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1 Article

2 **Al-rich titanites from Mont Blanc alpine fissures: witness of Ti-Nb-Y-REE mobility during water-rock interactions**

3 **Michel Cathelineau ¹, Chantal Peiffert ¹**

4 ¹ Université de Lorraine, CNRS, GeoRessources, Nancy, France ; michel.cathelineau@univ-lorraine.fr

5 * Correspondence: michel.cathelineau@univ-lorraine.fr

6 **Abstract:** Titanites can be excellent markers of element transfer in medium-temperature retrograde
7 metamorphism. Euhedral titanites from several alpine fissures from Mont Blanc, particularly those
8 of Périades and Courtes, crystallised at the end of the main quartz stage and are synchronous with
9 the formation of green biotites and albite before chlorite formation. Micro-XRF, SEM, electron
10 probe, and LA-ICP-MS analyses show that these titanites have a wide range of Al₂O₃ content from 1
11 to 8%, are dominated by -OH versus F and have a wide range of Nb (up to 4500ppm), Y (up to 3000
12 ppm), Zr (up to 1800 ppm) and Sn (up to 1400 ppm) concentrations. The allanite from the granite,
13 partly destabilised into epidote, is the most likely source of Nb, Y, Zr, Sn and REE. Titanites are
14 enriched in HREE and show variations in LREE depending on the studied sites. Like quartz, they
15 formed at around 400 ±20°C, compatible with the formation of green biotites after the destabilisa-
16 tion of granite Fe-Mg silicates. This early stage of fluid circulation, synchronous with the Mont
17 Blanc massif uplift, is therefore marked by the titanite formation at the transition between the
18 biotite and chlorite stability fields.

19 **Keywords:** titanite; niobium; REE

21 **1. Introduction**

22 Titanite (CaTiSiO₄)[O, OH, F] is a relatively ubiquitous mineral, crystallising both at the
23 magmatic stage, at the magmatic-hydrothermal transition (pegmatites) and during
24 metamorphism [1-4]. Titanite has also been described in several shear zone contexts (e.g.,
25 [5]). The mineral is frequently used for dating, particularly those related to magmatic
26 events and high-temperature water-rock interactions, such as skarn deposits. Hydro-
27 thermal titanite is less described than others from the point of view of genesis and crys-
28 tal-chemistry. As Ti is found in titanite in octahedral coordination, it is generally replaced
29 by Fe, Al, Nb, Ta, Mg, Zr, Sn, and to a lesser extent by V, Cr, U Th, while Y and REE
30 replace Ca. Fe, Al and F show the most significant variability in magmatic titanite
31 structure [4]. This extensive compilation of data makes it possible to evaluate the com-
32 positional fields of titanites from magmatic (plutonic or volcanic) and high-temperature
33 metamorphic facies (eclogite, in particular) origin. It also indicates that the number of
34 detailed examples of analyses of low to medium-temperature hydrothermal titanites
35 where the crystallisation conditions have been studied using independent approaches to
36 assess pressure, temperature and the nature of the fluids is much smaller than the num-
37 ber of studies of titanites of magmatic origin, affected or not by re-equilibration ([1,6-7].
38 In metamorphic rocks, Al-rich titanites seem more frequent. Some of them are charac-
39 terised by enrichment in Nb or V and an OH-dominated anion site (greenschist gneisses
40 from Andros island, [8]; the Salton Sea geothermal system, [9]. Regarding trace element
41 contents of titanites, abundant data concern magmatic rocks or relatively high tempera-
42 ture (> 600°C) metamorphic rocks, some related to water-rock interactions such as skarn
43 formation [10]. Data on titanites from lower-temperature hydrothermal systems are
44 scarce, except for the Salton Sea geothermal system [9].

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45
46 The aim here is to describe titanites crystallised from a hydrothermal/metamorphic fluid
47 set in motion during phases of deformation in an exhuming mountain range, the Alps,
48 under $400 \pm 20^\circ\text{C}$, 200-300 MPa. The example chosen is alpine fissures linked to defor-
49 mation near shear zones in the Mont Blanc massif around 22 Ma [11]. The physicochem-
50 ical conditions of these alpine fissures are reasonably well-defined thanks to previous
51 studies of fluid inclusions and paragenesis [12-14]. Titanites are formed from fluid in
52 open cavities and are sometimes covered with later minerals (chlorite). As they are well
53 preserved from deformation and alteration, they constitute one of the best-preserved
54 markers of elemental transfer during the late stages of exhumation of the outer crystalline
55 massifs in the French Alps. Titanite from alpine fissures unfortunately lacks precise and
56 detailed descriptions. Euhedral titanites of millimetric size from two localities (Periades,
57 Courtes, Fig. 1) have been selected because they are particularly representative,
58 well-formed and preserved. EDS chemical maps, micro-XRF, BSE-SEM electron images,
59 and LA-ICP-MS data were obtained on the same crystals. These data make it possible to
60 define the mobility of trace elements (Nb, Y, REE, Zr) during hydrothermal/metamorphic
61 fluid events during the formation of the alpine fissures.

62 2. Materials and Methods

63 2.1 Local geology

64 The Mont-Blanc massif is one of the Alpine external crystalline massifs (ECM) that form
65 the discontinuous belt observed at the periphery of the Alps, like that of the Aiguilles
66 Rouges (Figure 1). The Mont-Blanc massif mainly comprises a Variscan calc-alkaline
67 granite dated $316 \pm 19\text{Ma}$ (Rb/Sr ages, [15]). The Mont-Blanc area is one of the windows in
68 the Variscan basement beneath the Pennine and Helvetic nappes. Uplift of Mont Blanc
69 from depths of 15 to 20 km began around 22 Ma, an age that corresponds to ages identi-
70 fied by the formation of newly-formed biotites in the granites ($22.8 \pm 0.6\text{ Ma}$ and 22.4 ± 0.1
71 Ma, [11]).

72 To the south of the massif, the Mont Blanc granite is thrust onto the Jurassic-Cretaceous
73 sedimentary series (Fig. 1). To the north, the Mont-Blanc is separated from the Ai-
74 guilles-Rouges massif by a band of Mesozoic sedimentary rocks, commonly known as the
75 "Chamonix syncline", which outcrops in the Chamonix glacial valley. The contact zone is
76 a shear zone (MBSz), oriented NE-SW.

77 During the Alpine collision, the Mont Blanc granite was buried to a depth of around
78 twenty kilometres due to the thrusting of the Valaisan domain and then the Helvetic
79 nappes. The granite was deformed during these events, acquiring intense vertical schis-
80 tosity (flattening with vertical stretching). It was metamorphosed at nearly 450°C and 500
81 MPa [13,14]. The age of 29 Ma on allanite most probably indicates the age of maximum
82 granite burial beneath the nappes [16]. Temperatures peak at 450°C at that time and agree
83 with estimates for the base of the Morcles nappe. In the granite, the muscovite-chlorite
84 equilibrium in the thrust zone of the muscovite + biotite + chlorite + epidote association
85 gives P-T estimates of $0.5 \pm 0.05\text{ GPa}$ and $400 \pm 25^\circ\text{C}$ according to [13-14].

86 The alpine fissures formed during the thrusting of the Helvetic Nappe at around 22-20
87 Ma are generally close to areas of shearing and correspond to sub-horizontal tension
88 cracks, often developed in echelon, perpendicular to the shear planes, and compatible
89 with the SE-NW thrusting. The P-T conditions at the start of quartz crystallisation are
90 close to $400 \pm 20^\circ\text{C}$; 300-400 MPa [12, 17-20]. The fractures are filled with quartz, albite
91 and adularia, crystallising mainly by epitaxy onto the relics of granite feldspars on both

sides of the alpine fissures. The paragenetic succession is as follows: quartz Q1 (epidote), Q2-albite-adularia, chlorite, calcite-fluorite/ quartz Q3-muscovite-siderite/ zeolites [17].

