

Experimental determination of stability relations between monazite, fluorapatite, allanite, and REE-epidote as a function of pressure, temperature, and fluid composition

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ABSTRACT

The experimental alteration of monazite to allanite, REE-epidote, fluorapatite, and/or fluorapatite-britholite was investigated at 450 to 610 MPa and 450 to 500 °C. Experiments involved monazite + albite ± K-feldspar + muscovite ± biotite + SiO₂ + CaF₂ and variety of fluids including H₂O, (KCl + H₂O), (NaCl + H₂O), (CaCl₂ + H₂O), (Na₂Si₂O₅ + H₂O), 1 M HCl, 2 M NaOH, 2 M KOH, 1 M Ca(OH)₂, 2 M Ca(OH)₂, and (CaCO₃ + H₂O). The reaction products, or lack thereof, clearly show that the stability relations between monazite, fluorapatite, and allanite or REE-epidote are more dependent on the fluid composition and the ratio of silicate minerals than on the *P-T* conditions. A high Ca content in the fluid promotes monazite dissolution and the formation of fluorapatite and allanite or REE-epidote. Lowering the Ca content and raising the Na content in the fluid decreases the solubility of monazite but promotes the formation of allanite. Replacing Na with K in the same fluid causes fluorapatite, with a britholite component, to form from the monazite. However, allanite and REE-epidote are not formed. Monazite is stable in the presence of NaCl brines. In KCl brine, monazite shows a very limited reaction to fluorapatite. When the fluid is (Na₂Si₂O₅ + H₂O), strong dissolution of monazite occurs resulting in the mobilization of REEs, and actinides to form fluorapatite-britholite and turkestanite. These experimental results are consistent with natural observations of the partial to total replacement of monazite by fluorapatite, REE-epidote, and allanite in fluid-aided reactions involving the anorthite component in plagioclase at mid- to high-grade metamorphic conditions. In contrast, an alkali-bearing environment with excess Na prevents the growth of allanite and eventually promotes the precipitation of secondary monazite. The results from this study provide implications for geochronology and for deducing fluid compositions in metamorphic rocks.

Keywords: Monazite, fluorapatite, allanite, REE-epidote, experimental petrology

INTRODUCTION

Monazite [(REE,Th,U)PO₄], allanite [(CaREE)(Al₂Fe²⁺)Si₃O₁₂(OH)], and fluorapatite [Ca₅(PO₄)₃F] are relatively common accessory minerals in igneous and metamorphic rocks. They are also three of the principal hosts for the rare earth elements (Y+REE) in the Earth's crust and lithospheric mantle. The geochemical behavior of these minerals depends on pressure, temperature, fluid composition, and bulk rock composition (Spear and Pyle 2002; Gieré and Sorensen 2004; Harlov 2011). Monazite can be replaced by allanite during progressive low-grade metamorphism, followed by a reversed transition to form monazite at higher *P-T* (Gieré and Sorensen 2004). Mineral-fluid interactions leading to the replacement of monazite by fluorapatite, allanite, and/or epidote [Ca₂(Al₂Fe³⁺)Si₃O₁₂(OH)] have been recognized in a number of igneous and metamorphic rocks (e.g., Broska and Siman 1998; Finger et al. 1998; Claesson 2002; Wing et al. 2003; Broska et al. 2005; Janots et al. 2006, 2008, 2011; Majka and Budzyń 2006; Krenn and Finger 2007; Broska and Majka 2008; Harlov 2011). Recently, the formation

of secondary monazite and secondary fluorapatite with thorianite inclusions, at the expense of primary monazite in clasts of metamorphosed granites from the Carpathian flysch, was proposed to have occurred during retrograde metamorphism at 400 to 550 °C (Budzyń et al. 2010). In general, allanite did not form, although rare secondary textures of fluorapatite intergrown with allanite were observed. Under mid-greenschist facies conditions (ca. 350–400 °C), monazite breakdown also does not lead to the formation of allanite/epidote but rather to the secondary low-Th monazite growth (Rasmussen and Muhling 2007, 2009).

Previous experimental studies on monazite have been focused on monazite-fluid interactions (e.g., Teufel and Heinrich 1997; Ayers et al. 1999; Seydoux-Guillaume et al. 2002a, 2002b; Harlov et al. 2007, 2011; Harlov and Hetherington 2010; Hetherington et al. 2010) or the fluid-induced alteration of fluorapatite to form monazite inclusions (e.g., Harlov and Förster 2002; Harlov et al. 2002, 2003, 2005). In contrast, experimental studies involving allanite are limited to a series of allanite-zoisite [Ca₂Al₃Si₃O₁₂(OH)] experiments at 700 °C and 2000 MPa (Hermann 2002) and there are no experimental studies investigating monazite reacting to form fluorapatite. None of the previous experimental investigations has considered the stability

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of monazite in the complex mineral and fluid environment representative of natural granitoid rocks under low to moderate P - T conditions, except for work using experimental products from this study to constrain ages of experimentally altered monazite (Williams et al. 2011).

The goal of this study is to experimentally explore the geochemical relationship between monazite, fluorapatite, and allanite in the presence of silicate minerals typical of metapelites or quartzo-feldspathic rocks as a function of pressure and temperature at lower to middle amphibolite facies conditions using various metamorphic fluids. The P - T - X conditions for the experiments in this study were selected on the basis of the P - T conditions of the monazite-allanite transition reported in previous studies of Broska and Siman (1998), Finger et al. (1998), and Broska et al. (2005), monazite-to-secondary monazite transition (Budzyń 2009; Budzyń et al. 2010), as well as the P - T stability diagram for monazite and dissakisite [(CaLa)(Al₂Mg)Si₃O₁₂(OH)]-clinozoisite [Ca₂Al₃Si₃O₁₂(OH)] solid-solution as compiled by Janots et al. (2007). The results from this study, coupled with the application of in situ geochronology to monazite (e.g., Williams and Jercinovic 2002; Pyle and Spear 2003; Mahan et al. 2006; Williams et al. 2007; Dumond et al. 2008), allanite (Catlos et al. 2000; Gregory et al. 2007, 2009; Janots et al. 2009), and fluorapatite (Willigers et al. 2002), will further aid in helping to reconstruct the P - T - X - t evolution of greenschist- and lower-grade amphibolite-facies rocks.

EXPERIMENTAL AND ANALYTICAL METHODS

Experiments

Experiments involving alteration of monazite to allanite, REE-epidote and fluorapatite were conducted at the Deutsche GeoForschungsZentrum (Potsdam, Germany) utilizing cold-seal autoclaves on a hydrothermal line. Pressures and temperatures ranged from 450 to 610 MPa and 450 to 500 °C (Table 1). Three sets of experiments were performed. The first set (E1–E10) utilized monazite and albite + muscovite + amorphous quartz + CaF₂ (Table 1). Use of amorphous SiO₂ instead of quartz allowed for increased reaction rates. In experiments E11 through E23, biotite and K-feldspar were added to the assemblage.

The monazite used in the experiments was taken from a heavy mineral sand deposit located in Cleveland County, North Carolina (UCLA, Department of Geology mineral collection catalog number MS-1762) and is the same monazite used in the experimental monazite-fluid studies of Harlov and Hetherington (2010), Harlov et al. (2011), and Williams et al. (2011). The grains are 200 to 1000 µm in size, optically clear, light brown, euhedral to semi-euhedral crystals. In cross section, they show some faint zonation and patchiness under high-contrast back-scattered electron (BSE) imaging. The silicate minerals used in the experiments include a hydrothermal albite (Rožňava, Slovakia), gem quality sanidine (Eifel region, Germany), pegmatitic muscovite (Siedlimowice, Sudetes Mountains, Poland), and biotite (mica schist, Maine, U.S.A.).

The minerals were crushed and sieved to obtain a 50 to 100 µm fraction. Foreign and cloudy mineral grains were hand picked using a binocular microscope and removed. Fluids included doubly distilled H₂O, (KCl + H₂O), (NaCl + H₂O), (CaCl₂ + H₂O), (Na₂Si₂O₅ + H₂O), 1 M HCl, 2 M NaOH, 2 M KOH, 1 M Ca(OH)₂, 2 M Ca(OH)₂, and (CaCO₃ + H₂O) (Table 1). The exact amounts of monazite-(Ce), albite, sanidine, muscovite, biotite, SiO₂, CaF₂, Na₂Si₂O₅, and CaCO₃ used to prepare the solid mixture used in each experiment are listed in Table 1. Solid mixtures were prepared by mixing the individual minerals together in a dry state. The mixture was then slightly ground together in an agate mortar using ethanol and then dried at 105 °C. The mineral mixture plus fluid were loaded into 3 mm wide, 15 mm long Au capsules that were arc-welded shut using an argon plasma torch while the Au capsule was partially immersed in an ice-water bath. Capsules were checked for leaks by first weighing, then placing in a 105 °C oven for several hours, and then weighing again.

Experiments were performed in standard cold-seal, 6 mm bore, René metal

autoclaves with H₂O as the pressure medium. Three to four gently flattened Au capsules were placed in each autoclave. Temperatures, believed to be accurate to within ±5 °C, were measured externally with the thermocouple tip inserted into the end of the autoclave. Pressures were stable during the experiments except for one run with four capsules in the autoclave (E20–E23), where the pressure slowly decreased from 610 to 580 MPa over 16 days. The autoclaves were quenched after the run using compressed air. Temperatures of ca. 100 °C were reached within 1 min. Capsules were cleaned, weighed, opened, and dried at 105 °C and then re-weighed to determine the exact fluid content. The dry contents were then extracted from the Au capsule. Reacted mineral mixtures containing chlorides were washed several times in doubly distilled water to remove the salt. A portion of the experimental product was mounted in epoxy and polished. A second portion of the reacted mineral mixture was sprinkled on an adhesive carbon mount and carbon coated for backscattered electron (BSE) imaging.

Evaluation

Experimental products and the original mineral mixtures were evaluated using a series of scanning electron microscopes (SEM) equipped with energy-dispersive spectrometers (EDS) at the Deutsche GeoForschungsZentrum, Institute of Geological Sciences, Jagiellonian University (Kraków, Poland), and the Department of Mineralogy, Petrography, and Geochemistry, AGH–University of Science and Technology (Kraków, Poland).

Electron microprobe (EMP) analyses of the experimental products were performed utilizing a Cameca SX50 electron microprobe equipped with five wavelength spectrometers at the Department of Geosciences, University of Massachusetts in Amherst. Spot analyses were collected using a 15 kV accelerating voltage, 40 nA beam current, and ca. 1–5 µm beam size. The peak and background analytical times were 20 and 10 s, respectively, for all elements except Th and U, for which 30 and 15 s were used. Standards, spectral lines, WDS crystals, and detection limits are described in Budzyń et al. (2010). Additional analyses of monazite, turkestanite, REE-epidote, and fluorapatite were performed using the JEOL JXA-8500F Hyperprobe electron microprobe equipped with field emission gun and five wavelength spectrometers at the Deutsche GeoForschungsZentrum. The Hyperprobe was operated with a 15 kV accelerating voltage and 10 nA beam current. Analytical errors for each of the elements depend on the absolute abundances of each element in the mineral. Relative 1-σ errors are estimated to be <0.5% at the >10 wt% level, 5 to 10% at the >1 wt% level, 10 to 20% at the 0.2 to 1 wt% level, and 20 to 40% at the <0.1 wt% level. For concentrations below 0.1 wt%, the analytical precision for the actinides is approximately 10% higher. Results of the EMP analyses of starting material and reaction products are contained in Tables 2 through 9 and shown in Figure 1.

EXPERIMENTAL RESULTS

Experiments with H₂O

Monazite from experiments with H₂O (E1, 450 °C, 450 MPa; Mnz+Ab+Ms+SiO₂+CaF₂+H₂O; and E11, 500 °C, 450 MPa; Mnz+Ab+Kfs+Ms+Bt+SiO₂+CaF₂+H₂O) (see Appendix for mineral abbreviations) are homogeneous under high-contrast BSE imaging and the composition is unchanged compared to the starting monazite (Table 2; Fig. 2). Monazite grains do not reveal any signs of dissolution on the surface and have sharp edges. Feldspar and mica grains do not show any alteration and are similar in composition to the starting grains (Tables 3 and 5). REE-epidote occurs as a new phase present on the surface of a few monazite grains (Figs. 1 and 2). In experiment E1 only a few REE-epidote grains (up to several micrometers in size) were observed, whereas in experiment E11 higher amounts of euhedral single REE-epidote grains (up to ca. 100 µm long) are present.

Experiment with 1 M HCl

Monazite grains in experiment E6 (450 °C, 450 MPa; Mnz+Ab+Ms+SiO₂+CaF₂+1 M HCl) show evidence of partial dissolution, which takes the form of pits on the monazite grains surface (Table 2; Figs. 1 and 3a). However, neither the monazite

TABLE 1. Experimental conditions and starting materials (mg) over 16 days

Expt.	T (°C)	Mnz	Ab	Kfs	Ms	Bt	SiO ₂	CaF ₂	Na ₂ Si ₂ O ₅	CaCO ₃	Total solids	H ₂ O	2M KOH†	2M NaOH†	Ca(OH) ₂ 1M HCl†	NaCl	KCl	CaCl ₂	Total charge*	Mineral products	Remarks
P = 450 MPa																					
E1	450	5	7	–	4	–	4	5	–	–	25	4.97							25.95	REE-Ep	1
E2	450	5	7	–	4	–	4	5	–	–	25		5.26						28.28	FAp, FAp-Brt, Thn	2
E3	450	5	7	–	4	–	4	5	–	–	25			5.38					28.35	FAp-Brt, Mnz2, Thn	3
E4	450	5	7	–	4	–	4	5	–	–	25	5.17			0.38				28.86	FAp-Brt, REE-Ep	4
E5	450	5	7	–	4	–	4	5	5	–	30	5.17							33.70	FAp-Brt, Trk	5
E6	450	5	7	–	4	–	4	5	–	–	25					5.08			27.95	–	6
E7	450	5	7	–	4	–	4	5	–	–	25	5.08				0.30			29.56	–	6
E8	450	5	7	–	4	–	4	5	–	–	25	5.06					0.37		27.91	–	7
E9	450	5	7	–	4	–	4	5	–	–	25	5.01						0.20	27.93	–	8
E10	450	5	7	–	4	–	4	5	–	5	30	5.08							32.53	FAp, REE-Ep	9
E11	500	5	3	4	2	2	4	5	–	–	25	5.04							27.98	REE-Ep	10
E12	500	5	3	4	2	2	4	5	–	–	25		6.19						27.18	FAp, FAp-Brt	11
E13	500	5	3	4	2	2	4	5	–	–	25			5.62					28.08	FAp	12
E14	500	5	3	4	2	2	4	5	–	–	25	5.11			0.71				26.65	FAp, FAp-Brt, REE-Ep	13
E15	500	5	3	4	2	2	4	5	5	–	30	5.03							32.05	FAp-Brt, Trk	14
E16	500	5	3	4	2	2	4	5	–	–	25	5.09				0.28			27.64	–	6
E17	500	5	3	4	2	2	4	5	–	–	25	5.07					0.39		27.39	FAp	15
E18	500	5	3	4	2	2	4	5	–	–	25	5.15						0.52	28.57	FAp, Aln	16
E19	500	5	3	4	2	2	4	5	–	5	30	5.12							33.44	Aln, Thn	17
P = 610–580 MPa																					
E20	450	5	3	1	3	5	3	5	–	–	25		5.45						28.32	FAp	18
E21	450	5	3	1	3	5	3	5	–	–	25			5.42					28.96	FAp, Aln	19
E22	450	5	3	1	3	5	3	5	–	–	25	5.07				0.67			28.90	FAp, Aln	20
E23	450	5	3	1	3	5	3	5	5	–	30	5.03							34.26	Trk	21

Notes: Remarks =

- Starting minerals do not show any signs of alteration, except occasional grains of REE-epidote formed at the monazite surface.
- Monazite shows partial dissolution with delicate britholite-fluorapatite grains on the surface. High amounts of fluorapatite are present. Also rare thorianite is observed. Albite achieved K-feldspar overgrowths with inclusions of britholite-fluorapatite.
- Monazite shows partial dissolution with delicate britholite-fluorapatite grains on the surface. Albite achieved K-feldspar overgrowths with inclusions of secondary monazite. Thorianite is also formed.
- Monazite is partially dissolved. Up to ca. 20 µm REE-epidote grains are present on the monazite surface. Britholite-fluorapatite also occurs.
- Monazite shows strong dissolution on the surface and patchy internal zoning. The altered zones are depleted in Th, U, Ca, Y, and HREE. Large grains of britholite-fluorapatite and turkestanite are present. Also small amounts of K-feldspar has been formed. Delicate needle-like crystals with composition close to "glaucofane" are present. Muscovite is absent.
- Monazite shows dissolution pits on the surface.
- Monazite shows dissolution pits on the surface. Albite shows skeletal rims of K-feldspar
- No alterations are observed.
- Monazite shows delicate dissolution pits and is overgrown by REE-epidote. Rare <3 µm fluorapatite grains are present.
- Monazite shows partial dissolution. Large REE-epidote grains up to ca. 100 µm are found.
- Monazite shows dissolution pits on the surface and is overgrown by britholite-fluorapatite. Fluorapatite is present as minute inclusions in the K-feldspar overgrowths on albite. Muscovite has not been found within products. Delicate needle-like crystals with composition close to "glaucofane" are present.
- Small amounts of delicate apatite grains are found. Muscovite is gone.
- Monazite is partially dissolved, and portion of monazite grain has changed composition approaching composition of apatite. Up to ca. 20 µm REE-epidote grains are present on the monazite surface. Fluorapatite and britholite-fluorapatite are also found.
- Monazite shows strong dissolution on the surface and patchy internal zoning. The altered zones are depleted in Th, U, Ca, Y and HREE. Large grains of britholite-fluorapatite and turkestanite are present. Muscovite and biotite are absent. Delicate needle-like crystals with composition close to "glaucofane" are present.
- Monazite shows dissolution pits on the surface. Rare fluorapatite forms single grains.
- Monazite surface is strongly dissolved. Large amounts of up to ca. 40 µm allanite grains are present. Fluorapatite is formed. Albite shows etch pits on the surface.
- Monazite shows strong dissolution on the surface and patchy internal zoning. Monazite is overgrown by REE-Ep. Thorianite is formed. Muscovite is gone.
- Monazite is strongly dissolved on the surface. Fluorapatite is present within products.
- Monazite is overgrown by the allanite grains up to ca 40 µm. Fluorapatite grains (up to ca. 20 µm) are also found in the products.
- Monazite is partially dissolved. Up to ca. 20 µm REE-epidote grains are present on the monazite surface. Fluorapatite and britholite-fluorapatite are also found.
- Monazite shows strong dissolution. Rarely turkestanite is found. Muscovite and biotite are absent in the products. Delicate needle-like crystals with composition close to "glaucofane" are present.

