

INTERACTION OF RARE-METAL MINERALS WITH HYDROTHERMAL FLUIDS: EVIDENCE FROM QUARTZ–EPIDOTE METASOMATITES OF THE HALDZAN BURAGTAG MASSIF, MONGOLIAN ALTAI

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ABSTRACT

A quartz–epidote metasomatite from the Haldzan Buragtag massif, Mongolian Altai, provides evidence for the low-temperature hydrothermal alteration of rare-metal minerals. In what was essentially a continuous sequence of events during a complex evolutionary history, a peralkaline granitic pegmatite was metasomatized by hydrothermal fluids related to the associated intrusions. Minerals in the pegmatite, including fergusonite-(Y), chevkinite-(Ce), and members of the epidote supergroup, were recrystallized and texturally coarsened at temperatures in the range 318–446 °C. These phases were then altered by lower-temperature fluids (156–160 °C), with replacement of chevkinite-(Ce) by titanite–rutile–cerite-(Ce)–REE-carbonate assemblages and fergusonite-(Y) by complex hingganite–cerite–thorite assemblages. Late-stage veining included cerite-(Ce), fergusonite-(Y), and REE-carbonates. Generally, the light rare-earth elements (LREE) were replaced by Y, heavy rare-earth elements (HREE), and Ca as alteration proceeded. Mineral assemblages are interpreted to show that the hydrous fluids were acidic and oxidizing, contained significant amounts of CO₂, but were poor in F and Cl. The fluids may ultimately have been derived from basaltic magmas emplaced after formation of the pegmatite.

Keywords: chevkinite-(Ce), hydrothermal fluids, REE-bearing accessory phases, alteration.

INTRODUCTION

The strong enrichment in rare-earth elements (REE) and high-field-strength elements (HFSE) characteristic of Zr–Nb–REE deposits can be related to two processes: enrichment through extended fractional crystallization of alkaline magmas, and enrichment *via* hydrothermal processes. The hydrothermal fluids may be a free magmatic fluid, a later fluid containing a component of meteoric water, or a combination of both. The relative importance of the two processes varies between deposits and with time and place within individual deposits (Boily & Williams-Jones 1994, Schmitt *et al.* 2002, Salvi &

Williams-Jones 2005, 2006, Sheard *et al.* 2012, Louvel *et al.* 2014, Petrella *et al.* 2014).

The genesis of the granite-related Haldzan Buragtag Zr–Nb–REE deposit, Mongolia, has been a matter of debate. Kovalenko *et al.* (1985, 1995, 2009) argued that the deposit was formed solely by magmatic processes. Among their lines of evidence were the remarkable trace element levels in melt inclusions from the associated peralkaline granites, namely Zr ≤ 2.7 wt.%, Nb ≤ 0.6 wt.%, and REE ≤ 0.3 wt.% (Kovalenko *et al.* 1995). In contrast, Andreev *et al.* (1994), Andreev & Ripp (1996), and Kempe *et al.* (1999) related the enrichment up to ore concentrations to metasomatic alteration superimposed

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on the granites. This is consistent with the richest ores being found in metasomatically altered rocks but is not consistent with the presence of ore-free metasomatites in the host rocks of the pegmatites.

The Haldzan Buragtag deposit has certain features in common with other peralkaline granitic intrusions that host significant abundances of rare-metal minerals, such as Strange Lake, Canada (Salvi & Williams-Jones 2006, Gysi & Williams-Jones 2013); Amis, Namibia (Schmitt *et al.* 2002), Tamazeght, Morocco (Salvi *et al.* 2000); and Khan Bogd, Mongolia (Kynicky *et al.* 2011). These include evidence for the mobilization of REE and HFSE in hydrothermal fluids and the presence of late-stage Ca metasomatism. In contrast to these intrusions, the northern part of the Haldzan Buragtag massif, the subject of this study, does not contain abundant fluorite or show evidence of hydrothermal fluids rich in F or Cl.

In this report, we focus on two aspects of the hydrothermal fluids involved in the formation of the Haldzan Buragtag deposit. First, we discuss the formation of a series of quartz–epidote metasomatites which host some of the richest ores; second, we examine the nature of the lower-temperature fluids which altered the REE–HFSE minerals in the metasomatites. For this, particular attention is paid to minerals of the chevkinite group (CGM). The CGM are increasingly being recognized as important carriers of REE (with up to 50 wt.% REE_2O_3), HFSE, and, in some cases, actinides. They have the potential, therefore, to carry important records of the mobility of REE, HFSE, and actinides during the fluid-influenced post-magmatic stages of the Haldzan Buragtag deposit.

GEOLOGICAL SETTING

The Haldzan Buragtag Nb–Zr–REE deposit is located in the Mongolian Altai, some 45 km northeast of the city of Kobdo (Fig. 1). It is related to two bodies of peralkaline granite which are part of the multiphase Haldzan Buragtag peralkaline massif which is exposed in two oval-shaped outcrops (northern and southern) about 1 km apart (Kovalenko *et al.* 1995, Andreev & Ripp 1996). The massif, which is 30 km long and up to 8 km wide, intruded at ~ 385 Ma into Cambrian volcanic and sedimentary rocks and granites, and a series of dolerites and gabbros. It is partly covered by Devonian volcanic rocks. Eight intrusive events were recognized by Kovalenko *et al.* (1995): (1) quartz syenite (nordmarkite), (2) peralkaline granite, (3) peralkaline granitic pegmatites, and a slightly later peralkaline granite, (4) pantellerite dikes, (5) medium-grained rare-metal peralkaline granite, (6) mafic dikes, (7) miarolitic rare-metal peralkaline granite, and (8) leucite basalt and a stock-shaped body of leucosyenite. More recent work, however, has distinguished 12 intrusive phases, most clearly seen in the concentric structure of the southern body (P.M. Kartashov, unpublished).

In the Tsakhirin Khuduk occurrence at the northern end of the Haldzan Buragtag massif, quartz–epidote metasomatites form two types of body: linear zones

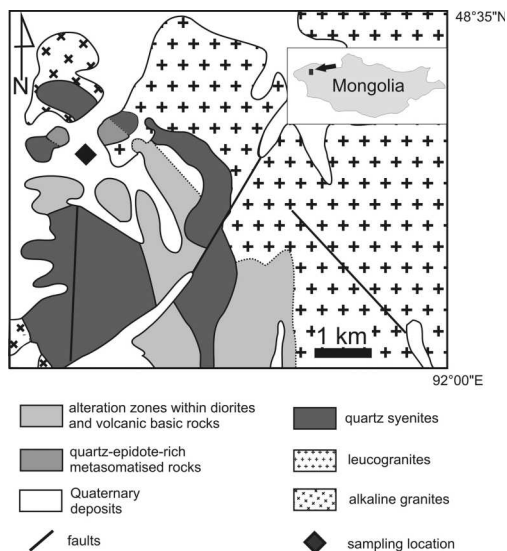


Fig. 1. Sketch map of the Tsakhirin Khuduk occurrence at the northern end of the Haldzan Buragtag massif. The metasomate was sampled from a trench at the site indicated.

0.5–20 m thick and up to 400 m long, and elliptical stockworks up to 150×200 m in size. Two linear zones (Western and Eastern) are more enriched in rare metals than the stockwork bodies. The zones occur at the exocontact of the massif, here represented by quartz syenites of the first intrusive phase, with Cambrian volcanic rocks, granites, and doleritic rocks. Field and petrographic evidence indicates that the linear zones are large, metasomatically altered pegmatite bodies (or series of subparallel pegmatitic veins) derived from peralkaline granites of intrusive phases 5 and 7 of Kovalenko *et al.* (1995), which are not exposed at the current erosion level. The metasomatites inherited the structural features, mineralogy, and rare-metal content of the pegmatites that they replaced. For example, different zones in the pegmatite can still be recognized, such as the outer part of the block zone through the inner part of the block zone to the quartz core. The host dolerites were, at the same time, replaced by actinolite–feldspar–epidote, actinolite–epidote, and epidote metasomatites.

There is no evidence that the pegmatites were able to autometasomatize themselves. In the northern part of the massif there are many unaltered granitic and syenitic pegmatites. Although some contain late epidote along fissures, there is no replacement of alkali feldspar or the primary mafic minerals. Moreover, feldspar and epidote have been found replacing the basic host rocks at some distance from the ore zones; they form a complex of ore-free metasomatites.

This study is focused on a quartz–epidote metasomate crossed by trench #4 in the Western ore zone,

where the metasomatite is particularly rich in rare-metal minerals. In addition to epidote, quartz, and calcite, the body contains fergusonite, zircon, columbite, titanite, fersmite, chevkinite, and epidote-supergroup minerals. Our samples come from the boundary between the former block zone and the quartz core of the pegmatite, where the chevkinite is up to $8 \times 2\text{--}3$ cm in size. This location was apparently extremely rich in metasomatized and recrystallized eudialyte [now represented by zircon–ferriallanite-(Ce) pseudomorphs], which trapped the bulk of the F in the rock. This had implications for later stages of alteration, as shown below.

ANALYTICAL METHODS

Mineral compositions were determined by electron microprobe at the Inter-Institute Analytical Complex at the Institute of Geochemistry, Mineralogy, and Petrology, University of Warsaw, using a Cameca SX-100 microprobe equipped with four wavelength-dispersive spectrometers. The accelerating voltage was 15 kV and the probe current was 40 nA. Counting times were 20 s on peak and 10 s on each of two background positions. The standards, crystals, and X-ray lines used and detection limits (for chevkinite, as an example) are given in Supplementary Table 1. The 'PAP' $\phi(\rho Z)$ program (Pouchou & Pichoir 1991) was used for corrections. Representative analyses are presented in Tables 1–6; the full data set is given in Supplementary Tables 2–4.

PETROGRAPHY OF THE PEGMATITE AND METASOMATITE

The primary pegmatites are closely similar to other, less altered, pegmatites in the area, notably Tatyana (Kartashov *et al.* 1993), Neprimetnyi (Kartashov *et al.* 2002), and Geophysicheskii (Sokolova *et al.* 2004). They contain quartz (40%), alkali feldspar (50%), riebeckite–arfvedsonite and aegirine (totaling 10 vol.% in the ratio 9:1), with eudialyte, zircon, fergusonite-(Y), chevkinite-(Ce), hingganite-(Y), and epidote-supergroup minerals. The aegirine formed later than the riebeckite–arfvedsonite, frequently overgrowing it. Eudialyte is a primary magmatic mineral within the large-block zone and along its boundary with the quartz core. Only rare crystals of eudialyte are found within the core. Minor primary zircon has been found in the outermost zones of the pegmatites (aplitic and pegmatoid zones); mostly the zircon is secondary after eudialyte. Fergusonite is a primary mineral, forming short, prismatic, honey-yellow crystals up to 1 mm in the intermediate zones (inner pegmatoid, block, and coarse-block zones). Fergusonite- β is a later, secondary mineral, tabular in form and up to 1 mm in size, associated with the alteration of eudialyte. Chevkinite-(Ce) is a late-stage mineral, found in the quartz core of the Tatyana pegmatite and in the pegmatoid and block zones of the Geophysicheskii pegmatite. It may be related to the alteration of eudialyte

but has not been observed in association with it. The largest crystal so far found is 10×1 mm in size. The epidote-supergroup minerals were formed by the alteration of eudialyte [ferriallanite-(Ce), allanite-(Ce), REE-epidote]. Its crystallization was partly coeval with, and partly post-dated, that of chevkinite-(Ce). It also occurs as hydrothermal phases precipitated along fissures and in cavities [allanite-(Ce), REE-epidote, and epidote]. Hingganite is also a relatively late phase, forming small anhedral aggregates of crystals.