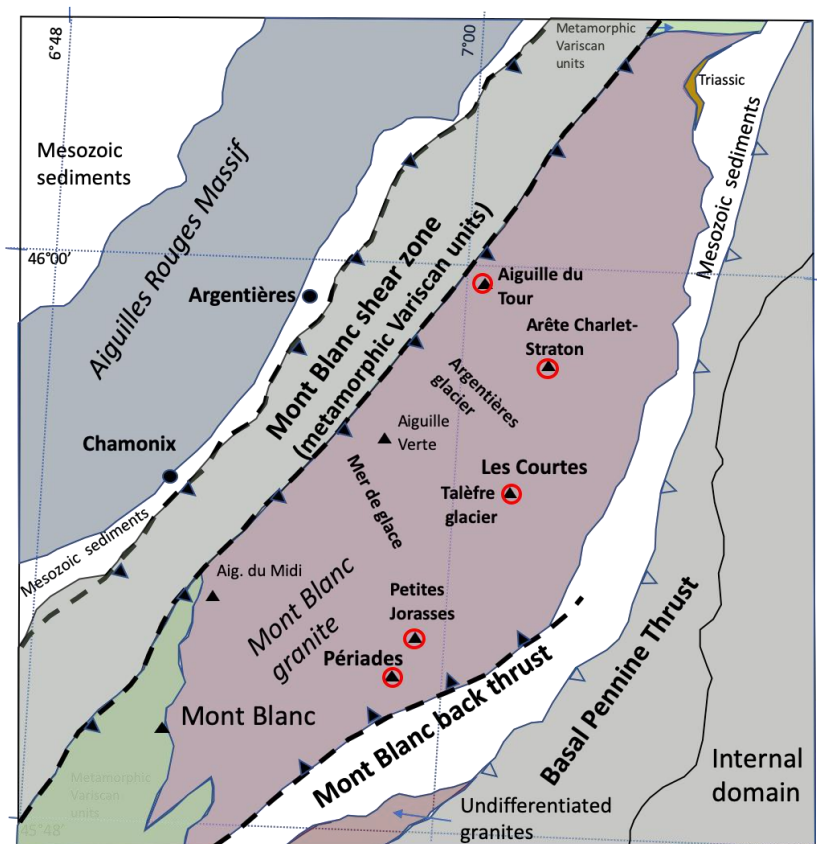


Figure 1. Map of the Mont Blanc massif (modified from [11]) with the locations of the studied titanites. A red circle indicates studied localities.

2.2 Historical works

Titanite was discovered relatively early in the Alps. Macroscopic titanite is found locally in some alpine fissures in the Mont Blanc massif. The first sample of titanite identified in France in 1780 was called "pictite" and corresponded to a prismatic form of titanite from the Mer de Glace sector. René Haüy studied a titanite crystal from Disentis near the Gotthard in 1801 and proposed calling it "sphene" in 1801 [21]. In his "Minéralogie de la France" [22], Alfred Lacroix described several specimens from the Mont Blanc massif, in particular from the area around the Talèfre glacier, and defined among other titanites reference crystals the following types: Type V, called the "pictite" variety, with crystals that are very elongated along the $e_{1/2}$ edge, and Type VIII, which characterises crystals that lack elongation and flattening and are generally rich in faces (Fig. 2). Since Lacroix, titanite has been found in fissures in various localities, primarily in the vicinity of Périades, along the Talèfre and Argentière basins (Les Courtes, Aiguille du Tour, Arête Charlet Straton, L'A. Neuve).

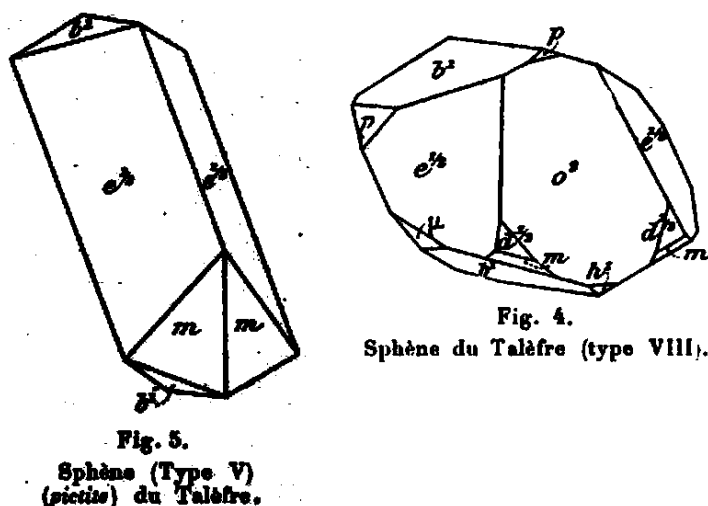


Figure 2. First historical drawing of titanite crystal types from the Talèfre glacier basin (Mont Blanc massif, location in Fig. 1) by [22] in his “Minéralogie de la France”.

2.3 Analytical methods

Polished sections and isolated crystals were prepared and mapped in transmitted light with a Keyence VHX microscope before micro-XRF mapping on selected samples to establish the paragenetic sequence of the hydrothermal mineral assemblages.

Micro-X-ray fluorescence (XRF) mapping was carried out using a Bruker-Nano M4 Tornado instrument (SCMEM, GeoRessources laboratory, Nancy, France). This system has a Rh X-ray tube with a Be side window and polycapillary optics, giving an X-ray beam with a 25–30 μm diameter on the sample. The X-ray tube was operated at 50 kV and 200 μA . A 30 mm² xflash® SDD detects X-rays with an energy resolution of <135 eV at 250,000 cps. All analyses were carried out at a 2 kPa vacuum. Main elements, such as Ti, Mg, Mn, Fe, Y, Zr, and Nb, were mapped, and composite chemical images were generated. The micro-XRF mapping made choosing the most representative crystals for SEM and LA-ICP-MS investigations easier.

Scanning electron microscope (SEM) investigations were performed on 14 samples at the SCMEM, GeoRessources laboratory (Nancy, France) using a JEOL FEG7600 apparatus 7600F (hot cathode) equipped with an Oxford Instruments SDD-type EDS spectrometer and WDS, allowing major element determination in titanite.

Electron Probe Microanalysis: Quantitative analysis of major elements was performed with a CAMECA SX100 EPMA equipped with five WDS spectrometers using an accelerating voltage of 15 kV, a probe current of 12 nA (accelerating voltage of 25 kV, a probe current of 150 nA for trace elements) and a beam diameter of 1 μm . Peak and background counting times were 10 and 5 s, respectively. The following crystals were used: TAP (F, Na, Mg, Al, Si, Rb), LPET (K, Cl, Nb), LIF (Mn, Fe), and PET (Cs). Standards were natural minerals and synthetic oxides: topaz (FK α), albite (Na, SiK α), olivine (MgK α), andradite (CaK α), Al₂O₃ (AlK α), orthoclase (KK α), MnTiO₃ (Mn, TiK α), Fe₂O₃ (FeK α), RbTiPO₅ (RbL α), SrSO₄ (SrL α), barite (BaL α).

