalciobritholite rims. Melt formed. Some starting albite, K-feldspar and biotite are preserved. Albite achieved Na-K feldspar rims. Titanite formed. Aggregates of secondary low-Ti biotite and secondary albite form post-garnet pseudomorphs. Delicate needle-like crystals of Na-(Fe-Mg)-amphibole are present. Garnet and muscovite are gone. |
| X12N-22, 750 °C, 600 MPa, 4 days. Xenotime-(Y) shows partial dissolution on the surface. Y-rich fluorocalciobritholite formed on xenotime-(Y) surface, partially replacing the xenotime-(Y). Melt formed. Aggregates of secondary low-Ti biotite are present in melt. Some starting albite preserved. Small crystals of amphibole with composition close to ferri-taramite are present. K-feldspar, albite, garnet and muscovite are gone. |
| X12N-21, 750 °C, 800 MPa, 4 days. Xenotime-(Y) shows partial dissolution on the surface. Y-rich fluorocalciobritholite formed on xenotime-(Y) surface, partially replacing the xenotime-(Y). Garnet and muscovite are not found. Y-rich fluorocalciobritholite grains show sector zoning with (Y,REE)-rich fluorapatite cores and Y-rich fluorocalciobritholite rims. Melt formed. Some starting albite, K-feldspar and biotite are preserved. Albite achieved Na-K feldspar rims. Titanite formed. Aggregates of secondary low-Ti biotite and secondary albite form post-garnet pseudomorphs. Delicate needle-like crystals of Na-(Fe-Mg)-amphibole are present. Garnet and muscovite are gone. |
| X12N-08, 650 °C, 1000 MPa, 6 days. Xenotime-(Y) shows partial dissolution on the surface. High amounts of Y-rich fluorocalciobritholite formed on xenotime-(Y) surface, partially replacing the xenotime-(Y). Melt formed. Some starting albite, K-feldspar and biotite are preserved. Aggregates of secondary low-Ti biotite are present in melt. Titanite formed. Delicate needle-like crystals of Na-(Fe-Mg)-amphibole are present. Garnet and muscovite are gone. |
| X12N-07, 550 °C, 1000 MPa, 8 days. Xenotime-(Y) shows partial dissolution on the surface. High amounts of Y-rich fluorocalciobritholite formed on xenotime-(Y) surface, partially replacing the xenotime-(Y). Garnet and muscovite are not found. Y-rich fluorocalciobritholite grains show sector zoning with (Y,REE)-rich fluorapatite cores and Y-rich fluorocalciobritholite rims. Melt formed. Some starting albite, K-feldspar and biotite are preserved. Albite achieved Na-K feldspar rims. Titanite formed. Aggregates of secondary low-Ti biotite and secondary albite form post-garnet pseudomorphs. Delicate needle-like crystals of Na-(Fe-Mg)-amphibole are present. Garnet and muscovite are gone. |
| X12N-18, 750 °C, 200 MPa, 4 days. Xenotime-(Y) shows partial dissolution on the surface. Y-rich fluorocalciobritholite formed on xenotime-(Y) surface, partially replacing the xenotime-(Y). Melt formed. Some starting biotite preserved. Secondary low-Ti biotite and pyroxene formed. Small crystals with composition of Na-(Fe-Mg)-amphibole are present. K-feldspar, albite, garnet and muscovite are gone. |
| X12N-19, 750 °C, 400 MPa, 4 days. Xenotime-(Y) shows partial dissolution on the surface. Y-rich fluorocalciobritholite formed on xenotime-(Y) surface, partially replacing the xenotime-(Y). Melt formed. Some starting biotite preserved. Secondary low-Ti biotite formed. Small crystals with composition of Na-(Fe-Mg)-amphibole are present. K-feldspar, albite, garnet and muscovite are gone. |
| X12N-20, 750 °C, 800 MPa, 4 days. Xenotime-(Y) shows partial dissolution on the surface. Y-rich fluorocalciobritholite formed on xenotime-(Y) surface, partially replacing the xenotime-(Y). Melt formed. Some starting biotite preserved. Secondary low-Ti biotite formed. Small crystals with composition of Na-(Fe-Mg)-amphibole are present. K-feldspar, albite, garnet and muscovite are gone. |