* Weight loss is due to transportation of mixed solids (Mnz+Ab±Kfs+Ms±Bt+SiO₂+CaF₂±Na₂Si₂O₅±CaCO₃) from the agate mortar to the capsule. See text for further explanation.

† Component in a liquid phase.

nor the other minerals show any signs of chemical alteration (Fig. 3b; Tables 2, 3, and 5).

Experiments with NaCl + H₂O

Experiments E7 (450 °C, 450 MPa; Mnz+Ab+Ms+SiO₂+CaF₂+NaCl+H₂O) and E16 (500 °C, 450 MPa; Mnz+Ab+Kfs+Ms+Bt+SiO₂+CaF₂+NaCl+H₂O) showed no alteration in mineral composition (Tables 2, 3, 5, and 6). Dissolution pits formed on the monazite grain surface with the degree of dissolution increasing with temperature (Figs. 4a and 4b).

Experiments with KCl + H₂O

The only reaction textures observed in runs E8 (450 °C, 450 MPa; Mnz+Ab+Ms+SiO₂+CaF₂+KCl+H₂O) and E17 (500 °C, 450 MPa; Mnz+Ab+Kfs+Ms+Bt+SiO₂+CaF₂+KCl+H₂O) (Tables 2–6; Fig. 1) were rare dissolution pits on the monazite grain surface (Fig. 4c). Rare fluorapatite takes the form of a single grain (Fig. 4d). Albite in run E8 has skeletal rims of K-feldspar (Fig. 4e). No other alterations or changes in mineral composition were observed.

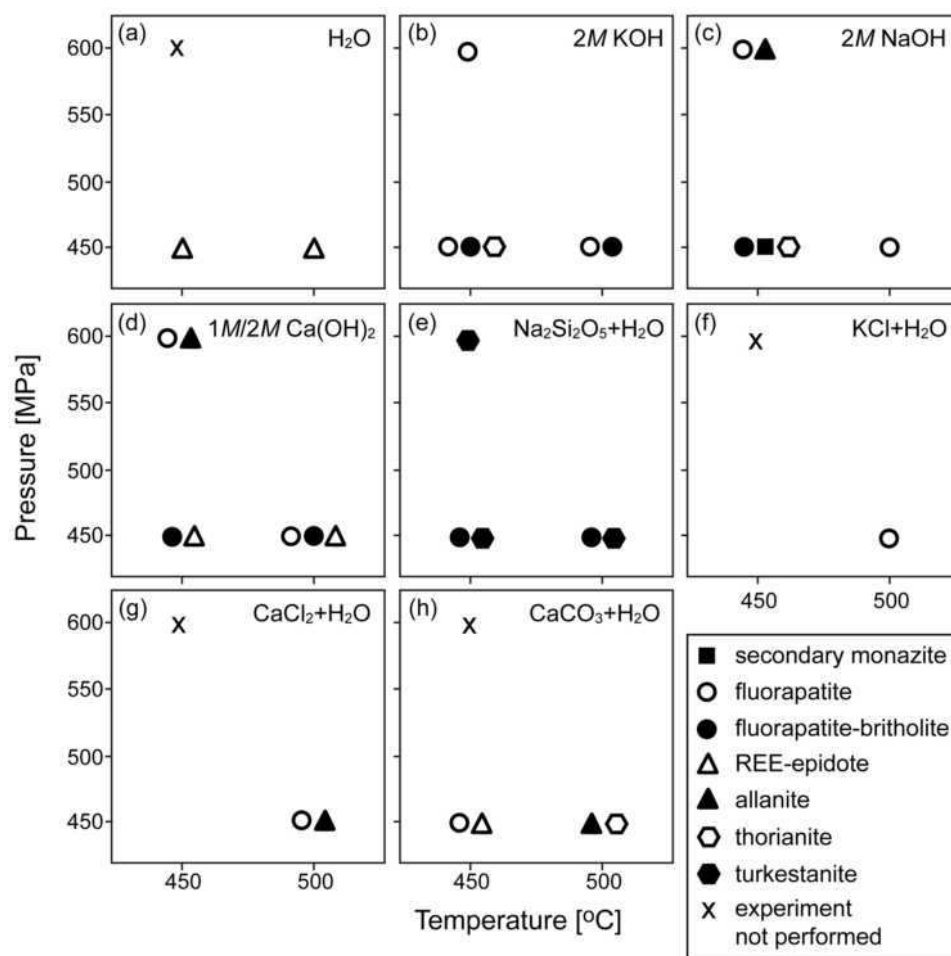


FIGURE 1. Simplified graphical compilation of the experimental results. (a) Experiments E1 and E11. (b) Experiments E2, E12, and E20. (c) Experiments E3, E13, and E21. (d) Experiments E4, E14, and E22. (e) Experiments E5, E15, and E23. (f) Experiments E8 and E17. (g) Experiments E9 and E18. (h) Experiments E10 and E19. Due to the fact that no new phases formed in experiments with 1 M HCl (E6) and (NaCl + H₂O) (E7 and E16), plots for these experimental runs are not shown.

Experiments with CaCl₂ + H₂O

The starting minerals were not altered in experiment E9 (450 °C, 450 MPa; Mnz+Ab+Ms+SiO₂+CaF₂+CaCl₂+H₂O) as opposed to run E18 (500 °C, 450 MPa; Mnz+Ab+Ms+SiO₂+CaF₂+CaCl₂+H₂O) (Tables 2–7; Fig. 1). Monazite in run E18 shows evidence of strong dissolution on the surface, but there is no alteration in the grain interiors such that the composition is unchanged. Large amounts of allanite (up to ca. 40 μm in size) are present (Table 7). Allanite is present both as grain aggregates as well as overgrowths on monazite (Fig. 4f). Etch pits formed on the crystal faces of the albite. The micas remained unchanged.

Experiments with CaCO₃ + H₂O

Alteration of monazite in experiments E10 (450 °C, 450 MPa; Mnz+Ab+Ms+SiO₂+CaF₂+CaCO₃+H₂O) and E19 (500 °C, 450 MPa; Mnz+Ab+Kfs+Ms+Bt+SiO₂+CaF₂+CaCO₃+H₂O) ranged from delicate dissolution pits to strong etching to complete dissolution of the grain surface (Tables 2–8; Figs. 1 and 5). The composition of the monazite, however, remains unchanged compared to the starting monazite (Table 2). Tabular crystals of REE-epidote and allanite overgrow the monazite (Fig. 5). EDS analyses indicate that the REE₂O₃ content of the REE-epidote increases from ca. 6.8 to 12.5 wt% (E10) to 13.7 to 18.3 wt% in allanite (E19) as a function of increasing temperature and grain size. The other minerals show no signs of alteration.

Experiments with 2 M KOH

Monazite shows partial to strong dissolution in runs with a 2 M KOH solution (Tables 2–8; Figs. 1 and 6a). However the monazite grains are homogeneous and their composition is similar to the starting monazite. Muscovite is not present in the products from run E12 (500 °C, 450 MPa; Mnz+Ab+Kfs+Ms+Bt+SiO₂+CaF₂+2 M KOH). Albite acquired overgrowths of K-feldspar (Fig. 6b). New phases include minerals whose grains are too small (ca. 0.5 × 3 μm; Fig. 6a) for EMP analysis. EDS analyses indicate that their composition reflects that of fluorapatite with a britholite component. Some of the fluorapatite-britholite needle-like grains are present directly on the monazite grain surface as individual grains (Fig. 6a) or as inclusions in the K-feldspar rims on albite (Fig. 6b). Another new phase is fluorapatite, which was observed only in runs E2 and E12 (Fig. 6b). It forms aggregates of euhedral grains up to several micrometers long in run E2, whereas in run E12 it formed inclusions in the K-feldspar rims on albite. Fluorapatite from run E2 contains ca. 5.29 wt% of SiO₂, 2.16 wt% of ThO₂, and 7.84 wt% of (Y+REE)₂O₃ (Table 8). Also, thorianite was observed as a single 3 μm size grain (Fig. 6b). In run E12, delicate needles of a mineral too fine grained for EMP analysis are present. Results from EDS analysis (52.93 wt% SiO₂, 0.73 wt% Al₂O₃, 18.93 wt% FeO, 7.72 wt% MgO, 0.95 wt% MnO, 2.01 wt% CaO, 6.47 wt% TiO₂, 2.71 wt% K₂O, 7.55 wt% Na₂O) suggest that these needles most likely are sodic clino-amphibole.

TABLE 2. Representative monazite compositions (wt%)