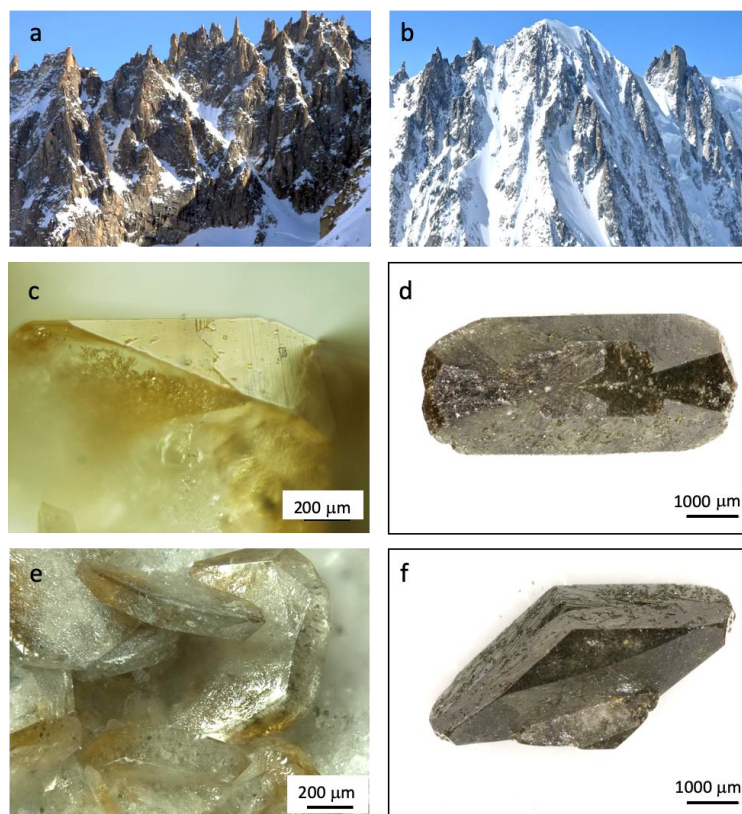
The titanite crystals were examined with A Dilor-Labram (Horiba Jobin Yvon, France) Raman micro-spectrometer (GeoRessources laboratory, Nancy, France) using a 514.5nm Ar⁺ laser emission line at a resolution of 2 cm⁻¹ in the 100–4000 cm⁻¹ range. Repeated acquisition using the highest magnification was accumulated to improve the sig-

145 nal-to-noise ratio. Raman spectra were obtained after generally five acquisitions of 10 to
146 20 s each. A long working-distance objective with a 50× magnification was used.

147 Titanites from Alpine fissures were analysed by LA-ICP-MS (GeoRessources laboratory)
148 to determine the trace element concentrations. Laser ablation utilised an ESI New Wave
149 Research UC 193 nm excimer laser at a frequency of 5 Hz. The ablated material was car-
150 ried by helium gas (0.5 l.min⁻¹), which was mixed with argon (0.9 l.min⁻¹) via a cyclone
151 mixer (volume of 9.5 cm³) before entering the ICP torch and analysed with an Agilent
152 7900 ICP-MS. External calibration was carried out using the NIST 610 and 612 glass
153 standards. Ti was used as an internal standard to calculate absolute concentrations. An-
154 alysed isotopes were: ⁵¹V, ⁵²Cr, ⁵⁵Mn, ⁸⁸Sr, ⁸⁹Y, ⁹³Nb, ¹¹⁸Sn, ¹⁷⁸Hf, ¹⁸¹Ta, ¹⁸²W, ²³²Th, ²³⁸U and
155 the REE. Data reduction was carried out using Iolite software (version 4) [23] following
156 the standard methods from [24].

157 3. Results

158 The two main samples chosen from extensive works on alpine fissures are relatively
159 large-size titanites, well-formed and preserved from two localities: Périades and Courtes
160 (Fig. 3a and b). The crystals of the Périades (Fig. 3c, e) are characterised by flattened
161 crystals of a light honey colour with slightly stronger colours at the edges. Numerous
162 inclusions of green biotite characterise the crystals from the north face of Courtes, making
163 them opaque and dark green. Some crystals show a twinning formed by two crystals
164 joining together by the plane {100} (Fig. 3d, f).



165
166 **Figure 3.** Main titanites studied and their sampling sites: a: Périades; b: Courtes (North
167 face); c, e: honey-coloured, tabular titanites from Périades; d, f: mottled titanite crystals
168 from Courtes.

A few samples showing small-size titanites representative of the assemblages found at the boundary of alpine fissures (Aiguille du Tour, Les Petites Jorasses, Arête Charlet Straton) were also studied by SEM.

3.1. Petrography

From a paragenetic point of view, titanite appears late and synchronous with the late quartz overgrowth that it also overlies. Titanite is ubiquitous in the altered boundaries of alpine fissures, where it is abundant euhedral crystals no larger than 100 μm (Fig. 4). A few samples were examined under SEM (Aiguille du Tour, Petites Jorasses and Arête Charlet Straton) which show the habitus and location of these small size titanites (Fig. 4). Titanite appears associated with albite and adularia (Fig. 4a, b). Euhedral apatite is in rare cases associated with titanite (Fig. 4b). In Fig. 4 a and b, clusters of tiny euhedral crystals around 20 to 40 μm are observed, and in a few instances, larger crystals around 100 μm are found (Fig. 4c). Vermicular chlorite when present is always located at the top of the titanite crystals and is later (Fig. 4d). Careful study of the chronological relationships between titanite and chlorite shows however that chlorite occurs later than titanite or only appears in the last growth band of the Qtz2 quartz and titanites. Then, it crystallises abundantly on top of titanite, quartz, and albite that have already been formed (Fig. 4).

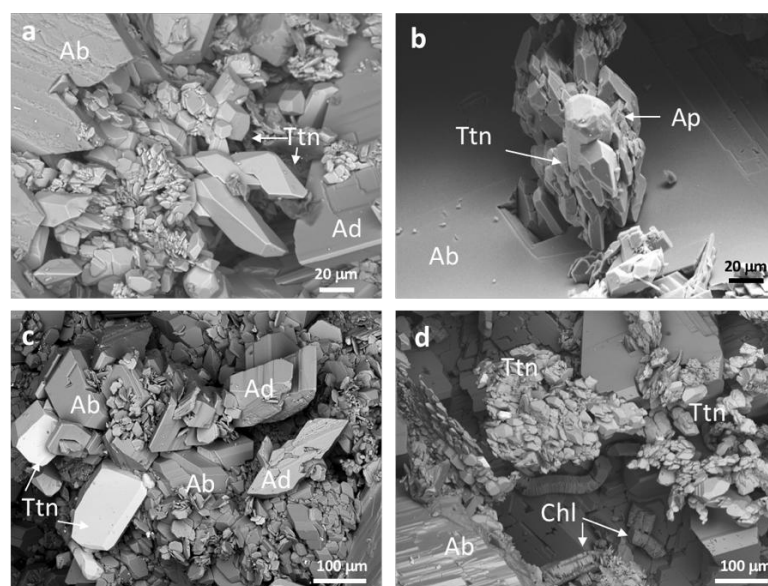
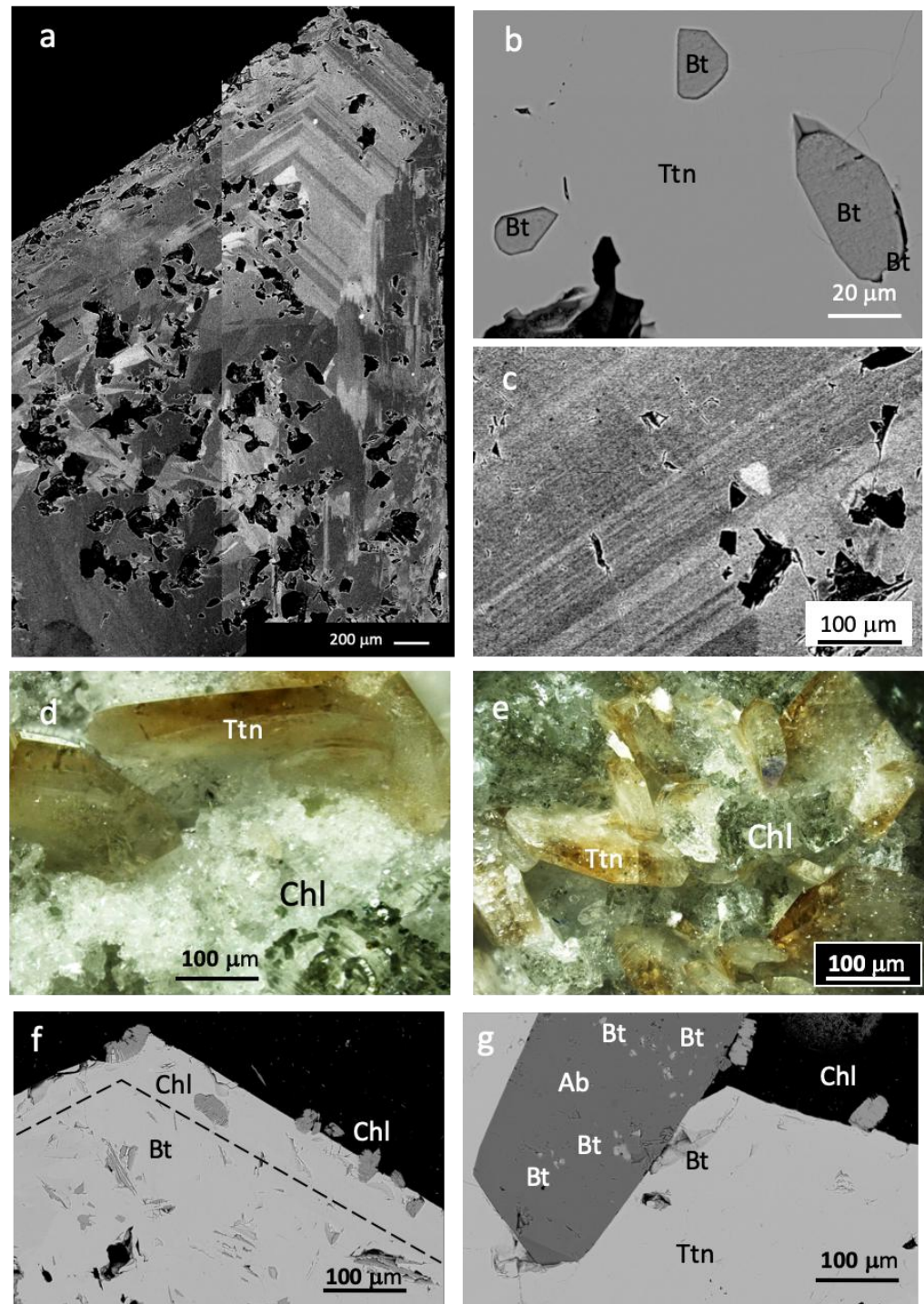


