

Prograde metamorphic sequence of REE minerals in pelitic rocks of the Central Alps: implications for allanite–monazite–xenotime phase relations from 250 to 610 °C

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ABSTRACT The distribution of REE minerals in metasedimentary rocks was investigated to gain insight into the stability of allanite, monazite and xenotime in metapelites. Samples were collected in the central Swiss Alps, along a well-established metamorphic field gradient that record conditions from very low grade metamorphism (250 °C) to the lower amphibolite facies (~600 °C). In the Alpine metapelites investigated, mass balance calculations show that LREE are mainly transferred between monazite and allanite during the course of prograde metamorphism. At very low grade metamorphism, detrital monazite grains (mostly Variscan in age) have two distinct populations in terms of LREE and MREE compositions. Newly formed monazite crystallized during low-grade metamorphism (< 440 °C); these are enriched in La, but depleted in Th and Y, compared with inherited grains. Upon the appearance of chloritoid (~440–450 °C, thermometry based on chlorite–chloritoid and carbonaceous material), monazite is consumed, and MREE and LREE are taken up preferentially in two distinct zones of allanite distinguishable by EMPA and X-ray mapping. Prior to garnet growth, allanite acquires two growth zones of clinozoisite: a first one rich in HREE + Y and a second one containing low REE contents. Following garnet growth, close to the chloritoid–out zone boundary (~556–580 °C, based on phase equilibrium calculations), allanite and its rims are partially to totally replaced by monazite and xenotime, both associated with plagioclase ($\pm$ biotite $\pm$ staurolite $\pm$ kyanite $\pm$ quartz). In these samples, epidote relics are located in the matrix or as inclusions in garnet, and these preserve their characteristic chemical and textural growth zoning, indicating that they did not experience re-equilibration following their prograde formation. Hence, the partial breakdown of allanite to monazite offers the attractive possibility to obtain *in situ* ages, representing two distinct crystallization stages. In addition, the complex REE + Y and Th zoning pattern of allanite and monazite are essential monitors of crystallization conditions at relatively low metamorphic grade.

Key words: allanite; central Alps; monazite; rare earth elements; xenotime.

INTRODUCTION

While *in situ* U–Pb dating of monazite has been possible for over a decade (e.g. Williams *et al.*, 1996), precise Th–Pb isotopic dating of allanite has only recently delivered satisfactory results (Catlos *et al.*, 2000; Gregory *et al.*, 2007). This now opens new avenues in geochronology because allanite has the potential to record low-temperature conditions, for which ages obtained using the Ar–Ar or Rb–Sr isotopic systems are often difficult to interpret. Moreover, allanite provides an alternative to xenotime and monazite already used as U–Th–Pb chronometers of low-temperature metamorphic conditions (Rasmussen, 2005; Sheppard *et al.*, 2007). Allanite is potentially a useful petrogenetic indicator because it occurs in a variety of low-temperature metamorphic environments; it is widespread in the greenschist facies (Smith & Barreiro,

1990; Wing *et al.*, 2003; Bollinger & Janots, 2006; Tomkins & Pattison, 2007), but is also common at blueschist to eclogite facies conditions (Hermann, 2002; Spandler *et al.*, 2003; Janots *et al.*, 2006). Importantly, allanite and monazite display phase relations that can be used to relate precise ages to well-constrained *P–T* conditions of reactions, provided these are identified and understood. One attempt is to compute phase diagrams for these minerals, using calorimetric data. Janots *et al.* (2007) presented such results for La end-members, but data are lacking for many REE phases. Hence, phase relationships of allanite and monazite are still mainly inferred from petrological data for natural phase relations. Smith & Barreiro (1990) were the first to analyse a sequence involving replacement of monazite by allanite at greenschist facies conditions, and to show that monazite reappears in metapelites at the staurolite-in

isograd. Wing *et al.* (2003) confirmed an allanite stability window under greenschist facies conditions, and added details of the possible reactions. They found that allanite formation from composite (detrital and metamorphic) monazite coincides with the appearance of biotite, whereas allanite breakdown to monazite is related to the formation of aluminosilicates (andalusite, kyanite, cordierite or staurolite). At higher pressure conditions (0.8–1.5 GPa), Janots *et al.* (2006) observed that monazite, stable at 350 °C, disappears in a prograde sequence and is replaced by allanite at temperatures of 420–450 °C. In the Nelson contact aureole, Tomkins & Pattison (2007) found evidence for an allanite-to-monazite reaction that occurs independently from, but close in temperature to the breakdown of muscovite + chlorite to either cordierite, andalusite or staurolite. However, allanite stability depends strongly on bulk-rock composition: while it breaks down at amphibolite facies conditions in metapelites, it can be preserved to higher temperatures in granitoids (Bingen *et al.*, 1996; Finger *et al.*, 1998). Although the allanite stability window is comparable in all of the metapelite sequence studied, the conditions of formation and breakdown of allanite remain under debate, and the parameters controlling the presence of allanite in metapelites are inadequately known. Indeed, while monazite can react to form allanite at temperatures ~400–450 °C (Smith & Barreiro, 1990; Wing *et al.*, 2003; Janots *et al.*, 2006), it is elsewhere preserved up to amphibolite facies (e.g. Rubatto *et al.*, 2001). Furthermore, there are questions regarding the role of allanite in the REE budget at low grade, prior to the appearance of amphibolite facies monazite. Some studies have proposed that LREE are contained in major silicate minerals. Monazite formation ascribed to reactions involving major silicate phases has been mainly inferred from: (1) the absence of a specific REE phase at lower grade (Kohn & Malloy, 2004); (2) relations of the compositional zoning between monazite and garnet (e.g. Foster & Parrish, 2003; Pyle & Spear, 2003); (3) coincidence of monazite appearance at mineral isograds, such as the staurolite appearance from garnet breakdown (Fitzsimons *et al.*, 2005). However, the significance of major silicates participating in monazite forming reactions is controversial. For example, Yang & Pattison (2006) concluded from mass balance calculations that LREE contents in garnet and major silicates are insufficient to form monazite in pelitic rocks. Rather than major metamorphic phases, allanite or other accessory REE minerals are proposed as the major precursors of monazite at amphibolite facies conditions (Simpson *et al.*, 2000; Rasmussen *et al.*, 2006; Yang & Pattison, 2006; Tomkins & Pattison, 2007).

The present contribution, based on metapelites of the Central Alps, aims to clarify whether LREE at low grade are contained in REE minerals or major silicates, to document the occurrence and composition of allanite in a prograde sequence, and to infer metamorphic

reactions responsible for allanite growth and breakdown. The investigation was carried out along a well-established metamorphic profile, recording conditions from very low grade metamorphism up to lower amphibolite facies (Frey, 1978), in an area that offers excellent exposures of regionally metamorphosed rocks. The metamorphic field gradient evolved in a single orogenic cycle from Mesozoic protoliths; the thermal peak was reached during the mid-Tertiary.

GEOLOGICAL SETTING

The central Alps of Switzerland are part of the Alpine orogen delimited by the Subalpine Swiss molasse to the north and the Insubric Line to the south (Fig. 1). This domain comprises pre-Alpine basement units shaped essentially by the Caledonian (470–445 Ma) and Variscan (360–260 Ma) orogenies (Schaltegger & Gebauer, 1999), as well as younger (meta)sedimentary rocks that record only the Alpine orogeny. Tertiary Barrovian metamorphism generated a thermal imprint, with grade increasing from north to south, as illustrated by the mineral zone boundaries and isograds (Fig. 1). Along a transect from the Helvetic pre-Alps to the Insubric Line, metamorphic conditions range from very low grade metamorphism to upper amphibolite facies (Frey, 1978; Frey & Ferreiro Mählmann, 1999).

In this study, the samples investigated derive from Triassic and Jurassic pelites (locally referred to as Quartenschiefer and Bündnerschiefer). They were collected along the metamorphic transect between the Helvetic Alps and the Northern Steep Belt of the Lepontine domain, recording a progressive metamorphic grade up to lower amphibolite facies (Fig. 1; Frey, 1978; Frey & Ferreiro Mählmann, 1999; Frey *et al.*, 1980). Quartenschiefer samples of the lowest metamorphic grade were collected at Quarten and Lauifurkel (Fig. 1). These two localities are within the Glarus Alps where temperature conditions reached between 240 and 260 °C (vitrinite reflectance at the pyrophyllite isograd; Frey, 1987) and 300–350 °C (equilibrium calculations on Prl–Sud–Cal–Dol–Qtz–Grt assemblages and thermometry on calcite–dolomite pairs; Livi *et al.*, 2002). The Urseren Zone corresponds to a band of Mesozoic metasedimentary rocks intercalated between the Aar massif and the Gotthard nappe, which has been sampled at Garvera. This locality is characterized by chloritoid-bearing assemblages. Physical conditions of the sub-greenschist facies metamorphism of Garvera are not precisely constrained in terms of pressure. Temperatures of 400–450 °C have been consistently obtained using chlorite–chloritoid and calcite–dolomite thermometers (Livi *et al.*, 2002). Pressure information is based only on fluid inclusions in veins of the Aar and Gotthard units, with the earliest populations yielding a range of temperatures 420–450 °C at pressures of 0.3–0.4 GPa (Mullis, 1996), but these should be regarded as

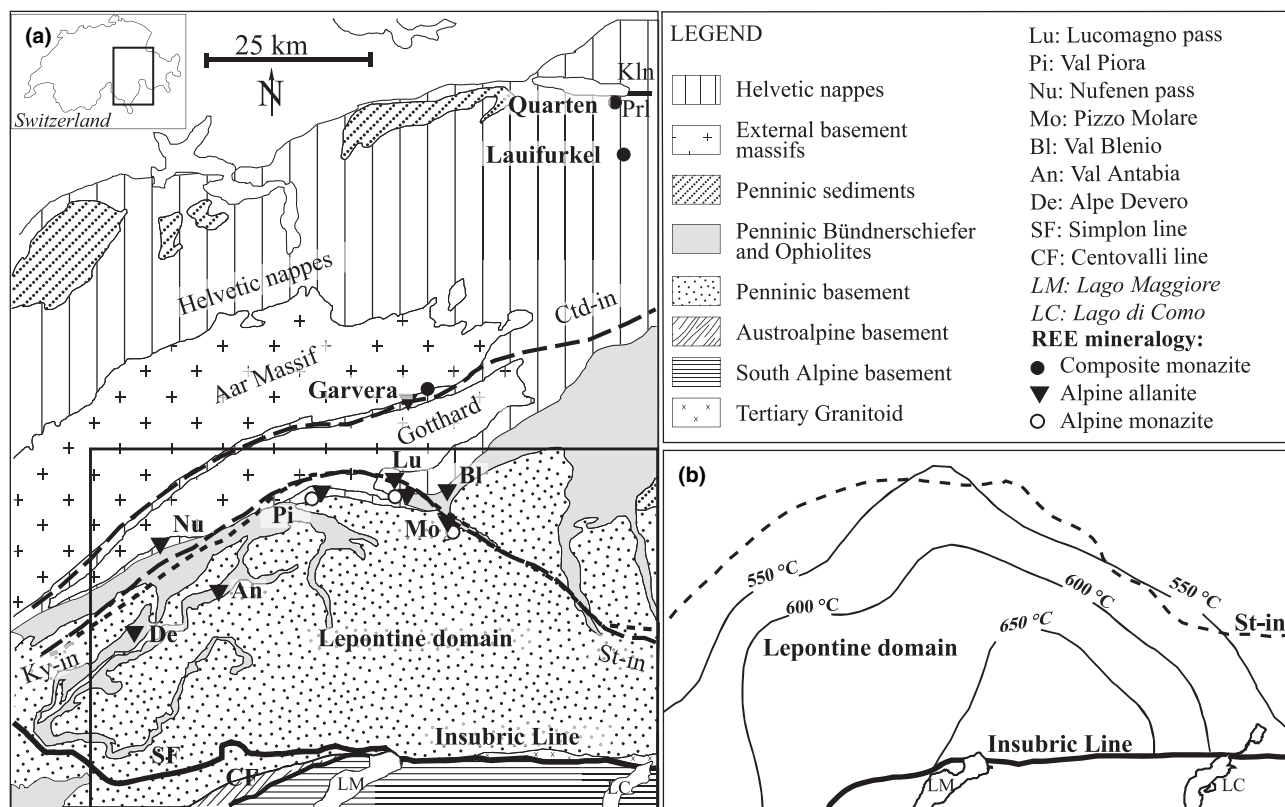


Fig. 1. Tectonic map of the central Alps in Switzerland showing (a) sample locations and mineral isograds (Frey, 1978) (b) isotherms in the Lepontine dome (Engi *et al.*, 1995).

minimum pressure values attending the metamorphic overprint.