Experiment	P (MPa)	T (°C)	Description	n	P ₂ O ₅	SiO ₂	ThO ₂	UO ₂	Y ₂ O ₃	La ₂ O ₃	Ce ₂ O ₃	Pr ₂ O ₃	Nd ₂ O ₃	Sm ₂ O ₃	Gd ₂ O ₃	Tb ₂ O ₃	Dy ₂ O ₃	Tm ₂ O ₃	CaO	PbO	Total
Starting Mnz			Starting Mnz	23	29.47	0.64	8.42	0.50	0.78	12.38	27.80	3.02	11.58	1.41	1.47		0.30	0.31	1.33	0.13	99.54
			<i>Cameca SX50</i>		<i>0.72</i>	<i>0.48</i>	<i>1.47</i>	<i>0.24</i>	<i>0.28</i>	<i>0.41</i>	<i>0.83</i>	<i>0.15</i>	<i>0.37</i>	<i>0.15</i>	<i>0.25</i>		<i>0.08</i>	<i>0.05</i>	<i>0.24</i>	<i>0.02</i>	
E1	450	450	unaltered Mnz	7	29.26	0.65	7.96	0.45	0.90	12.63	27.86	3.02	11.45	1.18	1.50		0.27		1.21	0.11	98.44
			<i>Cameca SX50</i>		<i>0.41</i>	<i>0.21</i>	<i>0.67</i>	<i>0.16</i>	<i>0.46</i>	<i>0.42</i>	<i>0.50</i>	<i>0.12</i>	<i>0.30</i>	<i>0.14</i>	<i>0.22</i>		<i>0.16</i>		<i>0.24</i>	<i>0.03</i>	
E2	450	450	unaltered Mnz	9	29.34	0.55	7.60	0.43	0.53	13.08	28.36	3.08	11.90	1.00	0.88	0.18		0.23	1.23	0.12	98.50
			<i>Cameca SX50</i>		<i>0.76</i>	<i>0.08</i>	<i>0.87</i>	<i>0.07</i>	<i>0.08</i>	<i>0.57</i>	<i>0.60</i>	<i>0.17</i>	<i>0.18</i>	<i>0.13</i>	<i>0.37</i>	<i>0.07</i>		<i>0.10</i>	<i>0.14</i>	<i>0.02</i>	
E3	450	450	unaltered Mnz	3	27.68	0.70	8.22	0.39	0.39	12.83	28.50	2.94	11.96	1.26	1.20				1.34	0.10	97.50
			<i>Cameca SX50</i>		<i>1.17</i>	<i>0.08</i>	<i>0.28</i>	<i>0.04</i>	<i>0.12</i>	<i>0.39</i>	<i>0.39</i>	<i>0.05</i>	<i>0.19</i>	<i>0.15</i>	<i>0.53</i>				<i>0.29</i>	<i>0.02</i>	
E4	450	450	unaltered Mnz	8	29.15	0.57	8.14	0.36	0.64	12.35	27.70	3.12	11.93	1.18	1.33				1.33	0.14	97.94
			<i>Cameca SX50</i>		<i>0.31</i>	<i>0.07</i>	<i>0.26</i>	<i>0.12</i>	<i>0.14</i>	<i>0.41</i>	<i>0.55</i>	<i>0.07</i>	<i>0.23</i>	<i>0.14</i>	<i>0.32</i>				<i>0.12</i>	<i>0.03</i>	
E5	450	450	altered Mnz	4	28.87	0.68	1.41	0.03	0.03	16.80	33.85	3.34	12.14	0.66	0.89				0.17		98.86
			<i>Cameca SX50</i>		<i>0.85</i>	<i>0.19</i>	<i>0.34</i>	<i>0.06</i>	<i>0.06</i>	<i>1.75</i>	<i>0.35</i>	<i>0.13</i>	<i>1.62</i>	<i>0.45</i>	<i>0.42</i>				<i>0.10</i>		
E5	450	450	unaltered Mnz	5	29.16	0.52	7.99	0.52	0.50	12.94	28.20	2.87	11.57	1.12	1.46		0.27	0.25	1.39	0.12	98.88
			<i>Cameca SX50</i>		<i>0.79</i>	<i>0.09</i>	<i>0.50</i>	<i>0.05</i>	<i>0.06</i>	<i>0.66</i>	<i>0.49</i>	<i>0.21</i>	<i>0.35</i>	<i>0.21</i>	<i>0.29</i>		<i>0.07</i>	<i>0.05</i>	<i>0.03</i>	<i>0.02</i>	
E6	450	450	unaltered Mnz	5	29.81	0.42	8.00	0.53	0.60	12.39	27.51	3.01	11.90	1.48	1.54		0.32	0.24	1.45	0.11	99.30
			<i>Cameca SX50</i>		<i>0.36</i>	<i>0.06</i>	<i>0.40</i>	<i>0.05</i>	<i>0.16</i>	<i>0.66</i>	<i>0.17</i>	<i>0.16</i>	<i>0.38</i>	<i>0.23</i>	<i>0.30</i>		<i>0.07</i>	<i>0.03</i>	<i>0.06</i>	<i>0.03</i>	
E7	450	450	unaltered Mnz	5	29.72	0.48	7.92	0.36	0.78	11.87	27.59	3.03	11.91	1.49	1.52		0.30	0.28	1.33	0.13	98.71
			<i>Cameca SX50</i>		<i>0.46</i>	<i>0.16</i>	<i>0.46</i>	<i>0.10</i>	<i>0.14</i>	<i>0.20</i>	<i>0.11</i>	<i>0.09</i>	<i>0.13</i>	<i>0.15</i>	<i>0.19</i>		<i>0.18</i>	<i>0.07</i>	<i>0.12</i>	<i>0.03</i>	
E8	450	450	unaltered Mnz	3	30.02	0.39	7.52	0.53	0.55	12.68	28.30	2.88	11.52	1.30	1.43			0.25	1.35	0.09	98.83
			<i>Cameca SX50</i>		<i>0.20</i>	<i>0.04</i>	<i>0.60</i>	<i>0.05</i>	<i>0.02</i>	<i>0.26</i>	<i>0.55</i>	<i>0.09</i>	<i>0.17</i>	<i>0.08</i>	<i>0.14</i>			<i>0.04</i>	<i>0.06</i>	<i>0.02</i>	
E9	450	450	unaltered Mnz	4	29.89	0.45	7.16	0.57	0.47	13.78	28.87	2.95	11.31	1.29	0.94	0.17	0.22	0.24	1.27	0.12	99.66
			<i>Cameca SX50</i>		<i>0.19</i>	<i>0.01</i>	<i>0.27</i>	<i>0.05</i>	<i>0.07</i>	<i>0.33</i>	<i>0.28</i>	<i>0.06</i>	<i>0.22</i>	<i>0.12</i>	<i>0.11</i>	<i>0.01</i>	<i>0.03</i>	<i>0.04</i>	<i>0.06</i>	<i>0.04</i>	
E10	450	450	unaltered Mnz	6	29.62	0.51	8.38	0.47	0.67	12.39	27.63	2.92	11.65	1.28	1.20		0.31	0.30	1.43	0.11	98.86
			<i>Cameca SX50</i>		<i>0.18</i>	<i>0.06</i>	<i>0.17</i>	<i>0.13</i>	<i>0.02</i>	<i>0.21</i>	<i>0.35</i>	<i>0.16</i>	<i>0.29</i>	<i>0.12</i>	<i>0.14</i>		<i>0.04</i>	<i>0.05</i>	<i>0.15</i>	<i>0.02</i>	
E11	450	500	unaltered Mnz	4	29.62	0.47	8.08	0.54	0.73	12.93	27.95	2.96	11.51	1.25	1.45		0.23	0.22	1.36	0.13	99.42
			<i>Cameca SX50</i>		<i>0.35</i>	<i>0.13</i>	<i>0.76</i>	<i>0.20</i>	<i>0.13</i>	<i>0.27</i>	<i>0.62</i>	<i>0.10</i>	<i>0.16</i>	<i>0.11</i>	<i>0.08</i>		<i>0.07</i>	<i>0.04</i>	<i>0.31</i>	<i>0.02</i>	
E12	450	500	unaltered Mnz	3	29.67	0.50	8.06	0.51	0.93	12.13	27.70	2.98	11.64	1.23	1.34		0.32	0.28	1.35	0.10	98.76
			<i>Cameca SX50</i>		<i>0.55</i>	<i>0.31</i>	<i>0.34</i>	<i>0.19</i>	<i>0.10</i>	<i>0.58</i>	<i>0.60</i>	<i>0.18</i>	<i>0.15</i>	<i>0.30</i>	<i>0.29</i>		<i>0.06</i>	<i>0.02</i>	<i>0.38</i>	<i>0.03</i>	
E13	450	500	unaltered Mnz	6	29.71	0.52	7.83	0.49	0.50	13.23	28.29	2.91	11.13	1.07	1.14		0.28		1.34	0.08	98.51
			<i>Cameca SX50</i>		<i>0.18</i>	<i>0.14</i>	<i>0.96</i>	<i>0.24</i>	<i>0.13</i>	<i>1.12</i>	<i>1.14</i>	<i>0.10</i>	<i>0.39</i>	<i>0.24</i>	<i>0.57</i>		<i>0.09</i>		<i>0.27</i>	<i>0.02</i>	
E14	450	500	unaltered Mnz	14	29.57	0.57	7.49	0.40	0.83	12.64	28.40	3.06	11.78	1.25	1.21		0.35	0.23	1.28	0.11	99.15
			<i>Cameca SX50</i>		<i>0.37</i>	<i>0.12</i>	<i>0.66</i>	<i>0.11</i>	<i>0.25</i>	<i>0.41</i>	<i>0.41</i>	<i>0.20</i>	<i>0.38</i>	<i>0.30</i>	<i>0.33</i>		<i>0.08</i>	<i>0.06</i>	<i>0.16</i>	<i>0.03</i>	
E15	450	500	altered Mnz	6	29.83	0.90	1.34			16.20	33.37	3.74	11.48	1.57	0.64			n.a.	0.10		99.17
			<i>JEOL JXA-8500F</i>		<i>0.13</i>	<i>0.08</i>	<i>0.37</i>			<i>0.36</i>	<i>0.52</i>	<i>0.17</i>	<i>0.24</i>	<i>0.09</i>	<i>0.10</i>				<i>0.03</i>		
E15	450	500	unaltered Mnz	12	29.77	0.61	7.38	0.50	0.53	13.05	28.38	3.31	10.97	2.00	1.15			n.a.	1.45	0.11	99.20
			<i>JEOL JXA-8500F</i>		<i>0.61</i>	<i>0.11</i>	<i>0.50</i>	<i>0.04</i>	<i>0.11</i>	<i>0.39</i>	<i>0.57</i>	<i>0.07</i>	<i>0.26</i>	<i>0.17</i>	<i>0.14</i>				<i>0.08</i>	<i>0.02</i>	
E16	450	500	unaltered Mnz	3	29.43	0.35	7.72	0.51	0.56	12.45	27.74	2.95	11.57	1.37	1.15		0.23		1.50	0.13	97.66
			<i>Cameca SX50</i>		<i>0.26</i>	<i>0.08</i>	<i>0.51</i>	<i>0.05</i>	<i>0.08</i>	<i>0.23</i>	<i>0.22</i>	<i>0.08</i>	<i>0.13</i>	<i>0.05</i>	<i>0.32</i>		<i>0.03</i>		<i>0.02</i>	<i>0.02</i>	
E17	450	500	unaltered Mnz	5	29.07	0.67	6.96	0.43	1.55	12.54	28.26	3.15	11.62	1.23	1.36		0.51	0.24	0.94	0.10	98.62
			<i>Cameca SX50</i>		<i>0.37</i>	<i>0.11</i>	<i>0.29</i>	<i>0.10</i>	<i>0.39</i>	<i>0.30</i>	<i>0.45</i>	<i>0.16</i>	<i>0.11</i>	<i>0.12</i>	<i>0.23</i>		<i>0.13</i>	<i>0.03</i>	<i>0.02</i>	<i>0.03</i>	
E18	450	500	unaltered Mnz	4	29.62	0.57	7.28	0.29	1.20	12.68	27.71	3.22	11.80	1.33	1.62		0.36		1.15	0.12	98.92
			<i>Cameca SX50</i>		<i>1.16</i>	<i>0.12</i>	<i>0.70</i>	<i>0.11</i>	<i>0.38</i>	<i>0.56</i>	<i>0.49</i>	<i>0.12</i>	<i>0.18</i>	<i>0.24</i>	<i>0.21</i>		<i>0.08</i>		<i>0.31</i>	<i>0.02</i>	
E19	450	500	unaltered Mnz	5	29.16	0.73	7.83	0.45	0.64	12.82	28.52	3.11	11.86	1.32	1.24		0.30	0.26	1.11	0.11	99.47
			<i>Cameca SX50</i>		<i>0.95</i>	<i>0.42</i>	<i>0.62</i>	<i>0.16</i>	<i>0.16</i>	<i>0.35</i>	<i>0.64</i>	<i>0.10</i>	<i>0.29</i>	<i>0.05</i>	<i>0.25</i>		<i>0.12</i>	<i>0.06</i>	<i>0.46</i>	<i>0.03</i>	
E20	610–580	450	unaltered Mnz	6	29.96	0.46	8.52	0.69	0.63	12.48	27.65	3.03	11.58	1.20	1.47		0.31	0.21	1.57	0.14	99.89
			<i>Cameca SX50</i>		<i>0.28</i>	<i>0.08</i>	<i>0.65</i>	<i>0.07</i>	<i>0.06</i>	<i>0.34</i>	<i>0.39</i>	<i>0.04</i>	<i>0.31</i>	<i>0.08</i>	<i>0.21</i>		<i>0.04</i>	<i>0.11</i>	<i>0.09</i>	<i>0.03</i>	
E21	610–580	450	unaltered Mnz	3	28.86	0.82	7.82	0.27	0.31	12.75	28.97	3.05	11.89	1.25	1.56			0.20	1.02	0.12	98.90
			<i>Cameca SX50</i>		<i>0.42</i>	<i>0.12</i>	<i>0.12</i>	<i>0.06</i>	<i>0.03</i>	<i>0.30</i>	<i>0.20</i>	<i>0.19</i>	<i>0.21</i>	<i>0.03</i>	<i>0.17</i>			<i>0.04</i>	<i>0.14</i>	<i>0.02</i>	
E22	610–580	450	unaltered Mnz	6	29.85	0.43	7.59	0.47	0.66	12.85	28.21	2.96	11.45	1.24	1.51		0.33		1.42	0.09	99.06
			<i>Cameca SX50</i>		<i>0.45</i>	<i>0.08</i>	<i>0.65</i>	<i>0.10</i>	<i>0.19</i>	<i>0.54</i>	<i>0.62</i>	<i>0.11</i>	<i>0.32</i>	<i>0.13</i>	<i>0.33</i>		<i>0.05</i>		<i>0.10</i>	<i>0.02</i>	
E23	610–580	450	unaltered Mnz	8	29.90	0.41	7.70	0.54	0.53	12.82	28.07	2.93	11.54	1.16	1.44		0.23		1.40	0.11	98.78
			<i>Cameca SX50</i>		<i>0.31</i>	<i>0.05</i>	<i>0.38</i>	<i>0.07</i>	<i>0.05</i>	<i>0.50</i>	<i>0.26</i>	<i>0.12</i>	<i>0.24</i>	<i>0.08</i>	<i>0.20</i>		<i>0.03</i>		<i>0.05</i>	<i>0.02</i>	

Notes: Blank = below EMP detection limit. n = mean of n spots on a random selection of Mnz grain fragments. Standard deviations are given in italics. All analyses of Eu, Ho, Er, Tm, and Yb are below detection limit and therefore not included in the table.

Experiments with 2 M NaOH

In experiments using 2 M NaOH (Tables 2–6, 8; Fig. 1) monazite was altered and new phases were formed (Figs. 6c–6h). Depending on the *P-T* conditions and starting materials, different mineral products were observed. In run E3 (450 °C, 450 MPa; Mnz+Ab+Ms+SiO₂+CaF₂+2 M NaOH), the monazite is overgrown by fluorapatite-britholite (Fig. 6c). Albite grains commonly have newly grown K-feldspar rims. Also, secondary monazite inclusions were observed in the outermost parts of the albite and their K-feldspar rims (Figs. 6d–6f). The orientation of the monazite inclusions is consistent with the cleavage orientation in the feldspar. Secondary monazite has a composition similar to the original monazite (Table 2). Rare grains of thorianite occur on the monazite grain surfaces. In experiment E13 (500 °C, 450 MPa; Mnz+Ab+Kfs+Ms+Bt+SiO₂+CaF₂+2

M NaOH) monazite rarely has dissolution pits on the surface and shows no internal alteration. No new minerals were found in run E13 except for tiny fluorapatite grains. In addition, the muscovite has disappeared. Experiment E21 (450 °C, 610–580 MPa; Mnz+Ab+Kfs+Ms+Bt+SiO₂+CaF₂+2 M NaOH) resulted in the formation of allanite and fluorapatite (Figs. 6g–6h; Table 8). Allanite grains up to ca. 40 µm long grew directly on the monazite grain surfaces. Fluorapatite forms grains up to ca. 20 µm long. The composition of the newly formed monazite is not changed compared to the starting monazite (Table 2). Feldspars and micas are not altered.

Experiments with 1 and 2 M Ca(OH)₂

Experiments utilizing 1 M Ca(OH)₂ at 450 °C, 450 MPa [E4; Mnz+Ab+Ms+SiO₂+Ca

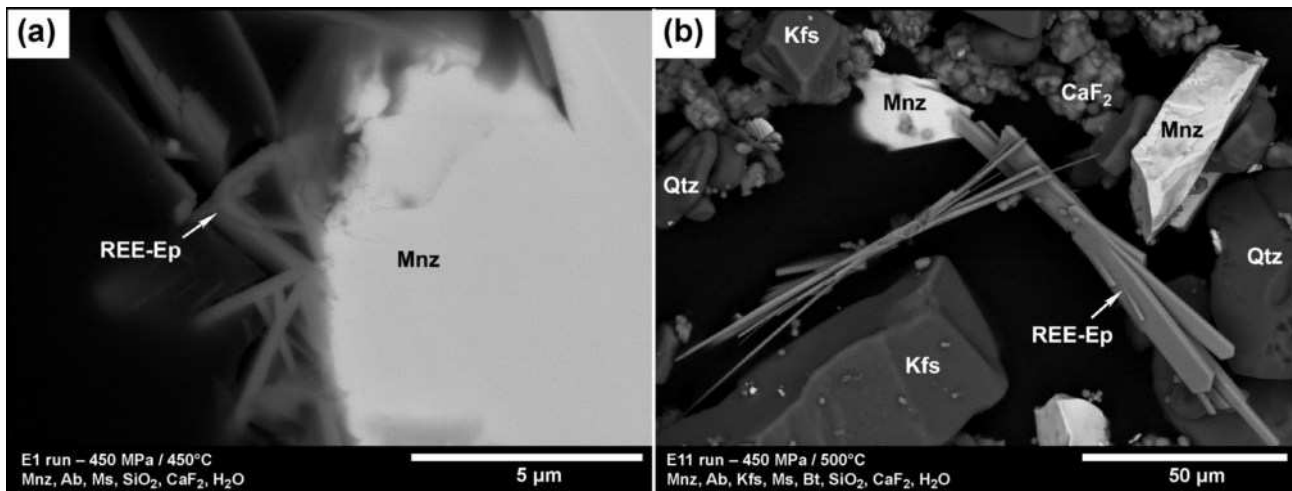


FIGURE 2. Experimental products from runs including only H₂O as the fluid. (a) REE-epidote overgrowing monazite; (b) newly formed REE-epidote grains.

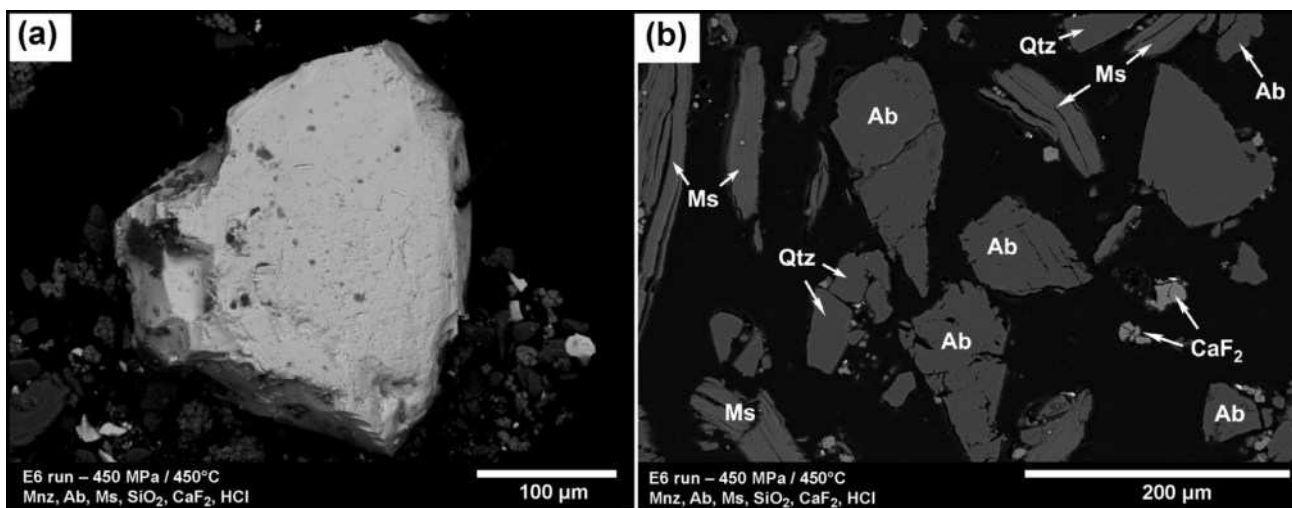


FIGURE 3. Experimental products from the run with 1 M HCl showing (a) etch pits on the monazite grain surface and (b) unaltered albite, muscovite, and quartz grains.

at 500 °C, 450 MPa [E14; Mnz+Ab+Kfs+Ms+Bt+SiO₂+CaF₂+2 M Ca(OH)₂] and 450 °C, 610–580 MPa [E22; Mnz+Ab+Kfs+Ms+Bt+SiO₂+CaF₂+2 M Ca(OH)₂] (Tables 2–8; Fig. 1) resulted in the growth of several new mineral phases. Monazite from all three runs is partially dissolved, but the overall composition is unchanged compared to the starting monazite (Table 2). REE-epidote or allanite are present on the monazite grain surface (Figs. 6k–6l). The REE₂O₃ content of the REE-epidote ranges from ca. 8.64 to 8.78 wt% in E4, to ca. 13.28 wt% in E14, and 14.27 wt% in E22 (Fig. 7; Table 7). Also, the grain size of the epidote group minerals increases with the increasing *P-T* from grains up to ca. 20 µm long in E4 to grains up to ca. 50 µm long in E14 and E22 (Fig. 6k). Elongated grains of a mineral with a chemical composition similar to that of fluorapatite-britholite occur in the products from run E4 (Table 8). Aggregates of fluorapatite grains, up to ca. 20 µm long, are present in experiments E14 (Fig. 6j) and E22 (Table 8). Moreover, portions of the monazite grain in E4 and E14 (Figs. 6i and 6l) appear to be partially replaced and/or overgrown by

fluorapatite. The other minerals were not altered, except in run E14 where muscovite was not present in the product mineral assemblage after the run.