Figure 4. Relationships between titanite and other mineral phases in the alpine fissures of Mont Blanc (electron microscope photographs in backscattered electron (BSE) mode). a: titanite showing the "wedge" profile in larger crystals (40-50 μm) surrounded by clusters of tiny crystals on adularia and albite, b: group of titanite spike crystals emerging from automorphic albite and topped by isogranular apatite, c: albite-adularia association and chunky titanite crystals (in white), d: automorphic albite and group of tiny agglomerated automorphic titanite crystals: vermicular chlorite is present in the background in the cavity in the form of "accordions" (vermicular shape) but is late. Ttn: titanite; Ab: albite; Ad: adularia; Ap: apatite; Chl: chlorite.

When titanite is present in the cracks (examples of Périades and Courtes), the crystals are usually unmottled, shiny and of a beautiful yellow to orange colour, sometimes intense, with sizes ranging from a few tens of micrometres to a few millimetres or even a few centimetres in exceptional cases. It crystallises on the large morion quartz Qtz2 that follows the quartz Qtz1-epidote, which is not always present.

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Figure 5. a: BSE images of Courtes titanite showing multiple inclusions of biotites (in black) with a magnification of biotite inclusions. b.: The zoning of the external growth domain is also shown magnified in c. d and e: vermicular chlorites found around titanite crystals (Périades), f: external growth band with chlorite in and out and internal part with biotite inclusions (Courtes sample), g: crystal from Courtes with biotite inclusions inside titanite and albite. Chlorite is found deposited onto the faces of the two minerals. Ttn: titanite; Ab: albite; Chl: chlorite; Bt: biotite.

Titanites show sectorial and locally oscillatory zonings, the most frequently in the late overgrowth bands. (Fig. 5a, b and c). Biotite crystals appear as black dots due to the chosen BSE contrast in Fig. 5a to reveal the titanite zoning. Biotite crystals trapped in titanite are euhedral, as shown by Fig. 5b, homogeneous in mean atomic number Z, and unaltered. They appear synchronous with the titanite growth.

In both localities, titanites are partially covered with vermicular chlorite, as shown in Fig. 5d, e. In the Courtes titanites, an interesting transition is observed between the main crystal, where biotites form inclusions trapped during crystal growth and the late crystal growth band, where appear a few vermicules of chlorites which crystallisation ends outside titanite, and then as free vermicular crystals (Fig. 5f, g). This sample represents, therefore, one of the best examples illustrating the relative timing of the biotite to chlorite transition.

3.2. Crystal-chemistry data

3-2-1 Major elements

Titanites from Mont Blanc Massif show quite contrasting levels of overall substitution of titanium by other elements (Al, Fe) (Fig. 6, Table 1 and Appendix A). In Figure 6a, which contrasts the occupation of the titanium site by the different chemical elements substituting it (Fe, Al), the titanites from Périades have the lowest level of titanium substitution, followed by those from Courtes and finally the other sites in the massif.

Wt. %	Périades				Courtes				Charlet St.	P. Jorasses	Ag. du Tour
	SiO ₂	30.11	30.31	30.17	30.19	31.27	30.71	30.61	30.49	30.96	32.97
CaO	28.34	28.05	28.26	29.65	28.86	28.67	28.86	28.32	31.10	28.66	30.46
TiO ₂	39.28	38.14	38.67	40.15	35.31	35.23	37.76	37.30	32.02	31.65	28.48
Al ₂ O ₃	1.32	1.72	2.11	1.02	3.60	3.80	1.65	1.70	5.91	6.72	7.75
Fe ₂ O ₃	0.11	0.17	0.16	0.10	0.81	0.63	0.44	0.33	0.00	0.00	0.00
Y ₂ O ₃	1.29	0.78	0.89	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Nb ₂ O ₃	0.45	0.23	0.13	0.02	0.00	0.00	1.16	0.99	0.00	0.00	0.00
ZrO ₂	0.13	0.04	0.10	0.00	0.00	0.00	0.30	0.39	0.00	0.00	0.00
F	0.00	0.00	0.00	0.00	0.82	0.96	0.52	0.54	0.00	0.00	0.00
total	101.05	99.62	100.61	101.43	99.77	98.98	99.28	98.11	99.99	100.00	100.01
a.p.f.u.											
Si	0.98	1.00	0.98	0.98	1.02	1.01	0.99	1.00	1.01	1.06	1.07
Ca	0.99	0.99	0.99	1.03	1.00	1.01	1.00	1.00	1.08	0.98	1.05
Ti	0.96	0.94	0.95	0.98	0.86	0.87	0.92	0.92	0.78	0.76	0.69
Al	0.05	0.07	0.08	0.04	0.14	0.15	0.06	0.07	0.23	0.25	0.29
Fe	0.00	0.00	0.00	0.00	0.02	0.02	0.01	0.01	0.00	0.00	0.00
Y	0.02	0.01	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Nb	0.01	0.00	0.00	0.00	0.00	0.00	0.02	0.01	0.00	0.00	0.00
Zr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00
F	0.00	0.00	0.00	0.00	0.04	0.05	0.03	0.03	0.00	0.00	0.00

Table 1: Representative chemical composition of titanites (oxides in wt%) and structural formulae calculated based on 5 oxygens. Total iron is expressed as FeO. b.d.l.: below detection limit. Charlet St: Charlet Straton, P. Jorasses: Petites Jorasses, Ag. Du Tour : Ai-guille du Tour. a.p.f.u. : atomic proportion per formula unit calculated.