Mesozoic metasedimentary rocks were also studied in the Northern Steep Belt, i.e. the northernmost part of the Central Alps (see Fig. 1a for samples locations). In the Lepontine domain as a whole (Fig. 1a, b), the metamorphic grade increases towards the south: greenschist facies is found at the external margin, whereas migmatites are observed near the Insubric line (Fig. 1). Isotherms between 500 and 650 °C form a concentric pattern truncated by the Insubric line (Fig. 1b; Todd & Engi, 1997). The pattern of isobars outlines a domal structure, with pressures decreasing both to the north and to the south (Todd & Engi, 1997). These pressures are thought to reflect the thermal peak of metamorphism (P at $T_{\max}$), not the (earlier) pressure peak. Typical Barrovian P – T paths were followed by most of the units studied here. A thin wedge of metasediments (Valaisian units, Bousquet *et al.*, 2002) had previously experienced high pressures at low temperatures during early Alpine subduction. The subsequent Barrovian evolution certainly post-dated the tectonic integration of these Valaisian slices in the Lepontine nappe stack, the polyphase deformation (Berger *et al.*, 2005) of which is particularly complex in the Northern Steep Belt. However, amphibolite facies assemblages in the present study are syn- to post-kinematic, with

porphyroblasts (e.g. garnet, staurolite) typically overgrowing the latest pervasive deformation structures.

METHODS

Whole-rock analyses were performed on 10 g to 1.0 kg of crushed and pulverized sample rock. Loss on ignition (LOI) was determined by weight difference after ignition at 1000 °C for 16 h. Major element compositions were obtained by XRF analysis (University of Fribourg, Switzerland). Trace elements were analysed by ICP mass spectrometry (ACME lab, Canada).

While P – T conditions for the Central Alps are well established, they were reassessed here for samples, in which reactions between REE minerals occur. The P – T conditions of the metamorphic peak were determined by several methods, depending on metamorphic grade. In sub-greenschist facies samples, temperatures were derived from chlorite–chloritoid thermometry (Vidal *et al.*, 1999). In the 330–650 °C range, the maturation of carbonaceous material was measured by Raman spectrometry, using the calibration of Beyssac *et al.* (2002). For both methods average temperatures and standard deviations (2σ) are reported; the latter do not include the dispersion in the calibration curves (estimated accuracy ± 50 °C). In the upper greenschist to amphibolite facies, pressure and temperature were

obtained using TWQ software (Berman, 1988, 1991). P – T results are given with a 2σ uncertainty, based on a minimum of three linearly independent reactions.

The REE minerals were identified on polished sections using optical microscopy and backscattered images of the electron microprobe (EMPA, Jeol JXA8200, University of Bern) and scanning electron microscope (CamScan SC4, University of Bern). Quantitative EMP analyses were obtained using the analytical scheme described by Scherrer *et al.* (2000). $K\alpha$ X-ray lines were used for Si, Fe, Ca, P and Al, $L\alpha$ lines for Y, Ce, La and Er, $L\beta$ lines for Pr, Dy, Sm, Ho, Gd, $M\alpha$ lines for Th and $M\beta$ line for U and Pb. For Nd the most intense $L\alpha$ line was preferred to the $L\beta$ line proposed by Scherrer *et al.* (2000) as interference with the $L\beta$ line of Ce is negligible ($<1\%$ error in the Nd elemental value, with lower background fixed to 3 mm). For all elements analysed, background was corrected by linear interpolation from background measurements on the two closest overlap-free positions. Standards included synthetic REE phosphates $\text{La}_{0.95}\text{Nd}_{0.05}\text{TiO}_3$ (La), NdGaO_3 (Nd), Y_2O_3 (Y), PbCrO_4 (Pb), huttonite (Th), uraninite (U), anorthite (Al, Ca), almandine (Si, Fe), albite (Na), ilmenite (Ti). The operating conditions were set to 25 kV, 50 nA for all REE analyses; $\phi(\rho Z)$ matrix correction was applied. For each monazite analysis, a chemical U–Th–Pb age was determined (Montel *et al.*, 1996). Chemical dating was not attempted on allanite as it incorporates high common lead concentrations. U, Th and Pb contents were measured with counting times (peak plus background) of 400 s for Pb, 300 s for U and 200 s for Th. The Th interference ($M\alpha$) with uranium measurement ($M\beta$) was taken into account using the correction factor determined on the huttonite standard:

$$U_{\text{cor}} = U_{M\beta\text{meas}} - (0.00417 * Th_{M\alpha\text{meas}})$$

Pb contents and standard deviations were measured on four spectrometers at the same time. Pb concentrations errors were propagated through the age equation to deduce ages at the 2σ level. Averaged ages were obtained using a weighted regression procedure (Isoplot/Ex software). X-ray maps were obtained for La, Ce, Nd, Th, U, Y, Mn, Mg in monazite and allanite, using the EMP with a beam set to 25 kV and 50 nA. Step size was $<1\ \mu\text{m}$ and the dwell time per pixel was 40 ms.

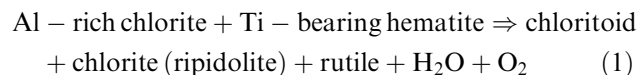
Major silicate minerals from select samples were analysed for REE by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at the Institute of Geological Sciences, University of Bern. The LA-ICP-MS facility consists of an Elan DRC-e ICP-MS and a Geolas Pro 193 nm ArF Excimer laser. Ablation was conducted with an energy density on the sample of $12\ \text{J cm}^{-2}$ using a beam diameter of $44\ \mu\text{m}$ and 8 Hz repetition rate. A He–H₂ gas mixture was used as the aerosol transport gas. The ICP-MS was tuned for low oxide production ($<0.5\%$ ThO) and robust plasma

conditions. External standardization was against NIST SRM 610 glass, using the reference values of Pearce *et al.* (1997). Data reduction was conducted according to Longerich *et al.* (1996) with ^{27}Al used as the internal standard for measurement of all major silicates.

COMPOSITION, MINERALOGY AND PHYSICAL CONDITIONS OF THE SAMPLES

Rare earth elements mineralogy was characterized in Mesozoic metapelites collected or obtained from the collection of the University of Basel (samples from M. Frey). Major- and trace element bulk-rock compositions are presented in Table 1. The major-element compositions are consistent with sediments of pelitic composition rich in Al-rich and Ca-poor compared with average shales (Fig. 2; Shaw, 1956), but compositions vary significantly in AFM space (Thompson, 1957), as shown in Fig. 3. Two metamorphs with higher bulk-rock CaO concentrations were studied as well (MF407 & MF208). As expected for metamorphic rocks of sedimentary origin, the REE contents are enriched relative to chondrite values (Fig. 4). The total REE + Y contents are between 122 and 411 p.p.m., for all samples except MF131, which has higher REE contents (826 p.p.m.). The chondrite-normalized trace element patterns decrease regularly from La to Sm and are nearly flat towards HREE. All samples show a negative Eu anomaly, but with variable intensity. In sample MF482, Ce presents a negative anomaly, whereas it is slightly enriched in samples MF47, MF94 and AMO0410.

The metamorphic sequence of major silicate phases in the samples is representative of the mineralogical changes established by Frey (1969, 1978) along the selected metamorphic transect of the Central Alps. In the Glarus Alps, mineral assemblages mainly include quartz, illite, muscovite and chlorite (MF16 & MF 47, Table 2). With the exception of sample MF407, samples from Garvera are characterized by the growth of chloritoid porphyroblasts (100–500 μm) with inclusions of quartz and rutile, in a matrix of micrometre-scale quartz, chlorite, muscovite and rutile. Apatite porphyroblasts (100–200 μm) feature a core rich in quartz and rutile inclusions, and an inclusion-free rim (Fig. 5a). Chloritoid is thought to form by the following reaction (Frey, 1969; Frey & Wiedeland, 1975):



Analyses of local associations of chlorite and chloritoid in sample MF482 yield an average temperature of $452 \pm 22\ ^\circ\text{C}$, whereas a maximum temperature of $438 \pm 22\ ^\circ\text{C}$ is derived from RAMAN spectra on proto-graphite in sample JGa0609 (Table 2). These results are consistent with those of Livi *et al.* (2002) who used chlorite–chloritoid and calcite–dolomite thermometers, and with fluid inclusion thermometry (Mullis, 1996).

Table 1. Major and trace elements whole-rock composition.

Sample	MF16	MF47 ^a	MF407 ^a	MF131 ^a	MF133	MF482	MF94 ^a	MF161 ^a	MF228 ^a	MF307 ^a	MF315 ^a	APi0413	SPi0306	SDe0303	ADe0301	SMo0407	AMo0410
Major oxide (%)																	
SiO ₂	67.90	61.80	66.50	58.30	67.83	56.54	56.50	52.90	53.00	59.00	54.60	47.75	53.28	57.57	55.05	49.84	59.29
TiO ₂	0.83	0.83	0.80	0.84	1.15	0.67	0.86	1.30	0.59	0.80	1.50	1.06	1.56	0.61	1.04	1.05	0.92
Al ₂ O ₃	17.45	18.80	17.90	19.70	15.33	15.79	24.70	29.70	20.60	20.30	27.90	25.22	26.35	21.13	22.85	25.41	21.92
FeO	3.75	3.40	2.90	8.70	8.90	8.93	8.45	4.70	8.80	6.80	10.30	8.87	8.32	7.25	7.90	10.32	7.38
MnO	0.01	0.03	0.02	0.08	0.00	0.03	0.05	0.02	0.05	0.02	0.05	0.02	0.04	0.50	0.10	0.79	0.34
MgO	1.76	3.20	2.20	2.60	1.83	2.29	1.50	1.50	3.90	5.90	1.40	6.72	1.59	1.50	3.25	2.40	1.93
CaO	0.30	0.27	0.55	0.88	0.48	5.65	0.52	0.35	7.30	1.80	0.31	1.38	1.32	1.76	2.40	1.65	1.05
Na ₂ O	3.46	0.87	0.57	0.73	1.44	2.30	1.20	2.20	2.20	1.60	1.80	3.40	3.11	1.89	0.83	3.05	2.26
K ₂ O	3.88	5.70	4.70	2.60	0.81	2.00	2.70	3.10	1.00	1.80	1.20	3.51	1.65	4.70	3.64	3.78	3.10
P ₂ O ₅	0.11	0.11	0.07	0.06	0.05	0.04	0.08	0.09	0.07	0.16	0.11	0.34	0.02	<0.01	0.18	0.04	<0.01
LOI	4.49	4.60	4.05	5.40	3.36	7.44	3.80	3.90	2.50	1.90	1.00	3.44	3.02	2.23	2.03	1.61	1.83
Σoxide	103.94	99.61	100.26	99.89	101.19	101.68	100.36	99.76	100.01	100.08	100.17	101.70	100.26	99.13	99.27	99.14	100.03
Ca/Ca _{shaw} ^b	0.14	0.12	0.25	0.40	0.22	2.59	0.24	0.16	3.35	0.83	0.14	0.63	0.61	0.81	1.10	0.48	0.76
Al/Al _{shaw} ^b	1.05	1.13	1.08	1.19	0.92	0.95	1.49	1.79	1.24	1.22	1.68	1.52	1.59	1.27	1.37	1.32	1.53
CaO/Na ₂ O	0.09	0.31	0.96	1.21	0.34	2.46	0.43	0.16	3.32	1.13	0.17	0.41	0.42	0.93	2.88	0.47	0.54
Rare earth element (p.p.m.)																	
Y	35.0	15.3	40.0	136.2	38.9	60.4	21.4				35.5	55.5					29.8
La	47.9	21.6	52.3	146.8	24.5	106.7	29.9				38.0	59.9					41.3
Ce	104.7	50.2	96.6	274.4	47.4	103.3	72.6				77.3	128.1					92.7
Pr	11.7	4.6	10.5	31.3	5.6	17.5	7.2				9.1	15.4					9.3
Nd	44.3	16.4	37.6	122.3	23.9	71.4	28.6				36.1	63.9					36.7
Sm	7.9	2.9	7.1	23.4	5.7	13.3	5.2				6.9	12.4					6.8
Eu	0.98	0.33	1.24	5.69	1.45	2.92	1.05				1.06	1.52					1.07
Gd	5.57	2.16	6.37	21.53	5.90	10.91	3.59				6.02	10.75					5.32
Tb	0.99	0.44	1.03	3.89	0.97	1.74	0.66				1.00	1.81					0.82
Dy	6.00	2.50	6.91	24.75	5.80	9.56	3.15				5.84	9.96					5.09
Ho	1.10	0.52	1.35	5.00	1.22	1.89	0.67				1.17	1.89					1.07
Er	3.83	1.95	4.33	14.83	3.71	5.63	2.27				3.87	5.22					2.90
Tm	0.58	0.36	0.63	2.19	0.54	0.88	0.38				0.56	0.76					0.46
Yb	3.45	2.03	4.12	11.98	3.26	4.32	1.86				4.07	4.02					2.80
Lu	0.51	0.32	0.64	1.86	0.49	0.69	0.32				0.56	0.56					0.38

^aMajor elements analyses from Frey (1969).^bCa and Al contents of the samples referenced to Shaw's (1956) average pelite.