Table 4 (continued)
The similar form and size of REE-rich fluorapatite-fluorocalciobritholite crystals in all the experiments indicate that their growth is relatively independent of the P-T conditions, although higher amounts of these crystals formed in high temperature runs with Na₃Si₂O₅ + H₂O, where REE-rich fluorapatite-fluorocalciobritholite were the primary phases replacing monazite-(Ce) (cf. Figs. 7a and e vs. 7f–j). REE enrichment in the product apatites is the result of two coupled substitution reactions REE³⁺ + Si⁴⁺ = Ca²⁺ + P⁵⁺ and REE³⁺ + Na⁺ = 2 Ca²⁺ (Pan and Fleet 2002). REE substitution into apatites from the 2 M Ca(OH)₂ experiments is dominated by Si (12.23–15.59 wt.% SiO₂, <0.01 wt.% Na₂O), whereas both REE substitutions occur in apatites from the runs with Na₃Si₂O₅ + H₂O (0.82–15.62 wt.% SiO₂, 0.58–4.52 wt.% Na₂O; supplementary Table S3). An increase in the REE concentration in apatite from the 2 M Ca(OH)₂ experiments from 27.66 to 44.09 wt.% (Y + REE)₂O₃ in runs from 450 to 750 °C (supplementary Table S3) indicates a direct correlation with increasing temperature conditions. The apatites from the experiments with Na₃Si₂O₅ + H₂O show similar increase from 14.25 to 39.47 wt.% (Y + REE)₂O₃ in the 450–550 °C runs to 36.94–42.60 wt.% (Y + REE)₂O₃ in the 650–750 °C runs (supplementary Table S3). These results also support those of Krenn et al. (2012) in a series of monazite-allanite-fluorapatite experiments. Krenn et al. (2012) documented an increase in the Na₂O-SiO₂-(Y + REE)₂O₃ content in fluorapatite [0.17–4.86 wt.% SiO₂, 0.47–3.38 wt.% Na₂O, 2.53–29.19 wt.% (Y + REE)₂O₃] with an increase in the pressure and temperature from 0.5 to 4 GPa and 650 to 900 °C. These experiments, along with the results from this study, support previous work suggesting that high activities of Si and Na in the fluid/melt promote the incorporation of REEs into apatite (Pan and Fleet 2002).

In the Na₃Si₂O₅ + H₂O experiments, the altered domains in the monazite-(Ce) are characterized by a fluid-induced, pervasive, interconnected nano- and micro-porosity (Figs. 7a and c and 8), which is characteristic of a coupled dissolution-reprecipitation process (Putnis 2002, 2009; Harlov et al. 2007, 2011; Putnis and Austrheim 2012). These domains are also characterized by depletion in Th and U, and the almost complete removal of Pb (supplementary Table S1) in runs at 450 °C, 200–1000 MPa; and 550 °C, 200–600 MPa. In runs at higher P-T conditions, a fluid-induced porosity occurs, along with numerous tiny inclusions of cheralite, apparently oriented parallel to a specific crystallographic plane in the monazite-(Ce) (Fig. 7g, k and l). The Burnet monazite-(Ce) (11.43 wt.% ThO₂, 0.34 wt.% UO₂, 0.59 wt.% PbO), used in these experiments, is relatively rich in Th, which would imply a greater degree of metamictization, and therefore a greater susceptibility to fluid-aided alteration via coupled dissolution-reprecipitation.

In the experiments utilizing Na₃Si₂O₅ + H₂O, altered domains in the monazite-(Ce) from the 450–550 °C experiments...
supplied Th and REE to the REE-rich steacyite, REE-rich fluorapatite, and Y-rich fluorcalciobritholite. The textural setting indicates that the Th was either transported by the fluid to form individual crystals of REE-rich steacyite, or that transport of Th was limited and REE-rich steacyte partially replaced monazite-(Ce). In the experimental replacement of