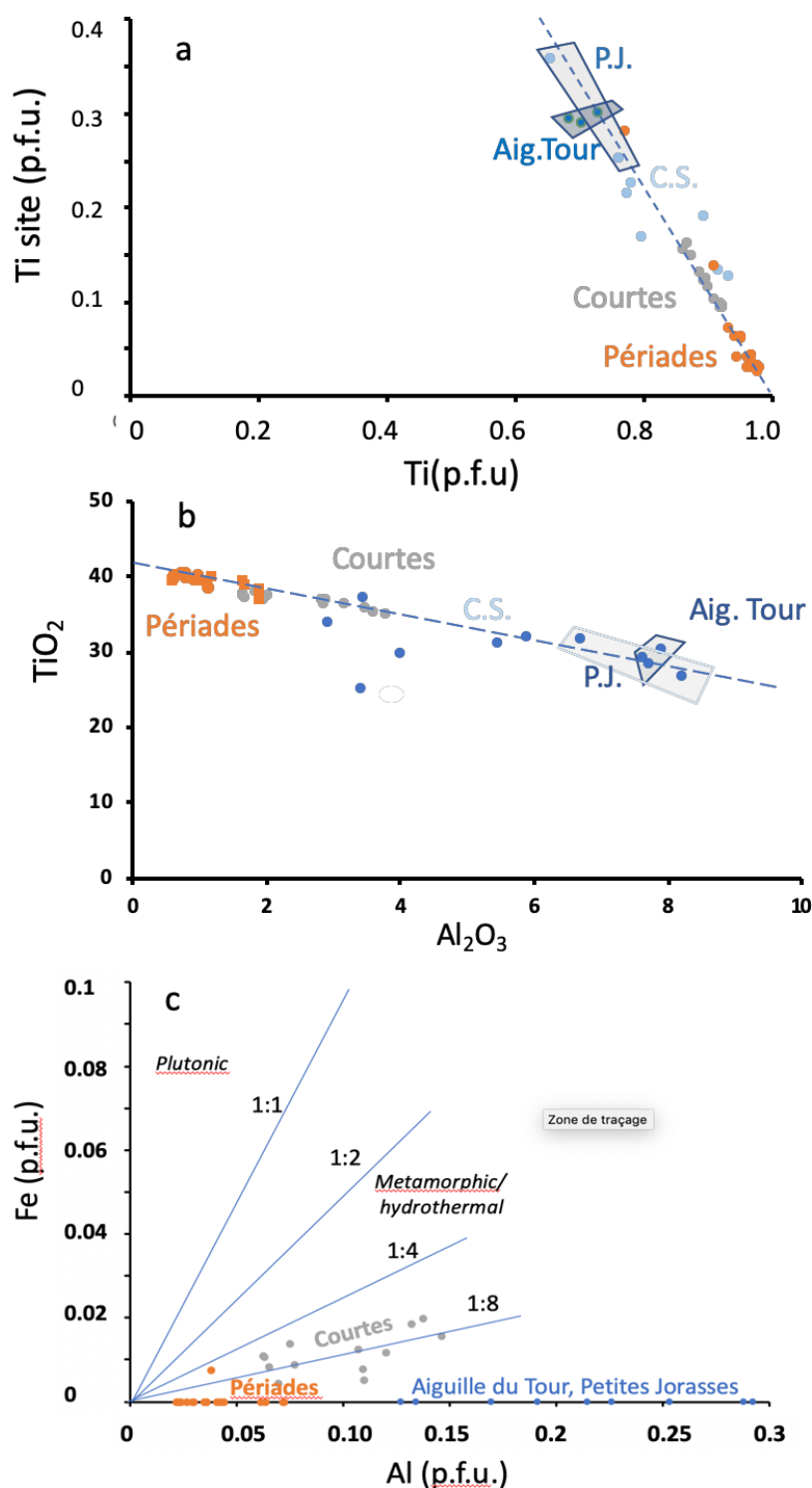


Figure 6. Crystal-chemical diagrams applied to Périades and Courtes titanites, and a few analyses performed on titanites from other localities (C.S.: Charlet Straton, P.J.: Petites Jorasses, Aig. Tour: Aiguille du Tour). a: Ti site infilling by other cations than Ti versus Ti content (p.f.u.: per formula unit.); b: TiO₂ versus Al₂O₃ diagram; c: Fe versus Al diagram from [4]. The main fields for plutonic or metamorphic/ hydrothermal are from [4].

In the TiO₂ versus Al₂O₃ diagram (Fig. 6b) proposed by [25], the titanites from the Mont Blanc have Al₂O₃ concentrations that range from 0.6 1% to 8% (data in Table 1 from supplementary material). Titanites have more restricted concentrations at the scale of a

crystal or a site. For example, the titanites from Périades have the lowest Al_2O_3 concentrations (0.77 to 0.97%), those at Les Courtes between 1.7 and 3.8% Al_2O_3 , while titanites from other localities, particularly those from l'Aiguille du Tour, reach 7.6 to 7.9%. Aluminium is, therefore, the main substituent for titanium in Mont Blanc titanites. In Courtes titanites, the F content is low and ranges from 0.45 to 0.95%, with a mode close to 0.8%. It is correlated positively with Al and Fe. Périades titanites are fluorine free, and have the lowest concentrations in Fe and Al.

In the Fe-Al diagram (Fig. 6c), many of the titanites analysed are characterised by low iron values, unlike those at Courtes, which show a Fe/Al correlation with a ratio of 1/8 and iron atomic concentrations between 0.01 and 0.02 p.f.u. (Figure 8c).

3-2-2 Trace elements

Two crystals from Périades exhibit interesting chemical zonings, illustrated in Fig. 7 and 8. The micro-XRF mapping of the titanite crystal has revealed their chemical zonations, particularly in trace elements such as Nb, Y, and Zr.

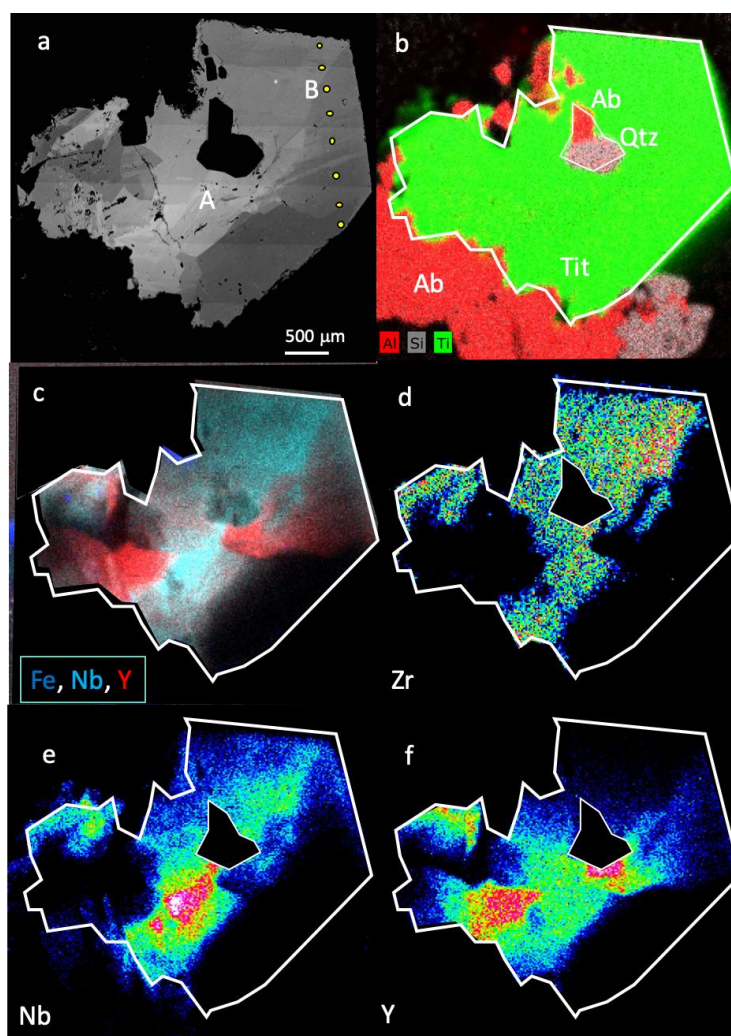
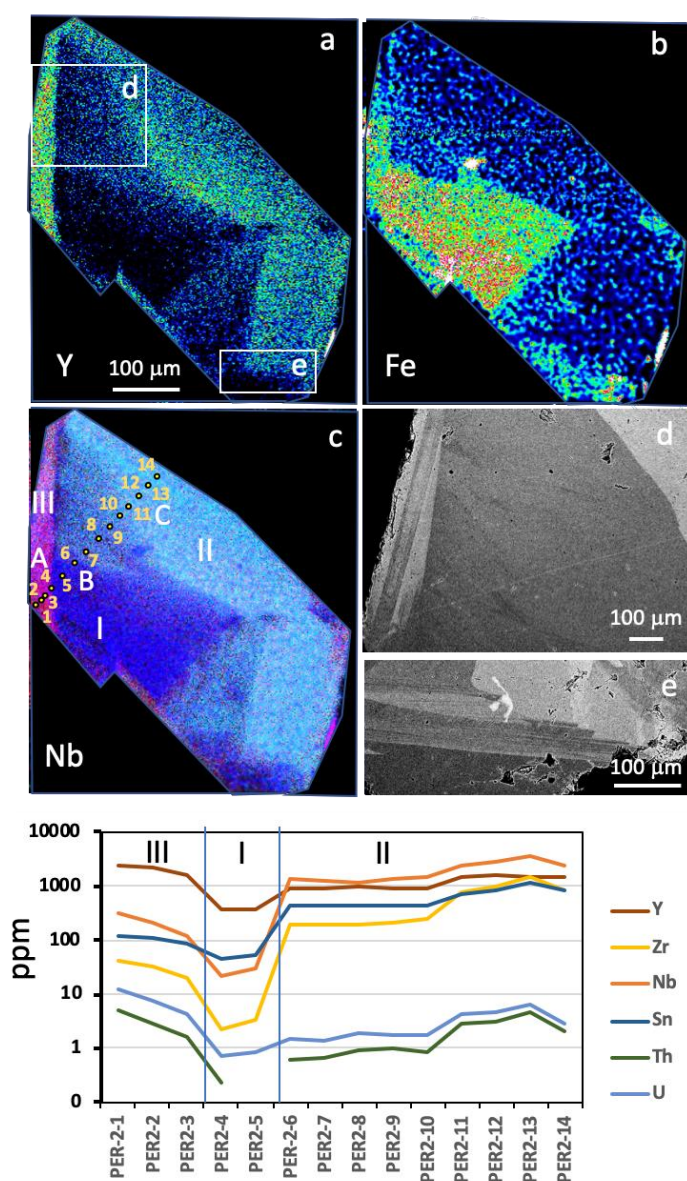