In the Northern Steep Belt, metamorphic conditions record the transition between greenschist facies and amphibolite facies, which is characterized by the progressive appearance of the biotite, garnet, kyanite and staurolite (Fig. 1). In all samples, garnet overgrew the main foliation, and porphyroblast evolution is associated with s-collisional folding. The reassessment of the *P*–*T* conditions yields similar temperatures (from 528 °C in MF161 from Lucomagno up to 610 °C in ADe0302 from Alpe Devero), but slightly higher pressures (*P*~0.8–1.0 GPa) compared with the smoothed values of Todd & Engi (1997).

COMPOSITION, TEXTURE, AND AGES OF REE MINERALS

From very low grade metamorphism up to the appearance of chloritoid

In the lowest grade sample studied (MF16), monazite occurs as rounded grains of 10–50 µm in size. Monazite grains often show fractured, porous textures filled with quartz, suggestive of dissolution processes (Fig. 5c). Two populations of monazite are distinguished based on their REE contents (Table 3). The first one is enriched in La and Ce, while the second one is enriched in Nd, Sm and Gd. Based on these variations in REE composition, monazite is here termed LREE monazite (relative enrichment in La and Ce; analyses 1 & 2 in

Table 3) or MREE monazite (relative enrichment in Nd, Sm and Gd; analysis 3 in Table 3). These two distinct monazite compositions were measured in distinct grains; element maps show no evidence of La or Nd zoning within grains. With the exception of one grain with a ThO₂ content of only 1.48%, LREE monazite has relatively high Th and low Y contents (Figs 6a & 7a; analysis 1 in Table 3). By comparison, MREE monazite grains have higher but variable Y contents. X-ray maps of Y in these grains shows that high Y contents occur mostly at grain boundaries. Chemical ages of the two populations are presented in Fig. 8, which shows age as a function of the La/Nd ratio. Ages range between 607 and 135 Ma (Table 4); the average of 330 ± 29 Ma excludes two outliers (discussed below). LREE monazite grains (La/Nd > 1.68) have similar ages, between 362 and 290 Ma, indicating that they formed during the Variscan orogeny (Fig. 8). Monazite grains with La/Nd ratios < 1.32 yield slightly older ages, between 412 and 314 Ma. The two outliers are at 607 ± 18 Ma, presumably a pre-Caledonian relic, and at 135 ± 48 Ma. This younger grain (analysis 2 in Table 3) is low in Th, and its Pb concentration is close to the detection limit, hence the high age uncertainty. Although intermediate in age between Variscan and Alpine values, the composition of this grain is typical of neoformed Alpine grains (Figs 6a & 7a).

Up to the appearance of chloritoid (samples MF47 & MF407), monazite always occurs as grains with

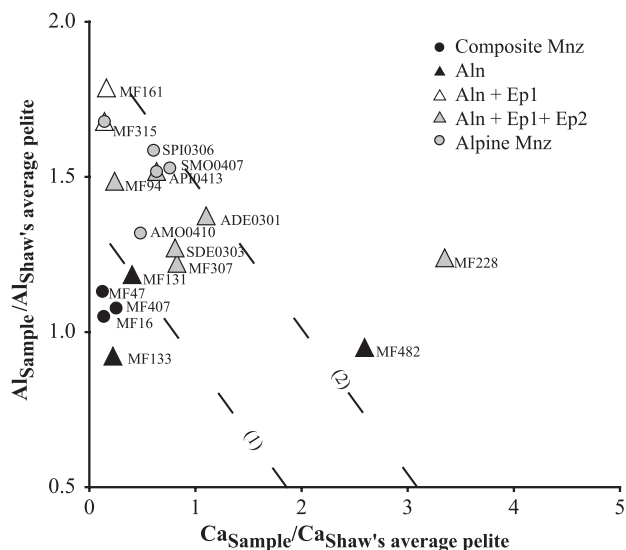


Fig. 2. Whole-rock Ca and Al contents of the samples relative to Shaw's (1956) data for average pelite. Symbols represent REE minerals observed for a given bulk-rock composition (sample numbers indicated): circles used for monazite, triangles for other members of the epidote group. Composite monazite (inherited plus newly formed under very low grade metamorphism) is distinguished from Alpine monazite (formed entirely during Alpine metamorphism at amphibolite facies conditions). Lines (1) and (2) delimit compositional domains that control the reactions between monazite and allanite inferred by Wing *et al.* (2003). According to that study, composite monazite can be preserved in the biotite and garnet zones for Al and Ca contents below line (1), whereas allanite reacts to monazite for Al and Ca contents below line (2) in samples from the And, Ky and Sil zones. In the samples, allanite formed in samples with chloritoid for composition below line (1) and is preserved in association with kyanite in some samples with Al and Ca contents below line (2).

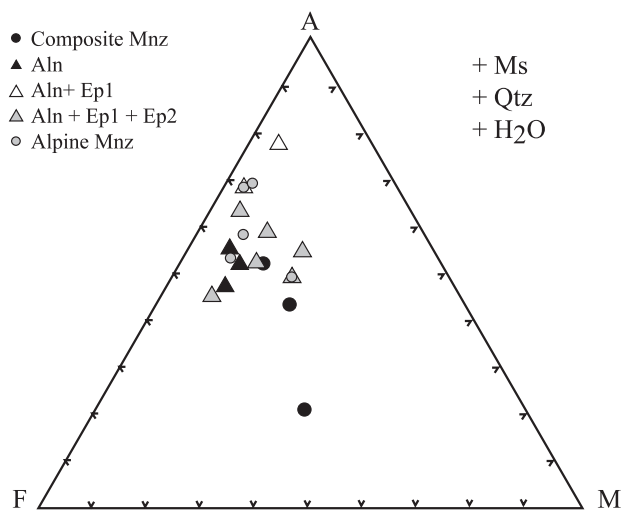


Fig. 3. Whole-rock compositions of samples plotted in the AFM diagram (Thompson, 1957). Symbols as in Fig. 2.

three habits: (1) rounded grains 10–15 μm in diameter; (2) irregularly shaped grains, 10–30 μm in size, associated with xenotime grains (Fig. 5d); (3) tiny grains

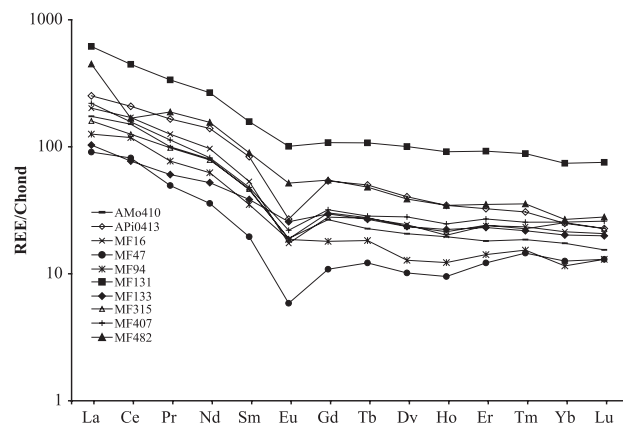


Fig. 4. Chondrite-normalized REE patterns of the samples. Chondrite data for normalization from McDonough & Sun (1995).

(diameter < 5 μm). In the cores of rounded and irregularly shaped grains, EMP analyses show MREE-rich compositions (Figs 6a & 7a) as in sample MF16 at the lowest grade. However, a few analyses of sample MF407 show LREE-rich compositions with high Th and Y contents (Figs 6a & 7a, analysis 5 of Table 3). As at lower grade, most monazite grains are detrital, with average chemical ages of 299 ± 43 and 319 ± 18 Ma in samples MF47 and MF407 respectively (Table 4, Fig. 8). Tiny monazite is very abundant (> 50 grains per thin section), but few EMP analyses are satisfactory owing to the micrometre-size of the grains (analyses 4 & 7 in Table 3). The tiny monazite grains show LREE-rich, Th–Y-poor compositions (Figs 6a & 7a). Chemical dating in samples MF47 and MF407 yields ages with no quantitative significance (Pb below detection limit; Table 4, analyses 21 & 7); in sample MF407 ages between the Alpine and Variscan cycles are found (Table 4, analysis 35). The systematic composition of the tiny grains compares well with one of the newly formed monazite in sample MF16. Where irregularly shaped monazite occurs, their micrometre-size rim cannot be analysed separately from the detrital monazite core. In this case, compositions are qualitatively evaluated from the X-ray maps of La, Nd, Th and Y. In Fig. 9, the element map presents a homogeneous monazite grain rimmed by a thin Nd-rich zone, with a border enriched in La and depleted in Y and Th. An adjacent grain of xenotime appears to contain Th (Fig. 9). Although the monazite rim was too thin to be dated, the chemical similarity with the tiny grains suggests that under these metamorphic conditions detrital monazite grains started recrystallizing at their periphery.

Greenschist facies: samples of chloritoid grade

With the appearance of chloritoid, monazite vanishes, and allanite is found instead as idiomorphic grains oriented in the main foliation (Fig. 5e) or as inclusions

Table 2. Mineralogy and *P–T* conditions of selected samples.