Experiments with Na₂Si₂O₅ + H₂O

Experiments involving (Na₂Si₂O₅ + H₂O) had the highest degree of monazite alteration of all the experiments (Tables 2–8; Figs. 1 and 8). New minerals include fluorapatite-britholite (Table 8) and turkestanite [Th(Ca,Na)₂(K_{1-x}□_x)Si₈O₂₀·nH₂O] (Fig. 8; Table 9). Monazite in experiments E5 (450 °C, 450 MPa; Mnz+Ab+Ms+SiO₂+CaF₂+Na₂Si₂O₅+H₂O) and E15 (500 °C, 450 MPa; Mnz+Ab+Kfs+Ms+Bt+SiO₂+CaF₂+Na₂Si₂O₅+H₂O) show indications of strong dissolution on the grain surfaces. Monazite crystal faces are rounded with multiple etches, and elongated depressions related to the growth of new minerals on the monazite grain surface (Fig. 8g). These include delicate, needle-like crystals whose composition most closely matches that of sodic clino-amphibole. BSE imaging of the monazite grains from both runs show a patchy texture (Figs. 8a and 8e). The bright

TABLE 3. Mean plagioclase compositions (wt%)

Sample	P (MPa)	T (°C)	No. pts	SiO ₂	Al ₂ O ₃	CaO	FeO	Na ₂ O	K ₂ O	Total	X _{An}	X _{Ab}	X _{Kfs}
Starting albite			6	70.27	19.80		0.06	9.82	0.04	99.99	0.000	0.998	0.002
				<i>1.36</i>	<i>0.23</i>		<i>0.03</i>	<i>0.88</i>	<i>0.02</i>		<i>0.000</i>	<i>0.001</i>	<i>0.001</i>
E1	450	450	2	72.24	20.35	0.03	0.01	8.28	0.05	100.96	0.001	0.994	0.004
				<i>2.60</i>	<i>0.44</i>	<i>0.01</i>	<i>0.01</i>	<i>1.80</i>	<i>0.01</i>		<i>0.000</i>	<i>0.001</i>	<i>0.001</i>
E2	450	450	5	71.49	20.22	0.06	0.01	9.86	0.11	101.76	0.003	0.989	0.008
				<i>2.30</i>	<i>0.31</i>	<i>0.03</i>	<i>0.01</i>	<i>0.56</i>	<i>0.06</i>		<i>0.002</i>	<i>0.004</i>	<i>0.003</i>
E3	450	450	2	68.69	19.79	0.06	0.03	10.77	0.05	99.38	0.003	0.994	0.003
				<i>0.59</i>	<i>0.25</i>	<i>0.01</i>	<i>0.01</i>	<i>0.35</i>	<i>0.01</i>		<i>0.000</i>	<i>0.001</i>	<i>0.001</i>
E6	450	450	2	72.17	20.33		0.01	8.35	0.03	100.88	0.000	0.997	0.003
				<i>0.23</i>	<i>0.13</i>		<i>0.01</i>	<i>1.33</i>	<i>0.01</i>		<i>0.000</i>	<i>0.000</i>	<i>0.000</i>
E7	450	450	4	72.72	20.20	0.04	0.02	9.04	0.05	102.07	0.002	0.994	0.004
				<i>0.81</i>	<i>0.25</i>	<i>0.02</i>	<i>0.01</i>	<i>1.08</i>	<i>0.01</i>		<i>0.001</i>	<i>0.002</i>	<i>0.001</i>
E8	450	450	2	70.12	19.85		0.03	10.08	0.06	100.15	0.000	0.996	0.004
				<i>1.77</i>	<i>0.92</i>		<i>0.02</i>	<i>0.86</i>	<i>0.01</i>		<i>0.000</i>	<i>0.000</i>	<i>0.000</i>
E9	450	450	3	71.44	19.22	0.01	0.01	10.62	0.05	101.35	0.001	0.996	0.003
				<i>1.10</i>	<i>0.75</i>	<i>0.01</i>	<i>0.01</i>	<i>1.13</i>	<i>0.01</i>		<i>0.001</i>	<i>0.001</i>	<i>0.000</i>
E10 feld 1	450	450	3	54.51	27.45	10.53	0.08	5.36	0.37	98.30	0.510	0.469	0.021
				<i>0.29</i>	<i>0.42</i>	<i>0.06</i>	<i>0.02</i>	<i>0.04</i>	<i>0.01</i>		<i>0.001</i>	<i>0.001</i>	<i>0.001</i>
E10 feld 2	450	450	1	70.96	20.23	0.07	0.02	9.31	0.07	100.66	0.004	0.991	0.005
				<i>0.09</i>	<i>0.04</i>	<i>0.01</i>	<i>0.01</i>	<i>0.06</i>	<i>0.01</i>				
E11	450	500	2	71.04	20.16	0.01	0.01	8.28	0.08	99.56	0.002	0.992	0.006
				<i>1.98</i>	<i>0.39</i>	<i>0.01</i>	<i>0.01</i>	<i>2.88</i>	<i>0.01</i>		<i>0.001</i>	<i>0.003</i>	<i>0.002</i>
E12	450	500	3	70.72	20.26	0.04	0.02	10.46	0.08	101.58	0.002	0.993	0.005
				<i>0.28</i>	<i>0.07</i>	<i>0.01</i>	<i>0.01</i>	<i>0.05</i>	<i>0.01</i>		<i>0.001</i>	<i>0.000</i>	<i>0.001</i>
E13	450	500	4	70.83	19.76	0.06	0.07	8.84	0.26	99.82	0.004	0.975	0.021
				<i>2.38</i>	<i>0.51</i>	<i>0.02</i>	<i>0.04</i>	<i>1.16</i>	<i>0.36</i>		<i>0.001</i>	<i>0.031</i>	<i>0.031</i>
E14	450	500	4	72.52	20.39		0.03	7.68	0.05	100.67	0.000	0.996	0.004
				<i>0.80</i>	<i>0.27</i>		<i>0.02</i>	<i>1.67</i>	<i>0.01</i>		<i>0.000</i>	<i>0.001</i>	<i>0.001</i>
E15	450	500	3	72.47	20.29		0.24	5.89	0.29	99.17	0.000	0.956	0.044
				<i>0.82</i>	<i>0.07</i>		<i>0.18</i>	<i>3.18</i>	<i>0.21</i>		<i>0.000</i>	<i>0.039</i>	<i>0.039</i>
E16	450	500	2	69.21	19.42		0.02	10.70	0.06	99.41	0.000	0.996	0.004
				<i>0.28</i>	<i>0.24</i>		<i>0.01</i>	<i>0.06</i>	<i>0.01</i>		<i>0.000</i>	<i>0.001</i>	<i>0.001</i>
E17	450	500	2	70.48	20.11		0.02	8.34	0.06	99.00	0.000	0.996	0.004
				<i>0.66</i>	<i>0.01</i>		<i>0.02</i>	<i>0.05</i>	<i>0.01</i>		<i>0.000</i>	<i>0.000</i>	<i>0.000</i>
E18	450	500	2	62.94	23.59	4.53	0.01	8.64	0.18	99.87	0.223	0.767	0.010
				<i>0.35</i>	<i>0.08</i>	<i>0.19</i>	<i>0.01</i>	<i>0.50</i>	<i>0.01</i>		<i>0.017</i>	<i>0.018</i>	<i>0.001</i>
E20	610–580	450	5	72.27	20.31	0.06	0.06	9.58	0.07	102.36	0.003	0.992	0.005
				<i>2.16</i>	<i>0.39</i>	<i>0.01</i>	<i>0.02</i>	<i>0.33</i>	<i>0.01</i>		<i>0.001</i>	<i>0.001</i>	<i>0.001</i>
E21	610–580	450	2	71.57	20.02		0.05	7.95	0.27	99.85	0.000	0.976	0.024
				<i>0.13</i>	<i>0.27</i>		<i>0.06</i>	<i>1.03</i>	<i>0.31</i>		<i>0.000</i>	<i>0.027</i>	<i>0.027</i>
E22	610–580	450	3	72.58	20.59		0.02	9.12	0.04	102.35	0.000	0.997	0.003
				<i>0.28</i>	<i>0.02</i>		<i>0.02</i>	<i>0.62</i>	<i>0.01</i>		<i>0.000</i>	<i>0.000</i>	<i>0.000</i>
E23	610–580	450	2	75.26	19.98	0.08	0.27	5.99	0.41	101.97	0.007	0.951	0.042
				<i>0.92</i>	<i>0.12</i>	<i>0.04</i>	<i>0.01</i>	<i>0.21</i>	<i>0.05</i>		<i>0.004</i>	<i>0.010</i>	<i>0.006</i>

Notes: Standard deviations are given in italics. Blank = below detection limit.

compositional domains in the monazite are unchanged compared to the starting monazite, whereas the dark compositional domains reveal significant differences (Fig. 9; Table 2). The average ThO₂ content is 1.41 wt% for the dark domains vs. 7.99 wt% for the bright domains in run E5 and 1.34 wt% in dark domains vs. 7.38 wt% in bright domains in run E15. Similar differences are seen for CaO, which average content varies from 0.17 wt% in the dark domains to 1.39 wt% in the bright domains in run E5 and from 0.10 wt% in the dark domains to 1.45 wt% in the bright domains in run E15. Uranium in the dark domains in both E5 and E15 is strongly depleted (<0.03 wt% UO₂) compared to the starting monazite. Furthermore, the Pb content in the dark domains areas in either experiment is below the detection limit, whereas the bright domains contain ca. 0.11 to 0.12 wt% PbO reflecting the Pb content for the original starting monazite.

At higher pressures, monazite in experiment E23 (450 °C, 610–580 MPa; Mnz+Ab+Kfs+Ms+Bt+SiO₂+CaF₂+Na₂Si₂O₅+H₂O) shows evidence of strong partial dissolution. Numerous delicate, needle-like crystals approximating a sodic clino-amphibole composition are present on grain surfaces. The monazite is not altered internally and the composition overall is not changed compared to the starting monazite (Table 2).

Experimental products from runs E5 and E15 include turkestanite (Table 9), which forms prismatic to anhedral grains with apparent sharply delineated zones of different compositions (Figs. 8b and 8f). These are commonly intergrown with monazite, CaF₂, or feldspars. The average ThO₂ content in turkestanite is 17.73 wt% in run E5, 20.70 wt% in run E15, and 19.30 wt% in run E23 (Table 9). The average REE₂O₃ content of turkestanite is 5.97 wt% in run E5, 4.00 wt% in run E15, and 2.96 wt% in run E23. Anhedral grains of turkestanite are also present in products from run E23.

Muscovite and biotite are not present in the product minerals from either run. Product minerals from run E5 include K-feldspar grains a few micrometers in size. K-feldspar grains in experiment E23 exhibit rim overgrowths of and/or partial replacement by albite (Fig. 8h).

DISCUSSION

Interpretation of experimental results

The rate of monazite dissolution has been observed to be relatively high in acidic fluids compared to neutral fluids (Ayers and Watson 1991; Oelkers and Poitrasson 2002; Schmidt et al. 2007;

TABLE 4. Mean K-feldspar compositions (wt%)

Sample	P (MPa)	T (°C)	No. pts	SiO ₂	Al ₂ O ₃	CaO	FeO	Na ₂ O	K ₂ O	Total	An	Ab	Kfs
Starting K-feldspar			2	66.51 <i>2.87</i>	18.53 <i>0.60</i>		0.21 <i>0.02</i>	1.49 <i>0.01</i>	13.43 <i>0.01</i>	100.16	0.000 <i>0.000</i>	0.144 <i>0.001</i>	0.856 <i>0.001</i>
E2	450	450	4	67.76 <i>2.07</i>	18.05 <i>0.35</i>	0.12 <i>0.05</i>	0.14 <i>0.06</i>	0.72 <i>0.68</i>	13.63 <i>2.09</i>	100.43	0.007 <i>0.003</i>	0.078 <i>0.081</i>	0.915 <i>0.082</i>
E3	450	450	3	64.76 <i>0.28</i>	17.60 <i>0.07</i>	0.08 <i>0.01</i>	0.25 <i>0.04</i>	1.41 <i>0.09</i>	13.66 <i>0.11</i>	97.76	0.005 <i>0.001</i>	0.135 <i>0.006</i>	0.861 <i>0.006</i>
E11	450	500	1	66.20 <i>0.09</i>	18.91 <i>0.04</i>		0.14 <i>0.01</i>	1.43 <i>0.06</i>	13.26 <i>0.01</i>	99.94	0.000	0.141	0.859
E12	450	500	2	66.75 <i>1.76</i>	17.83 <i>0.28</i>		0.22 <i>0.16</i>	0.81 <i>0.13</i>	14.11 <i>0.45</i>	99.71	0.000 <i>0.000</i>	0.081 <i>0.014</i>	0.919 <i>0.014</i>
E13	450	500	1	66.55 <i>0.09</i>	18.65 <i>0.04</i>		0.16 <i>0.01</i>	1.51 <i>0.06</i>	13.29 <i>0.01</i>	100.16	0.000	0.147	0.853
E14	450	500	5	65.87 <i>0.92</i>	18.55 <i>0.13</i>		0.15 <i>0.03</i>	1.45 <i>0.02</i>	13.22 <i>0.12</i>	99.25	0.000 <i>0.000</i>	0.143 <i>0.002</i>	0.857 <i>0.002</i>
E15	450	500	1	64.23 <i>0.09</i>	18.29 <i>0.04</i>		0.17 <i>0.01</i>	1.52 <i>0.06</i>	13.25 <i>0.01</i>	97.46	0.000	0.149	0.851
E17	450	500	1	65.87 <i>0.09</i>	18.91 <i>0.04</i>		0.13 <i>0.01</i>	1.46 <i>0.06</i>	13.22 <i>0.01</i>	99.59	0.000	0.143	0.857
E18	450	500	1	64.13 <i>0.09</i>	18.26 <i>0.04</i>		0.13 <i>0.01</i>	1.45 <i>0.06</i>	13.36 <i>0.01</i>	97.33	0.000	0.142	0.858
E19	450	500	2	64.83 <i>0.11</i>	18.45 <i>0.07</i>		0.15 <i>0.01</i>	1.45 <i>0.04</i>	13.30 <i>0.17</i>	98.17	0.000 <i>0.000</i>	0.142 <i>0.001</i>	0.858 <i>0.001</i>
E20	610–580	450	3	67.98 <i>1.39</i>	17.24 <i>0.19</i>	0.02 <i>0.02</i>	1.09 <i>0.22</i>	0.11 <i>0.02</i>	13.88 <i>0.10</i>	100.33	0.001 <i>0.001</i>	0.012 <i>0.002</i>	0.987 <i>0.003</i>
E21	610–580	450	2	64.66 <i>0.08</i>	18.48 <i>0.06</i>		0.18 <i>0.01</i>	1.49 <i>0.03</i>	13.58 <i>0.01</i>	98.38	0.000 <i>0.000</i>	0.143 <i>0.003</i>	0.857 <i>0.003</i>
E22	610–580	450	2	65.42 <i>0.29</i>	18.62 <i>0.04</i>		0.22 <i>0.01</i>	1.49 <i>0.04</i>	13.38 <i>0.01</i>	99.13	0.000 <i>0.000</i>	0.145 <i>0.003</i>	0.855 <i>0.003</i>
E23	610–580	450	2	62.49 <i>0.28</i>	18.26 <i>0.01</i>		0.16 <i>0.03</i>	1.46 <i>0.04</i>	13.29 <i>0.02</i>	95.65	0.000 <i>0.000</i>	0.143 <i>0.004</i>	0.857 <i>0.004</i>

Notes: Standard deviations are given in italics. Blank = below detection limit.