Figure 7. Périades titanite crystal (Per-Ti1). a: BSE-SEM images with the indication of the LA-ICP-MS profile and Raman analyses (A, B). b: composite chemical image showing that titanite has grown, including small quartz and albite crystals. c, d, e, and f: micro-XRF chemical maps of the same titanite crystal (Zr, Fe, Nb, Y composite). d and e: BSE-SEM images of the inset indicated in Figure 7a show oscillatory zoning of the external growth band.

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The first crystal from Périades (Fig. 7) indicates that quartz Qtz2 and albite may be incorporated within the titanite crystal during titanite growth. As shown in Fig. 7b, titanite grew probably because of aggregation of smaller crystals of microscopic size (several tens of microns), which then fuse into a single macroscopic crystal. The crystal shows sectorial zoning with zones enriched in Y and others enriched in Nb and Zr.

In the second crystal from Périades (Fig. 8 a, b, c), a core slightly enriched in Fe (zone I) is rimmed by a zone richer in Nb and Y (Zone II). A last growth band with oscillatory zoning is revealed by BSE-SEM images (Fig. 8 d and e). This band (zone III) shows similar trace element patterns than in zone II but still enriched in most elements such as Nb (3680 ppm in zone III compared to the 1200 - 2700 ppm range in zone II, Table 2, graph from the bottom of Fig. 8f).



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Figure 8. Périades titanite crystal (PER-Ti2). a: Y; b: Fe; c: Nb with an indication of the LA-ICP-MS profile and Raman analyses (A, B, C). d and e: BSE-SEM images of the inset indicated in the figure an oscillatory zoning in the external growth band. At the bottom of Figure (f), the chemical profile localised in c is provided.

Trace element concentrations obtained by LA-ICP-MS on two profiles from Périades and two profiles from Courtes were carried out after the micro-XRF mapping. They are shown in Table 2 and Fig. 9.

ppm	V	Cr	Mn	Sr	Y	Zr	Nb	Sn	Hf	Ta	W	Th	U
Périades													
PER2-1	142.8	12.2	470.7	38.9	2342.1	41.9	317.2	122.3	1.96	6.35	6.28	5.1	12.7
PER2-2	145.3	12.1	398.4	36.8	2252.2	33.6	203.5	108.6	1.67	6.15	2.40	2.8	7.6
PER2-3	141.9	13.8	372.0	36.7	1570.0	20.5	118.7	86.3	1.08	4.03		1.6	4.4
PER2-4	135.9	15.2	356.1	33.3	354.2	2.3	21.2	45.6	0.00		0.34	0.2	0.7
PER2-5	140.5	15.0	353.5	34.8	353.8	3.3	29.1	51.1		0.39			0.8
PER2-6	78.5	5.9	365.1	40.5	912.5	200.4	1313.6	425.9	8.95	27.6	1.24	0.6	1.5
PER2-7	79.0	5.4	365.0	40.2	863.1	190.0	1252.3	422.1	9.22	28.8	1.57	0.6	1.4
PER2-8	83.7	6.1	379.7	40.7	967.1	196.8	1162.5	449.9	8.92	18.7	5.71	0.9	1.9
PER2-9	85.1	5.6	371.8	39.8	925.8	212.9	1359.0	428.5	10.59	24.4	3.04	1.0	1.8
PER2-10	84.1	5.3	367.8	41.5	904.7	243.6	1462.2	423.5	13.80	37.6	1.73	0.9	1.8
PER2-11	80.0	5.4	344.7	45.7	1434.2	740.2	2313.9	720.6	34.44	93.9	1.14	2.7	4.4
PER2-12	82.3	6.0	334.1	49.7	1563.2	967.8	2691.8	839.7	43.48	122.2	1.27	3.2	4.7
PER2-13	77.6	5.0	344.3	52.5	1495.7	1420.1	3690.7	1143.2	57.60	163.5	1.21	4.7	6.2
PER2-14	81.4	5.5	322.8	52.1	1489.1	842.6	2300.2	796.1	46.47	150.8		2.1	2.8
PER1-1	79.3	5.1	352.2	58.9	1414.1	1339.4	4506.5	1078.0	58.72	169.3	0.52	3.8	4.9
PER1-2	67.8	5.3	369.1	53.6	1735.6	1790.3	4857.6	1365.7	62.15	141.9	2.04	6.4	11.5
PER1-3	65.3	6.8	463.5	55.4	3208.8	44.6	2411.9	551.1	1.87	38.38	85.8	18.3	41.4
PER1-4	84.0	12.3	605.4	50.7	3276.9	102.5	2054.6	605.5	4.87	28.2	55.4	12.4	76.9
PER1-5	98.0	9.5	500.5	49.5	2831.4	53.3	1637.6	417.6	2.15	23.3	123.1	15.3	41.2
PER1-6	138.4	12.5	452.5	38.0	2246.6	43.9	393.1	125.8	1.89	7.40	6.50	5.1	12.9
PER1-7	151.8	9.8	377.0	37.8	1623.8	22.2	150.8	96.9	1.17	4.80	1.46	1.8	5.1
PER1-8	167.4	13.3	351.1	36.5	231.4	1.4	24.6	44.0	0.00		0.08		0.4
Courtes													
B-1	430.8	42.2	305.2	21.1	187.8	21.0	109.5	137.1	1.24	3.17	1.27		7.4
B-2	383.9	71.5	375.5	26.3	1111.4	213.8	1735.6	742.3	6.88	6.98	269.8		717.5
B-3	384.0	64.9	305.6	27.9	1279.0	38.2	1917.8	406.4	1.48	8.67	65.62	0.7	148.6
B-4	473.0	58.2	289.9	20.3	772.0	51.0	531.1	178.7	1.68	2.36	63.04		93.1
B-5	473.9	59.4	308.7	21.7	802.5	59.5	692.8	252.4	1.94	3.30	76.84	0.1	159.1
B-6	445.1	55.6	287.1	20.8	720.7	54.0	509.7	225.1	0.69	2.39	60.78		82.0
B-7	462.4	61.1	309.1	23.9	887.2	35.3	993.3	265.1		5.06	51.55	0.0	60.1
C-1	442.2	19.7	239.3	22.3	208.9	25.6	115.3	156.0	1.07	3.14	1.53		3.9
C-2	418.3	52.6	234.4	18.2	432.5	18.2	137.3	116.5		0.76	3.70	0.0	8.3
C-3	405.4	47.0	249.6	19.1	580.4	47.9	276.3	198.6	2.29	1.51	6.85		15.1
C-4	504.0	39.9	334.0	21.8	1040.3	127.5	1025.3	374.9	5.37	4.37	100.7		415.6
C-5	382.7	62.9	335.9	25.5	1032.5	97.5	1727.8	475.4	4.67	9.69	80.4	0.0	105.2
C-6	435.0	91.6	364.5	24.0	1171.4	178.2	1080.0	706.2	10.53	5.23	2907.2	0.0	144.2
C-7	399.4	68.9	305.2	23.6	909.8	169.0	920.5	606.7	8.58	3.66	2285.0		94.7