Sample	Location	Chl	Carb.	Kfs	Pl (X_{An})	WM	Cld	Bt	Ky	St	Grt	Mnz	Xen	Aln	Ep1	Ep2	<i>T</i> (°C)	<i>P</i> (GPa)
MF16	Quarten	×	×	×								×	×					
MF47	Lauifurkel	×	×	×	×	×						×	×					
MF407	Garvera	×	×	×	×	×						×	×					
MF131	Garvera	×	×		×	×	×						×	×				
MF133	Garvera	×	×			×	×						×	×				
MF136	Garvera	×	×			×	×						×	×				
MF482	Garvera	×	×			×	×						×	×			452 ± 22 ^a	
JGa0609	Garvera	×	×			×	×							×			438 ± 22	
MF101	Lucomagno	×			×	×		×						×	×			
MF94	Lucomagno	×				×	×							×	×	×		
MF160	Lucomagno	×				×	×	×	×	×				×	×	×		
MF161	Lucomagno	×			0.27–0.28	×	×	±	×	×				×	×		528 ± 22 ^a	
MF228	Lucomagno	×			×		×	×	×	×				×	×	×		
MF307	Lucomagno	×			×		×	×	×	×				×	×	×		
ACb0301	Blenio	×			0.60–0.85	×		×			×			×	×	×	547 ^c	0.61 ^c
AAAn0401	Antabia	±			0.55–0.77	×		×			×			×	×	×	541 ± 10 ^c	0.69 ± 0.02 ^c
ANu0304	Nufenen	±	×			×	±	×			×			×	×	×	552	0.78
APi0413	Piora	±			0.10–0.28	×		×	×	×	×	×	×	×	×	×	556 ± 26 ^c	0.85 ± 0.05 ^c
AAAn0405	Antabia	±			0.53–0.63	×	±	×			×			×	×	×	567 ^c	0.70 ^c
MF315	Lucomagno	±			0.15–0.18	×		×	×	×	×	×	×	×	×	×	575 ± 28 ^c	0.88 ± 0.06 ^c
SMo0407	Molare	±			0.18–0.26	×		×	×	×	×	×		±	±	±	586	0.72
AMo0410	Molare	±			0.13–0.15	×		×	×	×	×	×		±	±	±	595 ± 14 ^c	0.85 ± 0.5 ^c
AMo0504	Molare	±			0.76–0.86	×		×			×			±	×	×	586 ± 16 ^{b,c}	0.72 ^c
SDe0303	Devero	±			0.29–0.31	×		×	×		×			×	×	×	589 ± 22 ^a	
SPi0306	Piora	±			0.18–0.29	×		×	×	×	×	×		±	±	±	592 ^c	0.83 ^c
ADe0301	Devero	±			0.40–0.86	×		×	×		×			×	×	×	601 ± 25 ^c	0.80 ± 0.07 ^c
ADe0302	Devero	±			0.23–0.26	×		×			×			×	×	×	611 ± 26 ^c	1.04 ± 0.07 ^c

×, mineral occurrence; ±, mineral occurrence as relics in inclusions or as late-stage phase; quartz is present in all of the samples, illite and hornblende are found only in sample MF16 and samples MF228 and MF307 respectively. WM, white mica; Xen, xenotime; Ep1 and Ep2, the two distinct clinozoisite rims.

^aChl–Cld thermometry.

^bRAMAN spectrometry on carbonaceous material.

^cThermobarometry using multi-equilibrium reactions (Twq calculations).

in chloritoid porphyroblasts (Fig. 5f). Numerous tiny xenotime grains (1–5 μm) occur in the close vicinity of allanite, at 5–20 μm distance. In sample MF482, allanite is > 20 μm in diameter, whereas in the other samples of the Garvera zone it is observed as grains < 10 μm containing quartz inclusions. As for low-grade monazite, the analyses yield two groups, but with a more pronounced fractionation of the LREE and MREE proportions (Table 5). This effect is illustrated in Figs 6b and 7b. In sample MF482, the Ce content of allanite is lower than in other samples ($\text{Ce}_2\text{O}_3 = 6\text{--}7\%$), and peculiar La-dominant and Nd-dominant grains of allanite are found. Compared with monazite, allanite is drastically depleted in HREE + Y, and it shows lower Th contents (Figs 6b & 7b). LREE zoning in allanite is reproducible within each grain: X-ray maps show a core of allanite enriched in Nd, surrounded by a rim richer in La (Fig. 10a, b). The two different zones are outlined by at least two Th-rich rims (Fig. 10c), which may account for the variable Th contents measured in allanite. The Y content of the mapped allanite grain is low, and high Y concentrations indicate the presence of tiny grains of xenotime (Fig. 10d).

Transition from greenschist to lower amphibolite facies conditions

In the Northern Steep Belt, for conditions ranging between 528 and 550 °C and 0.5–0.9 GPa (Table 2),

allanite is preserved, but it occurs with rims of other members of the epidote group. For bulk-rock compositions poor in Ca ($\text{CaO} < 0.3\%$), only one rim is observed around allanite grains (Fig. 5g), whereas two consecutive rims are present (Fig. 5h) in samples of higher Ca contents ($0.3\% < \text{CaO} < 7.0\%$). In contrast to samples previously described, xenotime is not associated with allanite. The textural position of allanite and its rims oriented in the main foliation, or as inclusions in garnet, demonstrates that these phases grew prior to or during the main foliation-forming stage. Compositions of allanite and the epidote domains are consistent from sample to sample. EMP analyses (Table 6) and maps of allanite show that these grains preserve the REE zoning documented at lower degrees of metamorphism, as described in the previous paragraph (Fig. 11). Allanite has a core rich in MREE, an edge richer in LREE, and homogeneously low HREE contents (Fig. 11a, b). By comparison, the two successive rims have compositions dominated by clinozoisite ($\sum \text{REE} < 0.20$ atom per formula unit). The first rim (Ep1) is significantly enriched in Y, HREE and U with respect to allanite (Table 6, Figs 7d & 11d). Some of the analyses of the allanite and HREE-rich rim show high Th contents (Fig. 6d). This variability results from the Th-rich zone at the limit between allanite and the first rim of epidote, rather than variable Th contents within an epidote zone (Fig. 11e). The outer rim (Ep2) corresponds to clinozoisite with very low REE contents ($\sum \text{REE} < 0.02$ atom per formula unit).

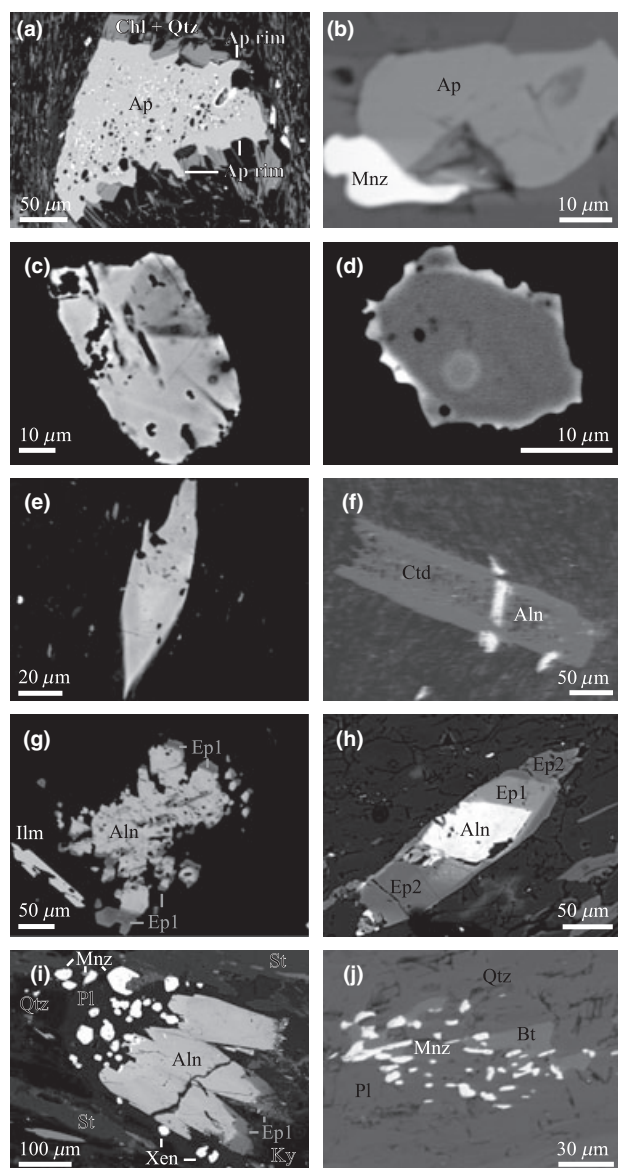


Fig. 5. BSE images of REE minerals observed successively along the metamorphic transect through the central Alps. (a) Apatite grain showing a core studded with rutile and quartz inclusions; the rim is devoid of inclusions in samples of chloritoid grade; (b) Contact of apatite and monazite grains at lower amphibolite facies conditions; (c) Round detrital monazite under very low grade metamorphic conditions (Quarten); (d) Corroded detrital monazite with newly formed rim (Garvera); (e, f) Idiomorphic allanite at chloritoid grade (Garvera) located (e) in the main foliation, and (f) as an inclusion in a chloritoid porphyroblast; (g–j) are images of REE minerals in the Northern Steep Belt, i.e. at higher grade: (g) allanite clusters with a first rim Ep1; (h) allanite with two consecutive rims of clinozoisite (Ep1 & Ep2), all oriented in the main foliation; (i) *in situ* breakdown of allanite to a monazite aggregate associated with plagioclase, staurolite, kyanite and quartz; (j) monazite clusters associated with plagioclase, biotite and quartz. Abbreviations: Ep1, first epidote rim enriched in HREE; Ep2, second clinozoisite rim; Xen, Xenotime.

Lower amphibolite facies

At equilibrium temperatures higher than 550 °C for pressures of 0.78–1.0 GPa, the REE mineralogy is controlled by local variations of the mineral assemblages, i.e. local bulk composition.

In metapelites with minor kyanite and no staurolite (Table 2), allanite and epidote are the only REE minerals up to 610 °C (Table 2). They have similar compositions as allanite and epidote rims found at lower grade condition, with the exception of the Mn-rich sample SDe0303 (Table 6, up to 1.34% MnO in allanite).

In metapelites containing the mineral assemblage kyanite–garnet–staurolite–biotite without chlorite and chloritoid, allanite reacted partially or totally to form aggregates of monazite and xenotime. Associations of allanite, monazite and xenotime are found in two samples (APi0413 & MF315; Fig. 5i, j), with equilibration temperatures below 580 °C (TWQ; Table 2). At higher temperatures, allanite disappeared completely from the matrix and was replaced by monazite clusters (Table 2; Fig. 5j). In these samples (Table 2), allanite is locally preserved in garnet, whereas monazite remains only where included in biotite or staurolite porphyroblasts. In samples with coexisting allanite and monazite, *in situ* breakdown of allanite is observed to be texturally associated with xenotime, plagioclase, white mica, kyanite, biotite, staurolite and quartz (Fig. 5i). Even after partial replacement, relic epidote retains its growth zones acquired at greenschist facies conditions (Table 7, Figs 6d & 7d). Elemental maps of *in situ* allanite breakdown to monazite (Fig. 12) show that the original allanite had a MREE-rich core and a LREE-rich edge outlined by a Th-rich zone, separating allanite from the first epidote rim. X-ray maps of La, Nd and Y show that the spatial organization of MREE- and LREE-rich monazite and xenotime reflects the successive breakdown of epidote zones (Fig. 12a, b & d). MREE-rich monazite is restricted to the centre of the aggregate, LREE monazite grains are distributed more externally, and xenotime islands are found exclusively at the periphery of the aggregates. In sample APi0413 (Table 4), monazite clearly remained fractionated in LREE and MREE, whereas this effect is less visible in sample MF315 (Table 4 and Figs 6c & 7c). Monazite has Y contents ~1–2% at the contact of xenotime grains (sample APi0413, Table 3, Fig. 7c). Using the thermometer of Pyle *et al.* (2001) and Gratz & Heinrich (1997), Y and HREE (Gd and Dy) contents in monazite yield a temperature of 485 ± 54 °C and 461 ± 80 °C (data repository). These results are consistent with phase equilibrium calculations for sample APi0413, albeit with higher 1σ uncertainty. The data dispersion partly results from high-temperature values determined in monazite grains with high Th contents (Table 3, analysis 11). Experimental calibration of the influence of Th on monazite–xenotime

Table 3. Electron microprobe analysis of detrital and metamorphic monazite.