TABLE 5. Mean muscovite compositions (wt%)

Experiment	P (MPa)	T (°C)	No. pts	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	K ₂ O	Na ₂ O	H ₂ O	F	sum	O=F	Total
Starting muscovite			8	48.73 <i>1.12</i>	0.16 <i>0.04</i>	33.50 <i>0.68</i>	2.62 <i>0.61</i>	0.06 <i>0.02</i>	0.93 <i>0.43</i>	9.42 <i>0.13</i>	0.56 <i>0.05</i>	4.41 <i>0.07</i>	0.15 <i>0.07</i>	100.54	0.06	100.48
E1	450	450	4	48.61 <i>0.63</i>	0.26 <i>0.14</i>	33.78 <i>1.29</i>	1.99 <i>0.72</i>	0.03 <i>0.01</i>	0.66 <i>0.51</i>	9.38 <i>0.12</i>	0.60 <i>0.05</i>	4.39 <i>0.01</i>	0.16 <i>0.01</i>	99.85	0.07	99.78
E2	450	450	5	49.02 <i>0.80</i>	0.11 <i>0.03</i>	32.84 <i>0.39</i>	2.66 <i>0.14</i>	0.07 <i>0.02</i>	0.99 <i>0.08</i>	9.39 <i>0.10</i>	0.50 <i>0.06</i>	4.41 <i>0.08</i>	0.14 <i>0.08</i>	100.13	0.06	100.08
E3	450	450	1	48.00 <i>0.06</i>	0.15 <i>0.01</i>	33.22 <i>0.04</i>	2.78 <i>0.04</i>		1.21 <i>0.01</i>	9.56 <i>0.05</i>	0.56 <i>0.01</i>	4.42 <i>0.05</i>	0.10 <i>0.05</i>	100.00	0.04	99.96
E4	450	450	3	48.44 <i>0.99</i>	0.14 <i>0.01</i>	33.42 <i>0.26</i>	2.66 <i>0.03</i>	0.03 <i>0.01</i>	1.16 <i>0.02</i>	9.12 <i>0.39</i>	0.62 <i>0.06</i>	4.35 <i>0.05</i>	0.20 <i>0.05</i>	100.14	0.08	100.05
E6	450	450	5	48.25 <i>0.15</i>	0.18 <i>0.03</i>	32.55 <i>0.31</i>	2.65 <i>0.03</i>	0.07 <i>0.03</i>	1.17 <i>0.03</i>	9.30 <i>0.20</i>	0.60 <i>0.11</i>	4.38 <i>0.03</i>	0.12 <i>0.03</i>	99.28	0.05	99.23
E7	450	450	2	48.48 <i>0.09</i>	0.14 <i>0.02</i>	32.93 <i>0.01</i>	2.81 <i>0.01</i>	0.09 <i>0.01</i>	1.12 <i>0.05</i>	9.44 <i>0.13</i>	0.59 <i>0.04</i>	4.38 <i>0.04</i>	0.15 <i>0.04</i>	100.11	0.06	100.04
E8	450	450	3	47.89 <i>0.58</i>	0.16 <i>0.01</i>	33.49 <i>0.62</i>	2.49 <i>0.48</i>	0.05 <i>0.01</i>	0.97 <i>0.36</i>	9.38 <i>0.12</i>	0.47 <i>0.08</i>	4.38 <i>0.06</i>	0.13 <i>0.06</i>	99.41	0.05	99.35
E9	450	450	3	48.21 <i>0.73</i>	0.12 <i>0.01</i>	33.07 <i>0.45</i>	2.58 <i>0.06</i>	0.06 <i>0.01</i>	1.05 <i>0.02</i>	9.48 <i>0.03</i>	0.57 <i>0.04</i>	3.01 <i>2.39</i>	1.49 <i>0.12</i>	99.64	0.63	99.01
E10	450	450	3	47.48 <i>1.95</i>	0.16 <i>0.01</i>	33.23 <i>0.42</i>	2.64 <i>0.03</i>	0.05 <i>0.01</i>	1.10 <i>0.03</i>	9.45 <i>0.28</i>	0.59 <i>0.06</i>	4.36 <i>0.06</i>	0.12 <i>0.06</i>	99.16	0.05	99.11
E11	450	500	4	48.82 <i>0.60</i>	0.14 <i>0.04</i>	33.92 <i>1.76</i>	1.99 <i>0.74</i>		0.67 <i>0.54</i>	9.05 <i>0.23</i>	0.58 <i>0.05</i>	4.47 <i>0.02</i>	0.08 <i>0.02</i>	99.70	0.03	99.67
E16	450	500	2	48.69 <i>0.21</i>	0.12 <i>0.01</i>	31.08 <i>0.33</i>	2.58 <i>0.01</i>		1.17 <i>0.01</i>	9.37 <i>0.11</i>	0.66 <i>0.02</i>	4.35 <i>0.04</i>	0.10 <i>0.04</i>	98.09	0.04	98.05
E17	450	500	6	48.89 <i>0.69</i>	0.16 <i>0.03</i>	32.30 <i>0.49</i>	2.79 <i>0.25</i>	0.05 <i>0.02</i>	1.04 <i>0.18</i>	9.37 <i>0.15</i>	0.52 <i>0.04</i>	4.38 <i>0.05</i>	0.14 <i>0.05</i>	99.64	0.06	99.58
E18	450	500	5	47.79 <i>0.71</i>	0.14 <i>0.05</i>	33.01 <i>0.68</i>	2.83 <i>0.29</i>	0.08 <i>0.03</i>	1.20 <i>0.10</i>	9.53 <i>0.08</i>	0.55 <i>0.14</i>	4.28 <i>0.07</i>	0.22 <i>0.03</i>	99.63	0.09	99.53
E21	610–580	450	3	48.85 <i>0.84</i>	0.09 <i>0.01</i>	32.87 <i>0.07</i>	2.73 <i>0.05</i>	0.04 <i>0.01</i>	1.20 <i>0.02</i>	9.57 <i>0.07</i>	0.60 <i>0.03</i>	4.41 <i>0.07</i>	0.13 <i>0.02</i>	100.49	0.06	100.43
E22	610–580	450	2	48.70 <i>0.70</i>	0.11 <i>0.01</i>	32.89 <i>0.61</i>	2.72 <i>0.04</i>		1.21 <i>0.01</i>	9.57 <i>0.01</i>	0.61 <i>0.04</i>	4.47 <i>0.02</i>	0.07 <i>0.02</i>	100.32	0.03	100.29

Notes: Standard deviations are given in italics. Blank = below detection limit. All analyses of Ca and Cl are below detection limit and therefore not included.

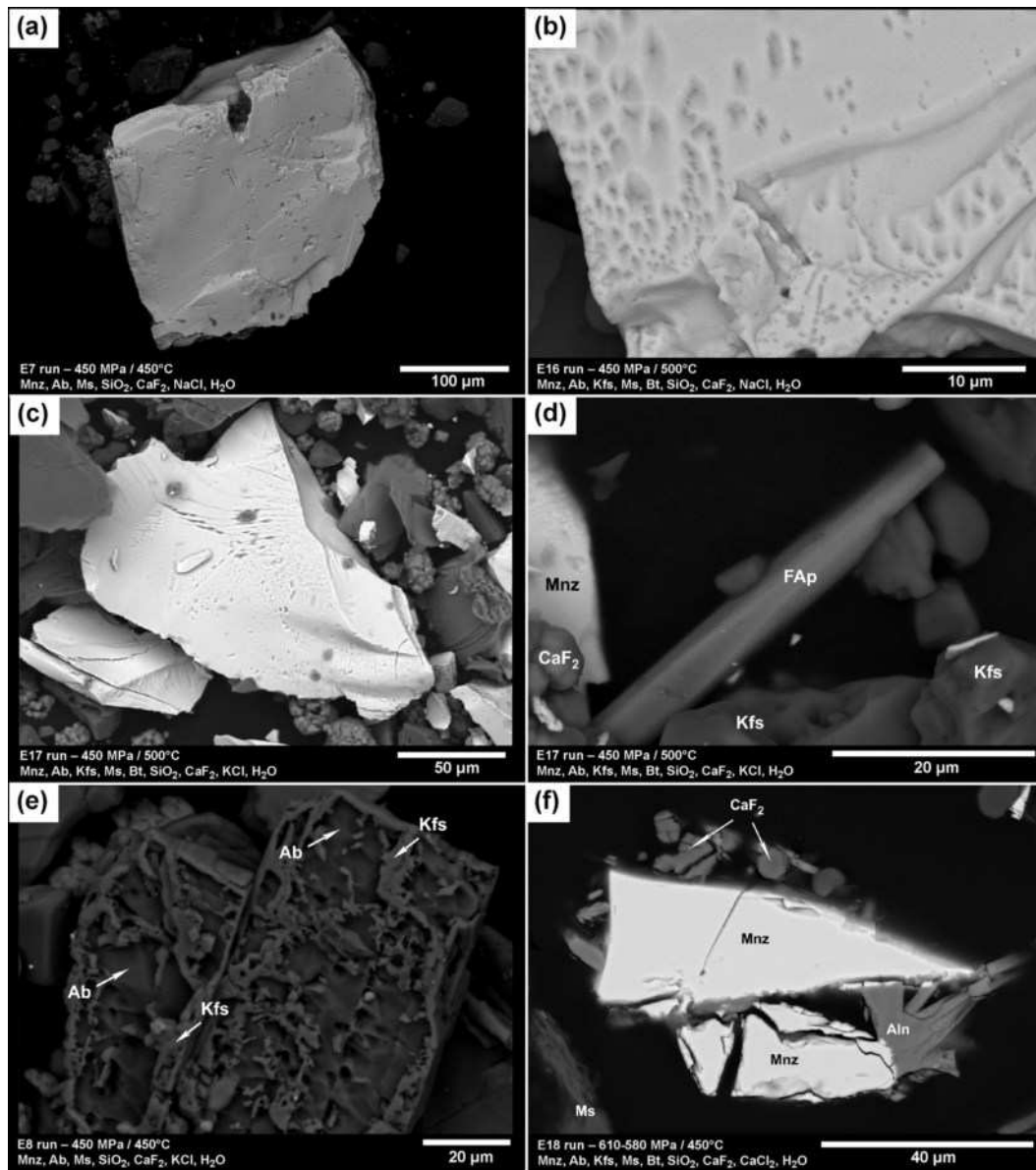


FIGURE 4. Products from experiments involving brines. (a–c) Etch pits on the monazite surface. (d) Newly formed fluorapatite grain. (e) Skeletal overgrowths of K-feldspar on albite. (f) Newly formed allanite grains overgrowing monazite.

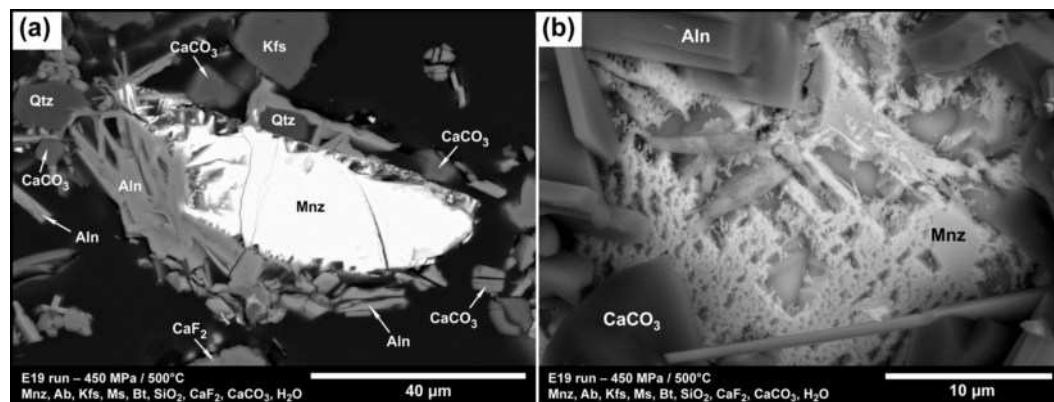


FIGURE 5. Experimental products from the run with (CaCO₃+H₂O). Monazite grains are strongly dissolved on the surface and overgrown by allanite.

TABLE 6. Mean biotite compositions (wt%)

Experiment	P (MPa)	T (°C)	No. pts	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	K ₂ O	Na ₂ O	H ₂ O	F	Cl	sum	O=F	O=Cl	Total
Starting biotite			7	37.64 <i>0.76</i>	3.75 <i>0.15</i>	18.07 <i>0.42</i>	20.40 <i>0.51</i>	0.18 <i>0.02</i>	6.83 <i>0.59</i>	8.82 <i>0.09</i>	0.16 <i>0.02</i>	3.68 <i>0.06</i>	0.28 <i>0.01</i>	0.04 <i>0.01</i>	99.86	0.12	0.01	99.73
E12	450	500	5	38.28 <i>0.78</i>	3.52 <i>0.23</i>	17.56 <i>0.23</i>	20.12 <i>0.18</i>	0.22 <i>0.02</i>	6.96 <i>0.21</i>	8.72 <i>0.16</i>	0.19 <i>0.04</i>	3.66 <i>0.06</i>	0.30 <i>0.01</i>	0.05 <i>0.01</i>	99.58	0.13	0.01	99.44
E13	450	500	10	38.90 <i>0.81</i>	3.36 <i>1.04</i>	17.19 <i>0.84</i>	20.50 <i>1.22</i>	0.23 <i>0.07</i>	7.00 <i>0.61</i>	8.38 <i>0.66</i>	0.21 <i>0.09</i>	3.64 <i>0.22</i>	0.34 <i>0.01</i>	0.04 <i>0.01</i>	99.80	0.14	0.01	99.64
E14	450	500	6	37.65 <i>0.58</i>	3.81 <i>0.06</i>	17.95 <i>0.36</i>	19.83 <i>0.73</i>	0.25 <i>0.02</i>	6.91 <i>0.19</i>	8.74 <i>0.24</i>	0.15 <i>0.01</i>	3.63 <i>0.08</i>	0.31 <i>0.01</i>	0.05 <i>0.01</i>	99.26	0.13	0.01	99.12
E16	450	500	3	37.30 <i>0.37</i>	3.85 <i>0.10</i>	17.84 <i>0.26</i>	20.53 <i>0.27</i>	0.20 <i>0.01</i>	6.92 <i>0.01</i>	8.75 <i>0.05</i>	0.17 <i>0.02</i>	3.53 <i>0.08</i>	0.41 <i>0.01</i>	0.05 <i>0.01</i>	99.55	0.17	0.01	99.36
E17	450	500	4	37.36 <i>0.43</i>	3.66 <i>0.04</i>	18.33 <i>0.08</i>	20.13 <i>0.09</i>	0.23 <i>0.01</i>	6.93 <i>0.07</i>	8.68 <i>0.03</i>	0.15 <i>0.01</i>	3.60 <i>0.02</i>	0.35 <i>0.01</i>	0.05 <i>0.01</i>	99.47	0.15	0.01	99.31
E19	450	500	4	37.71 <i>0.37</i>	3.73 <i>0.05</i>	18.07 <i>0.24</i>	20.37 <i>0.17</i>	0.21 <i>0.01</i>	6.95 <i>0.38</i>	8.68 <i>0.11</i>	0.17 <i>0.01</i>	3.75 <i>0.03</i>	0.22 <i>0.01</i>	0.05 <i>0.01</i>	99.89	0.09	0.01	99.79
E20	610–580	450	3	36.24 <i>0.77</i>	4.20 <i>0.05</i>	18.00 <i>0.05</i>	20.83 <i>0.24</i>	0.21 <i>0.01</i>	6.88 <i>0.06</i>	8.75 <i>0.09</i>	0.15 <i>0.02</i>	3.67 <i>0.03</i>	0.24 <i>0.01</i>	0.05 <i>0.01</i>	99.22	0.10	0.01	99.11
E21	610–580	450	3	36.66 <i>0.10</i>	3.96 <i>0.05</i>	17.86 <i>0.18</i>	20.99 <i>0.11</i>	0.24 <i>0.01</i>	7.06 <i>0.06</i>	8.75 <i>0.10</i>	0.17 <i>0.01</i>	3.65 <i>0.07</i>	0.28 <i>0.01</i>	0.05 <i>0.01</i>	99.67	0.12	0.01	99.54
E22	610–580	450	4	36.50 <i>1.12</i>	3.76 <i>0.10</i>	17.68 <i>0.35</i>	20.52 <i>0.46</i>	0.22 <i>0.02</i>	6.83 <i>0.22</i>	8.59 <i>0.30</i>	0.18 <i>0.01</i>	3.65 <i>0.02</i>	0.22 <i>0.01</i>	0.05 <i>0.01</i>	98.19	0.09	0.01	98.08

Notes: Standard deviations are given in italics. Blank = below detection limit. All analyses of Ca are below the detection limit and therefore not included.