The metasomatite consists mainly of quartz and epidote, with subordinate amounts of fergusonite, zircon, allanite, columbite, titanite, fersmite, chevkinite, and hingganite. Calcite formed very late, as cavity fillers with quartz $\pm$ hingganite. The epidote formed by the breakdown of feldspar, arfvedsonite, and aegirine in the pegmatite. The feldspar alteration is clearly visible in hand specimen and petrographically as finely granular epidote rims. The alteration of arfvedsonite and aegirine was reported by Andreev *et al.* (1994). The fergusonite forms spear-like, dipyrnidal crystals up to 2–3 cm long and spherulitic aggregates up to 4 cm in diameter. The chevkinite-(Ce) forms prismatic crystals up to 8×1.5 cm, tabular crystals up to $4 \times 3 \times 1$ cm, and rounded grains up to 3.5 cm across. The titanite formed by the breakdown of chevkinite-(Ce) and, in the samples described here, occurs at the contact between chevkinite and allanite and as pseudomorphs in the allanite zone. It was in turn partially replaced by rutile. Cerite-(Ce) and REE-carbonates are late phases.

An important observation is that in the unaltered pegmatites, fergusonite, chevkinite, and zircon largely form disseminated grains never exceeding 1 mm in size. In the metasomatite, the same phases are cm in size and formed by recrystallization and enlargement of the same minerals found in the primary pegmatite. Hingganite did not, apparently, behave like the other rare-metal minerals. Although present in the original pegmatite, it did not recrystallize with the formation of large crystals. The largest cluster of crystals so far recorded, in a calcite-filled cavity, measures 3 mm across. In contrast, hingganite in the Tatyana pegmatite forms abundant 4–7 mm (occasionally up to 2×1.2 cm) crystals and granular masses up to $8 \times 8 \times 5$ cm in size (Kartashov *et al.* 1993).

ALTERATION ASSEMBLAGES

The thin section presented in Figure 2 can broadly be separated into three zones. Zone A, appearing relatively bright in back-scattered electron (BSE) images, is composed mainly of chevkinite-(Ce). Towards and crossing its boundary with Zone C, the zone contains abundant crystals of cerite-(Ce), often filling fractures in the chevkinite-(Ce), occasionally accompanied by Nb,Y-oxides (Fig. 3A). In places, the cerite-(Ce) forms complexly zoned altered areas up to 100 μm across (Figs. 3B, C, D). In the grain in the center of Figure 3B, the oscillatory-zoned core has been truncated and

TABLE 1. REPRESENTATIVE ANALYSES (wt.%) OF CHEVKINITE-(Ce) AND EPIDOTE-SUPERGROUP MINERALS

	chevkinite-(Ce)				epidote-supergroup					
	1	2	3	4	5	6	7	8	9	10
wt. %										
Nb ₂ O ₅	2.79	2.61	2.35	2.43	bd	bd	bd	bd	bd	bd
Ta ₂ O ₅	0.15	0.15	bd	0.13	bd	bd	bd	bd	bd	bd
SiO ₂	18.33	18.31	18.46	18.51	33.21	36.19	35.95	29.77	30.27	29.62
TiO ₂	15.17	15.35	15.66	15.81	0.79	0.10	0.19	1.65	1.10	2.71
ZrO ₂	0.41	0.42	0.42	0.22	bd	bd	bd	bd	bd	bd
ThO ₂	0.44	0.27	0.28	0.26	bd	bd	bd	bd	bd	bd
Al ₂ O ₃	bd	bd	bd	bd	16.56	23.98	21.15	11.85	13.28	9.69
Y ₂ O ₃	0.74	0.73	0.65	0.61	3.57	1.65	3.40	bd	bd	bd
La ₂ O ₃	11.35	11.49	10.86	10.81	0.74	0.93	0.07	6.82	7.19	8.15
Ce ₂ O ₃	23.70	23.79	23.76	23.81	2.29	1.57	0.11	13.85	14.33	15.32
Pr ₂ O ₃	2.52	2.37	2.25	2.48	bd	0.18	bd	1.36	1.37	1.14
Nd ₂ O ₃	8.40	8.51	9.02	8.85	2.35	0.74	0.31	3.63	3.53	2.43
Sm ₂ O ₃	1.37	1.27	1.50	1.42	1.26	0.25	0.13	0.23	bd	0.20
Gd ₂ O ₃	0.75	0.65	0.75	0.76	1.62	0.54	0.53	0.23	bd	bd
MgO	bd	bd	bd	bd	bd	bd	bd	0.08	0.12	0.37
CaO	0.26	0.27	0.31	0.25	15.85	20.39	19.97	10.16	10.09	9.29
MnO	1.04	1.06	1.11	1.06	bd	bd	bd	bd	bd	bd
FeO*	10.85	10.84	10.86	10.72	16.19	8.93	13.20	16.85	15.60	17.39
SrO	0.43	0.41	0.43	0.35	bd	bd	bd	bd	bd	bd
Na ₂ O	0.09	0.06	0.10	0.08	bd	bd	bd	bd	bd	bd
Total	95.76	95.74	96.32	95.92	94.43	95.45	95.01	96.48	96.88	96.31
<i>Formulae on the basis of 22 O pfu</i>					<i>Formulae on basis of 12.5 O pfu</i>					
Ca	0.061	0.063	0.072	0.058	1.577	1.847	1.841	1.112	1.088	1.033
Sr	0.054	0.052	0.054	0.044	0.000	0.000	0.000	0.000	0.000	0.000
Na	0.038	0.025	0.042	0.034	0.000	0.000	0.000	0.000	0.000	0.000
La	0.914	0.926	0.871	0.867	0.025	0.029	0.002	0.257	0.267	0.312
Ce	1.895	1.904	1.892	1.897	0.078	0.049	0.003	0.518	0.528	0.582
Pr	0.201	0.189	0.178	0.197	0.000	0.006	0.000	0.051	0.050	0.043
Nd	0.655	0.664	0.701	0.688	0.078	0.022	0.010	0.132	0.127	0.090
Sm	0.103	0.096	0.112	0.106	0.040	0.007	0.004	0.008	0.000	0.007
Gd	0.054	0.047	0.054	0.055	0.050	0.015	0.015	0.008	0.000	0.000
Y	0.086	0.085	0.075	0.071	0.176	0.074	0.156	0.000	0.000	0.000
Th	0.022	0.013	0.014	0.013	0.000	0.000	0.000	0.000	0.000	0.000
Fe ²⁺	1.981	1.981	1.975	1.950	1.257	0.631	0.949	1.439	1.313	1.509
Mn	0.192	0.196	0.204	0.195	0.000	0.000	0.000	0.000	0.000	0.000
Mg	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.012	0.018	0.057
Nb	0.275	0.258	0.231	0.239	0.000	0.000	0.000	0.000	0.000	0.000
Ta	0.009	0.009	0.000	0.008	0.000	0.000	0.000	0.000	0.000	0.000
Zr	0.044	0.045	0.045	0.023	0.000	0.000	0.000	0.000	0.000	0.000
Ti	2.491	2.522	2.561	2.586	0.055	0.006	0.012	0.127	0.083	0.212
Al	0.000	0.000	0.000	0.000	1.812	2.390	2.144	1.427	1.575	1.185
Si	4.003	4.001	4.015	4.027	3.083	3.060	3.092	3.041	3.046	3.074
Σ cations	13.07	13.07	13.10	13.06	8.22	8.14	8.23	8.13	8.10	8.10
Sum A	4.08	4.06	4.07	4.03	Sum A	2.02	2.05	2.03	2.09	2.06
Sum B	1.99	2.01	2.02	2.00	Sum M	3.12	3.03	3.11	3.00	2.99
Sum C	2.00	2.00	2.00	2.00	Sum T	3.08	3.06	3.09	3.04	3.05
Sum T	4.00	4.00	4.01	4.03	-	-	-	-	-	-

FeO*, all Fe as Fe²⁺. bd, below detection.

Explanation: 1–4, random points in main chevkinite zone; 5–10, regions of different BSE intensity in allanite zone (B).

TABLE 2. REPRESENTATIVE ANALYSES (wt.%) OF HINGGANITE

	1	2	3	4	5	6	7	8
wt. %								
Nb ₂ O ₅	bd	0.09	bd	bd	bd	bd	bd	0.24
Ta ₂ O ₅	0.08	0.09	bd	0.09	0.05	0.06	bd	bd
SiO ₂	24.32	26.00	25.90	24.40	24.38	24.72	24.18	26.48
TiO ₂	0.06	bd	0.03	bd	bd	bd	0.04	0.09
ThO ₂	bd	bd	bd	bd	bd	bd	bd	0.46
Y ₂ O ₃	6.83	13.72	23.29	4.56	8.36	15.03	9.15	28.34
La ₂ O ₃	2.06	0.84	0.70	4.03	1.97	0.96	1.60	0.23
Ce ₂ O ₃	13.94	6.83	4.60	19.63	13.10	7.31	11.32	1.32
Pr ₂ O ₃	3.09	1.92	1.16	3.25	3.15	1.97	2.73	0.28
Nd ₂ O ₃	18.46	13.50	7.05	16.52	16.82	12.65	17.12	2.93
Sm ₂ O ₃	6.31	6.16	4.58	4.24	6.45	7.09	6.35	3.27
Gd ₂ O ₃	4.70	6.62	6.75	3.42	5.27	7.39	6.00	7.66
Tb ₂ O ₃	0.35	0.56	0.78	0.20	0.49	0.67	0.48	0.90
Dy ₂ O ₃	1.59	2.71	3.98	1.12	2.04	3.55	2.14	5.35
Ho ₂ O ₃	bd	0.43	0.32	0.32	bd	0.33	0.34	0.70
Yb ₂ O ₃	bd	0.22	0.41	bd	bd	bd	bd	0.25
BeO*	10.12	10.82	10.78	10.15	10.14	10.28	10.06	11.02
CaO	1.14	3.15	1.56	1.7	1.2	1.11	1.34	2.27
FeO*	1.86	2.15	1.58	1.91	1.90	1.23	1.54	1.82
Cl	0.06	0.04	bd	0.05	0.05	0.04	0.06	bd
Total	94.97	95.85	93.47	95.59	95.37	94.39	94.45	93.61
<i>Formula on basis of Si = 2 and Be = 2</i>								
Si	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
Ca	0.100	0.260	0.129	0.149	0.105	0.096	0.119	0.184
La	0.062	0.024	0.020	0.122	0.060	0.029	0.049	0.006
Ce	0.420	0.192	0.130	0.589	0.394	0.217	0.343	0.037
Pr	0.093	0.054	0.033	0.097	0.094	0.058	0.082	0.008
Nd	0.542	0.371	0.194	0.484	0.493	0.366	0.506	0.079
Sm	0.179	0.163	0.122	0.120	0.182	0.198	0.181	0.085
Gd	0.128	0.169	0.173	0.093	0.143	0.198	0.165	0.192
Tb	0.009	0.014	0.020	0.005	0.013	0.018	0.013	0.022
Dy	0.042	0.067	0.099	0.030	0.054	0.093	0.057	0.130
Ho	0.000	0.011	0.008	0.008	0.000	0.008	0.009	0.017
Yb	0.000	0.005	0.010	0.000	0.000	0.000	0.000	0.006
Y	0.299	0.562	0.957	0.199	0.365	0.647	0.403	1.139
Th	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.008
Nb	0.000	0.003	0.000	0.000	0.000	0.000	0.000	0.008
Ta	0.002	0.002	0.000	0.002	0.001	0.001	0.000	0.000
Ti	0.004	0.000	0.002	0.000	0.000	0.000	0.002	0.005
Fe ²⁺	0.128	0.138	0.102	0.131	0.130	0.083	0.107	0.115
Be	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
Cl	0.008	0.005	0.000	0.007	0.007	0.006	0.009	0.000
Σ cations	6.01	6.04	6.00	6.03	6.03	6.01	6.03	6.04
*□	0.872	0.862	0.898	0.869	0.870	0.917	0.893	0.885

FeO*, all Fe as Fe²⁺. BeO*, calculated from Be = 2 *apfu*. bd, below detection. *□, vacancy in X site.