Sample	MF16			MF407			MF47		MF315		APi0413	
Analyses	1	2	3	4 (tiny grain)	5	6	7 (tiny grain)	8	9	10	11	12
P ₂ O ₅	29.82	31.12	32.92	30.81	30.22	30.44	32.18	33.10	31.36	29.00	32.29	31.47
SiO ₂	1.03	0.57	0.21	1.71	0.98	0.19	3.15	0.36	0.14	0.40	0.24	0.12
ThO ₂	7.65	1.48	4.92	2.74	13.75	4.62	1.96	4.04	1.55	3.63	6.12	2.21
UO ₂	0.41	0.01	0.76	0.06	0.91	0.89	0.17	0.66	0.10	0.39	0.33	0.17
Y ₂ O ₃	0.01	0.20	3.15	0.16	1.92	2.90	0.21	0.59	0.92	1.84	1.47	1.24
La ₂ O ₃	17.37	17.01	13.65	18.54	13.79	13.27	15.83	14.71	18.33	15.67	18.14	11.17
Ce ₂ O ₃	28.89	30.97	25.82	31.46	23.91	25.73	34.34	28.14	30.37	27.16	24.10	28.63
Pr ₂ O ₃	2.64	2.87	2.71	2.75	2.34	2.87	2.74	3.31	2.91	2.85	2.28	3.74
Nd ₂ O ₃	9.84	10.46	11.03	9.48	8.00	11.74	9.47	11.99	11.18	11.79	9.61	15.41
Sm ₂ O ₃	0.94	1.56	1.66	0.99	1.11	2.15	1.22	2.04	1.56	1.98	1.84	3.01
Gd ₂ O ₃	0.31	1.12	1.63	0.34	0.88	2.27	0.59	1.47	0.99	1.64	1.76	1.73
Dy ₂ O ₃	0.00	0.04	0.72	0.00	0.42	0.98	0.01	0.07	0.30	0.55	0.51	0.22
CaO	1.28	0.46	1.34	0.34	2.85	1.27	0.41	0.96	0.28	0.72	1.32	0.39
PbO	0.11	0.01	0.10	0.02	0.21	0.10	0.00	0.10	0.01	0.00	0.01	0.01
Total	100.31	97.93	100.62	100.40	101.28	99.42	102.27	101.55	100.00	97.62	100.42	99.52
<i>A.p.f.u</i>												
ΣREE	0.85	0.92	0.84	0.87	0.74	0.89	0.84	0.85	0.94	0.93	0.83	0.92
XLREE	0.82	0.80	0.69	0.83	0.76	0.67	0.83	0.74	0.78	0.72	0.74	0.67
XMREE	0.18	0.20	0.23	0.16	0.18	0.25	0.17	0.24	0.20	0.23	0.21	0.30
XHREE + Y	0.00	0.01	0.09	0.00	0.06	0.08	0.00	0.01	0.02	0.05	0.04	0.03
<i>T</i> (°C) ^a									334	532	578	447

^aTemperatures calculated from $X_{HREE} + Y = (Y + Gd + Dy) / \sum(REE + Y)$ using the thermometer of Pyle & Spear (2003).

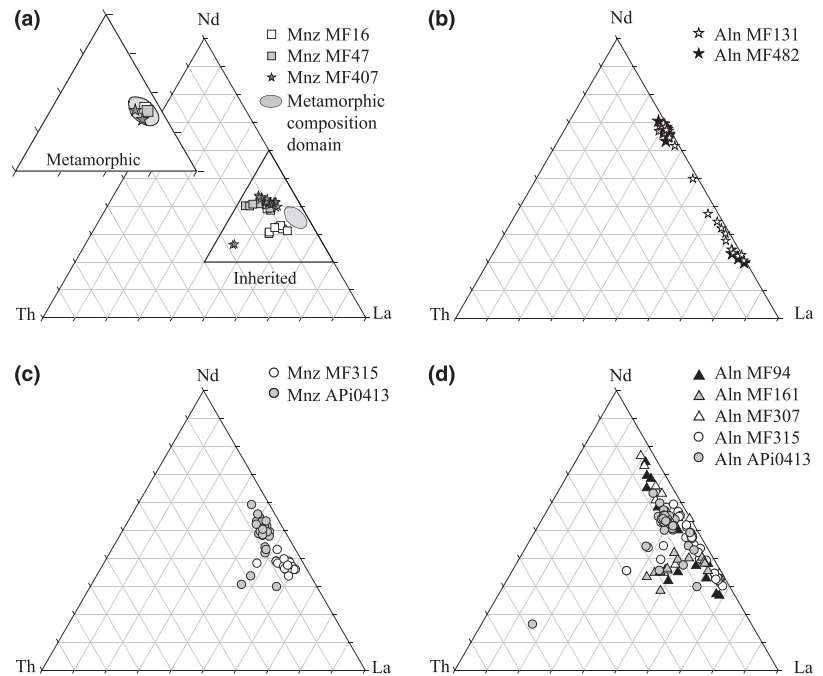


Fig. 6. La–Nd–Th diagram (mol.%) of EMP analyses for monazite and allanite. (a) Monazite under low-grade metamorphic conditions up to chloritoid grade. Analyses of metamorphic monazite (Pb below or close to detection limit) are presented separately in the small triangle, whereas analyses of inherited monazite are plotted in the regular triangle. The grey domain illustrates compositions of metamorphic monazite for comparison with inherited monazite; (b) allanite at chloritoid grade; (c) monazite at lower amphibolite facies; (d) allanite at lower amphibolite facies.

thermometry at 2 kbar shows that monazite analysis with 10% of huttonite component can be overestimated by ~50 °C (Seydoux-Guillaume *et al.*, 2002). In some aggregates, a Th silicate is present. For all monazite measured, Pb contents are below detection limit (~100 p.p.m.) of the EMPA. Considering the high Th contents (up to 11.0% ThO₂), this confirms that these monazite grains formed during Alpine metamorphism (e.g. Montel *et al.*, 2000).

DISCUSSION

LREE distribution in Alpine metasedimentary rocks

Recognition of the phases that control the REE distribution is essential to understand the reactions among REE minerals. In the Alpine pelites studied, the REE minerals observed and their textural relations suggest that involvement of major silicate phases as

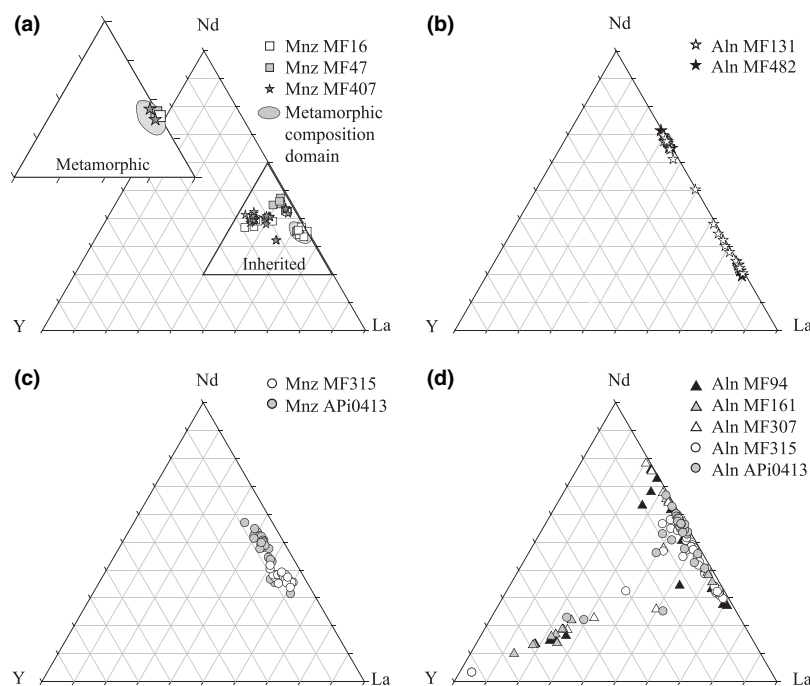


Fig. 7. La–Nd–Y diagram (mol.%) of EMP analyses for monazite and allanite. (a–d) as in Fig. 6.

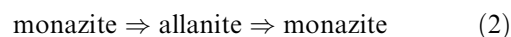
sources of LREE is small and, as will be shown below, may be negligible in the reactions between monazite and allanite. This conclusion is supported by the correlation between mineral and bulk REE contents observed in sample MF482. In this sample, allanite has uniquely low Ce concentrations and is dominated by La- and Nd components (Table 5); anomalies that are also observed in the REE pattern of the bulk sample (Fig. 4).

Potential LREE contributions of major silicates to the monazite were assessed from REE concentrations in major silicates measured by LA-ICP-MS (Table 7). For this purpose, the REE concentrations were deter-

mined in a sample where allanite has partially reacted to form monazite (API0413) and in another sample where allanite is preserved at 600 °C (ADe0301). In both samples, major silicate minerals (kyanite, garnet, white mica, biotite, staurolite and plagioclase) contain low LREE contents. These data can be used to constrain the contribution of major silicates to the LREE budget of the bulk rock. It is evident from analyses in Table 7 that even metapelites composed essentially of white mica (as shown in Table 7) would contain only some 5 p.p.m. LREE. In these samples, major silicates contribute negligibly to the 100–300 p.p.m. measured for the LREE in the bulk rock (Table 1), and to monazite formed in metapelites at lower amphibolite facies conditions (Yang & Pattison, 2006).

Formation and breakdown of allanite

From very low-grade metamorphism up to conditions of the lower amphibolite facies, the phase relations between monazite and allanite conform with the sequence already described from various metapelites (review by Gieré & Sørensen, 2004) and calculated from thermodynamic data (Janots *et al.*, 2007), i.e.



Under low-grade conditions, the mineralogy of REE-rich phases found in this study is similar to other samples from the Central Alps (Livi *et al.*, 2002). Both studies document REE phosphates in the Glarus Alps and the appearance of allanite at Garvera. In the temperature interval $260 < T < 440$ °C, monazite is found mainly as detrital grains, but also as newly formed tiny crystals or overgrowths on corroded relics

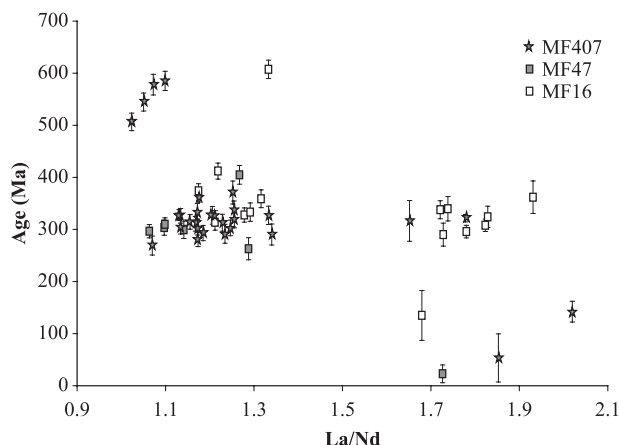


Fig. 8. EMP chemical ages of monazite found below chloritoid grade. Error bars on the age reflect propagated Pb uncertainties (2σ). Ages are expressed as a function of the La/Nd ratio to illustrate age variation with monazite composition.

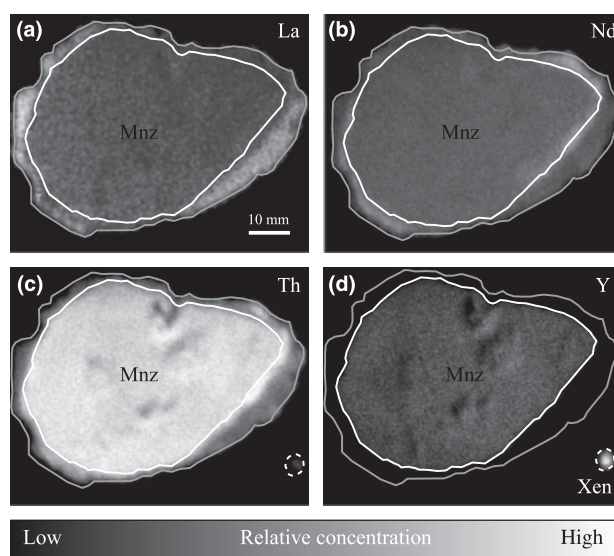
Table 4. EMP analysis and chemical ages (with 2σ uncertainty) of monazite from the Glarus Alps (MF16 and MF47) and the Garvera zone (MF407).