TABLE 7. Mean and representative allanite and REE-epidote compositions (wt%)

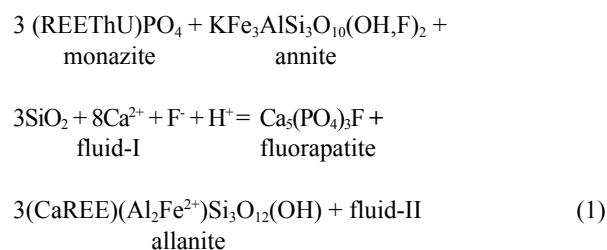
Experiment	T (°C)	No. pts	P ₂ O ₅	SiO ₂	TiO ₂	ThO ₂	Al ₂ O ₃	La ₂ O ₃	Ce ₂ O ₃	Pr ₂ O ₃	Nd ₂ O ₃	Sm ₂ O ₃	MgO	CaO	MnO	FeO	SrO	K ₂ O	F	Total	REE ₂ O ₃
P = 450 MPa																					
E4	450	3	1.23	34.83	0.10	0.55	21.76	2.08	4.41	0.46	1.69		1.08	19.70	0.02	4.40				92.32	8.64
<i>Cameca SX50</i>			<i>1.29</i>	<i>3.15</i>	<i>0.05</i>	<i>0.45</i>	<i>2.20</i>	<i>0.94</i>	<i>2.01</i>	<i>0.29</i>	<i>0.86</i>		<i>0.57</i>	<i>0.95</i>	<i>0.03</i>	<i>0.58</i>					
E4	450	2	0.64	34.73	n.a.	0.38	24.28	1.96	4.34	0.63	1.50	0.35	18.74	0.12	3.81	0.08				91.53	8.78
<i>JEOL JXA-8500F</i>			<i>0.07</i>	<i>0.83</i>		<i>0.03</i>	<i>0.70</i>	<i>0.40</i>	<i>0.67</i>	<i>0.10</i>	<i>0.06</i>	<i>0.01</i>	<i>0.19</i>		<i>0.03</i>	<i>0.21</i>	<i>0.05</i>				
E14	500	6	0.52	32.52	0.42	1.29	19.92	3.18	6.79	0.71	2.61		1.11	16.48	0.06	8.26			0.07	93.91	13.28
<i>Cameca SX50</i>			<i>0.82</i>	<i>1.53</i>	<i>0.16</i>	<i>0.70</i>	<i>1.18</i>	<i>0.82</i>	<i>1.28</i>	<i>0.22</i>	<i>0.45</i>		<i>0.32</i>	<i>0.88</i>	<i>0.04</i>	<i>0.87</i>			<i>0.11</i>		
E18	500	6	0.10	30.25	0.64	0.40	21.45	3.65	7.86	0.95	3.23		0.35	14.39	0.08	8.61		0.08	0.10	92.12	15.69
<i>Cameca SX50</i>			<i>0.02</i>	<i>0.98</i>	<i>0.26</i>	<i>0.18</i>	<i>0.51</i>	<i>0.13</i>	<i>0.31</i>	<i>0.13</i>	<i>0.22</i>		<i>0.07</i>	<i>0.31</i>	<i>0.01</i>	<i>0.28</i>		<i>0.04</i>	<i>0.08</i>		
E19	500	3	0.05	32.01	0.32	0.68	22.60	3.70	8.16	0.87	3.21		1.82	14.75		5.17			0.23	93.57	15.94
<i>Cameca SX50</i>			<i>0.01</i>	<i>1.02</i>	<i>0.13</i>	<i>0.09</i>	<i>1.80</i>	<i>0.49</i>	<i>0.64</i>	<i>0.17</i>	<i>0.14</i>		<i>0.24</i>	<i>1.10</i>		<i>0.36</i>			<i>0.09</i>		
E19	450	3	0.12	35.24		0.42	21.93	2.79	5.19	0.86	1.87		11.17		0.14	6.32	0.09	0.05		86.18	10.72
<i>Cameca SX50</i>			<i>0.05</i>	<i>0.51</i>		<i>0.08</i>	<i>0.42</i>	<i>0.25</i>	<i>0.51</i>	<i>0.19</i>	<i>0.30</i>		<i>0.37</i>		<i>0.02</i>	<i>0.48</i>	<i>0.05</i>	<i>0.07</i>			
P = 610–580 MPa																					
E22	450	6	0.31	31.94	0.75	0.89	18.79	3.36	7.30	0.84	2.77		0.92	16.30	0.10	9.42			0.43	94.11	14.27
<i>Cameca SX50</i>			<i>0.25</i>	<i>1.45</i>	<i>0.18</i>	<i>0.14</i>	<i>0.56</i>	<i>0.28</i>	<i>0.44</i>	<i>0.11</i>	<i>0.25</i>		<i>0.18</i>	<i>0.67</i>	<i>0.02</i>	<i>0.90</i>			<i>0.22</i>		

Notes: Standard deviations are given in italics. Blank = below detection limit. All analyses of U, As, Y, Eu, Gd, Er, Tb, Dy, Ho, Tm, Yb, Lu, Na, and Cl are below the detection limit and therefore not included.

Hetherington et al. 2010). Previous results from simple monazite-fluid experiments showed that the 1 M HCl may cause partial dissolution and rounding of monazite with reprecipitation of very small monazite grains with the same composition at 500 MPa and 600 °C and 1000 MPa and 900 °C (Hetherington et al. 2010). In our study, monazite, accompanied by muscovite, albite, and SiO₂, behaves in a similar way in the presence of 1 M HCl exhibiting some partial dissolution and no formation of new phases. Similarly, while there was some dissolution of monazite in most of the brine experiments (NaCl + H₂O, KCl + H₂O, CaCl₂ + H₂O), no reaction to other minerals occurred. Although monazite dissolution tends to increase with increasing P-T conditions (cf. Ayers and Watson 1991; Hetherington et al. 2010), the presence of NaCl + H₂O seems to be effective in stabilizing monazite. The KCl + H₂O experiment at 450 MPa and 450 °C (run E8; Mnz+Ab+Ms+SiO₂+CaF₂+KCl+H₂O) gave a similar result, whereas at 500 °C and the same pressure (run E17; Mnz+Ab+Kfs+Ms+Bt+SiO₂+CaF₂+KCl+H₂O) a small amount of fluorapatite formed (Fig. 4d). Because no other new phases are present, REE released from partially dissolved monazite presumably went into solution.

Experiments involving CaCl₂ + H₂O gave several results. In run E9 (450 MPa, 450 °C; Mnz+Ab+Ms+SiO₂+CaF₂+CaCl₂+H₂O), monazite showed no alteration compared to run E1 (450

MPa, 450 °C; Mnz+Ab+Ms+SiO₂+CaF₂+H₂O) where REE-epidote did form (Fig. 2). Increasing the temperature to 500 °C for the same pressure and CaCl₂ + H₂O fluid (E18; Mnz+Ab+Ms+SiO₂+CaF₂+CaCl₂+H₂O) promoted the formation of fluorapatite and allanite probably due to reactions such as (Broska and Siman 1998):



The experimental products from the CaCO₃ runs at 450 MPa, E10 at 450 °C (Mnz+Ab+Ms+SiO₂+CaF₂+CaCO₃+H₂O) and E19 at 500 °C (Mnz+Ab+Kfs+Ms+Bt+SiO₂+CaF₂+CaCO₃+H₂O), i.e., fluorapatite and REE-epidote or allanite (Fig. 5) are interpreted to also have formed according to reaction 1. In general, these results indicate that (in the presence of F) high Ca activity in the system destabilizes monazite and promotes the formation of fluorapatite and REE-epidote or allanite.

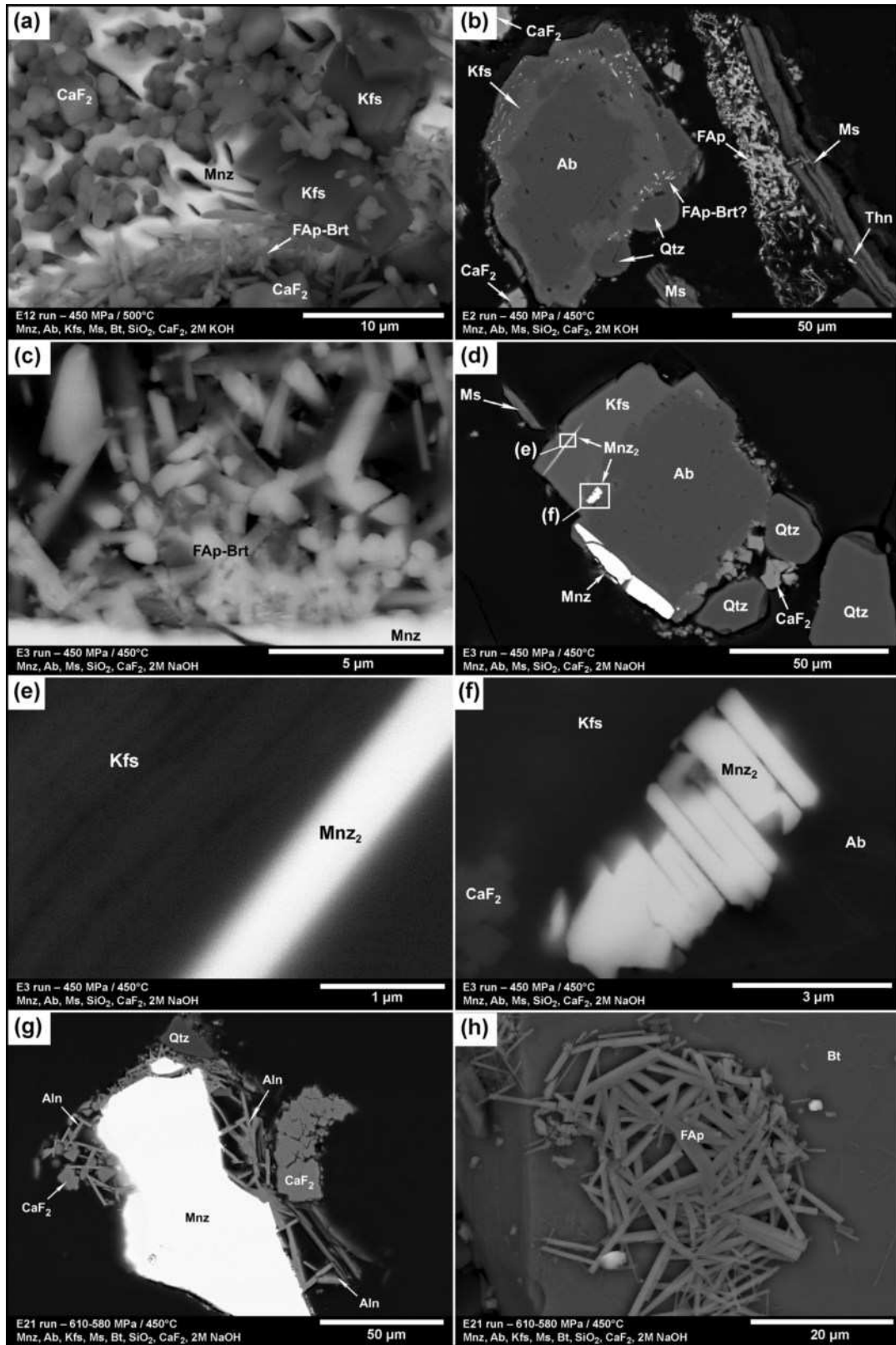


FIGURE 6. Experimental products from runs with hydroxides. **(a)** The newly formed fluorapatite-britholite present on the strongly dissolved monazite surface. **(b)** Fluorapatite-britholite inclusions in a newly formed K-feldspar overgrowth on albite, and thorionite and apatite grains. **(c)** Newly formed fluorapatite-britholite grains on monazite. **(d–f)** Albite with a K-feldspar rim overgrowth and secondary monazite inclusions. **(g)** Allanite grains overgrowing monazite. **(h)** Newly formed fluorapatite grains.

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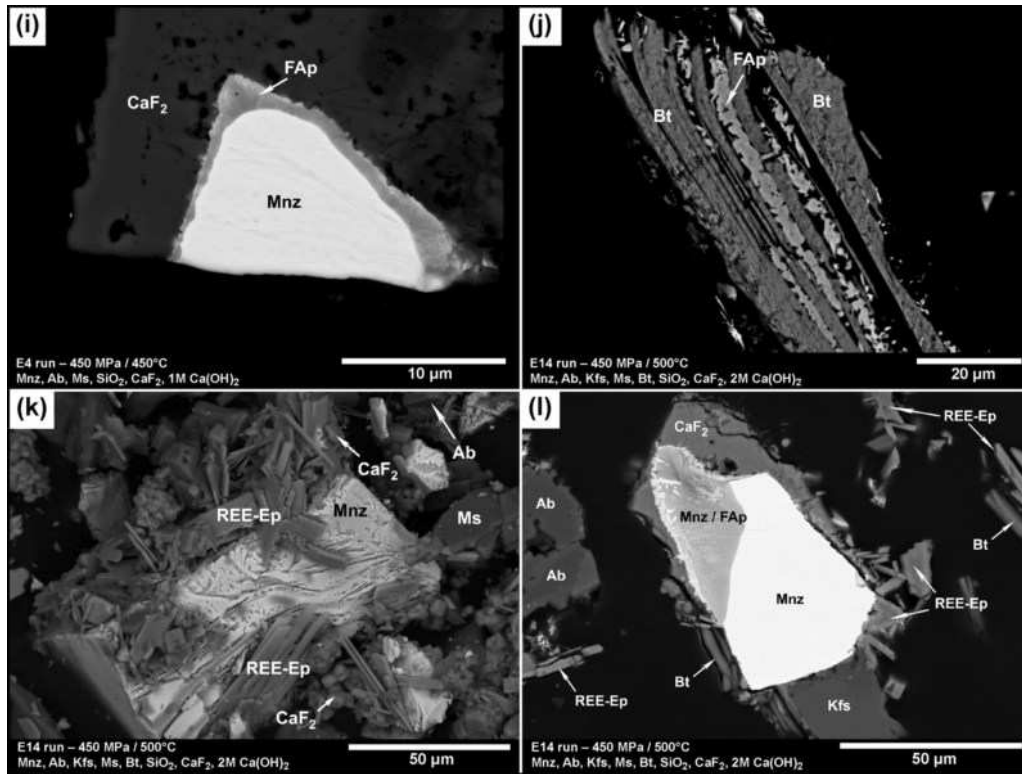


FIGURE 6.—*CONTINUED* (i, l) Monazite grain partially replaced and or overgrown by fluorapatite. (j) Newly formed fluorapatite within biotite cleavage plains. (k) Strongly dissolved monazite grain overgrown by REE-epidote.

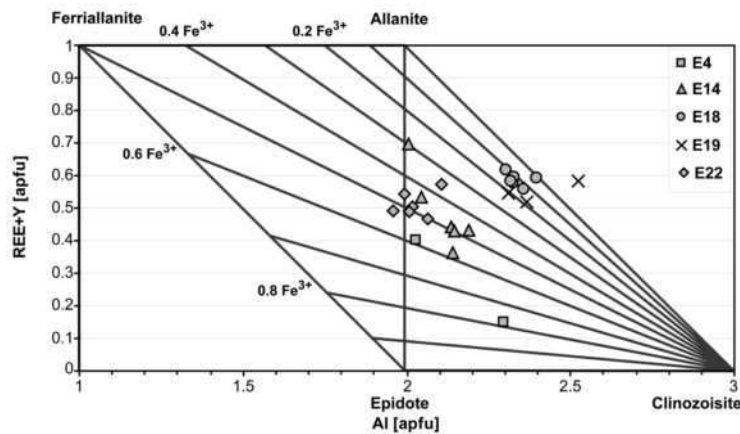


FIGURE 7. Al vs. REE+Y diagram after Petrik et al. (1995) reflecting compositional distribution of the epidote group minerals formed during the experiments.

Experiments involving alkali-bearing fluids were highly reactive, which is consistent with previous experimental work involving monazite and alkali-bearing fluids (e.g., Oelkers and Poirasson 2002; Hetherington et al. 2010; Harlov and Hetherington 2010; Harlov et al. 2011). In the majority of the experiments, monazite dissolution occurred accompanied by the formation of new minerals (Fig. 1). For example, REE-enriched fluorapatite formed in the presence of 2 M KOH at 450 °C and 450 and 610 MPa (Fig. 6b; E2 Mnz+Ab+Ms+SiO₂+CaF₂+2 M KOH; E20 Mnz+Ab+Kfs+Ms+Bt+SiO₂+CaF₂+2 M KOH) or 500 °C and 450 MPa (Figs. 8c–8d, 8f; E15; Mnz+Ab+Kfs+Ms+Bt+SiO₂+CaF₂+Na₂Si₂O₅+H₂O) indicating that REE released from the monazite were incorporated into the fluorapatite structure according to the coupled substitution reactions (Pan and Fleet 2002):

CaF₂+Na₂Si₂O₅+H₂O) indicating that REE released from the monazite were incorporated into the fluorapatite structure according to the coupled substitution reactions (Pan and Fleet 2002):



Fluorapatite-britholite primarily grew directly on the surface of the monazite grains (Fig. 6a; E2, E12, and E20 runs; Table 8) most likely via the reaction proposed by Gieré and Sorensen (2004):

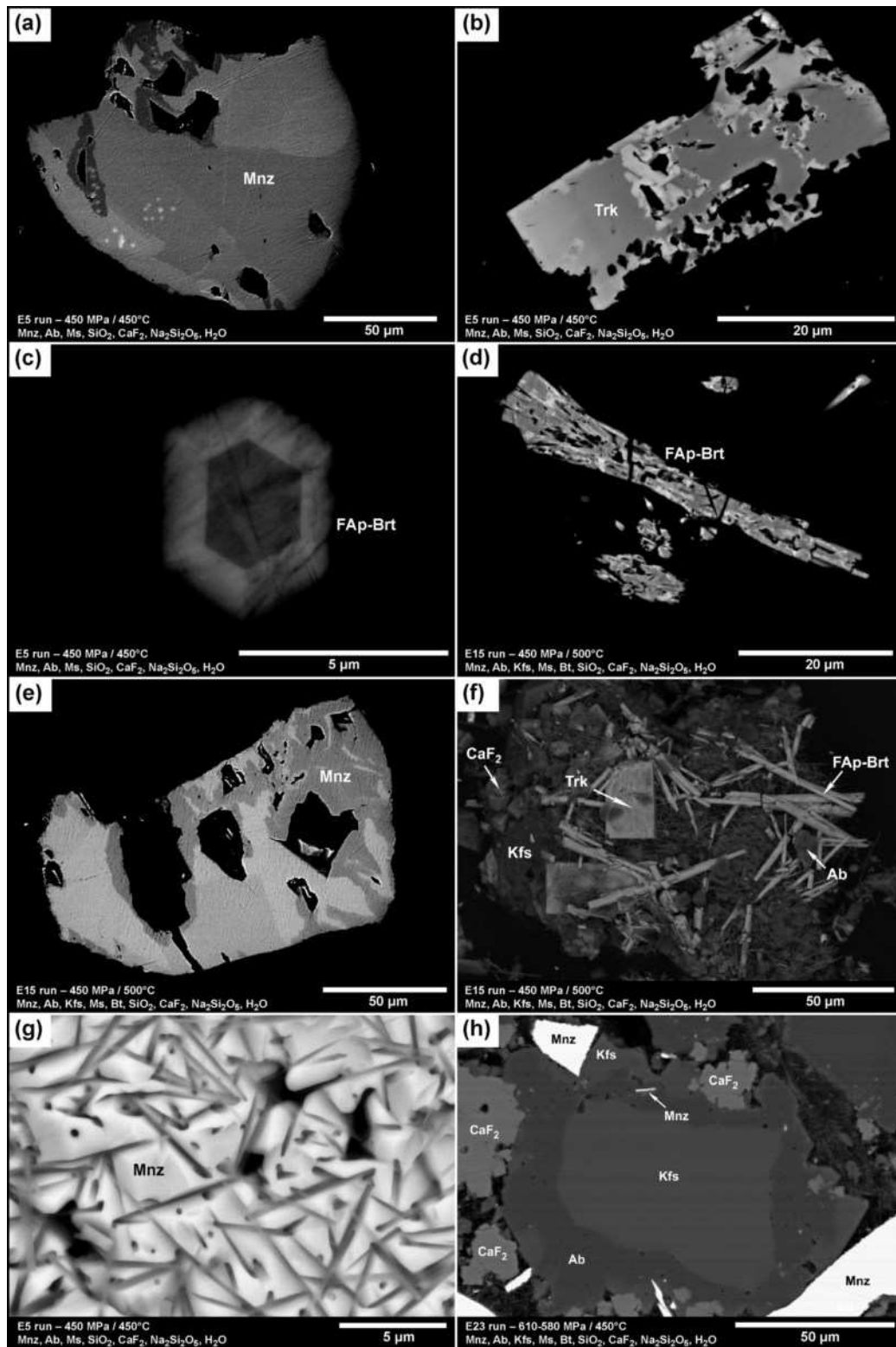


FIGURE 8. Experimental products from runs with $(\text{Na}_2\text{Si}_2\text{O}_5 + \text{H}_2\text{O})$. **(a, e)** High-contrast images of reacted monazite showing internal inhomogeneity related to coupled dissolution-precipitation. Bright areas represent the original monazite compositions (bright compositional domains = BCD). Dark regions are depleted in Th (dark compositional domains = DCD). **(b)** The newly formed turkestanite reflecting sharply delineated zones. **(c–d)** The zoned fluorapatite-britholite formed during experiments. **(f)** The prismatic turkestanite and fluorapatite-britholite grains. **(g)** The monazite grain surface with indentations related to the growth of new minerals, which are present as aggregates of needle-like crystals in the products. **(h)** Partial albitization of K-feldspar.