Explanation: 1, patch in fergusonite-(Y); 2, rimming fergusonite-(Y); 3, patch in fergusonite-(Y); 4, 5, oval patch in fergusonite-(Y); 6, 7, 8, anhedral, composite grain.

TABLE 3. REPRESENTATIVE ANALYSES (wt.%) OF TITANITE AND RUTILE

	titanite						rutile			
	1	2	3	4	5	6	7	8	9	10
Nb ₂ O ₅	1.64	0.27	3.53	6.61	2.67	0.67	3.24	0.52	1.23	1.80
SiO ₂	29.98	30.20	29.58	30.00	30.09	30.11	bd	bd	0.04	0.08
TiO ₂	37.12	39.49	32.72	33.84	36.79	37.45	95.10	98.14	95.89	94.64
ZrO ₂	bd	bd	3.12	bd	0.15	bd	bd	bd	0.61	bd
SnO ₂	0.31	0.20	bd	bd	bd	bd	bd	bd	bd	bd
Al ₂ O ₃	1.06	0.66	0.46	0.47	0.90	0.91	bd	bd	bd	bd
Fe ₂ O ₃ *	0.42	0.43	1.18	1.24	0.43	0.43	-	-	-	-
Y ₂ O ₃	bd	bd	bd	bd	bd	0.28	bd	bd	bd	bd
Ce ₂ O ₃	0.21	0.13	bd	bd	bd	bd	bd	bd	bd	bd
Nd ₂ O ₃	0.35	bd	bd	bd	bd	bd	bd	bd	bd	bd
Sm ₂ O ₃	0.14	bd	bd	bd	bd	bd	bd	bd	bd	bd
MgO	bd	bd	0.02	bd	0.02	bd	bd	0.02	bd	bd
CaO	27.97	28.54	27.35	27.33	28.33	27.67	0.30	0.93	1.00	0.61
FeO*	-	-	-	-	-	-	1.46	0.62	0.36	0.98
F	bd	bd	0.47	bd	0.29	0.40	bd	bd	bd	bd
Sum	99.20	99.92	98.43	99.49	99.67	97.92	100.10	100.23	99.13	98.11
O = F	0.00	0.00	0.20	0.00	0.12	0.17	0.00	0.00	0.00	0.00
Total	99.20	99.92	98.23	99.49	99.55	97.75	100.10	100.23	99.13	98.11
<i>Formulae</i>	<i>on basis of 5 oxygens</i>						<i>on basis of 2 oxygens</i>			
Nb	0.025	0.004	0.054	0.100	0.040	0.010	0.020	0.003	0.008	0.011
Si	0.995	0.990	1.002	1.001	0.992	1.004	0.000	0.000	0.001	0.001
Ti	0.927	0.973	0.833	0.849	0.913	0.939	0.965	0.986	0.977	0.975
Zr	0.000	0.000	0.052	0.000	0.002	0.000	0.000	0.000	0.004	0.000
Sn	0.004	0.003	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Al	0.041	0.025	0.018	0.018	0.035	0.036	0.000	0.000	0.000	0.000
Ce	0.003	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Nd	0.004	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sm	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Y	0.000	0.000	0.000	0.000	0.000	0.005	0.000	0.000	0.000	0.000
Ca	0.995	1.002	0.993	0.977	1.001	0.989	0.004	0.013	0.015	0.009
Fe ³⁺	0.010	0.011	0.030	0.031	0.011	0.011	-	-	-	-
Fe ²⁺	-	-	-	-	-	-	0.016	0.007	0.004	0.011
Mg	0.000	0.000	0.001	0.000	0.001	0.000	0.000	0.000	0.000	0.000
F	0.000	0.000	0.050	0.000	0.030	0.042	0.000	0.000	0.000	0.000
Σ cations	3.01	3.01	2.98	2.98	3.00	2.99	1.01	1.01	1.01	1.01

FeO*, all Fe as Fe²⁺. Fe₂O₃*, all Fe as Fe³⁺. bd, below detection; dash, not determined. Explanation: 1, 2, dark regions in Zone C; 3, 4, in vein cutting chevkinite-(Ce); 5, in patch of allanite in Zone C; 6, with hingganite in Zone B; 7, dark needle in Zone B; 8, in rectangular strip in Zone B; 9, 10, with hingganite in Zone B.

patchily replaced by a slightly brighter phase in the BSE image. The grain in Figure 3C is dominated by a bright area with residual stripes of a darker phase, whilst at the top of the grain, a darker material is intergrown with a lighter phase. Nb,Y-oxides occur as ragged patches associated with the cerite in Figure 3B; small veinlets penetrating the cerite may indicate that it formed later.

Zone B is dominated by minerals of the epidote supergroup. Allanite-(Ce)-ferriallanite-(Ce) dominates,

but epidote occurs locally, filling cavities between allanite crystals (Fig. 2). In detail, the allanite-(Ce) appears as a patchy zone of lighter and darker material in BSE images, especially near cerite and/or REE-carbonate veins (Fig. 4A). The zone contains dark Y-shaped aggregates and rectangular strips of titanite and rutile, with inclusions of Nb,Y-oxides, usually with rather sharp junctions against the allanite (Fig. 4B). It is suggested below that these are pseudomorphs, possibly

TABLE 4. REPRESENTATIVE COMPOSITIONS OF FERGUSONITE

fergusonite-	Ce 1	Nd 2	Y 3	Y 4	Y 5	Y 6	Y 7	Y 8
wt. %								
WO ₃	0.32	0.62	5.01	0.26	0.13	0.32	0.87	0.24
Nb ₂ O ₅	44.21	45.51	41.94	45.75	45.26	44.51	32.20	46.08
Ta ₂ O ₅	0.06	0.11	1.06	1.52	0.44	0.12	0.34	0.79
SiO ₂	0.48	0.17	0.71	0.39	0.34	0.46	10.19	0.48
TiO ₂	0.36	0.48	1.56	0.43	0.60	0.73	6.04	1.19
ZrO ₂	0.10	bd	0.51	bd	bd	bd	0.56	bd
ThO ₂	0.15	0.70	1.56	1.99	2.87	1.12	6.44	1.53
UO ₂	0.22	0.14	0.29	0.57	0.38	0.84	0.25	0.32
Y ₂ O ₃	4.73	8.24	27.40	20.65	17.59	12.00	10.33	20.02
La ₂ O ₃	4.33	1.91	0.14	0.29	0.46	1.28	1.54	0.22
Ce ₂ O ₃	17.06	11.76	0.86	2.57	2.68	7.43	5.09	1.39
Pr ₂ O ₃	2.82	2.67	0.14	0.54	1.37	1.87	bd	0.42
Nd ₂ O ₃	13.36	14.04	1.98	6.07	7.14	10.21	5.41	5.09
Sm ₂ O ₃	4.00	4.95	1.22	3.03	4.26	4.80	2.96	4.45
Eu ₂ O ₃	0.62	0.71	0.82	1.24	1.08	1.03	0.69	1.22
Gd ₂ O ₃	4.44	4.94	2.40	4.03	5.38	5.33	3.59	5.67
Tb ₂ O ₃	bd	0.29	0.50	0.62	0.89	0.58	0.36	0.81
Dy ₂ O ₃	1.46	1.79	3.53	3.88	4.24	3.17	2.56	4.52
Ho ₂ O ₃	bd	bd	1.14	1.08	0.89	0.90	0.27	1.01
Er ₂ O ₃	0.56	0.69	2.78	2.62	2.26	1.55	1.40	2.38
Yb ₂ O ₃	0.60	0.47	1.90	1.59	1.57	1.51	0.57	1.54
Lu ₂ O ₃	0.26	0.19	0.37	0.35	0.47	0.50	0.32	0.54
CaO	0.21	0.36	0.53	0.27	0.62	0.39	3.10	0.64
Total	100.35	100.74	98.35	99.74	100.92	100.65	95.08	100.55
<i>Formulae on basis of (Nb + Ta + Ti) = 1 apfu</i>								
Ca	0.011	0.018	0.028	0.014	0.032	0.020	0.173	0.031
La	0.079	0.034	0.003	0.005	0.008	0.023	0.030	0.004
Ce	0.308	0.206	0.016	0.044	0.047	0.131	0.097	0.023
Pr	0.051	0.046	0.003	0.009	0.024	0.033	0.000	0.007
Nd	0.235	0.239	0.035	0.102	0.122	0.176	0.101	0.083
Sm	0.068	0.081	0.021	0.049	0.070	0.080	0.053	0.070
Eu	0.010	0.012	0.014	0.020	0.018	0.017	0.012	0.019
Gd	0.073	0.078	0.039	0.063	0.085	0.085	0.062	0.086
Tb	0.000	0.005	0.008	0.010	0.014	0.009	0.006	0.012
Dy	0.023	0.028	0.056	0.059	0.065	0.049	0.043	0.067
Ho	0.000	0.000	0.018	0.016	0.013	0.014	0.004	0.015
Er	0.009	0.011	0.047	0.042	0.037	0.026	0.025	0.037
Yb	0.009	0.007	0.029	0.023	0.023	0.022	0.009	0.022
Lu	0.004	0.003	0.006	0.005	0.007	0.007	0.005	0.007
Y	0.124	0.209	0.719	0.518	0.446	0.309	0.287	0.488
Th	0.002	0.008	0.018	0.021	0.031	0.012	0.077	0.016
U	0.002	0.001	0.003	0.006	0.004	0.009	0.003	0.003
Nb	0.986	0.982	0.935	0.975	0.976	0.973	0.760	0.954
Ta	0.000	0.001	0.007	0.010	0.003	0.001	0.002	0.005
Ti	0.013	0.017	0.058	0.015	0.022	0.027	0.237	0.041
Zr	0.002	0.000	0.012	0.000	0.000	0.000	0.014	0.000
W	0.002	0.004	0.036	0.002	0.001	0.002	0.007	0.002
Si	0.024	0.008	0.035	0.018	0.016	0.022	0.532	0.022
Σ cations	2.04	2.00	2.14	2.03	2.06	2.05	2.54	2.01

Explanation: 1, bright, 2, 3, intermediate, and 4, dark components of fergusonite-(Y) (Fig. 4c); 5, ragged grain in Zone B; 6, vein in chevkinite-(Ce); 7, 8, darker and brighter components of striped grain (Fig. 5c). bd, below detection.