Analysis	PbO	ThO ₂	UO ₂	La/Nd	Age (Ma)
<i>MF16</i>					
4 ^a	0.009	1.48	0.012	1.68	135 ± 48
12	0.060	4.69	0.048	1.73	290 ± 22
46	0.105	7.42	0.293	1.78	296 ± 12
2	0.115	7.65	0.359	1.82	308 ± 12
20	0.088	4.29	0.712	1.21	314 ± 15
11	0.067	4.71	0.043	1.83	324 ± 20
57	0.101	4.92	0.728	1.28	328 ± 14
22	0.082	4.36	0.454	1.29	333 ± 18
19	0.086	5.52	0.152	1.72	338 ± 17
10	0.079	5.24	0.071	1.74	340 ± 23
18	0.066	4.08	0.066	1.93	362 ± 31
17	0.123	4.34	1.053	1.17	374 ± 14
16	0.137	4.26	1.105	1.22	412 ± 15
48 ^a	0.158	4.8	0.396	1.33	607 ± 18
Average					330 ± 29
<i>MF47</i>					
21 ^a	b.d.	1.96	0.157	1.73	—
18	0.050	2.63	0.569	1.29	263 ± 21
14	0.112	7.98	0.300	1.06	297 ± 13
13	0.084	5.80	0.250	1.14	299 ± 17
16	0.099	6.80	0.274	1.10	303 ± 14
15	0.115	7.26	0.465	1.10	310 ± 13
20	0.105	4.04	0.632	1.27	405 ± 18
Average					299 ± 43
<i>MF407</i>					
7 ^a	b.d.	2.39	0.078	1.85	—
35 ^a	0.017	2.74	0.042	2.02	142 ± 20
5	0.061	3.11	0.697	1.07	269 ± 18
11	0.090	4.4	0.978	1.17	281 ± 13
29	0.061	3.63	0.401	1.34	290 ± 20
7	0.064	3.36	0.557	1.23	292 ± 18
23	0.078	4.18	0.656	1.18	293 ± 15
25	0.206	13.75	0.821	1.78	297 ± 7
19	0.086	4.3	0.756	1.25	303 ± 15
24	0.083	4.24	0.679	1.17	305 ± 15
10	0.092	4.3	0.876	1.13	306 ± 14
4	0.097	4.62	0.861	1.17	311 ± 14
17	0.086	4.19	0.707	1.23	313 ± 16
9	0.098	4.65	0.835	1.16	315 ± 14
8	0.039	2.79	0.046	1.65	316 ± 39
8	0.081	3.61	0.735	1.26	321 ± 17
26	0.220	13.37	0.854	1.78	322 ± 7
6	0.103	4.41	0.958	1.21	323 ± 13
12	0.101	4.48	0.882	1.13	326 ± 14
14	0.086	4.11	0.638	1.21	327 ± 17
34	0.081	3.41	0.754	1.33	327 ± 18
32	0.146	4.03	2.014	1.13	328 ± 10
22	0.095	4.11	0.811	1.17	334 ± 16
1	0.095	4.14	0.763	1.25	338 ± 16
31	0.173	4.45	2.102	1.18	362 ± 10
13	0.079	3.19	0.570	1.25	371 ± 22
38	0.133	4.85	0.412	1.02	507 ± 17
40	0.140	5.01	0.308	1.05	545 ± 17
37	0.140	4.66	0.306	1.07	578 ± 20
39	0.152	5.06	0.317	1.10	585 ± 18
Average					319 ± 18

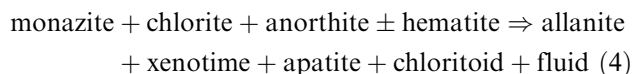
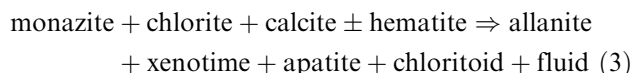
b.d., below detection limit.

^aRejected analysis from averaged age using Isoplot/Ex.

(Fig. 13). With the appearance of chloritoid, monazite gives way to allanite–xenotime associations, and newly formed rims of apatite are found (Garvera, ~430–450 °C, Figs 5a, e & 10). Based on these observations, we propose that the LREE, HREE and phosphate released by monazite breakdown are taken up by allanite, xenotime, and apatite respectively. In these samples, the allanite-forming reaction coincides with

**Fig. 9.** X-ray maps of monazite and newly formed xenotime in sample MF407 (sub-greenschist facies conditions): (a) La; (b) Nd; (c) Th; and (d) Y. Note homogeneous core of monazite finely rimmed by successive zones rich in Nd and La, but depleted in Y and Th.

the growth of chloritoid from chlorite + hematite (Frey & Wiedeland, 1975), suggesting that these ferromagnesian phases balance the silicate–phosphate reaction between monazite and allanite. The Ca-bearing phase involved in forming allanite and apatite correspond to carbonates in metamarl and, in metapelites devoid of carbonate minerals, to detrital plagioclase and/or an aqueous fluid. These observations in Alpine metapelites lead us to propose two (unbalanced) prograde reactions:

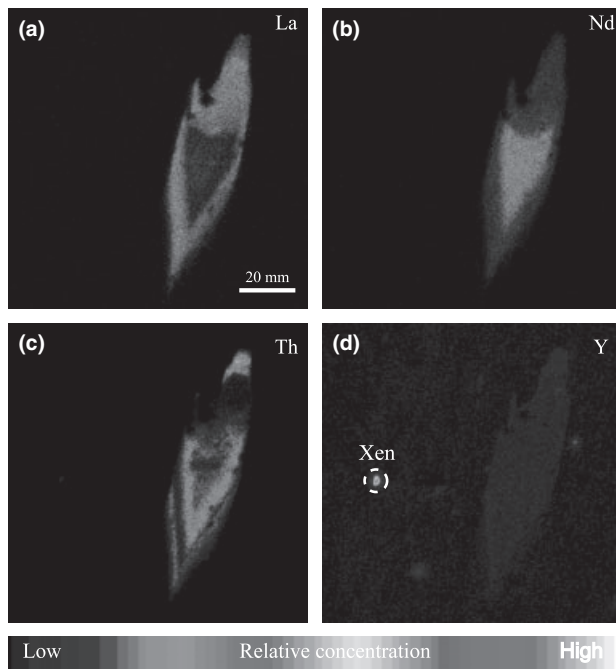


Reaction (3) is more relevant for metamarl, Eq. (4) for metapelites (Fig. 13).

In metapelites, (Smith & Barreiro, 1990) and Wing *et al.* (2003) observed that monazite disappears and is replaced by allanite exactly at the biotite isograd. In Alpine metasediments, monazite breakdown occurs at chloritoid grade. This may reflect allanite formation at lower metamorphic conditions (below biotite grade), perhaps due to differences in fluid composition (X_{CO_2}) or in sample compositions compared with those encountered in the earlier studies. At greenschist facies conditions, Wing *et al.* (2003) and Krenn & Finger (2007) documented that monazite, rather than being replaced by allanite, may be preserved for some bulk compositions low in Al and Ca. For such compositions (e.g. samples MF131 & MF133; Fig. 2), no monazite grains

Table 5. Electron microprobe analysis of allanite from greenschist up to lower amphibolite facies conditions.

Sample	MF482		MF131		MF307				MF94			MF161	
Ep-comp	Aln	Aln	Aln	Aln	Aln	Aln	Ep1	Ep2	Aln	Aln	Ep1	Aln	Ep1
SiO ₂	34.28	33.45	36.14	34.30	34.44	34.53	36.89	37.22	33.76	34.62	37.16	34.42	36.85
TiO ₂	b.d.	0.80	0.35	0.42	b.d.	0.23	0.06	0.76	0.13	b.d.	0.03	b.d.	0.06
ThO ₂	0.11	0.13	0.11	0.29	0.50	0.36	0.20	b.d.	0.63	0.41	0.33	0.39	0.43
UO ₂	0.02	b.d.	b.d.	b.d.	b.d.	0.01	0.27	b.d.	0.03	0.02	0.22	0.02	0.42
Al ₂ O ₃	21.21	20.86	22.45	20.39	21.86	22.64	25.48	26.54	23.10	23.14	26.46	23.61	27.85
Y ₂ O ₃	0.03	0.01	0.06	0.05	0.08	0.09	1.30	0.01	0.11	0.06	1.53	0.11	1.80
La ₂ O ₃	9.37	3.65	6.13	2.98	1.57	2.82	0.49	0.04	6.02	1.62	0.59	4.62	0.66
Ce ₂ O ₃	7.04	6.37	8.45	9.79	7.06	8.69	0.73	0.08	9.77	8.29	1.12	9.07	1.38
Pr ₂ O ₃	0.75	1.53	0.53	1.43	1.20	0.87	0.12	0.00	0.53	1.30	0.14	1.00	0.10
Nd ₂ O ₃	2.49	8.14	1.55	5.96	6.34	3.74	0.38	0.05	2.40	5.60	0.46	3.19	0.52
Sm ₂ O ₃	0.09	1.81	0.22	1.04	2.19	0.22	0.16	0.06	0.16	1.58	0.11	0.36	0.12
Gd ₂ O ₃	0.21	0.58	0.00	0.44	0.93	0.22	0.43	0.01	0.17	0.97	0.39	0.25	0.51
Dy ₂ O ₃	0.16	0.06	0.10	0.11	0.03	0.17	0.70	0.00	0.15	0.00	0.33	0.14	0.58
MgO	0.07	0.00	0.09	0.07	0.13	0.09	0.06	0.00	0.12	0.09	0.13	0.42	0.20
CaO	12.68	11.62	13.16	11.40	13.00	13.52	19.28	22.66	13.06	13.08	18.05	13.12	17.97
MnO	0.06	0.06	0.18	0.12	0.09	0.06	0.08	0.05	0.04	0.01	0.03	0.01	0.05
FeO	10.86	10.57	11.83	11.08	9.99	9.19	4.78	1.05	8.09	8.49	5.83	8.03	5.90
Fe ₂ O ₃	0.67	0.00	0.00	0.00	0.00	0.00	4.10	7.48	0.00	0.00	0.00	0.00	0.00
SrO	0.14	0.06	0.05	0.02	0.17	0.29	0.14	0.19	0.10	0.12	0.03	0.09	0.11
PbO	0.01	0.01	0.03	0.02	0.03	0.03	0.02	0.02	0.00	0.02	0.02	0.01	0.01
Na ₂ O	0.02	0.09	0.03	0.03	0.09	0.02	b.d.	b.d.	0.03	0.05	0.04	0.04	0.01
H ₂ O	1.69	1.65	1.75	1.66	1.69	1.69	1.82	1.88	1.68	1.70	1.78	1.70	1.82
Total	101.98	101.49	103.26	101.65	101.40	99.51	97.73	98.10	100.33	101.22	95.09	100.83	97.76
ΣREE (A.p.f.u.)	0.65	0.72	0.53	0.71	0.62	0.54	0.14	0.01	0.63	0.62	0.16	0.60	0.19
XLREE	0.86	0.53	0.89	0.66	0.52	0.74	0.28	0.50	0.85	0.59	0.35	0.79	0.34
XMREE	0.13	0.47	0.10	0.33	0.48	0.24	0.19	0.45	0.14	0.41	0.17	0.20	0.17
XHREE + Y	0.01	0.00	0.01	0.01	0.01	0.02	0.53	0.05	0.02	0.00	0.48	0.01	0.49

**Fig. 10.** X-ray maps of allanite and xenotime in sample MF482 (chloritoid grade, cf. Fig. 5e): (a) La; (b) Nd; (c) Th; and (d) Y. Note Nd-rich core and La-rich rim, outlined by at least two Th-rich zones; high Y contents indicate xenotime grains.

appear to have survived above chloritoid grade, i.e. at >430–450 °C. Contrary to the proposition by Wing *et al.* (2003), these observations imply that monazite

Table 6. Electron microprobe analysis of allanite at lower amphibolite facies ($T > 560$ °C).