TABLE 8. Representative fluorapatite and fluorapatite-britholite compositions (wt%)

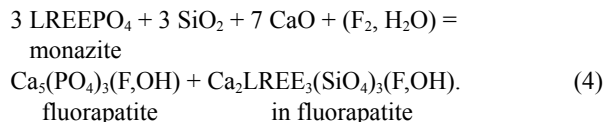
Experiment	P (MPa)	T (°C)	P ₂ O ₅	SiO ₂	ThO ₂	UO ₂	Al ₂ O ₃	Y ₂ O ₃	La ₂ O ₃	Ce ₂ O ₃	Pr ₂ O ₃	Nd ₂ O ₃	Sm ₂ O ₃	Gd ₂ O ₃	Dy ₂ O ₃	FeO	CaO	SrO	Na ₂ O
E2	450	450	31.01	5.29	2.16	0.27		0.37	1.31	3.49	0.49	1.73	0.45				45.06		4.28
E5	450	450	28.68	4.07	0.28			0.31	6.64	15.10	2.09	6.80	0.71	1.07			29.53		1.49
E5	450	450	27.66	3.79	0.32			0.27	5.65	15.10	2.16	7.65	1.04	1.88			28.29		2.51
E5	450	450	23.78	6.42	0.50			0.31	7.43	17.45	2.27	8.05	1.27	1.63	0.43		23.41		3.02
E5	450	450	23.63	6.36	0.37			0.24	7.87	18.23	2.34	7.95	1.07	1.35	0.34		23.94		2.89
E14	450	500	25.73	0.47	6.90			0.37	2.70	18.50	1.01	3.97	0.56				35.11		1.11
E14	450	500	24.49	0.43	7.48	0.48		0.22	3.62	18.52	0.94	4.70	0.50				33.35		1.09
E14	450	500	26.10	0.55	7.68	0.41		0.24	3.12	19.55	0.97	4.29	0.67				32.22		0.51
E14	450	500	35.62	3.16				0.15	0.82	1.71							52.50		1.99
E14	450	500	35.32	2.88				0.16	0.64	1.31							53.00		2.49
E14	450	500	33.61	3.69				0.18	1.03	2.30							52.05		2.52
E15	450	500	28.58	5.31	0.25			1.17	5.13	14.36	1.89	8.40	1.66	1.85	0.54	0.54	24.39	0.20	2.01
E15	450	500	26.49	5.35	0.19			1.34	4.57	14.96	2.06	9.24	1.85	2.06	0.63	0.20	24.84		2.98
E15	450	500	23.94	7.34	0.17		0.22	0.61	6.35	17.37	2.27	9.15	1.97	1.28	0.29		22.70		2.75
E19	450	500	31.54	3.32	0.24			0.24	1.42	3.13	0.28	1.14				0.10	52.77		2.02
Standard deviation			0.10	0.02	0.05	0.04		0.03	0.07	0.10	0.08	0.07	0.08	0.20	0.04	0.01	0.09	0.02	0.04

Notes: Blank = below detection limit; n.a. = not analyzed. Results for Eu, Tb, Ho, Tm, Er, Yb, Lu, Mn, S, and Cl are below the detection limit and are not included.

TABLE 9. Mean and representative turkestanite compositions (wt%)

Experiment	T (°C)	No. pts	SiO ₂	TiO ₂	ThO ₂	UO ₂	Al ₂ O ₃	Y ₂ O ₃	Ce ₂ O ₃	Nd ₂ O ₃	Sm ₂ O ₃	Gd ₂ O ₃	Dy ₂ O ₃	CaO	FeO	SrO	Na ₂ O	K ₂ O	Total
P = 450 MPa																			
E5	450	11	53.90		17.73	1.02	0.04	1.00	0.47	1.74	1.89	0.68	0.86	0.32	8.43		2.89	4.35	95.34
<i>Cameca SX50</i>			<i>1.32</i>		<i>2.35</i>	<i>0.18</i>	<i>0.01</i>	<i>0.26</i>	<i>0.26</i>	<i>0.92</i>	<i>0.63</i>	<i>0.13</i>	<i>0.32</i>	<i>0.11</i>	<i>0.67</i>		<i>0.41</i>	<i>0.27</i>	
E15	500	6	53.88	0.08	20.70	1.48	0.05	0.68	0.42	1.47	1.09	0.32	0.51	0.20	7.48	0.42	3.26	3.90	95.91
<i>Cameca SX50</i>			<i>0.66</i>	<i>0.13</i>	<i>2.54</i>	<i>0.26</i>	<i>0.02</i>	<i>0.10</i>	<i>0.32</i>	<i>0.96</i>	<i>0.50</i>	<i>0.07</i>	<i>0.22</i>	<i>0.09</i>	<i>0.62</i>	<i>0.82</i>	<i>0.26</i>	<i>0.15</i>	
P = 610–580 MPa																			
E23	450	2	52.91	n.a.	19.30	2.47	0.56	0.29	0.33	1.22	0.71	0.30	0.39		7.35	0.44	0.17	4.28	95.90
<i>JEOL JXA-8500F</i>			<i>1.45</i>		<i>2.33</i>	<i>0.04</i>	<i>0.37</i>	<i>0.10</i>	<i>0.21</i>	<i>0.55</i>	<i>0.49</i>	<i>0.02</i>	<i>0.05</i>		<i>0.10</i>	<i>0.22</i>	<i>0.01</i>	<i>0.23</i>	<i>0.06</i>

Notes: Standard deviations are given in italics. Blank = below detection limit. n.a. = not analyzed. Results for P, As, Pr, Eu, Tb, Ho, Er, Tm, Yb, Mg, Mn, S, F, and Cl are below the detection limit and are not included.



In addition, fluorapatite-britholite also occurred as inclusions within overgrowths of K-feldspar on albite from run E2 (450 °C, 450 MPa; Fig. 6b).

The very thin monazite inclusion in the K-feldspar overgrowth on albite (Figs. 6d and 6e) from run E3 at 450 °C and 450 MPa with 2 M NaOH fluid (Mnz+Ab+Ms+SiO₂+CaF₂+2 M NaOH) indicates that the monazite precipitated from the fluid during growth of the K-feldspar. The textural position of the monazite inclusions located at the K-feldspar-albite interface in Figures 6d and 6f and oriented parallel to the albite cleavage suggest simultaneous growth with, or shortly before, K-feldspar and consequently a secondary origin. Overgrowth of albite by K-feldspar indicates the breakdown of the muscovite, which was the only source of K. At a higher pressure of 610–580 MPa and 450 °C, allanite growth (Fig. 6g; E21 Mnz+Ab+Kfs+Ms+Bt+SiO₂+CaF₂+2 M NaOH) was presumably at the expense of monazite, muscovite, and/or biotite. The fluorapatite and allanite are interpreted to have formed according to reaction 1. Some of the released monazite components, including Th, U, and REE, appear to have been mobilized in the fluid and not incorporated into any mineral.

The presence of 1 and 2 M Ca(OH)₂ also promoted the strong dissolution of monazite and subsequent growth of fluorapatite and REE-epidote or allanite (Figs. 6i–6l). Compared to run E4 at 450 MPa and 450 °C [Mnz+Ab+Ms+SiO₂+CaF₂+1 M Ca(OH)₂], an increase either in pressure to 610–580 MPa

at 450 °C [E22 Mnz+Ab+Kfs+Ms+Bt+SiO₂+CaF₂+2 M Ca(OH)₂] or in temperature to 500 °C at 450 MPa [E14 Mnz+Ab+Kfs+Ms+Bt+SiO₂+CaF₂+2 M Ca(OH)₂] increased the substitution of REE in the epidote (Table 7) probably via the coupled substitution reactions (Gieré and Sorensen 2004):



and



Run E22 contained the highest amount of biotite (5 mg) compared to 2 mg in E14 and no biotite in E4. The presence of biotite as the principal source of Fe promoted coupled substitution reactions 5 and 6, which could explain the fact that REE-epidote/allanite in E22 contains the highest amount of REE.

The greatest extent of monazite alteration was achieved when the fluid consisted of (Na₂Si₂O₅ + H₂O). This alteration consisted of Th-, U-, and Pb-depleted patches with sharp compositional boundaries in the monazite (Figs. 8a and 8e). Internal textures such as these are interpreted to be the result of compositional alteration driven by fluid-mediated coupled dissolution-reprecipitation (cf. Putnis 2002, 2009; Harlov et al. 2003, 2005, 2007, 2011; Hetherington and Harlov 2008; Harlov and Hetherington 2010). Coupled dissolution-reprecipitation is characterized by a pervasive fluid-filled porosity in the altered regions coupled with a sharp compositional boundary between the altered and original mineral (Putnis 2002, 2009). The formation of these patches, and their specific composition, depends on the fluid chemistry and surrounding mineral chemistry and is related to the redistribution of the cheralite [CaTh(PO₄)₂] and huttonite (ThSiO₄) components. These textures, either enriched

TABLE 8.—EXTENDED

Experiment	F	H ₂ O	sum	O=(F+Cl)	total	(Y+REE) ₂ O ₃
E2	4.98	1.20	102.09	2.10	99.99	7.84
E5	4.13	1.21	102.11	1.74	100.37	32.72
E5	3.93	1.24	101.49	1.65	99.84	33.75
E5	3.91	1.13	101.01	1.65	99.36	38.84
E5	4.01	1.09	101.68	1.69	99.99	39.39
E14	5.18	0.56	102.17	2.18	99.99	27.11
E14	6.63	0.00	102.45	2.79	99.66	28.50
E14	2.67	1.63	100.61	1.12	99.49	28.84
E14	6.34	0.79	103.56	2.67	100.89	3.16
E14	6.42	0.74	103.15	2.70	100.45	2.30
E14	6.37	0.71	103.13	2.68	100.45	4.18
E15	3.71	1.37	101.36	1.56	99.80	35.00
E15	3.91	1.23	101.90	1.65	100.25	36.71
E15	3.43	1.36	101.20	1.45	99.75	39.28
E19	4.82	1.30	102.32	2.03	100.29	6.21
Standard deviation	0.18					

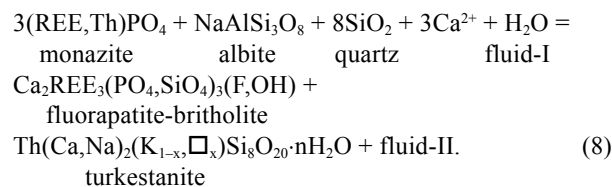
or depleted in Th+U+Si+Ca, have been reported extensively in various metamorphic and igneous rocks (e.g., Watt and Harley 1993; Watt 1995; Bingen and van Breemen 1998; Förster and Harlov 1999; Hawkins and Bowring 1999; Terry et al. 2000; Harlov and Förster 2002; Spear and Pyle 2002; Goncalves et al. 2005; Kelly et al. 2006; Kohn et al. 2005; Mahan et al. 2006; Finger and Krenn 2007; Hansen and Harlov 2007) as well as in monazite that has experienced late- to post-magmatic hydrothermal alteration (e.g., Poitrasson et al. 1996; Townsend et al. 2000; Petrik et al. 2006; Petrik and Konečný 2009).

In experiments E5 and E15, the altered patches in the monazite are depleted in Th, Y, and Ca and enriched in Ce and La compared to the unaltered areas in the monazite (Table 2; Fig. 9) via the coupled substitution reaction (Förster 1998; Linthout 2007):



The remaining Th in the altered monazite areas takes the form of the huttonite component (Fig. 9). Simultaneously, U has been also mobilized and removed from the altered areas. The presence of Ni metal spacing rods in the autoclave buffered the experiments to Ni-NiO oxidizing conditions and may have been responsible for the mobilization of U as U (VI) (cf. Shock et al. 1997). Furthermore, the presence of CaF₂ probably also helped to promote the mobilization of both U and Th (cf. Keppler and Wyllie 1990).

The monazite-fluid experiments with (Na₂Si₂O₅ + H₂O) at 900 °C and 1000 MPa, from the study of Harlov et al. (2011) showed that monazite incorporates Th in preference to the (Y+REE), which remain in the fluid. The altered areas also retain the original USiO₄ component. In contrast, the monazite in experiments in this study releases Th in preference to the REEs (Fig. 9). This implies that in addition to the *P-T* conditions and oxidation state, mobilization of actinides and (Y+REE) depends on the local mineral and/or fluid chemistry. In experiments E5, E15, and E23, the mobilized Th was incorporated mostly by turkestanite (Table 9), a rare Th-bearing mineral known only from several alkali-rich localities (Kabalov et al. 1998; Petersen et al. 1999; Pautov et al. 1997, 2004). The (Y+REE) released from monazite were incorporated into the fluorapatite-britholite via reactions such as:



The formation of turkestanite corresponds to natural observations, where the high-Th minerals crystallize under extremely alkali-rich hydrothermal conditions and temperatures not lower than 350 to 400 °C (Ermolaeva et al. 2007). Furthermore, a decrease in the alkali-activity may result in a decrease in the Th activity (Ermolaeva et al. 2007). This is consistent with observations from other experiments in this study. Thorium-rich phases did not form nor was the monazite composition altered in the experiments except when the fluid was Na₂Si₂O₅ + H₂O (experiments E5, E15, and E23).

Implications for geochronology

During the last two decades, Th-U-Pb dating of monazite by EMP has gained wide acceptance (Suzuki and Adachi 1991, 1994; Montel et al. 1996; Konečný et al. 2004; Jercinovic and Williams 2005; Pyle et al. 2005; Suzuki and Kato 2008; Jercinovic et al. 2008; Spear et al. 2009). This dating technique is based on the assumption that the newly formed monazite contains negligible amounts of common Pb relative to radiogenic Pb such that all of the measured Pb is assumed to be the result of radiogenic decay from Th and U (Parrish 1990; Williams et al. 2007). The extremely slow volume diffusion rate of Th and Pb at 800 to 900 °C implies that the monazite Th-U-Pb system is closed over geologic time scales even at high-grade conditions (Cherniak et al. 2004; Gardes et al. 2006; Cherniak and Pyle 2008).

However, in nature, diagenesis (e.g., Cuney and Mathieu 2000), hydrothermal alteration (e.g., Poitrasson et al. 1996, 2000; Hecht and Cuney 2000), and weathering processes (Read et al. 2002; Berger et al. 2008) can cause remobilization of U, Th, Pb, and REE in monazite. In particular, fluid driven coupled dissolution-reprecipitation has been demonstrated as a process that can dramatically alter the Th-U-Pb system in monazite during metamorphism (e.g., Teufel and Heinrich 1997; Seydoux-Guillaume 2002a; Harlov et al. 2007, 2011; Catlos et al. 2010; Harlov and Hetherington 2010; Hetherington et al. 2010; Williams et al. 2011). In addition, isotopic analysis has shown that the interaction of monazite with fluids can lead to a significant disturbance in the U-Pb system resulting in age discordance (Bosch et al. 2002; Corfu and Evins 2002; Seydoux-Guillaume et al. 2003; Yi and Cho 2009).