TABLE 5. REPRESENTATIVE COMPOSITIONS OF CERITE AND REE-CARBONATE

	cerite						REE-carbonate	
	1	2	3	4	5	6	7	8
wt. %								
P ₂ O ₅	0.11	0.11	0.31	0.12	0.05	bd	-	-
SiO ₂	21.99	22.93	18.71	22.05	23.67	25.85	0.97	0.26
ThO ₂	bd	bd	1.36	0.16	bd	bd	bd	bd
Al ₂ O ₃	0.28	0.06	0.52	0.42	bd	bd	-	-
Y ₂ O ₃	0.71	1.20	1.82	0.91	5.79	15.54	0.87	0.69
La ₂ O ₃	11.89	14.65	11.16	11.74	2.40	0.84	12.96	11.71
Ce ₂ O ₃	34.06	32.09	33.01	32.59	15.52	5.66	30.16	28.09
Pr ₂ O ₃	3.66	3.25	3.15	3.60	3.57	1.56	3.41	2.53
Nd ₂ O ₃	15.28	11.11	10.88	16.03	19.65	12.33	14.29	11.12
Sm ₂ O ₃	1.85	1.63	1.88	1.82	5.48	5.16	2.29	1.72
Gd ₂ O ₃	0.78	1.12	1.57	1.06	4.59	6.51	1.67	0.77
Tb ₂ O ₃	bd	bd	bd	bd	0.37	0.59	-	-
Dy ₂ O ₃	bd	bd	0.41	bd	1.39	2.54	bd	bd
Yb ₂ O ₃	bd	bd	0.25	bd	0.17	0.28	bd	bd
MnO	bd	0.13	0.22	bd	bd	bd	-	-
FeO*	1.17	1.82	1.09	1.23	1.83	2.45	0.63	bd
MgO	1.01	0.81	0.69	0.88	bd	bd	-	-
CaO	3.27	5.32	4.17	3.61	0.94	3.38	9.07	6.21
SrO	bd	bd	bd	bd	bd	bd	2.47	2.48
F	0.58	0.53	0.42	0.59	bd	bd	bd	0.51
Cl	0.04	0.04	0.24	0.06	0.05	0.04	-	-
Sum	96.68	96.80	91.86	96.87	85.47	82.73	78.79	66.09
O = F + Cl	0.00	0.00	0.00	0.26	0.00	0.00	0.00	0.21
Total	96.68	96.80	91.86	96.61	85.47	82.73	78.79	65.88
<i>Formulae</i>	<i>on the basis of 17 cations pfu</i>						<i>on basis of 4 cations pfu</i>	
Ca	1.117	1.745	1.517	1.225	0.355	1.179	1.061	0.915
Sr	0.000	0.000	0.000	0.000	0.000	0.000	0.156	0.198
Th	0.000	0.000	0.105	0.012	0.000	0.000	0.000	0.000
La	1.398	1.654	1.397	1.372	0.312	0.101	0.522	0.594
Ce	3.975	3.597	4.103	3.780	2.001	0.675	1.206	1.415
Pr	0.425	0.363	0.390	0.416	0.458	0.185	0.136	0.127
Nd	1.739	1.215	0.319	1.813	2.472	1.434	0.558	0.546
Sm	0.203	0.172	0.220	0.199	0.665	0.579	0.086	0.082
Gd	0.082	0.114	0.177	0.111	0.536	0.703	0.061	0.035
Tb	0.000	0.000	0.000	0.000	0.043	0.063	-	-
Dy	0.000	0.000	0.045	0.000	0.158	0.266	0.000	0.000
Yb	0.000	0.000	0.026	0.000	0.018	0.028	0.000	0.000
Y	0.120	0.196	0.329	0.153	1.085	2.693	0.050	0.050
Fe	0.316	0.473	0.314	0.330	0.547	0.677	0.058	0.000
Mn	0.000	0.034	0.063	0.000	0.000	0.000	-	-
Al	0.105	0.022	0.208	0.157	0.000	0.000	-	-
Mg	0.480	0.370	0.349	0.415	0.000	0.000	-	-
Sum M	9.960	9.955	9.562	9.983	8.650	8.583	3.894	3.961
Si	7.009	7.019	6.351	6.984	8.336	8.417	0.106	0.036
P	0.030	0.028	0.089	0.032	0.015	0.000	-	-
Sum T	7.039	7.047	6.440	7.016	8.351	8.417	0.106	0.036
F	0.585	0.513	0.451	0.591	0.000	0.000	0.000	0.222
Cl	0.022	0.021	0.140	0.033	0.030	0.022	-	-

FeO*, all Fe as Fe²⁺. bd, below detection; -, not determined.

Explanation: 1, prism in Zone A; 2, rectangular crystal at A/C boundary; 3, in complexly zoned crystal at Zones A/C boundary (Fig. 3b); 4, patch at A/C boundary; 5, 6, patchily zoned crystal in Zone B (Fig. 3d); 7, 8, in large fergusonite-(Y) (Fig. 4c).

TABLE 6. REPRESENTATIVE ANALYSES (wt.%) OF THORITE

	1	2	3	4	5
ThO ₂	67.06	66.45	64.25	61.52	67.17
UO ₂	1.65	1.75	1.90	1.21	2.24
PbO	0.26	0.82	0.28	0.22	0.31
La ₂ O ₃	0.17	0.13	bd	0.44	0.16
Ce ₂ O ₃	0.36	0.34	0.33	1.50	0.22
Pr ₂ O ₃	bd	bd	bd	0.29	bd
Nd ₂ O ₃	0.32	0.21	0.72	2.11	0.38
Sm ₂ O ₃	0.39	bd	0.64	0.74	0.29
Gd ₂ O ₃	1.17	0.57	0.61	1.02	0.50
Dy ₂ O ₃	0.46	0.68	0.48	0.42	0.61
Yb ₂ O ₃	0.34	bd	0.48	0.21	bd
Y ₂ O ₃	3.77	2.04	3.70	2.43	3.47
CaO	1.34	0.47	1.25	1.46	1.32
TiO ₂	bd	0.04	0.04	0.08	0.05
FeO*	0.17	0.08	0.06	0.48	0.10
MnO	bd	bd	bd	bd	bd
SiO ₂	16.48	17.13	17.94	17.42	18.88
Al ₂ O ₃	0.12	bd	0.10	0.14	0.06
MgO	bd	bd	bd	0.02	bd
P ₂ O ₅	0.72	0.68	0.84	0.64	0.72
Total	94.78	91.39	93.62	92.35	96.48
<i>Formulae on basis of 4 O pfu</i>					
Th	0.845	0.862	0.790	0.771	0.799
U	0.020	0.022	0.023	0.015	0.026
Pb	0.004	0.013	0.004	0.003	0.004
La	0.003	0.003	0.000	0.009	0.003
Ce	0.007	0.007	0.007	0.030	0.004
Pr	0.000	0.000	0.000	0.006	0.000
Nd	0.006	0.004	0.014	0.041	0.007
Sm	0.007	0.000	0.012	0.014	0.005
Gd	0.021	0.011	0.011	0.019	0.009
Dy	0.008	0.012	0.008	0.007	0.010
Yb	0.006	0.000	0.008	0.004	0.000
Y	0.111	0.062	0.106	0.071	0.097
Ti	0.000	0.002	0.002	0.003	0.002
Ca	0.080	0.029	0.072	0.086	0.074
Fe ²⁺	0.008	0.004	0.003	0.022	0.004
Mn	0.000	0.000	0.000	0.000	0.000
Mg	0.000	0.000	0.000	0.002	0.000
Sum	1.128	1.030	1.059	1.104	1.045
Si	0.913	0.976	0.969	0.959	0.987
Al	0.008	0.000	0.006	0.009	0.004
P	0.034	0.033	0.038	0.030	0.032
Sum T	0.954	1.009	1.014	0.998	1.023
Σ cations	2.08	2.04	2.07	2.10	2.07

All analyses from bright grains in large fergusonite-(Y) crystal (Fig. 4c). FeO*, all Fe as Fe²⁺. bd = below detection.

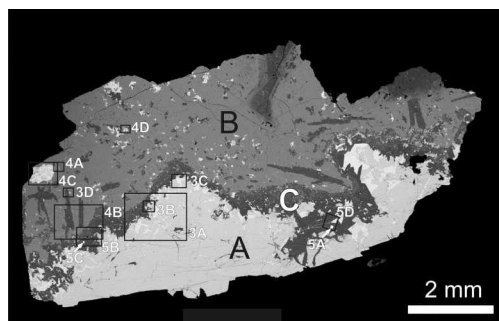


FIG. 2. Photomicrograph of a section of sample chev7, showing the three main zones (A to C) in the hydrothermally altered quartz-epidote metasomate. The locations of BSE images referred to in the text are outlined. The darker areas in the upper center and upper right are epidote, perhaps filling cavities between (ferri)allanite crystals.

after a chevkinite-group mineral. A large ($500 \times 440 \mu\text{m}$) grain of fergusonite-(Y) is partially altered internally to cerite-(Ce) and, generally nearer the rim, to Nd-dominant hingganite and hingganite-(Y) (Fig. 4C). The grain also contains small, bright grains of thorite (Fig. 4C) and anhedral patches of REE-carbonate. Figure 4D shows an intimate intergrowth of cerite-(Ce) and hingganite. The hingganite is patchily zoned, with a darker phase replacing a lighter phase. REE-carbonate minerals occur as veinlets and occasional patches (not shown on Fig. 4).

Zone C, up to ~ 1 mm thick, mantles and locally penetrates Zones A and B and also contains relict patches of chevkinite-(Ce). It is composed mainly of titanite, comprising a patchy intergrowth of phases showing slightly different brightness on BSE images; in the example shown in Figure 5A, the darker component (Ttn2) has replaced the lighter component (Ttn1) along fractures and as disseminated strips. Slight differences in brightness in the titanite host reflect compositional differences (see below). The zone becomes increasingly crowded with white veinlets, mainly of cerite-(Ce) with some bright grains of Nb,Y-oxides, towards Zone B (Figs. 4B, 5B) and there is partial replacement of titanite by rutile (Fig. 5B). An unusual texture in an Nb-Y-oxide comprises alternating strips of brighter and darker material (Fig. 5C). In Figure 5D, REE-carbonate veins rim and cut a cerite-(Ce) crystal.

MINERAL COMPOSITIONS

Chevkinite-(Ce)

The general formula of chevkinite and perrierite, the two most common members of the chevkinite-group of minerals, is $A_4BC_2D_2(\text{Si}_2\text{O}_7)_2\text{O}_8$, where the dominant

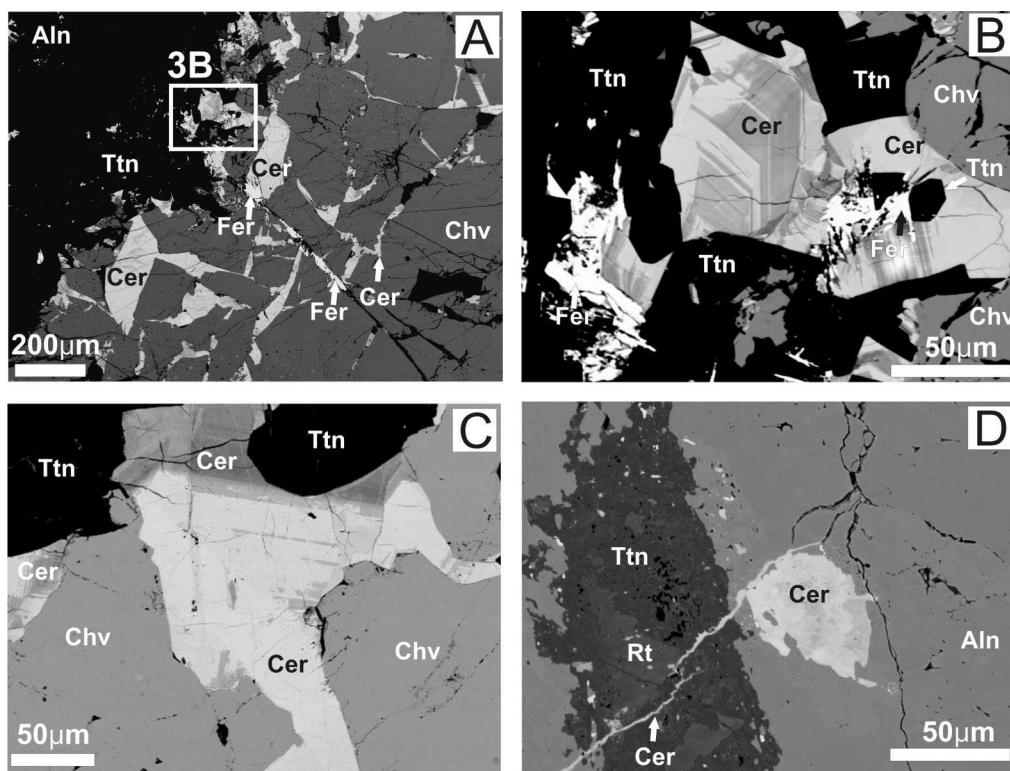


FIG. 3. BSE images of textural relationships involving cerite-(Ce) (Cer). (A) Cerite-(Ce) occupying fractures in chevkinite-(Ce) (Chv). Also shown is a thin vein of fergusonite (Fer). The location of Figure 3B is indicated. Zone C here is relatively thin and is composed mainly of titanite (Ttn). (B) Complexly zoned cerite-(Ce), patchily intergrown with fergusonite-(Y) at the boundary between Zones A and C. The dark material is titanite; at this brightness the patchy nature cannot be seen. (C) Zoned cerite-(Ce) crossing the boundary between Zones A and C. (D) Zoned altered cerite-(Ce) in allanite (Aln), Zone B. The dark area to the left is an intergrowth of titanite and rutile (Rt; slightly lighter). The bright spots in all three phases are mainly Nb, Y-oxides.

cations at each site are: A—Ca, REE, Th; B—Fe²⁺; C—Fe²⁺, Fe³⁺, Ti; and D—Ti. Electron microprobe analyses of chevkinite-(Ce) are presented in Supplementary Table 2a, with representative compositions in Table 1. The mineral has been classified as chevkinite using the empirical discriminant of Macdonald *et al.* (2009). Oxide totals range from 97.64 to 98.79 wt.% and the sums of cations from 13.06–13.11 *apfu*, close to the theoretical 13 *apfu*. Higher oxide totals and sums of cations of 13 *apfu* would be achieved by recalculating some Fe²⁺ to Fe³⁺.