Fig. 10 BSE images of run products from experiments with xenotime-(Y) and 2 M Ca(OH)₂: a, b slightly altered xenotime-(Y) overgrown by small crystals of Y-rich fluorcalciobritholite (450 °C, 200 MPa, 16 days); c fractured xenotime-(Y) with Y-rich fluorcalciobritholite filling the fractures (450 °C, 400 MPa, 18 days); d Y-rich fluorcalciobritholite almost completely replacing altered xenotime-(Y) (450 °C, 800 MPa, 16 days); e labradorite partially replaced by K-feldspar (550 °C, 200 MPa, 12 days); f numerous hexagonal prisms of Y-rich fluorcalciobritholite formed on the surface of the xenotime-(Y) (550 °C, 400 MPa, 6 days); g hexagonal, sector-zoned, prismatic crystals of (Y,REE)-rich fluorapatite and Y-rich fluorcalciobritholite, which have formed on the xenotime-(Y) surface (550 °C, 800 MPa, 8 days); h (Y,HRREE)-rich epidote formed at the expense of altered xenotime-(Y) (hexagonal prisms of Y-rich fluorcalciobritholite formed on the xenotime-(Y) surface (550 °C, 800 MPa, 8 days); i, j Y-rich fluorcalciobritholite overgrowths on altered xenotime-(Y) (650 °C, 200 MPa, 6 days); k (Y,HRREE)-rich epidote formed at the expense of altered xenotime-(Y) in experiments at 650 °C, 800 MPa, 6 days (k) and 650 °C, 1000 MPa, 6 days (l); m altered xenotime-(Y) overgrown by Y-rich fluorcalciobritholite (650 °C, 1000 MPa, 6 days); n recrystallized muscovite in run at 650 °C, 1000 MPa, 6 days; o small crystals of pyroxene formed in melt (750 °C, 1000 MPa, 4 days); p slightly altered xenotime-(Y) with overgrowths of minute Y-rich fluorcalciobritholite crystals (750 °C, 200 MPa, 4 days); altered garnet is partially replaced by an aggregate of secondary low-Ti biotite and iron oxides.
monazite-(Ce), mobility of Th has also been documented by the formation of REE-rich steacyite at 250–350 °C and 200–400 MPa by Budzyń et al. (2015) or turkestanite \{(K,□)(Ca,Na)\color{red}_2(Th,U)\color{blue}_{\text{Si}}\color{green}_8O_{\text{20}}\}nH_2O\} at 450–500 °C, 450–610 MPa (Budzyń et al. 2011). Natural occurrences of steacyite and turkestanite are known from several alkaline complexes (Pautov et al. 1997, 2004; Kabalov et al. 1998; Petersen et al. 1999; Vilalva and Vlach 2010).

In Na_2Si_2O_5 + H_2O experiments at 650–750 °C, reacted areas in the monazite-(Ce) are characterized by a REE-rich fluorapatite-, Y-rich fluorcalciobritholite- and cheralite-filled lenticular porosity (Fig. 7f, g, k and l). The lenticular shape of the pores (Fig. 7l) suggests preferred dissolution along a certain crystallographic direction (or crystallographic plane) in the monazite-(Ce). Cheralite formation, along inner pore surfaces in the reacted monazite-(Ce), indicates that Th transport occurred over only short distances, whereas REE were mobilized across the pore volumes to form REE-rich fluorapatite and Y-rich fluorcalciobritholite.

The experiments also document the albitization of K-feldspar grain rims (Figs. 3i and 7b and j) via coupled dissolution-reprecipitation (e.g. Putnis 2002, 2009; Norberg et al. 2011, 2013). The re-equilibrated albite domains in the K-feldspar are characterized by both a micro-porosity and the
presence of REE-rich fluorapatite or fluorcalciobritholite inclusions. These suggest fluid-aided mass transfer of P, Ca, and REE from the outside the feldspar structure into the albitized regions, which would have then allowed for these inclusions to form.

Previous experimental data have shown that monazite solubility increases in felsic melts under water-saturated conditions (Montel 1993), whereas it is low in peraluminous melts (Montel 1986; Wolf and London 1995). In a series of monazite alteration experiments, Harlov et al. (2011) showed that an increase in the Al content in the fluid/melt limits the reactivity of monazite. In the experiments from this study, feldspars and micas partially to completely broke down to provide the components for a peraluminous melt in the high-temperature experiments (supplementary Tables S7, S16). However, no decrease in the reactivity of monazite-(Ce) was seen despite the melt composition. This would imply that the dissolution and reactivity of monazite is mostly related to the actual fluid/melt chemistry with no direct dependence on the Al content.