Sample	SDe0303			APi0413				MF315		
Ep-comp	Aln	Ep1	Ep2	Aln	Aln	Ep1	Ep2	Aln	Aln	Ep1
SiO ₂	33.66	36.66	36.36	34.14	34.13	35.96	37.75	34.13	34.61	36.86
TiO ₂	0.00	0.06	0.13	0.47	0.00	0.47	0.11	0.20	0.17	0.00
ThO ₂	1.39	0.39	0.27	1.49	1.29	4.00	0.05	0.26	0.25	0.16
UO ₂	0.05	0.14	0.12	0.05	0.02	0.29	0.00	0.00	0.02	0.35
Al ₂ O ₃	21.75	25.77	27.47	22.41	22.70	25.35	28.87	23.15	24.52	27.07
Y ₂ O ₃	0.16	0.64	0.05	0.12	0.09	0.96	0.06	0.12	0.19	2.15
La ₂ O ₃	3.95	0.86	0.52	4.74	3.12	0.60	0.20	6.37	2.56	0.12
Ce ₂ O ₃	10.65	1.88	1.23	8.26	8.73	0.94	0.19	9.42	7.42	0.25
Pr ₂ O ₃	0.93	0.12	0.00	0.93	1.16	0.04	0.07	0.91	0.90	0.00
Nd ₂ O ₃	3.68	0.63	0.42	3.49	4.90	0.61	0.10	2.88	4.06	0.12
Sm ₂ O ₃	0.37	0.12	0.01	0.49	0.74	0.37	0.00	0.46	0.72	0.00
Gd ₂ O ₃	0.33	0.08	0.11	0.19	0.52	0.98	0.06	0.29	0.47	0.60
Dy ₂ O ₃	0.19	0.30	0.01	0.19	0.05	0.70	0.06	0.07	0.05	0.78
MgO	0.41	0.45	0.07	0.14	0.15	0.10	0.00	0.17	0.11	0.07
CaO	10.62	16.13	19.94	12.69	12.36	16.88	22.51	12.21	13.20	17.94
MnO	1.34	1.01	0.17	0.04	0.09	0.01	0.07	0.03	0.01	0.08
FeO	9.93	6.66	2.68	8.96	8.94	6.20	1.37	8.49	8.01	6.51
Fe ₂ O ₃	0.00	5.39	3.71	0.00	0.00	1.37	3.97	0.00	0.00	0.38
SrO	0.13	0.33	0.35	0.21	0.32	0.20	0.18	0.06	0.10	0.07
PbO	0.03	0.00	0.03	0.01	0.01	0.01	0.01	0.02	0.01	0.00
Na ₂ O	0.18	0.00	0.10	0.08	0.12	0.06	0.01	0.03	0.07	0.02
H ₂ O	1.67	1.83	1.82	1.68	1.68	1.76	1.89	1.68	1.71	1.80
Total	101.62	99.64	95.68	101.00	101.40	98.02	97.65	101.15	99.31	95.78
ΣREE (A.p.f.u.)	0.66	0.15	0.07	0.60	0.62	0.17	0.02	0.67	0.52	0.15
XLREE	0.77	0.59	0.75	0.76	0.68	0.29	0.61	0.82	0.67	0.08
XMREE	0.21	0.17	0.22	0.22	0.31	0.34	0.20	0.17	0.31	0.14
XHREE + Y	0.02	0.25	0.03	0.02	0.01	0.37	0.18	0.01	0.02	0.79

preservation under greenschist and amphibolite facies conditions is not simply controlled by the Ca/Al ratio. The occurrence of allanite in metapelites, with CaO

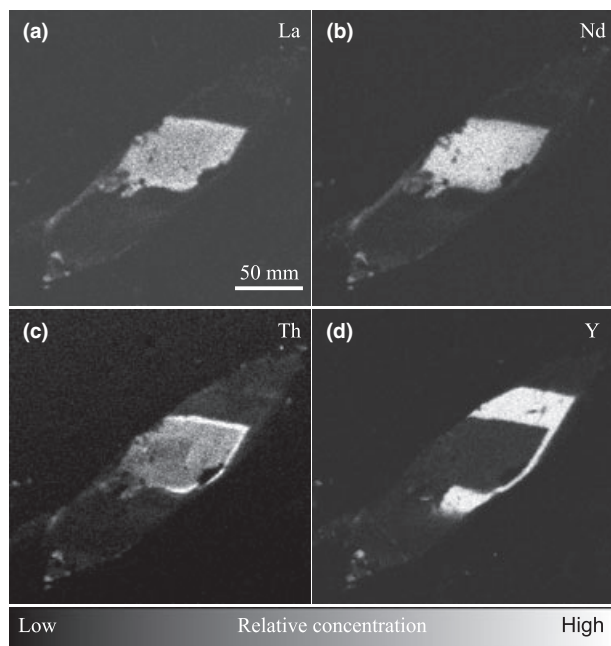
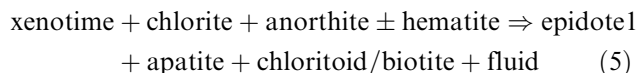


Fig. 11. X-ray maps of allanite shown in Fig. 5h (lower amphibolite facies conditions): (a) La (b) Nd (c) Th and (d) Y contents. Core of allanite enriched in Nd and La, separated from the first Ep1 rim (enriched in Y) by a thin Th-rich zone. The second rim Ep2 is present, but not distinguishable on these X-ray maps.

contents as low as 0.3 wt%, demonstrates that a low Ca content is not a valid criterion to exclude allanite as the precursor of monazite in amphibolite facies rocks.

Allanite is preserved up to biotite grade, but at $> 528^{\circ}\text{C}$ and depending on the $\text{CaO}/\text{Na}_2\text{O}$ ratio of the sample (Fig. 13), it shows one or two overgrowth rims of clinozoisite, the first of which is HREE rich. As xenotime is no longer present in these samples (Table 2), we infer that its breakdown acted as the source of Y and HREE for the first epidote rim. A reaction similar

to the monazite breakdown, involving chloritoid or biotite as products, is envisaged for the temperature interval $450\text{--}528^{\circ}\text{C}$:



This xenotime breakdown appears to occur before the onset of garnet growth, as indicated by the presence of HREE-rich epidote in samples without garnet and, once garnet occurs, as inclusions therein (Table 2). The consistent succession of allanite and HREE-rich clinozoisite demonstrates that xenotime is stable towards higher temperatures than monazite in pelites, at least under Barrovian conditions.

In samples containing garnet, biotite, staurolite and kyanite assemblages, allanite breaks down at temperatures above 556°C , while in samples without staurolite allanite is preserved up to temperatures $\sim 600\text{--}610^{\circ}\text{C}$ (Fig. 13). Although allanite breakdown to monazite has been repeatedly documented, this is the first time to our knowledge that the breakdown of HREE-rich clinozoisite to xenotime is reported. The absence of monazite inclusions in garnet from five of these samples suggests that monazite grew after garnet. We propose that allanite breakdown occurs close to but slightly above the staurolite or kyanite zone boundaries, at minimum temperatures of 556°C based on: (1) the equilibrated metamorphic assemblages associated with the allanite breakdown; (2) the absence of monazite at lower grade conditions, even in samples with kyanite or staurolite (MF161, Table 2). Several products of allanite and epidote breakdown were identified from textural relations, including monazite, xenotime, plagioclase and either biotite or staurolite. Although apatite is not observed paragenetically associated with the allanite breakdown, it is the most abundant phosphate phase in all of the samples and thus a most likely reactant in monazite and xenotime

Table 7. Averaged REE contents (p.p.m.) of major silicates determined by LA-ICP-MS in samples APi0413 and ADe0301.

Elements (p.p.m.)	APi0413 St (2)	APi0413 Grt (5)	APi0413 Bt (2)	APi0413 Ky (1)	APi0413 WM (2)	APi0413 Pl (2)	ADe0301 Grt (5)	ADe0301 Bt (2)	ADe0301 Ky (1)	ADe0301 WM (3)
La	<0.015	0.05	0.11	<0.05	1.23	1.66	0.02	0.05	<0.02	0.06
Ce	0.03	0.14	0.18	<0.06	0.17	0.97	0.06	0.10	<0.03	0.11
Pr	<0.015	0.03	0.05	0.03	0.53	0.09	0.01	0.02	<0.02	0.03
Nd	<0.08	0.13	0.13	0.18	2.31	0.41	0.05	0.07	<0.11	0.15
Sm	<0.11	0.26	0.17	0.09	0.71	0.12	0.07	<0.06	<0.13	0.10
Eu	0.04	0.15	0.05	<0.07	<0.41	0.51	0.04	<0.01	<0.02	<0.06
Gd	<0.09	2.81	0.19	<0.24	2.08	0.19	0.39	0.05	<0.10	0.05
Tb	<0.02	0.88	0.02	<0.03	0.43	0.02	0.15	<0.01	<0.01	0.01
Dy	0.04	7.69	0.23	<0.11	1.90	0.11	1.36	0.03	<0.08	0.08
Ho	<0.01	2.00	0.04	<0.05	0.36	0.02	0.36	0.01	<0.02	0.02
Er	<0.08	8.12	0.11	0.15	0.78	0.07	1.36	<0.02	<0.04	0.06
Tm	<0.02	1.43	0.03	<0.02	0.10	0.02	0.25	<0.01	<0.01	0.01
Yb	<0.04	13.6	0.10	<0.17	0.50	0.14	2.26	<0.05	<0.06	0.08
Lu	<0.02	2.63	0.02	<0.02	0.05	0.02	0.43	<0.01	<0.01	0.02
Y	<0.03	53.6	0.84	<0.05	6.44	0.40	10.01	0.07	<0.03	0.13
Sum LREE	<0.29	0.78	0.68	<0.48	5.36	3.76	0.26	<0.31	<0.33	0.55
Sum LREE ^a	0	0	1–10		2–20	5–50	0	1–10		2–20

Numbers in brackets correspond to the number of analyses; WM stands for white mica.

^aCorresponds to the sum of LREE of major silicates reported in metapelites and summarized by Yang & Pattison (2006).

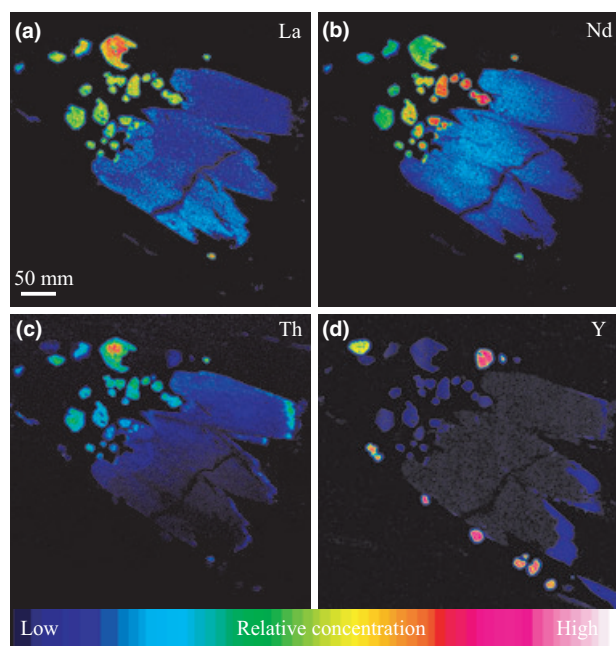
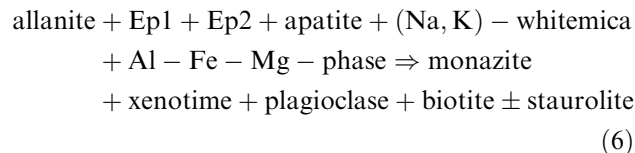


Fig. 12. X-ray maps of allanite breaking down *in situ* to monazite in sample APi0413 (lower amphibolite facies conditions, cf. Fig. 5i): (a) La (b) Nd (c) Th and (d) Y contents. Allanite core preserves low-grade La–Nd zoning, the first Ep1 rim is enriched in Y. The replacement by Nd-rich monazite, La-rich Mnz and xenotime shows a spatial organization reflecting the successive breakdown of epidote zones. MREE-rich monazite is restricted to the centre of the aggregate, LREE monazite grains lie more externally, and xenotime islands are found exclusively at the periphery of the aggregate.

formation. Direct textural evidence is sparse, as grain contact of apatite and monazite has been found in only one sample (AMo0410, Fig. 5b). Plagioclase is the calcic phase observed that may take up the Ca supplied by the breakdown of allanite (and apatite), for garnet growth predates monazite formation. Clusters of monazite and xenotime occur mostly associated with

biotite or staurolite porphyroblasts. Based on the textural observations and mass balance for alkalis, we attribute these phosphates in clusters with biotite to the formation of plagioclase. From textural observations, it is not clear whether quartz and kyanite associated with the allanite breakdown were produced or consumed. Considering the chemical compositions of major and accessory minerals, a possible reaction involves:



where the Al–Mg–Fe phase in reaction (6) may correspond to chlorite, chloritoid or garnet (the (Mg, Fe) phases observed at lower *P–T* conditions).