The chevkinite-(Ce) has notably low Ca contents (Ca 0.058–0.073 *apfu*) and correspondingly high REE contents (Σ REE 3.81–3.92 *apfu*). Thorium contents are low (0.010–0.022 *apfu*). Thus, the REE occupy >95% of the A-site. Divalent Fe is the dominant cation at the C-site, which also has moderate amounts of Nb (0.216–0.283 *apfu*). A simplified average composition can be expressed as (LREE_{3.76}HREE_{0.13}Ca_{0.07}) Σ _{3.96}Fe²⁺(Fe²⁺_{0.99}Ti_{0.54}Nb_{0.25}Mn_{0.19}) Σ _{1.97}Ti_{2.00}(Si_{2.01}O₇)₂O₈, with Ce

the dominant REE (1.90 *apfu*). Chondrite-normalized REE patterns indicate strong LREE enrichment, with elements heavier than Gd being below detection levels (Fig. 6A). There are small positive Ce anomalies (Ce/Ce* 1.07–1.24; average 1.13).

Epidote-supergrout minerals

Compositions of epidote-supergrout minerals are given in Table 1 and Supplementary Table 2b. Oxide totals are in the range 94.43–97.44 wt.%, partly because total Fe is presented as Fe²⁺, whereas there is significant Fe³⁺ (see below), and perhaps partly because the minerals have been secondarily hydrated during metamictization. The cation sums range from 8.04–8.23 *apfu* (average 8.13 *apfu*), slightly higher than the theoretical value of 8 *apfu* but again partly a result of presenting all Fe as Fe²⁺. We specifically looked for F but it was below detection (~0.25 wt.%) in all analyses.

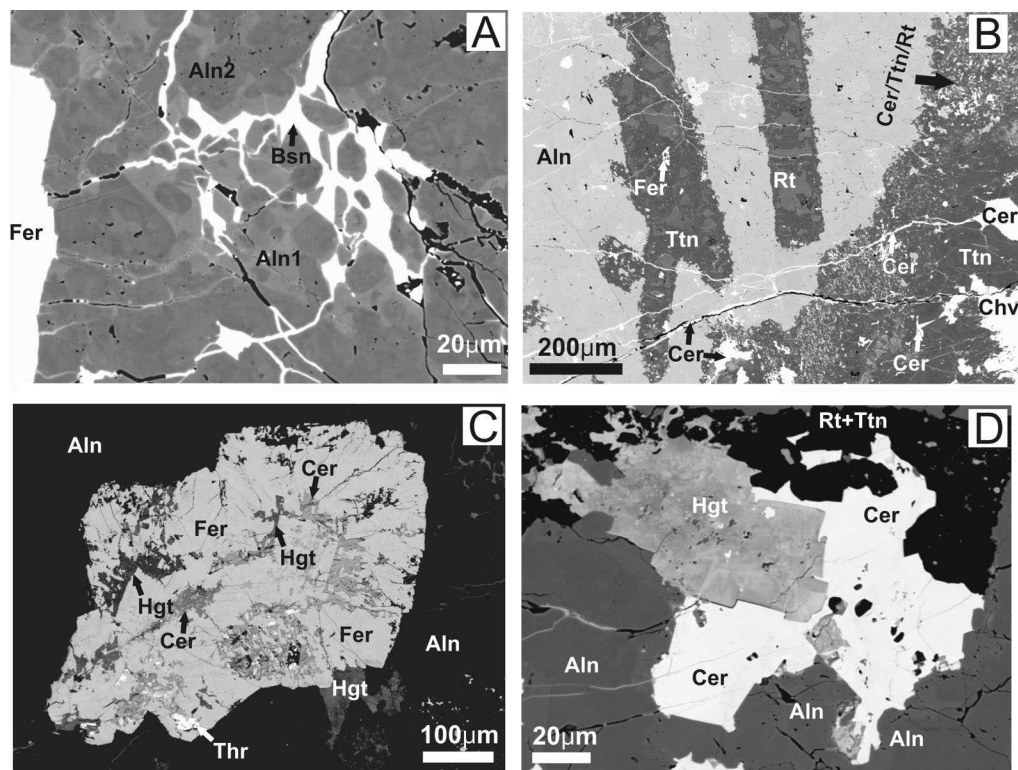


FIG. 4. BSE images of selected textural relationships in Zone B. (A) Patchy intergrowth of lighter and darker varieties of ferriallanite-(Ce) (Aln1 and Aln2), veined by REE-carbonates (Bsn). (B) The dark strips are intergrowths of titanite and rutile (slightly lighter), with bright inclusions of fergusonite-(Y) and REE-carbonates. The light-colored veins cutting the titanite-rutile pseudomorphs are REE-carbonate. (C) Crystal of fergusonite-(Y) in the (ferri)allanite zone, partly altered to fergusonite with higher Y and HREE contents, cerite-(Ce), hingganite-(Y), and Nd-dominant hingganite (Hgt). Hingganite also forms rimming material at the lower right. Bright crystals are thorite (Thr) and REE-carbonate. (D) Aggregate of cerite-(Ce), hingganite, titanite, and rutile in Zone B.

The compositions of the epidote-supergroup minerals are plotted in the (REE + Sr + Th) versus Al diagram of Petrik *et al.* (1995) in Figure 7. The phase in Zone B plots along the allanite-(Ce)–ferriallanite-(Ce) join, reflecting the range of compositions from more to less REE-rich. Some points have $\Sigma\text{REE} > 1$, *i.e.*, plot above the allanite–ferriallanite join. They do not have sufficient Al to fill the *M*(2) site, reflected in the sum of *M* cations being less than 3. Similar features were described by Vlach & Gualda (2007) for allanite from A-type granites of the Graciosa Province, south Brazil. The phase filling cavities between ferriallanite-(Ce) crystals (Fig. 2) is epidote. Oxidation ratios $[\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}^{2+})]$, calculated from stoichiometry, vary from ~ 0.1 in ferriallanite-(Ce) to ~ 0.7 in epidote (Supplementary Table 2b).

The ferriallanite-(Ce)–allanite-(Ce) is strongly LREE-enriched, with the HREE commonly below detection level. In contrast, Y is the dominant REE in the epidote (0.074–0.176 *apfu*). Chondrite-normalized REE plots contrast the sharp decrease from La to Gd in the allanite with the concave-upward form of the epidote patterns

(Fig. 6B), indicating accumulation of HREE compared to LREE. In the transition allanite to ferriallanite, there is an overall increase in $[\text{La}/\text{Nd}]_{\text{CN}}$ ratio (where CN is chondrite-normalized) from ~ 3 to 7. The overall allanite patterns are similar to those of chevkinite-(Ce) but at lower LREE contents (Figs. 6A, B). The chevkinite is also less depleted in the MREE than the allanite. The ferriallanite–allanite shows positive Ce anomalies ($\text{Ce}/\text{Ce}^* 1.02\text{--}1.47$; average 1.16), similar to those in chevkinite-(Ce). An epidote crystal has, however, a small negative anomaly ($\text{Ce}/\text{Ce}^* 0.94$).

An example of the replacement of LREE by HREE occurs near the REE-carbonate veins shown in Figure 4 A; the darker phase (aln2) has replaced a brighter phase richer in LREE (aln1), strongly suggestive of local REE mobility.

Hingganite-(Y) and Nd-dominant hingganite

Hingganite, a member of the gadolinite–datolite group, has the simplified formula $\text{REE}_2(\square, \text{Fe}^{2+})$

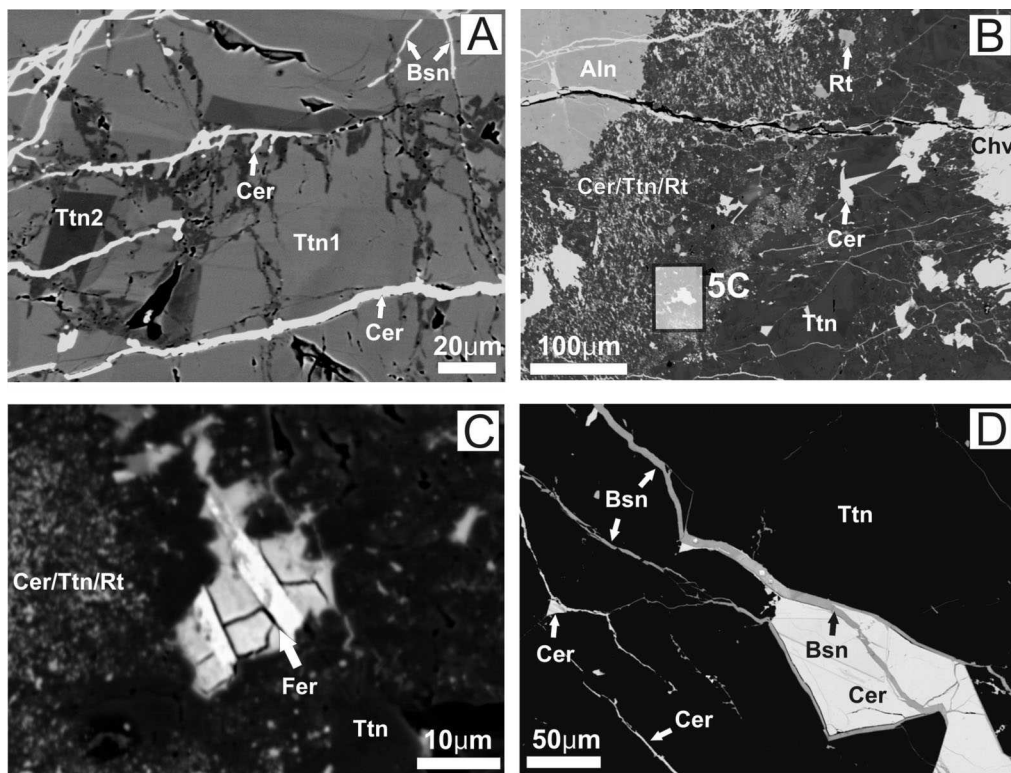


FIG. 5. BSE images of selected textural relationships in Zone C. (A) The darker, lower-Nb titanite generally forms disseminated veinlets in the lighter, higher-Nb titanite. The bright veinlets are mainly cerite-(Ce), with lesser REE-carbonate (Bsn). (B) A small area of chevkinite-(Ce) appears at the far right. Zone C comprises titanite to the right, but towards Zone B (Aln) is a mix of titanite and rutilite and becomes progressively crowded with small grains of cerite-(Ce), which also forms larger, anhedral grains throughout Zone C. (C) Striped fergusonite in Zone C, the darker stripes being heavily altered (see text). (D) REE-carbonate (Bsn) veining and rimming cerite-(Ce) in titanite host. Brighter veins are cerite.