Table 2: Representative LA-ICPMS analyses of titanite trace elements from the two mostly studied sites, Périades and Courtes. (all elements in ppm)

Nb, Zr, and Y concentrations reach thousands of ppm in some growth bands (LA-ICP-MS, confirming the X-ray microfluorescence data and the maps shown in Fig. 7 and 8. Nb concentrations range from 20 to 5000 ppm, Y from 180 to 330 ppm, Zr from 1 to 1800 ppm and Sn from 35 to 1400 ppm. Nb, Zr and Sn are positively correlated to Y. A single profile from Périades stands out from the others in a zone of Périades titanite, for which the Y concentration is much higher than the others, covering the 1500 - 3300 ppm range and corresponds to the sectorial zoning enrichment shown in Fig. 7 d and e. Even higher Y values may be expected in this crystal, as the profile crosscuts the sector but not at the maximal mapped enrichments. The Périades titanites are enriched in most metals compared to those from Courtes, W, U, V, and Cr excepted and correspond to the titanites with the lowest Fe and Al contents.

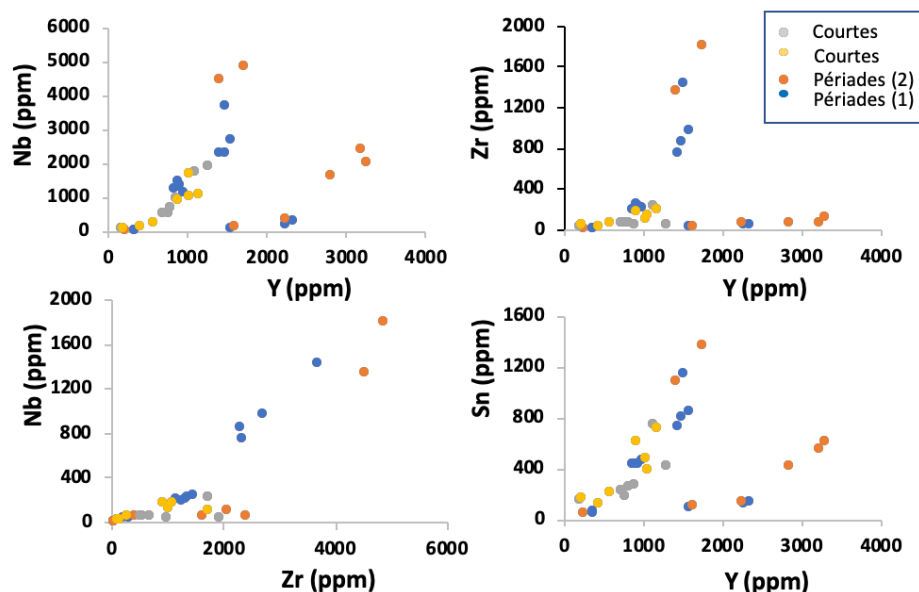


Figure 9. Trace elements analysed by LA-ICP-MS in titanites from Courtes (2 crystals) and Périades (2 profiles, one by crystals shown in Fig. 5 and 6).

The sum of REE reaches ranges from 300 to 2800 ppm. In Périades titanites, the spectra normalised to the chondrites are not very fractionated and show a moderate negative Eu anomaly. In Courtes titanites, the REE spectrum is much more fractionated, with a relatively low LREE content and slight inflexion at the Eu level. Overall, the spectrum is fractionated in favour of HREE, which reaches values close to, but lower than those of Périades titanites by a factor of 2.

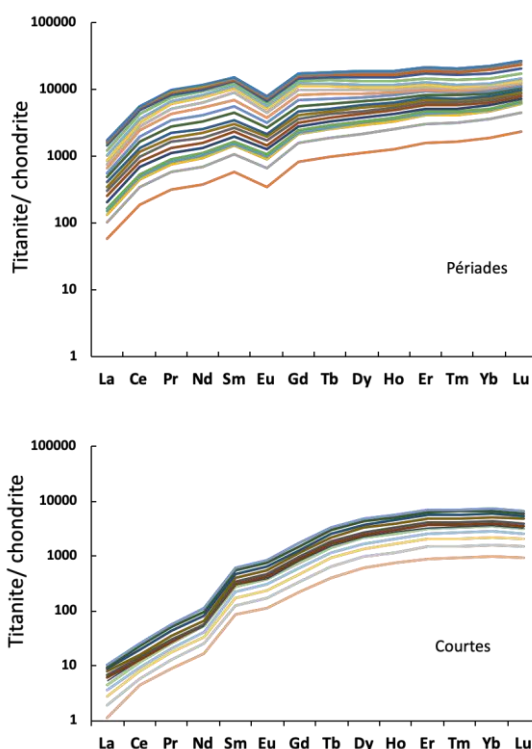


Figure 10. REE spectra normalised to chondrite of titanites from Périades and Courtes.