The results from this study have implications with regard to monazite Th-U-Pb geochronology. Previous experiments have shown that fluid-aided coupled dissolution-reprecipitation alteration can disturb the Th-U-Pb system in monazite (Teufel and Heinrich 1997; Seydoux-Guillaume et al. 2002; Harlov et al. 2007, 2011; Harlov and Hetherington 2010; Hetherington et al. 2010; Grand’Homme et al. 2016). In experiments utilizing Na$_2$Si$_2$O$_5$ + H$_2$O, partial loss of Pb in the altered areas of the monazite-(Ce) was seen at 250–350 °C, 200–400 MPa (Budzyń et al. 2015). Here, for the same mineral assemblage and fluid (Na$_2$Si$_2$O$_5$ + H$_2$O), Pb in altered areas of the monazite-(Ce) is almost completely removed for experiments at 450 °C, 200–1000 MPa and 550 °C, 200–600 MPa (Fig. 4c and d; supplementary Table S1), which is in good agreement with similar results reported by Williams et al. (2011). These temperatures are far below the diffusional closure temperature for Pb (i.e. above 800–900 °C; Cherniak et al. 2004; Gardes et al. 2006). However, in both the 2 M Ca(OH)$_2$ and Na$_2$Si$_2$O$_5$ + H$_2$O experiments, the unreacted monazite-(Ce) cores show no evidence of having experienced solid-state diffusion over the entire range of temperatures and pressures considered in these experiments. This indicates that significant dissolution, alteration, and partial replacement of the monazite-(Ce) grain by altered monazite-(Ce) or new phases does not affect the composition of the core over the duration of the experiment, even under conditions of 650–750 °C and subsequent partial melting of the initial mineral mix. Instead, the monazite-(Ce) core (or unaltered domains in patchy zoned grains) retains its original composition, within EPMA detection limits, in an alkali-rich fluid environment in a P-T window from 450 to at least 750 °C, and 200 to 1000 MPa.

**Interpretation of the experimental results: runs with xenotime-(Y)**

Similar to the experiments involving monazite-(Ce), the experiments involving xenotime-(Y) indicate that it is highly reactive with both 2 M Ca(OH)$_2$ and Na$_2$Si$_2$O$_5$ + H$_2$O and that the reaction products are relatively similar to those found for experiments involving monazite-(Ce) over the same P-T range (Tables 1 and 3). Yttrium-rich fluorcalciobritholite always formed either as individual crystals or, more commonly, formed overgrowths on xenotime-(Y) grains indicating relatively high mobilization of Y + REE, more specifically Y + HREE. However, Y + REE abundances in Y-rich fluorcalciobritholite show no obvious pattern relative to the P-T conditions (supplementary Table S11) unlike the apatites from the experiments involving monazite-(Ce). The higher abundance of unaltered xenotime-(Y) grains in the low temperature run products, compared to the paucity of unreacted
grains in high P-T runs, suggests that xenotime-(Y) reactivity is relatively temperature dependent. Some experiments also document partial replacement of the xenotime-(Y) by Y-rich fluorocalciobritholite, which could be interpreted as having been...
driven, at least partially, by coupled dissolution-reprecipitation (Figs. 10c and i and 12i and m).

Previous experiments involving the metasomatic alteration of xenotime-(Y) in the presence of alkali-bearing fluids (Na$_2$Si$_2$O$_5$ + H$_2$O, NaF + H$_2$O), along with the addition of SiO$_2$, Al$_2$O$_3$, ThO$_2$, and ThSiO$_4$, has documented enrichment in ThSiO$_4$ in altered areas of the xenotime-(Y) via coupled dissolution-reprecipitation (Harlov and Wirth 2012). More recent experiments at 250–350 °C and 200–400 MPa have also resulted in the strong alteration of xenotime-(Y) in the presence of Na$_2$Si$_2$O$_5$ + H$_2$O (Budzyń and Kozub-Budzyń 2015). In the experiments from this study, altered areas within the xenotime-(Y), enriched or depleted in REE, were not observed. This indicates that the components released from the altered xenotime-(Y) were incorporated primarily into the Y-rich fluorcalcicobritholite.