$\text{Be}_2\text{Si}_2\text{O}_8(\text{OH})_2$, where $\square$ is vacancy at the X site. The species currently approved by the IMA are hingganite-(Y), hingganite-(Yb), and hingganite-(Ce). A distinction from the other members of the gadolinite–datolite group has been made on a plot of $^{\text{W}}(\text{REE} + \text{Y})/^{\text{W}}(\text{REE} + \text{Y} + \text{Ca})$ versus $^{\text{X}}\square/(^{\text{X}}\square + \text{Fe}^{2+})$ (e.g., Pršek *et al.* 2010, Chakrabarty *et al.* 2013). Compositions of hingganite may be found in Table 2 and Supplementary Table 2c. Lacking data for H_2O , formulae have been calculated on the basis of $\text{Si} = 2$ apfu. Beryllium has been assumed to be 2 apfu and it has also been assumed that there has been no substitution of Be by B. This is consistent with the absence of any B mineral from the Haldzan Buragtag massif. Calculated BeO values are in the range 9.42–11.02 wt.%.

Hingganite-(Y) and a Nd-dominant form are both present in the metasomatite, often occurring in the same crystal; in the patchily zoned crystal shown in Figure 4D, the darker component, inferred to be later, is hingganite-(Y), replacing the lighter, Nd-dominant hingganite. A single example of hingganite-(Ce) also occurs in the

same crystal. The coexistence of hingganite-(Ce) and hingganite-(Y) in the same crystals was earlier recorded in a granitic pegmatite at Hirukawa-mura, Gifu Prefecture, Japan by Miyawaki *et al.* (2007). The first report of Nd-dominant hingganite, without structural data, was by Kartashov & Lapina (1994), from the Tatyana pegmatite, Haldzan Buragtag massif. A second occurrence, also without a structural analysis, was from the Bacúch magnetite deposit in Slovakia, where it occurs in banded and disseminated magnetite mineralization in quartz lenses (Pršek *et al.* 2010).

Both species of hingganite are Fe-poor (<0.14 apfu) and the $^{\text{X}}\square/(^{\text{X}}\square + \text{Fe}^{2+})$ ratios are correspondingly high (0.86–0.92). Calcium contents are modest, in the range 0.065–0.260 apfu, indicating a small datolite component. Whilst there are minor amounts of Cl, F is below detection level in all analyses. The sum of $(\text{REE} + \text{Y} + \text{Ca})$, 1.81–1.94 apfu, is lower than the ideal 2 apfu and indicates partial vacancies at the W site. There is a continuous spread of compositions from Nd-dominant hingganite to hingganite-(Y) (Fig. 8), but

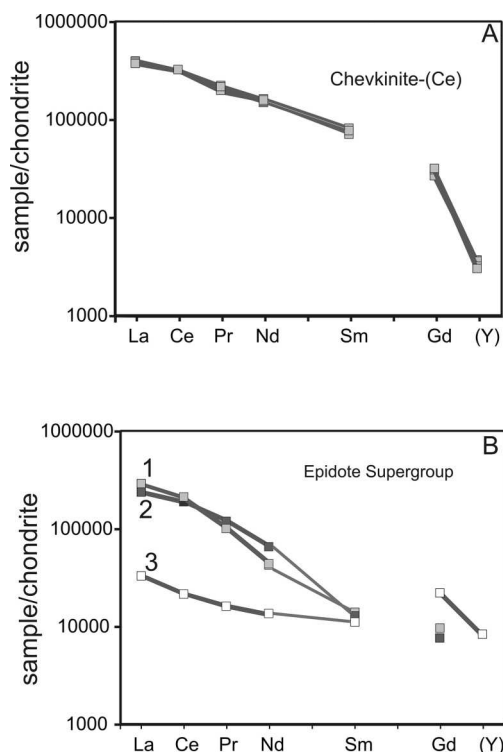


FIG. 6. Chondrite-normalized REE patterns for (A) chevkinite, (B) (ferri)allanite/epidote, with Y proxying for Ho. Normalizing factors from Sun & McDonough (1989). Patterns 1 and 2 are for (ferri)allanite-(Ce) and pattern 3 for epidote. Analyses used: chevkinite, Supplementary Table 2a, nos. 1, 7, 12, 13 (with major overlap of plotted points); epidote-supergroup, Supplementary Table 2b, nos. 5, 8, 13.

there are slight differences between the two species. As well as elevated Y contents, hingganite-(Y) has higher Ca and HREE (from Gd to Yb) and lower REE (from La to Nd) than Nd-dominant hingganite. The analytical totals are, on average, 1 wt.% lower (93.71 and 94.81 wt.%, respectively). These features can be interpreted as replacement of LREE by HREE and addition of some Ca during interaction with fluids (*i.e.*, to the darker phase in Fig. 4D). This is neatly demonstrated in the chondrite-normalized REE patterns (Fig. 9A). In Nd-dominant hingganite, the patterns peak at Nd; with inferred progressive alteration [towards hingganite-(Y)], the peak moves towards the HREE. Both types show positive Ce anomalies, with Ce/Ce* in the ranges 1.26–1.40 (Nd-dominant) and 1.17–1.37 (Y-dominant). The patterns for the Nd-dominant phase compare well with those of Nd-dominant hingganite from the Bacúch magnetite deposit (Pršek *et al.* 2010).

Titanite and rutile

Electron microprobe analyses of titanite are presented in Supplementary Table 3a, with representative compositions in Table 3. Two types can be broadly distinguished; a higher-Nb variety has Nb > 0.05 *apfu* (Nb₂O₅ > 3.5 wt.%) and is brighter on BSE images (Fig. 5A). It also has higher Fe and lower Ti contents than the darker variety. Other elements (Zr, Sn, Ce, Nd, Sm, Y, and Mg) are present in abundances ≤ 0.03 *apfu*. The two varieties are invariably associated texturally; where discernible, the lower-Nb phase appears to be replacing the higher-Nb type (Fig. 5A), for example along fractures.

Compositions of rutile are presented in Table 3. Oxide totals are in the range 98.11–101.78 wt.% and the sum of cations is 1.01 *apfu*. The composition is close to ideal TiO₂ (Ti_{0.96–0.99}). All other elements, where detectable, are < 0.02 *apfu*, but there is a small replacement of Ti by Nb, Ca, and Fe.

Fergusonite

Members of the fergusonite group have the general formula ABO₄, where A stands for REE and Y and B for Nb and Ta. In the metasomatite, minerals of the group occur as the large crystal in Zone B (Fig. 4C), as small ragged grains in Zones B and C, and as a veinlet and patches associated with cerite-(Ce) at the junction of Zones A and C (Fig. 3A, B). Selected compositions are given in Table 4; the full data set is available in Supplementary Table 3b. Formulae were calculated on the basis of (Nb + Ta + Ti + W) = 1 *apfu*. Oxide analytical totals are, with the exception of three point analyses discussed below, in the range 98.34–101.58 wt.% (average 99.86 wt.%). Total cations are between 1.97 and 2.15 *apfu* (average 2.04 *apfu*), close to the theoretical 2 *apfu*.

The great majority of point analyses are of fergusonite-(Y), although two are of fergusonite-(Ce) and one of fergusonite-(Nd). All three varieties occur in the large fergusonite-(Y) crystal (Fig. 4C), which shows an almost continuous compositional spread from fergusonite-(Y) through fergusonite-(Nd) to fergusonite-(Ce) (Fig. 10). Despite the differences in composition, there seems to be no systematic relationship to the brightness in BSE images. There are, however, different chondrite-normalized patterns (Fig. 9B), of which a notable feature is the replacement in the fergusonite-(Y) of a negative Eu anomaly (Eu/Eu* 0.44–0.91) by a positive anomaly (Eu/Eu* 1.03–1.67) that is positively correlated with the Y content. With three exceptions, they show positive Ce anomalies (Ce/Ce* ≤ 1.70) that are negatively correlated with Y content. The fergusonite-(Ce) pattern shows a modest negative Eu anomaly (Eu/Eu* 0.57) and a positive Ce anomaly (Ce/Ce* 1.25). Textural relationships do not

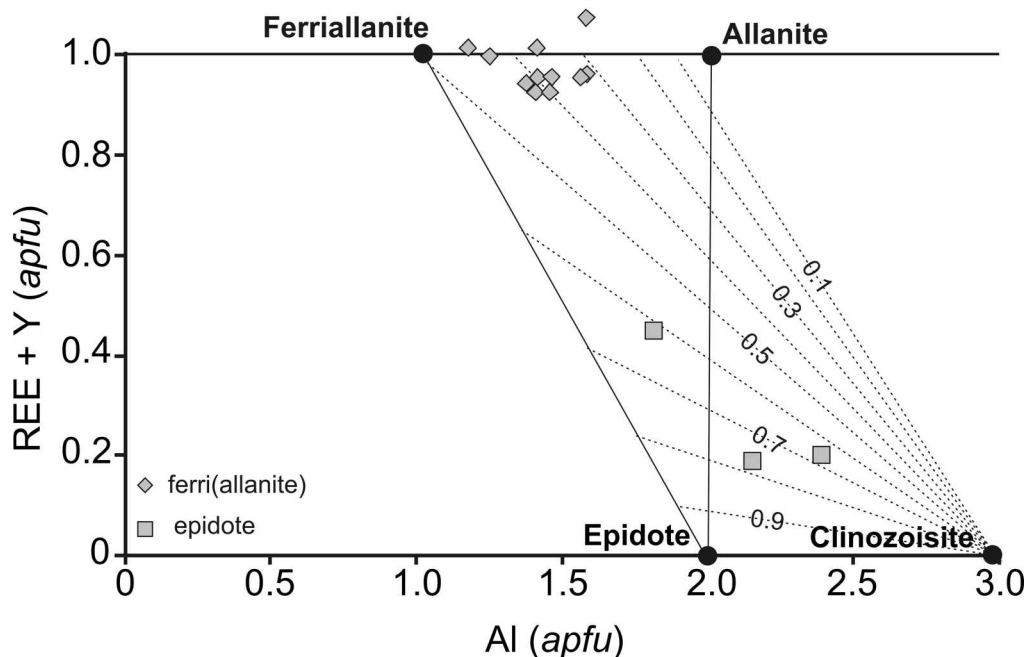


Fig. 7. Epidote-group minerals plotted in the (REE + Th + Mn + Sr) versus Al diagram of Petrik *et al.* (1995), contoured with isolines of the ratio $\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}^{2+})$. The general increase in oxidation ratio from (ferri)allanite-(Ce) to epidote is in keeping with the ratios calculated from stoichiometry. Data from Supplementary Table 2b.

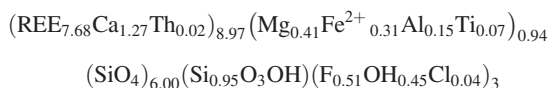
give a clear answer to the relative ages of the Y-dominant and LREE-dominant varieties. However, the positive correlation between the Y content and the positive Eu anomaly might suggest that the fergusonite-(Y) was later. Kartashov *et al.* (1993), for example, described late-formed REE-epidote extremely enriched in Eu in the Tatyana pegmatite. The feature was explained by release of Eu during recrystallization of plagioclase in host basic rocks during the main metasomatizing event. If such a process is applicable, for example, to the Eu-rich fergusonite-(Ce) in the metasomatite, it provides evidence that the different stages of the alteration process took place essentially simultaneously.