In experiments E5 and E15, the altered areas are depleted in Th and depleted in Pb to below the EMP detection limit (Table 2). These areas represent a complete resetting of the monazite geochronometer due to the action of fluids via coupled dissolution-reprecipitation (cf. Williams et al. 2011). This has far-reaching implications with respect to dating. Presuming that Th-depleted textures in natural monazite are due to fluid-induced alteration, the total removal of Pb during alteration would reset the Th-U-Pb clock so that these textures could be used to date metasomatic events over the geologic history of the monazite grain and potentially the host rock itself.

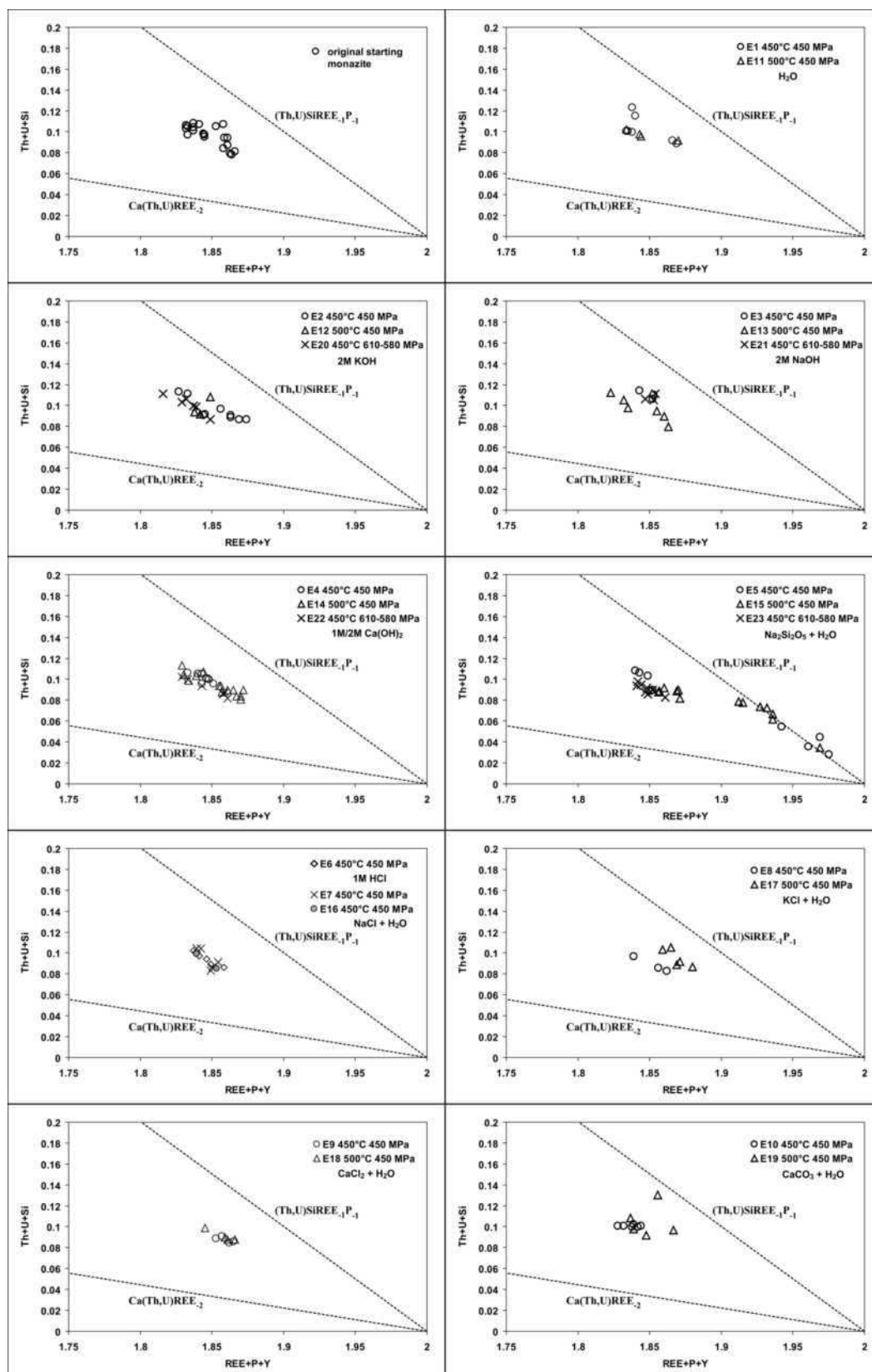


FIGURE 9. Plots of formula proportions (REE + Y + P) vs. (Th + U + Si) calculated on the basis of four O atoms for the original starting monazite and product monazite. Dashed lines represent the huttonitic substitution $(Th,U)SiREE_{1.1}P_{.1}$ and cheralitic substitution $Ca(Th,U)REE_2$ (Förster 1998; Linthout 2007). The plots show significant compositional modifications resulting from the dissolution-reprecipitation driven alteration of monazite from the E5 and E15 runs with $Na_2Si_2O_5 + H_2O$ comparing to all other runs where monazite internal composition was not altered.

Implications for the natural occurrence of the monazite-fluorapatite-allanite-REE-epidote assemblage

The results from these experiments support the premise that, at mid-crustal *P-T* conditions, alkali- and alkaline-bearing fluids were responsible for the alteration of monazite in gneiss clasts from the Western Outer Carpathian flysch (Budzyń 2009; Budzyń et al. 2010) to (texture 1) fluorapatite with thorianite inclusions + secondary monazite and (texture 2) fluorapatite with thorianite inclusions + REE epidote or allanite. Because monazite is present both as a reactant and a product in texture 1, the reaction had to be controlled by changing the chemical conditions after the fluorapatite formed, i.e., dissolution of primary monazite followed by reprecipitation of secondary monazite. The experiments from this study have demonstrated that conversion of monazite to fluorapatite occurs in the presence of alkali- and alkaline-bearing fluids, such as $\text{Na}_2\text{Si}_2\text{O}_5 + \text{H}_2\text{O}$, NaOH, KOH, and $\text{Ca}(\text{OH})_2$. In the gneiss clasts, the predominant source of P, Ca, and F for fluorapatite formation comes from the monazite, the anorthite component in plagioclase, and the biotite, respectively (cf. Broska and Siman 1998; Finger et al. 1998; Broska et al. 2005). The undersaturation of the fluid in Ca^{2+} ions, due to the crystallization of the fluorapatite, and possible oversaturation in Na^+ , released from plagioclase, resulted in changing the original chemical conditions to those that promoted precipitation of secondary monazite from a fluid oversaturated in REE^{3+} and PO_4^{3-} . Such a scenario is supported by the experiment with NaOH (E3, $\text{Mnz} + \text{Ab} + \text{Ms} + \text{SiO}_2 + \text{CaF}_2 + 2 \text{M NaOH}$) where secondary monazite formed at 450 MPa and 450 °C, similar to the estimated 400 to 550 °C for secondary monazite formation in the gneiss clasts. The alkali-bearing fluid and oxidizing conditions due to the Ni-NiO buffer also promoted thorianite formation in experiment E3, suggesting that the precipitated secondary thorianite in the gneisses was stabilized under relatively oxidizing conditions. Texture 1, with secondary monazite, is the most common in these gneisses, whereas texture 2, with secondary epidote or allanite, is relatively rare. This suggests that a localized increase in the Ca content (on the scale of several 100 to 1000 μm), probably promoted local epidote or allanite formation. The increased Ca concentration had a source either in the fluid or possibly from the anorthite component in the plagioclase (cf. Broska and Siman 1998).

Another example of monazite alteration in mid-crustal rocks involves coronas of secondary fluorapatite, allanite, and epidote formed during monazite-fluid interactions, e.g., in the amphibolite-facies granite gneiss from the Tauern Window (500–600 °C and 400–700 MPa; Finger et al. 1998) or migmatite and metagranite from the Tatra Mountains (500–600 °C and 800–1000 MPa; Broska and Siman 1998). The elements necessary for monazite breakdown and subsequent formation of allanite are released mainly from biotite and the anorthite component in plagioclase (Broska and Siman 1998; Finger et al. 1998). In this study, the approximated granitoid mineral assemblage used in the experiments confirms that high Ca activity can promote allanite and/or fluorapatite formation at pressure conditions as low as 450 MPa and temperatures of 450 °C (E1, E4, E10) or 500 °C (E11, E14, E19). Furthermore, the fluorapatite is characterized by a high REE content, which increases with increasing pressure from 450 to 500 MPa.

The significance of Ca activity for the relative stability of monazite, allanite, and fluorapatite documented in this study has been previously described in granitic rocks (Lee and Dodge 1964; Lee and Bastron 1967; Bea 1996; Broska et al. 2000; Claesson 2002) as well as in metapelites where the $\text{CaO}/\text{Na}_2\text{O}$ ratio is one of the factors controlling the stability of monazite relative to allanite (Janots et al. 2008, 2009). In Alpine metasediments, monazite has been observed to break down to allanite or epidote at the chloritoid isograd (440–450 °C) followed by the replacement of allanite by monazite above 556 °C for bulk rock $\text{CaO}/\text{Na}_2\text{O} < 0.54$, although allanite can be preserved up to 610 °C for $\text{CaO}/\text{Na}_2\text{O} > 0.93$ (Janots et al. 2008). Similarly in Barrovian-type sediments from central Korea, allanite has been reported in the garnet and staurolite zones, whereas monazite occurs in the kyanite zone (Kim et al. 2009). Monazite breakdown and allanite formation during progressive metamorphism has been documented at the biotite isograd (500–525 °C) in metapelites with average or above average Ca contents (Smith and Barreiro 1990; Wing et al. 2003). In contrast, monazite replaces allanite in the presence of either andalusite or kyanite, or in rocks containing staurolite or cordierite (Wing et al. 2003). Recent thermodynamic evaluation of the MnNCKFMASHPCe system, utilizing end-member mineral thermochemical data, imply that the allanite to monazite transition occurs at 400 to 550 °C at 200 to 1000 MPa in metapelites with 2.17 wt% of CaO (Spear 2010). However, doubling the Ca content to 4.34 wt% CaO increases the stability field of allanite relative to monazite such that the allanite to monazite transition now ranges from 500 to 750 °C at 200 to 1000 MPa (Spear 2010).

Monazite growth during amphibolite facies metamorphism has been assigned to the simultaneous breakdown of garnet and subsequent formation of staurolite (Kohn and Malloy 2004; Fitzsimons et al. 2005). In contrast, allanite replacement by monazite in pelites from the Nelson contact aureole (southern British Columbia) occurs close to, but below, the cordierite-in, andalusite-in, and staurolite-in isograds. Here the reactions involving andalusite, cordierite, staurolite, and/or garnet apparently did not directly promote the formation of monazite (Tomkins and Pattison 2007). Although some studies have indicated that both Ca and Al affect monazite and allanite stability in metapelites (Foster and Parrish 2003; Wing et al. 2003; Krenn and Finger 2007), preservation of monazite under upper greenschist to lower amphibolite facies conditions seems to be not simply a matter of the Ca/Al ratio (Janots et al. 2008). For example, sandstones metamorphosed under greenschist facies conditions (ca. 350 °C) contain different products from monazite alteration depending on the Ca bulk content (Rasmussen and Muhling 2009). In sandstones with moderate to high Ca bulk compositions, detrital allanite is preserved, whereas detrital monazite is replaced by secondary allanite, fluorapatite, and ThSiO_4 (Rasmussen and Muhling 2009). Moreover, low- to medium-grade metamorphism can induce the formation of rhabdophane (Nagy et al. 2002) or allanite (Krenn and Finger 2007) replacing monazite though the extent of the rhabdophane stability field remains a matter of a discussion.

The experimental results from this study support natural observations that the relationship between monazite and allanite/epidote depends on both the Ca and Na content. All of the

experiments are characterized by a relatively high Ca activity due to the presence of CaF_2 . In experiments with 1 and 2 M $\text{Ca}(\text{OH})_2$ (E4, 450 MPa, 450 °C; E14, 450 MPa, 500 °C; E22, 610–580 MPa, 450 °C), $\text{CaCl}_2 + \text{H}_2\text{O}$ (E18, 450 MPa, 500 °C), and $\text{CaCO}_3 + \text{H}_2\text{O}$ (E10, 450 MPa, 450 °C; E19, 450 MPa, 500 °C) an increase in the Ca content resulted in the formation of allanite/REE-epidote as well as fluorapatite. Diluting the Ca content from CaF_2 with Na from 2 M NaOH stabilized the newly formed fluorapatite-britholite, and secondary monazite at 450 MPa and 450 °C (E3 run) and retarded the growth of allanite. The presence of $\text{CaF}_2 + 2$ M NaOH does not promote REE-epidote or allanite growth under these *P-T* conditions. Although at 450 MPa and 500 °C only fluorapatite formed in run E13, both secondary fluorapatite and allanite (from monazite) are stable in run E21 (610–580 MPa, 450 °C). In addition to pressure and temperature, the Ca/Na ratio in the alkali- and alkaline-bearing fluid and the mineral ratio are interpreted to have been the controlling factors. These observations are consistent with conclusions from previous works concerning the importance of the Ca bulk content (Janots et al. 2007, 2008; Spear 2010) and the Ca/Na ratio in the monazite-allanite stability relationship (Janots et al. 2008) mentioned above. Furthermore, increasing the ratio of mica to feldspar in run E21 would have resulted in an increased Al bulk content that could have affected the relative stabilities of monazite and allanite (cf. Foster and Parrish 2003; Wing et al. 2003; Krenn and Finger 2007). However, because pressure also increased, it is difficult to say whether pressure or the Al content is more crucial with regard to promoting allanite formation. The experimental results also reveal the significance of K on monazite stability in alkali-bearing fluids. Experiments with 2 M KOH suggest that the presence of excess Ca and K in the fluid maintain the stability of primary monazite such that allanite does not form.

The partitioning of LREEs between monazite and fluorapatite become more efficient in experiments where neither allanite nor REE-epidote formed. Natural observations reveal that fluorapatite may incorporate LREEs from monazite during progressive high-grade metamorphism (Spear and Pyle 2002; Finger and Krenn 2007; Krenn et al. 2009). For example, Finger and Krenn (2007) have documented the preferential partitioning of LREE from monazite into fluorapatite at 2600 MPa and 830 °C. The enrichment of fluorapatite in LREEs and Th related to the breakdown of monazite or allanite has also been documented in high-grade terranes at the Opx-in isograd, e.g., the amphibolite- to granulite-facies transition from the Rogaland-Vest-Agder sector of the Sveconorwegian province, southwest Norway (Bingen et al. 1996). Our experimental results demonstrate that fluorapatite can incorporate REEs in relatively large amounts even at low- to middle-grade metamorphic conditions. Although there is some evidence that the substitution of the britholite component increases with pressure, the REE content in fluorapatite also appears to be dependent on the fluid composition. High Ca, Na, and Si activities in experiments E5 and E15 resulted in fluorapatite with the highest britholite component via coupled substitution reactions 2 and 3. In contrast to previous studies on high-grade rocks (e.g., Krenn et al. 2009), the results from this study indicate that the fluid composition plays a greater role in the incorporation of (Y+REE) into fluorapatite than the *P-T* conditions.

Future experimental work on the monazite-fluorapatite-allanite-REE-epidote system involving alkali- and alkaline-bearing fluids should expand on the *P-T* range considered here. Such an expansion would help to better define both the allanite-monzite stability field, as outlined by Janots et al. (2007) and Spear (2010), as well as the monazite-fluorapatite stability field as described, in part, by Finger and Krenn (2007) and Krenn et al. (2009) as well as Bingen et al. (1996). Such experiments would help to define the degree to which (Y+REE) incorporation into fluorapatite is a function of fluid composition or *P-T* conditions or both. The experiments would need a starting mineral assemblage similar to that used in this study. Once the monazite-allanite and monazite-fluorapatite stability fields have been defined in *P-T* space for a specific fluid composition, varying the fluid compositions, per speculations based on natural monazite-allanite-fluorapatite assemblages, presumably would have an effect on the stability fields of these minerals overall and thus lead to greater insights into the fluids responsible for monazite-allanite-fluorapatite textures for specific rock compositions under various metamorphic *P-T* conditions.

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APPENDIX

Mineral abbreviations (cf. Whitney and Evans 2010). Ab = albite, Aln = allanite, Brt = britholite, Bt = biotite, Ep = epidote, FAp = fluorapatite, Kfs = K-feldspar, Mnz = monazite, Ms = muscovite, Qtz = quartz, Pl = plagioclase, Thn = thorianite, Trk = turkestanite. The term allanite is used for newly grown epidote-group minerals with REE > 0.5 apfu, and the “REE-epidote” name is used if REE < 0.5 apfu (cf. Gieré and Sorensen 2004).

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