Although the 2 M Ca(OH)$_2$ fluid was highly aggressive in all runs, only three runs (550 °C, 800 MPa; 650 °C, 800 and 1000 MPa) resulted in the formation of (Y,HREE)-rich epidote, which suggests certain differences in the stability relations between xenotime-(Y) – (Y,HREE)-rich epidote compared to monazite – allanite. The experimental data first indicate that the P-T conditions are a crucial factor in controlling the relative stabilities between xenotime-(Y) and (Y,HREE)-rich epidote. Furthermore, the (Y + REE)$_2$O$_3$ content in (Y,HREE)-rich epidote increases from 2.31 wt.% at
800 MPa to 5.76 wt.% at 1000 MPa (supplementary Table S12). This suggests that the substitution of these elements is to some degree a function of pressure. However, because of the small crystal size, accurate analyses of (Y,HREE)-rich epidote could only be obtained in two runs. Hence these experimental results should be used only as a guide when applied to natural interpretations.

Monazite – allanite – fluorapatite and xenotime-(Y) – (Y,HREE)-rich epidote – (Y,HREE)-rich fluorapatite assemblages in nature

The influence of the Ca activity on the stability relations between monazite, allanite, and fluorapatite has been previously described in various rocks of granitic composition (Lee and Dodge 1964; Lee and Bastron 1967; Bea 1996; Bingen et al. 1996; Broska and Siman 1998; Finger et al. 1998; Broska et al. 2000, 2005; Claeson 2002) and metapelites (Janots et al. 2008, 2009). Temperature conditions controlling monazite–allanite phase relations have been constrained to ~400–450 °C in metapelites, where progressive metamorphic reactions involve the breakdown of monazite to form allanite (Smith and Barreiro 1990; Wing et al. 2003; Janots et al. 2006, 2008). In some cases these breakdown reactions were later followed by a reversed reaction resulting in the formation of monazite at the andalusite or kyanite isograd (Wing et al. 2003) or under temperature conditions of ~550–650 °C (Janots et al. 2008; Finger et al. 2016). Thermodynamic modeling by Spear (2010), utilizing Shaw’s (1956) average pelite bulk composition, predicted that increasing CaO from 2.17 to 4.34 wt.% would shift the allanite-(Ce) to monazite-(Ce) transition from 400 °C at 200 MPa and 550 °C at 1000 MPa, to 480 °C at 200 MPa and 750 °C at 1000 MPa (Fig. 6 in Spear 2010).

The experiments with 2 M Ca(OH)₂ confirm that a high CaO bulk content (10.08 wt.%, Table 2) shifts the stability of allanite-(Ce) towards higher temperatures and pressures up to the limits set by these experiments, i.e. 750 °C and 1000 MPa. In contrast, the experiments with Na₂Si₂O₅ + H₂O, also characterized by a high 5.91 wt.% CaO bulk content, produced no REE-rich epidote or allanite-(Ce) indicating that, depending on the bulk composition, a high Ca content is not necessarily one of the main factors controlling the monazite-(Ce)-to-allanite-(Ce) transition. Spear’s (2010) thermodynamic modeling also demonstrated the significant impact of Al, showing that the temperature of the allanite-(Ce)-to-monazite-(Ce) transition increases with a decrease in the Al₂O₃ bulk content. Hence, the increased stability of allanite-(Ce) in the experiments to high temperatures might also have been promoted by the low Al₂O₃ bulk content [10.04 and 7.74 wt.% in experimental sets (1) and (2), respectively, Table 2] compared to 16.57 wt.% Al₂O₃ in Shaw’s average pelite.

However, in general, the whole rock activity of Na, relative to that of Ca, appears to be one of the major factors in controlling the relative stabilities of monazite vs. allanite and xenotime-(Y) vs. (Y,HREE)-rich epidote. For example, in amphibolite-facies Alpine metapelites, both temperature and the bulk CaO/Na₂O ratio control the relative stabilities of allanite, monazite, and xenotime-(Y) (Janots et al. 2008). An increase in temperature to above 586 °C, during progressive metamorphism, resulted in the total breakdown of allanite and the formation of monazite and xenotime-(Y) for CaO/Na₂O < 0.54, while allanite remained stable up to 610 °C for CaO/Na₂O > 0.93 (Janots et al. 2008). In this study, the CaO/Na₂O ratios in the experimental runs with monazite-(Ce) and xenotime-(Y) and 2 M Ca(OH)₂ were 13.3 and 13.7, respectively (Table 2), which is much higher than that found to the Alpine metapelites (0.09–3.32 CaO/Na₂O; Janots et al. 2008).
Consequently, the allanite-(Ce) stability field was shifted to higher temperatures up to and probably higher than 750 °C. In contrast, neither epidote nor allanite-(Ce) formed in the monazite-(Ce) and xenotime-(Y) Na$_2$Si$_2$O$_5$ + H$_2$O experiments with significantly lower CaO/Na$_2$O ratios of 1.0, though still high concentrations of 5.91 and 5.56 wt.% CaO, and low concentrations of 7.74 and 9.25 wt.% Al$_2$O$_3$ (Table 2), respectively, compared to Spear’s (2010) model. The results from these experiments demonstrate that while the CaO/Na$_2$O ratio is important, the total whole rock composition is also important. This implies that the monazite-(Ce)-allanite-(Ce)-fluorapatite thermodynamic model of Spear (2010) should be only applied to those rocks whose whole rock composition approximates Shaw’s (1956) average pelite bulk composition.