Our observations confirm the notion that allanite begins to break down close to the appearance of staurolite and/or kyanite and that the whole-rock composition controls the temperature of this reaction of allanite (Foster & Parrish, 2003; Wing *et al.*, 2003). Similarly to Tomkins & Pattison (2007), we find that allanite replacement occurs at temperatures close to the breakdown of chlorite and/or chloritoid, but without being linked to the formation of either kyanite or staurolite. Fitzsimons *et al.* (2005) associated the appearance of monazite with the breakdown of garnet and infer a strong influence of the AFM composition. We find that, for low-Ca metapelites the first monazite grew under similar conditions in samples of contrasting composition in AFM space (Fig. 3), suggesting that at least the Fe–Mg ratio has a limited influence on monazite stability (Rasmussen *et al.*, 2006). By contrast, the allanite stability domain does appear to be influenced by the CaO contents of the rocks, as previously stated by Foster & Parrish (2003) and Wing *et al.* (2003). We find allanite preserved to higher

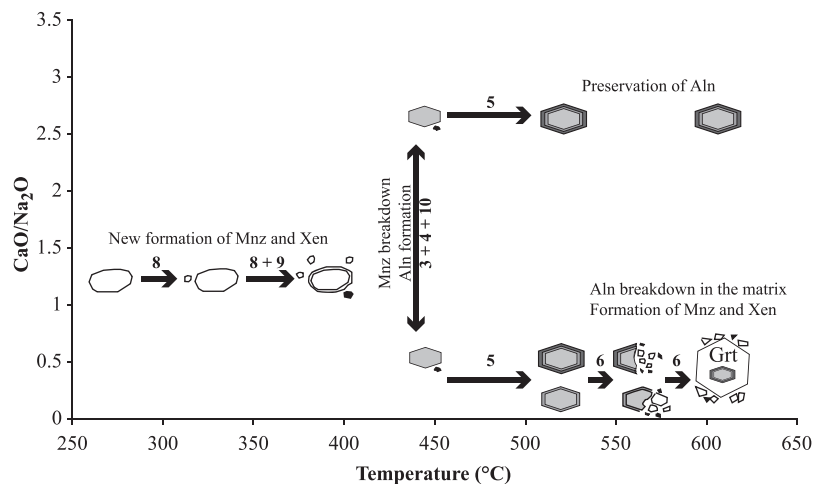


Fig. 13. Prograde metamorphic sequence of monazite, xenotime and allanite as a function of temperature and CaO/Na₂O ratio. REE minerals are depicted using different filling colours: monazite in white, xenotime in black and allanite (with one or two rims of epidote) in grey. Number above arrows refers to reaction described in the text. Two major effects of bulk-rock composition emerge: (1) only one rim of epidote is present for CaO/Na₂O < 0.17, two rims of epidote are found for other compositions; (2) for CaO/Na₂O > 0.93 allanite is preserved up to 610 °C, whereas it reacted partially (556–575 °C) to totally (> 586 °C) in the matrix with CaO/Na₂O < 0.54. Note that in these former samples allanite can be preserved as inclusions in garnet.

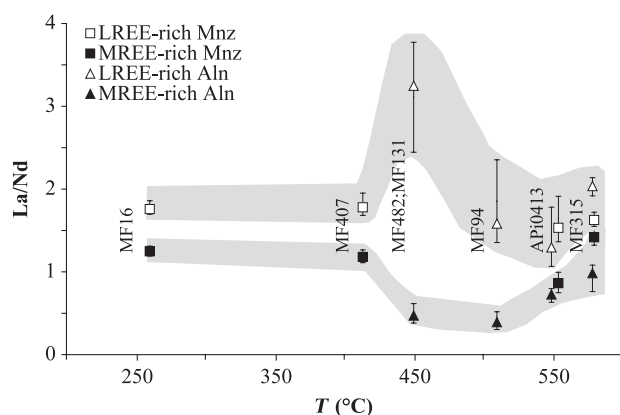
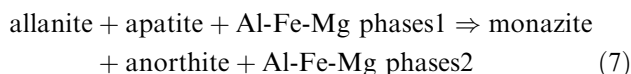


Fig. 14. Evolution of the La/Nd ratios in LREE- and MREE-rich monazite and LREE- and MREE-rich allanite with increasing temperature.

temperatures (600–610 °C) in rocks with the highest CaO contents. Various reactions have been reported in the literature to account for the breakdown of allanite; in the studied samples, replacement of allanite by plagioclase as the Ca-bearing phase is systematic, whereas different AlFeMg phases may be involved (as reactants and products). A generalized prograde reaction may be written as:



Differences in the specific AFM phases aside, plagioclase produced in low-Ca samples has a lower anorthite activity than in samples with higher Ca contents; hence the above equilibrium is shifted to the left, which accounts for the breakdown of allanite at lower temperatures. This effect ought to be dependent not just on CaO contents, but on the Ca/Na ratio of the samples (Fig. 13). This is precisely as observed (Tables 1 & 2):

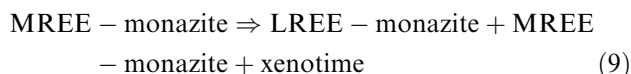
- (a) in metapelites with low Ca/Na ratios, containing plagioclase with An contents <0.18, monazite is formed;
- (b) in samples of intermediate to high Ca/Na ratios, with X_{An} varying from 0.23 to 0.86, allanite is preserved towards higher temperatures.

The ratio CaO/Na₂O may be more important than AFM compositional parameters in controlling allanite breakdown. If the REE elements are transferred from monazite to allanite, and Fe/Mg ratios are not key to the stability of allanite, the phase stability may have similar characteristics as epidote/clinozoisite minerals. The respective stability of epidote and clinozoisite depends on the Ca/Na ratio, and the reactions all have intermediate slopes in *P*–*T* space (Holdaway, 1972; Goldsmith, 1982). The effect of pressure on the temperature of reaction (6) is not well known at the moment.

Element distribution among metamorphic REE minerals

An unexpected outcome of this study is the significant fractionation of LREE, MREE, HREE + Y and Th amongst REE minerals, under conditions of low-grade metamorphism.

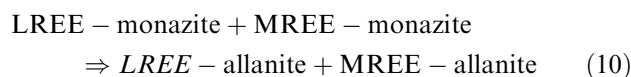
Contrary to recently held beliefs, formation of monazite below greenschist facies conditions is now well established; such monazite growth has been documented from various precursors, such as detrital monazite (Wing *et al.*, 2003; Rasmussen *et al.*, 2007), aluminophosphates (Janots *et al.*, 2006) and allanite (Pan, 1997; Bollinger & Janots, 2006; Krenn & Finger, 2007). In the present study, low-grade monazite appears to have grown from the destabilization of detrital monazite, and two initial populations of detrital grains retain separate characteristics during metamorphism (La/Nd ratios are summarized in Fig. 14). While the LREE-rich population of detrital monazite (which is mostly rich in Th as well) is resorbed, the MREE-rich one is essentially conserved, with some newly formed overgrowth (Fig. 8). Hence, newly formed tiny grains of LREE-rich monazite depleted in Y and Th (Figs 6 & 7) are interpreted to result from destabilization of LREE-rich detrital monazite. Overgrowths on detrital MREE monazite show an Nd-rich rim deposited prior to the La-rich (Th-poor) rim, as described by Rasmussen & Muhling (2007). The decay of detrital monazite lead to newly formed xenotime which, apart from using the Y, may have incorporated the Th released (Fig. 9c, d). The observed compositions and textures at low grade suggest two reactions:



Reaction (9) indicates that two coexisting monazite populations may form. As the LREE monazite is preferentially resorbed, reaction (8) is dominant. The high Th contents of detrital LREE monazite (of igneous and/or high-grade metamorphic origin) may induce this reaction at low-temperature conditions (Rasmussen & Muhling, 2007). Monazite recrystallization actually may be driven by this chemical disequilibrium, rather than an extraneous fluid (Poitrasson *et al.*, 1996), for which there is no evidence in our samples. In this case, monazite with low Th and/or Y reflects monazite recrystallization during low-grade metamorphism, without major hydrothermal causes being involved in this process.

Above 440–450 °C, the appearance of allanite and its succession of complexly zoned rims reflect several discrete reactions of prograde growth. The reproducibility of the composition and texture of these epidote group phases in the Alpine metapelites suggest that the allanite was formed by comparable reactions in the

greenschist facies. The prograde zoning pattern confirms previous observations of allanite cores with clinozoisite rims, described from metapelites (recent report in Janots *et al.*, 2006; Krenn & Finger, 2007). It is this reproducible zoning pattern of allanite, acquired during prograde metamorphism and showing no signs of re-equilibration after its formation, which opens an important avenue for allanite geochronology: where such allanite is preserved, it allows an early stage of prograde metamorphism to be dated, under greenschist facies conditions. The reason behind the LREE and MREE fractionation in the epidote group minerals is not well understood at present. It may or may not be related to monazite zoning at lower metamorphic grade, according to the partition coefficient between monazite and allanite. However, one general reaction can be written:



with the fractionation of LREE and MREE being more pronounced in allanite compared with monazite (Fig. 14).

Above 556 °C, metamorphic reactions either preserve REE zoning or redistribute the LREE and MREE into monazite. In sample MF315, the La/Nd ratio in monazite grains is uniform (Fig. 14), whereas in sample APi0413 monazite preserves the La/Nd fingerprint of the allanite precursor (sample APi0413, Figs 12 & 14). By comparison, these two samples show different textures, with *in situ* breakdown of allanite in APi0413, whereas the two minerals are not observed in mutual contact in MF315. Inheritance of compositional variations indicates that zoning in monazite cannot be interpreted in all cases as reflecting metamorphic growth. Partial HREE + Y equilibration is also indicated by the results of monazite–xenotime thermometers, which are consistent with phase equilibrium calculations, albeit with high uncertainties.

SUMMARY AND CONCLUSIONS

The LREE distribution in pelitic rocks from very low grade metamorphism up to amphibolite facies conditions shows that these elements are essentially transferred between allanite and monazite during prograde evolution; only a small fraction of the LREE appears to be stored in the major silicate minerals of such rocks.

Allanite initially appears at temperatures of 440–450 °C. It is then overgrown by one or two rims of epidote which form at < 528 °C. In all of the samples studied and the compositions they encompass, both monazite and xenotime fully break down to allanite/epidote in the biotite zone. The temperature of allanite breakdown is more complex to interpret as this phase is observed over a larger temperature range (560 < *T* < 610 °C), depending notably on the bulk

CaO contents and Ca/Na ratio. The breakdown products of allanite (and its rims) invariably include monazite, commonly plagioclase and xenotime are involved as well.

The reproducible zoning pattern of allanite acquired during prograde metamorphism is commonly preserved without signs of re-equilibration after its formation, suggesting that allanite isotopic dating (*in situ*, using the ion microprobe or LA-ICP-MS) should record the age of prograde metamorphism at greenschist facies conditions, specifically the temperature interval of allanite growth. With careful petrological documentation, combined age data for allanite and monazite appear as a powerful tool to derive ages of distinct stages from a single metamorphic cycle. Especially, the *in situ* breakdown of allanite to monazite offers an attractive possibility to derive the rate and duration of the metamorphic evolution from a single suitable sample. The complex zoning patterns of LREE, MREE, HREE + Y and Th which emerge from this study, present additional clues to correlate ages with *P–T* conditions of allanite and monazite under low-grade metamorphic conditions.

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SUPPLEMENTARY MATERIAL

The following material is available online at <http://www.blackwell-synergy.com>:

Table S1. Monazite analyses from sample APi0413 with Y and HREE thermometry.

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