The fergusonite-(Y) occurring in association with the titanite-rutile pseudomorphs in Zone B and as late grains in Zone C has compositions within the range shown in the large fergusonite-(Y). The replacement of a higher-Nb titanite by a lower-Nb type (above) and the formation of late-stage Nb,Y-oxides suggest that the mobility of Nb became limited at this stage. Reference was made earlier to three point analyses showing low oxide totals (84.50–95.76 wt.%; Supplementary Table 3b). They also have slightly high cation sums (2.30–2.54 *apfu*). The occurrence of this phase is unusual; it forms zones, dark on BSE images, in a composite grain with more normal fergusonite-(Y) (Fig. 5C). The compositions are different from others in the data set in having lower Nb, Ta, Y, and REE from Eu to Yb, and higher Ca, Ti, Zr, Th, W, La,

Ce, and SiO_2 . The levels of SiO_2 (≤ 10.19 wt.%) seem extraordinarily high but Papoutsas & Pe-Piper (2013) recorded up to 4.45 wt.% SiO_2 in aeschynite-(Y) from the Wentworth pluton, Nova Scotia. Although La and Ce have fractionated from the other REE, there was not a marked decrease in total REE. This grain appears to have undergone a rather different alteration history from the other fergusonite crystals, late in the alteration record, with extensive hydration and addition of Si and Al, as demonstrated by Ercit (2005) for various Nb,Y-oxides.

Cerite-(Ce)

The presence of cerite in the metasomatite has been confirmed by powder X-ray diffraction patterns, with characteristic peaks at 2.95, 1.95, 2.83, and 3.47 Å, and by the tabular-rhombohedral habit of the crystals. Representative compositions are given in Table 5 and the full data set in Supplementary Table 3c. Oxide totals, with two exceptions (below), are in the range 94.51–97.51 wt.% (average 96.69 wt.%), the deficit being mainly due to the non-determination of water. Structural formulae have been calculated on the basis of 17 cations *pfu*. The average composition has the formula:



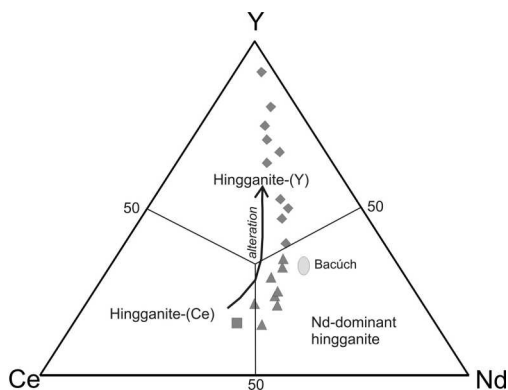


FIG. 8. Y–Ce–Nd plot for hingganite. The trend from Ce- to Y-dominance, shown by the arrow, was a result of progressive hydrothermal alteration. Data from Supplementary Table 2c.

Cerium is the dominant REE and the phase is thus cerite-(Ce). In several point analyses (and in the average analysis) F exceeds calculated OH.

The sum of (REE + Y + Ca) is in the range 7.91–9.23 *apfu* (average 8.94 *apfu*). Calcium levels vary from 0.35–1.74 *apfu* and are negatively correlated with REE + Y (Fig. 11A). Shown for comparison are data for cerite-(Ce) from the Norberg district, Bergslagen mining region, Sweden, which Holtstam & Andersson (2007) noted is relatively Ca-poor. Magnesium and Fe^{3+} abundances in the cerite-(Ce) range from 0.29–0.58 *apfu* (with two exceptions, noted below) and 0.18–0.47 *apfu*, respectively, and are crudely negatively correlated. On the basis of a clear negative correlation between the elements in the Norberg cerite, Holtstam & Andersson (2007) proposed the possible exchange mechanism $\text{Fe}^{3+} + \text{Ca}^{2+} = \text{Mg}^{2+} + \text{REE}^{3+}$. The mechanism is also applicable to the cerite-(Ce) in the metasomatite (Fig. 11B). There are significant levels of Al (0.022–0.229 *apfu*), but it is always subordinate to Fe and Mg. Chondrite-normalized patterns show peaks at Ce and then a steady decrease through the heavier REE (Fig. 12). There are small positive Ce anomalies ($\text{Ce}/\text{Ce}^* = 1.14\text{--}1.37$), which tend to be higher in the more Fe-rich compositions.

In the strikingly zoned crystal shown in Figure 3B, the darker material has higher Mn, Ti, P, Nb, Th, Cl, and HREE contents, lower LREE and Si contents, and lower oxide totals than the lighter material. The compositional modifications may have been a result of hydrothermal mineralization, although the possibility cannot be precluded that the higher Nb and Ti values reflect contamination by the neighboring phases. Both the darker and lighter material in the patchily zoned grain shown in Figure 3D have very low oxide totals (85.61, 82.73 wt.%) and high Si values (8.32–8.42 *apfu*). The darker material has a low Ca content (0.157

apfu) and a low La/Nd atomic ratio [0.13 as opposed to 0.33–1.53 in the other cerite-(Ce) analyses]. Our interpretation of the relationship is that the crystal developed growth zonation but that one composition in the zones was unstable and underwent selective metamictization and hydration, probably accompanied by absorption of non-structural components (*e.g.*, Nb and Ti). It appears that Ca was removed from this darker phase and La (and Ce) replaced by heavier REE, especially Nd, and Si. The exchange is strongly reflected in the chondrite-normalized REE patterns (Fig. 12). The Ce anomalies are larger than in the unaltered material ($\text{Ce}/\text{Ce}^* = 1.93, 2.15$).

Thorite

Thorite is relatively uncommon in the metasomatite, presumably a result of the Th-poor nature of the unaltered

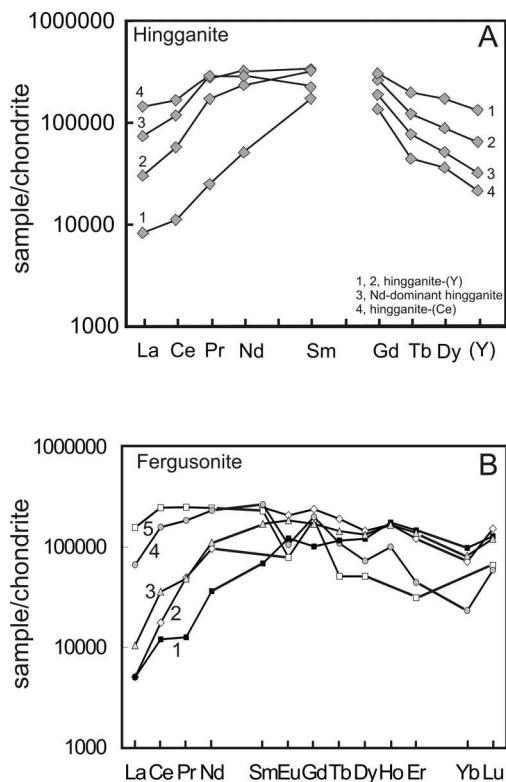


FIG. 9. Representative chondrite-normalized REE patterns for (A) hingganite and (B) fergusonite-(Y). Y is used as a proxy for Ho in (A). Normalizing factors from Sun & McDonough (1989). (A) Patterns 1 and 2, hingganite-(Y); pattern 3, Nd-dominant hingganite; pattern 4, hingganite-(Ce); Supplementary Table 2c, numbers 18, 10, 1, 19). (B) All analyses from large fergusonite-(Y) crystal (Fig. 4C); patterns 1–4 are fergusonite-(Y), pattern 5 for fergusonite-(Ce). Supplementary Table 3b, numbers 2, 5, 7, 11, and 15.

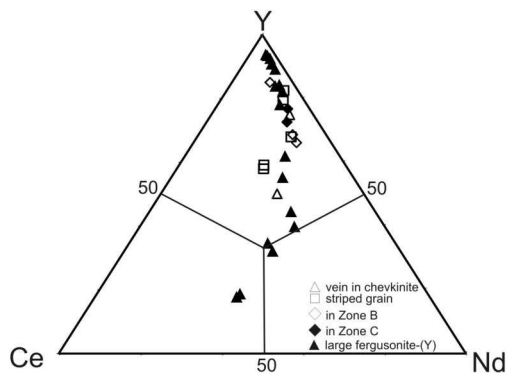


FIG. 10. Ce–Y–Nd plot for fergusonite. There is an almost continuous range of compositions; the full range is found in the crystal shown in Figure 4C. Data from Supplementary Table 3b.

chevkinite-(Ce) (≤ 0.022 apfu). Analyses are available (Table 6) of five small, bright grains enclosed in the large, primary fergusonite-(Y) crystal shown in Figure 4C. Oxide totals are low (91.39–96.48 wt.%) and it seems likely that the thorite has been variably hydrated, perhaps during and after metamictization. The average composition is $(\text{Th}_{0.81}\text{Y}_{0.09}\text{Ca}_{0.07})\Sigma_{0.97}(\text{Si}_{0.96}\text{P}_{0.03})\Sigma_{0.99}\text{O}_4$. Uranium levels are low (0.015–0.026 apfu; 1.21–2.24 wt.% UO_2), with Th/U ratios in the range 31–52. REE contents are significant (ΣREE 0.099–0.201 apfu; $\Sigma\text{REE}_2\text{O}_3$ 3.97–9.16 wt.%), with Y the dominant cation (up to 0.11 apfu; 2.04–3.77 wt.% Y_2O_3). Chondrite-normalized patterns (not shown) are convex, peaking at Gd. One pattern shows a small positive Ce anomaly (Ce/Ce* 1.03). The ranges of $[\text{La}/\text{Nd}]_{\text{CN}}$ and $[\text{La}/\text{Y}]_{\text{CN}}$ values (0.41–1.21 and 0.32–1.30, respectively) indicate some fractionation between the LREE and of LREE from HREE.

REE-carbonates

Three point analyses have been made of REE-carbonate in the large fergusonite-(Y) crystal shown in Figure 4C (Table 5; Supplementary Table 4). It is hydroxylbastnäsite-(Ce), with significant levels of Ca (0.25 apfu) and Sr (< 0.04 apfu), on a 1-cation basis. Fluorine levels are below detection level. Two point analyses have also been made of a veinlet cutting and rimming a cerite-(Ce) crystal in the allanite zone (Fig. 5D; Supplementary Table 4). It is hydroxylbastnäsite-(Ce), with detectable F (0.04 apfu).

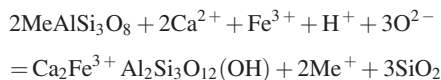
MINERAL ASSEMBLAGES

The following sequence of events during formation of the pegmatite and its subsequent interaction with hydrothermal fluids may be deduced from this, and previous, studies:

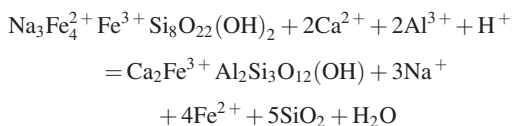
(1) Peralkaline granite pegmatite is formed, including the crystallization of rare-metal minerals such as chevkinite-(Ce), ferriallanite-(Ce), and fergusonite-(Y). Crystallization in the sequence chevkinite-(Ce)–ferriallanite-(Ce)–allanite-(Ce)–epidote points to the progressive depletion of the mineral-forming fluid in Ti, REE, and Fe and a relative enrichment in Ca and Al (*cf.* Jiang 2006, Vlach & Gualda 2007, Macdonald *et al.* 2013). There was also a decrease in LREE/HREE ratios and, in the epidote, a positive Ce anomaly was replaced by a negative anomaly. As to the origin of the granular/Y-shaped aggregates of titanite and rutile in Zone B (Fig. 4b), their form suggests that they pseudomorphed a primary phase of the pegmatite, replacing it with a very small change of volume. This phase may have been a member of the chevkinite group, perhaps the Ca analogue of matsubaraita $[(\text{Ca},\text{REE})_4(\text{Ti},\text{Nb},\text{Fe})_5(\text{Si}_2\text{O}_7)_2\text{O}_8]$. Its association with (ferri)allanite-(Ce) indicates that it crystallized rather later than the chevkinite-(Ce).