Compared to numerous studies on monazite, little has been described regarding the alteration of xenotime-(Y) in nature. The fluid-mediated breakdown and replacement of xenotime-(Y) by (Y,HREE)-rich fluorapatite and (Y,HREE)-rich epidote have been documented in metamorphosed granitic rocks (Broska et al. 2005). However, the P-T conditions of such alterations remain a matter of some speculation. Fluid-aided, compositional alteration of xenotime-(Y) at 450 °C has been described in a quartz-muscovite-chlorite schist, which included metamorphic overgrowths on detrital xenotime-(Y) (Rasmussen et al. 2011). In Alpine metapelites, xenotime-(Y) has been described as being replaced by HREE-rich epidote and fluorapatite at 450–528 °C, followed by a reverse reaction at 560–610 °C, depending on the CaO bulk content and Ca/Na ratios (Janots et al. 2008). These observations are confirmed by the breakdown of xenotime-(Y) to (Y,HREE)-rich epidote in the same temperature range in the 2 M Ca(OH)$_2$ experiments (Fig. 2c; Table 3). In general, the results from the xenotime-(Y) experiments in this study could potentially provide important data for petrological constraints regarding xenotime-(Y) breakdown to (Y,HREE)-rich apatite and (Y,HREE)-rich epidote during the formation of the Veporíc nappe system in the Tatric unit, Tribeč Mountains (Broska et al. 2014).

The partitioning of REE and actinides between monazite-(Ce), fluorapatite, and fluorcalciobritholite played a significant role in the experiments. In nature, fluorapatite is an important carrier of REE and actinides with increasing metamorphic grade (Bingen et al. 1996; Spear and Pyle 2002; Finger and Krenn 2007; Hansen and Harlov 2007; Krenn et al. 2009, 2012). The results from this study show that REE can substitute into fluorapatite in extensive amounts under conditions replicating medium- to high-grade metamorphism. However, only minor amounts of REE-rich fluorapatite formed in the experiments, whereas fluorcalciobritholite or Y-rich fluorcalciobritholite were the main products due to high Y + REE bulk content. In nature, these phases are relatively uncommon, and have been reported in post-magmatic assemblages including britholite-(Y), fluorbritholite-(Y), fluorcalciobritholite, secondary monazite, and REE carbonate minerals formed during low-temperature alteration of primary magmatic fluorapatite and allanite-(Ce) in A-type granites from the Western Carpathians in Slovakia (Uher et al. 2015). Britholites also occur in various alkaline rocks such as alkali granites (Lyalina et al. 2014), pegmatites associated with peralkaline granites (Pekov et al. 2011), nepheline syenites (Liferovich and Mitchell 2006; Dumańska-Slokow et al. 2012), and carbonatites (Ahijado et al. 2005; Doroshkevich et al. 2009). The predominance of fluorcalciobritholite or Y-rich fluorcalciobritholite in the products from these experiments appears to have been related to the high percentage of monazite-(Ce) and xenotime-(Y) in the starting mineral mix, as well as the high alkalinity of the starting bulk composition, which includes the fluids used, i.e. 2 M Ca(OH)$_2$ and Na$_2$Si$_2$O$_5$ + H$_2$O. High compositional variations in the REE-rich fluorapatite and fluorcalciobritholite prevent us from making speculations regarding P-T control of REE substitution in the fluorapatite and britholite phases.

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