(2) Initial fluid-induced alteration of the pegmatite resulted in the formation of a quartz–epidote metasomate. The alteration of the primary feldspar, arfvedsonite, and aegirine may have proceeded through reactions of the type:

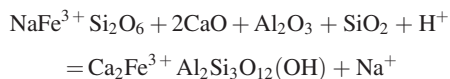
(a) feldspars $\rightarrow$ epidote



(b) arfvedsonite $\rightarrow$ epidote



(c) aegirine $\rightarrow$ epidote



The rare-metal minerals, with the exception of hingganite, were partially mobilized and recrystallized, and, in most cases, enlarged.

(3) During further hydrothermal interactions, there was replacement of chevkinite-(Ce) by titanite and rutile along the chevkinite–allanite boundary (Zone C; Fig. 2), with abundant Nb,Y-oxides and REE-carbonate occurring towards Zone B, accompanied by the partial replacement of all three zones, including alteration of the fergusonite-(Y) in Zone B to a complex hingganite–cerite–REE-carbonate assemblage (Fig. 4C). The Nb and Ti in the titanite and rutile and the LREE in the carbonate were clearly derived from the chevkinite-(Ce).

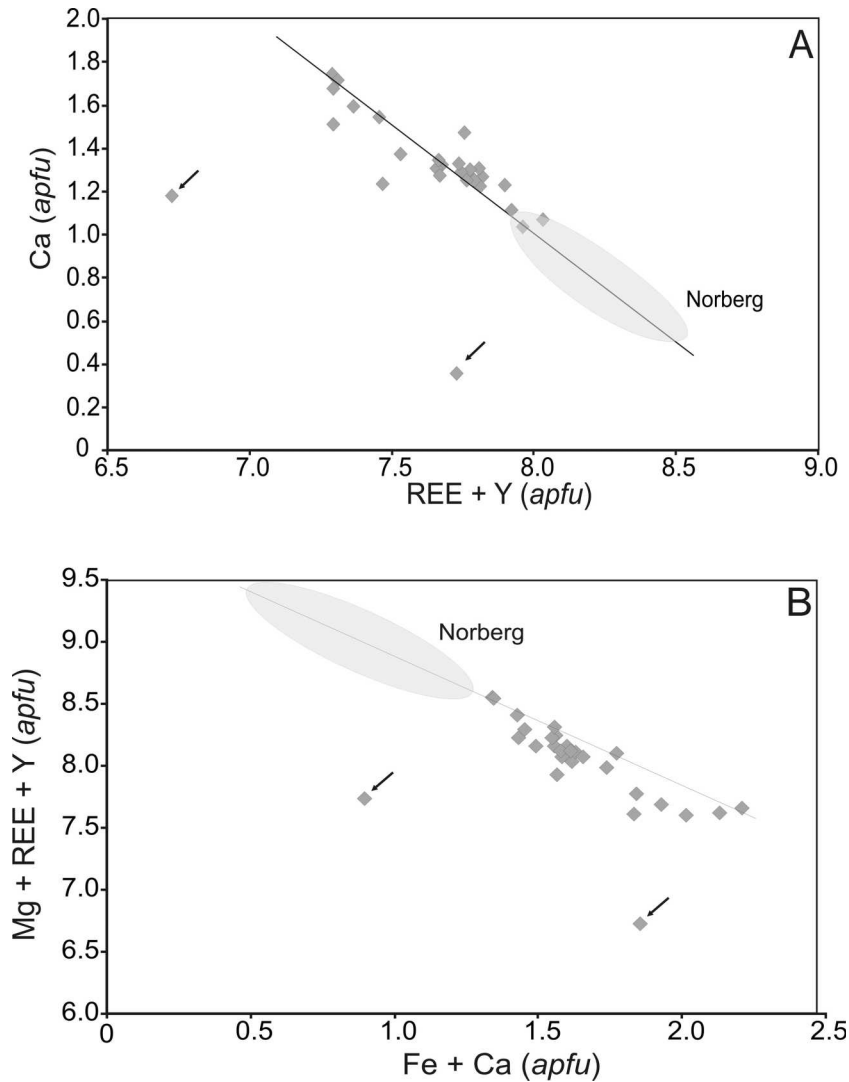
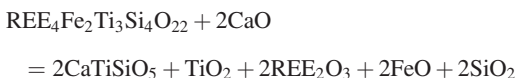


FIG. 11. (A) Variation of Ca against REE+Y in cerite-(Ce). Data from Supplementary Table 3c. The field for cerite from the Norberg District, south-central Sweden, is from data in Holtstam & Andersson (2007). The solid line is for an ideal (REE + Y + Ca) value of 9 *apfu*. (B) The substitution mechanism proposed by Holtstam & Andersson (2007) for the Norberg cerite is also applicable to cerite-(Ce) in the metasomatite. The solid line indicates (Mg + REE + Y + Fe + Ca) values of 10 *apfu*. The arrowed points in both plots are for the strongly altered crystal shown in Figure 3D (Supplementary Table 3c, nos. 26, 27).

A much simplified scheme of the chevkinite alteration to titanite (and rutile) is:



The elements were released, accompanied by an input of Ca, Mg, Be, and F, then formed hingganite-(Y), Nd-dominant hingganite, cerite-(Ce), and hydroxylbastnäsite-(Ce). Formation of these phases limited the mobility of the LREE, which were effectively trapped in the system. Textural features in the hingganite were interpreted above

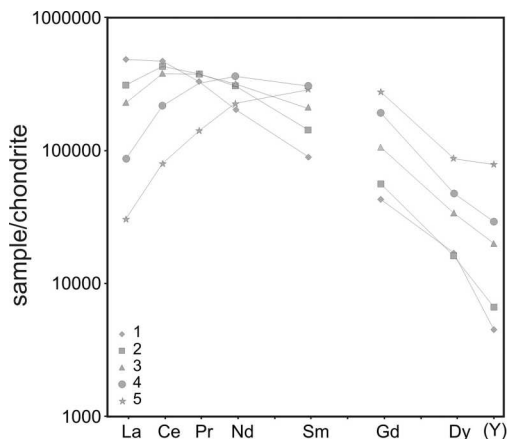


FIG. 12. Chondrite-normalized REE patterns for cerite-(Ce), with Y proxying for Ho. The point analyses showing Y + HREE enrichment relative to LREE (patterns 1 and 2) are from a strongly altered crystal (see text). They are the arrowed points in Figure 11. Normalizing factors from Sun & McDonough (1989). Source data (including textural information) for patterns 5, 4, 3, 2, 1 are from Supplementary Table 3c, nos. 11, 16, 23, 26, 27.

as indicating replacement of LREE by Y + HREE and addition of some Ca during interaction with the fluids.

The late-stage leaching of LREE during fluid-rock interaction and their replacement by Ca, HREE, and Y has previously been reported from peralkaline silica-oversaturated intrusions by Salvi *et al.* (2000), Salvi & Williams-Jones (2006), Kynicky *et al.* (2011), and Gysi & Williams-Jones (2013).

NATURE OF HYDROTHERMAL FLUIDS

Temperature

In a study of aqueous, CO_2 -bearing, L + V inclusions in quartz and epidote in the metasomatites, Andreev *et al.* (1994) recognized primary and secondary inclusions. The primary inclusions in the epidote are rectangular, with vapor/liquid ratios varying from 30:70 to 40:60. The inclusions homogenized at 434–453 °C. Primary inclusions in quartz are rounded, ellipsoidal, or rectangular and are located along growth zones in the crystals. They homogenized at 422–446 °C. Primary quartz crystals in the recrystallized quartz core of the pegmatite have vapor/liquid ratios of 25:75 to 30:70; they homogenized at 318–364 °C. The temperature range 318–446 °C has been taken to be that of formation of the metasomatite and thus of chevkinite recrystallization and growth.

Late-stage alteration proceeded under rather different conditions. The secondary fluid inclusions in quartz have rounded or ellipsoidal forms, are located along healed fractures, are binary and ternary, and have vapor/liquid ratios from 20/20/60 to 10/20/70

(Andreev *et al.* 1994). On heating the first liquid CO_2 disappeared at 156–160 °C; this range may be taken as that of chevkinite alteration.

Alkalinity

Various features indicate that the hydrothermal fluids were acidic. The equations given above for the formation of metasomatic epidote involved incorporation of H ions from the fluids. The formation of thorite as a secondary phase during the alteration of fergusonite suggests that the fluids were acidic (pH ~ 2), where Th has a low solubility (Oelkers & Poitrasson 2002, Harlov & Hetherington 2010). The presence of abundant cavities (porosity) infilled by quartz and calcite may well have been produced by acidic fluids (Gysi & Williams-Jones 2013).

$f\text{O}_2$

Virtually all the REE-bearing phases show positive Ce anomalies (Figs. 9, 12). This is consistent with oxidizing conditions, where Ce^{3+} is converted to Ce^{4+} and thus fractionates from the trivalent LREE (Gieré & Sorensen 2004, Mayer *et al.* 2014). Specifically, the Ce anomalies in altered cerite are larger than in the unaltered material ($\text{Ce}/\text{Ce}^* = 1.93, 2.15$), which possibly reflects alteration under more oxidizing conditions. This feature is also consistent with the increasing oxidation in the replacement of ferriallanite-(Ce) by allanite-(Ce) and then by epidote.

CO_2 , F, and Cl

Direct evidence of the presence of CO_2 during metasomatism comes from the fluid inclusions in quartz and epidote (Andreev *et al.* 1994). REE-carbonates occur as patches in fergusonite-(Y), but mainly as late-stage veinlets, possibly indicating that CO_2 was an important component of the fluids during the latest stages of alteration. This is consistent with the alteration of titanite to rutile (Fig. 4B), pointing to relatively high $f\text{CO}_2$ and reactions of the type: titanite + CO_2 + REE $\rightarrow$ rutile + REE-carbonates + SiO_2 (Wang *et al.* 2001). Furthermore, calcite was the latest hydrothermal phase, occurring in cavities.

Fluorine was undoubtedly a component of the fluids in the later stages of alteration of the metasomatite, although it may not have been dominant. The cerite-(Ce) contains significant levels of F, but some of the bastnäsite-(Ce) is a hydroxyl variety, implying low F activity (Hsu 1992), and F is absent from the hingganite. Fluorite occurs as a very late phase, in cavities with quartz and calcite. Although there is a general absence of fluorite from the rocks of the northern part of the Haldzan Buragtag massif, it was suggested above that our study locality was rich in metasomatized and recrystallized eudialyte that trapped the bulk of the F in the rock. The F was trapped in the volume of rock until captured by cerite. Petrographic evidence, such as the presence of late-stage fergusonite-(Y), indicates

that Nb showed rather limited mobility during alteration and was retained within the system. This is consistent with a low content of F in the fluid: Timofeev *et al.* (2015) demonstrated experimentally that the solubility of Nb₂O₅ (solid) in aqueous fluids increases with increasing HF concentration. Apart from minor amounts in hingganite and cerite, Cl is absent from the metasomate phases and seems not to have been an important component of the hydrothermal fluids.

The question remains: what was the ultimate source of the hydrothermal fluids? The primary pegmatites were formed during intrusive phases 5 and 7 of Kovalenko *et al.* (1995). Metasomatism was therefore related to one or more of the remaining five phases. Numerous late intrusions of mantle-derived basaltic magma were emplaced over this period and may have been the source of low-temperature fluids with the very simple composition H₂O–CO₂–Ca, with minor amounts of Mg.

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