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3-2-2 Raman spectra

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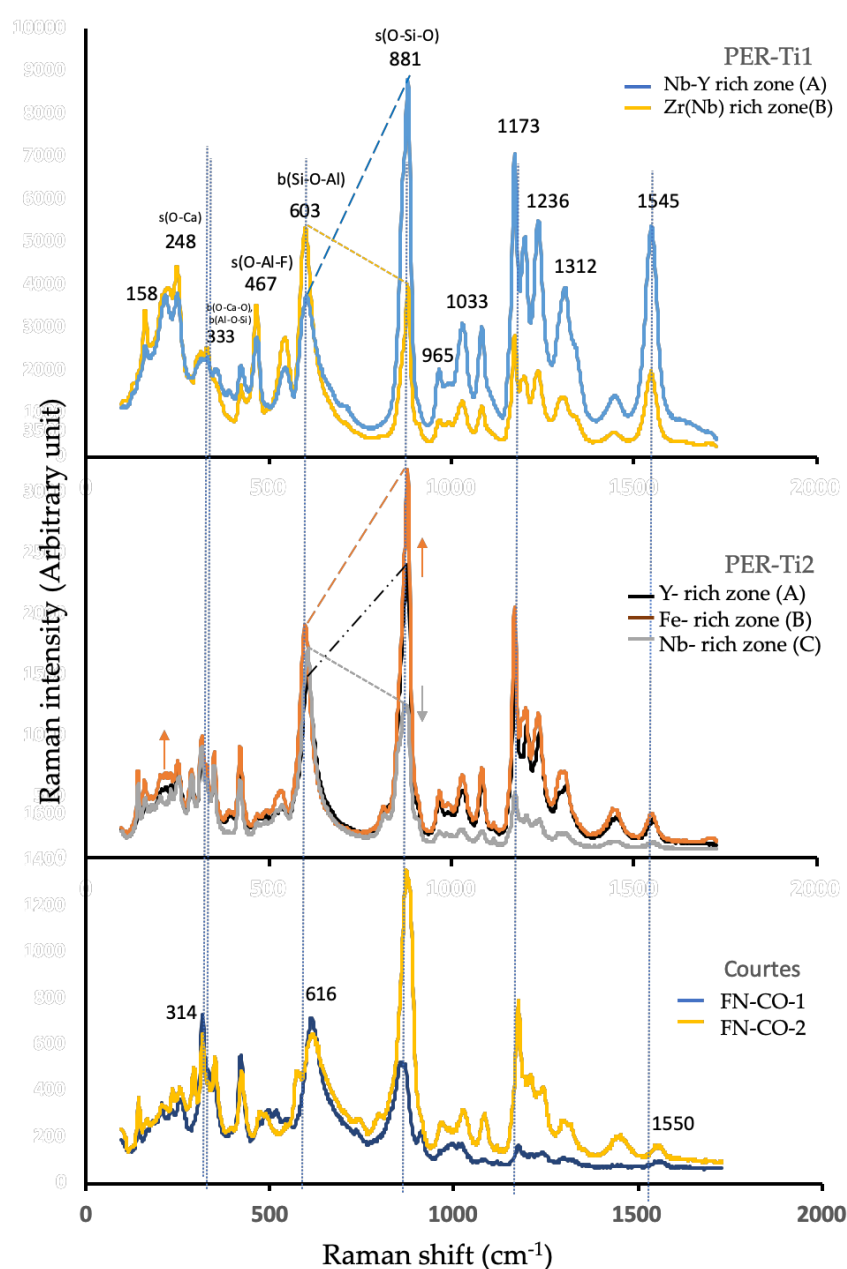
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Representative Raman spectra obtained from the analyzed titanite samples are shown in Fig. 12 and correspond to areas characterised by contrasted trace element distribution: two Raman spectra for titanite Per-Ti1 with a zone enriched in Zr (noted A) and a zone enriched in Nb (noted B), three Raman spectra obtained on Per-Ti-2 (Fig. 8 for location) corresponding to zones enriched in Y and Fe (A), Fe (B) and Nb (C), and finally two representative Raman spectra of Courtes titanites which do not display any significant zoning.



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Figure 12. Raman spectra of Mont Blanc titanites. Périades: crystals PER-Ti1 and PER-Ti2 (location of analyzed zones in figures 7 and 8, respectively), and Courtes (2 crystals, FN-CO-1 and FN-CO2). Band assignment follows [31,32].

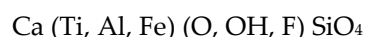
All spectra exhibit characteristic peaks near 248, 333, 603, 881, 965, 1033, 1173, 1236, 1312, and 1545 cm^{-1} . The main differences between spectra concern the relative intensity of some bands, particularly the two intense bands at 603 and 881 cm^{-1} . Another difference concerns the bands 217-229 and 248 cm^{-1} , which display similar intensities or increased intensity of the 248 cm^{-1} band.

4. Discussion

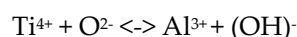
4.1 Incorporation of trace elements into the titanite structure

Titanite is a nesosilicate in which the isolated silica tetrahedra (SiO_4^{4-}) are bonded to cations or anionic groups and not to other silica tetrahedra. The isolated silica tetrahedra are bonded to a folded chain of TiO_6 octahedra, which shares the corners and is parallel to the crystallographic axis.

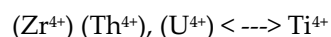
There are several possible substitutions in each site of titanite. The most common substitution of quadrivalent Ti is by trivalent Fe and Al, leading to a formula of the type:



This results in a charge imbalance generally compensated by a coupled substitution of F or OH^- for the oxygen (called O1) underbonded relative to the other oxygens in the structure [26,25]. The suggested substitution to maintain the electrical equilibrium is:



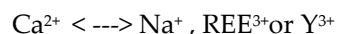
Ti site: besides Al^{3+} , titanium can also be replaced by the following elements [[8, 26-28]: Mg^{2+} , Fe^{2+} , (Cr^{3+}) , (Zr^{4+}) , (V^{5+}) , Nb^{5+} , (Ta^{5+}) , (Th^{4+}) , (U^{4+}) . In this site, substitutions may occur at a constant charge:



Or, by the introduction of trivalent and pentavalent cations to maintain the charge balance [25,27,30]:



Ca site: calcium ions occupy relatively large cavities with unusual sevenfold coordination [28]. It can be substituted by Na^+ and large cations, including Sr^{2+} , Ba^{2+} , Y + MREE, (U, Th, Mn, and Pb) [29]. The introduction of monovalent and trivalent cations maintains the charge balance:



Si site: $(\text{P}^{4+}), (4\text{H}^+)$;

O1site: $\text{OH}, \text{F}, (\text{Cl})$

The elements written in bold are those identified in the Mount Blanc titanites in significant amounts. In the Mont Blanc titanites, mainly Al is substituted for titanium, with Fe remaining low. Compared with the reference titanites analyzed by [25], the Mont Blanc titanites display an Al content which covers the entire worldwide range. The titanites have high concentrations at the crystal or site scale. The titanites of Périades are the lowest in Al₂O₃ (0.77 to 0.97%), those of Courtes between 1.7 and 3.8% Al₂O₃, while the titanites of other localities, in particular that of the Aiguille du Tour, reach 7.6 to 7.9%.

The iron content is low so that in the Fe-Al diagram of [4], the low to very low Fe/Al ratios place the Mont Blanc titanites broadly within the wide range of hydrothermal to metamorphic titanites defined by these authors but at the lowest Fe content. The very low Fe values are typical in the compiled data on eclogitic formations [4], which do not correspond to the Mont Blanc geological context. According to [4], the charge balance in metamorphic, hydrothermal and pegmatitic titanite due to the substitution of Fe³⁺ and Al³⁺ in the Ti⁴⁺ site is achieved mainly by the coupled substitution of F⁻ for O²⁻, which is only partially the case in Courtes and not the case in Périades. In Courtes titanite, F is correlated with Al, with a F/Al ratio 1/3.3. As Al is trivalent and three times (in p.f.u.) more abundant than fluorine, the contribution of fluorine is relatively low (1/10) to the electric balance.

4.2 Raman data

Raman spectra of Mont Blanc titanites exhibit the same bands as those predicted by numerical modelling and those from RRUFF Pakistan titanites. Main bands are attributable by analogy to data from [31,32]: at 248-252 cm⁻¹ to translational vibration of [SiO₄]⁴⁻, around 580-600 cm⁻¹ to O-Si-O and Si-O-Al bending modes, and around 881 cm⁻¹ to O-Si-O symmetric stretching bonds. It is rather difficult to correlate the shift in the bands' intensities to chemical changes observed in the crystals, which mainly concern trace elements and Al-Fe content. The differences cannot be due to a different crystallographic orientation, as analyses were done in single crystals. Therefore, the crystallographic orientation must be similar between the analyzed points. However, differences in band intensities are not easily related to the changes in trace element contents.

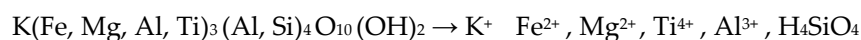
The spectra are identical to the spectrum R050114 from RRUFF [32], which corresponds to titanite from Skardu (Roundu, Gilgit, Pakistan), e.g. Alpine-cleft-type metamorphic deposits, similar to the Alpine clefts. The cleft in Pakistan formed in granite and amphibolite lithologies during the tectonic deformation associated with the Main Karakoram Thrust. As in Mont Blanc, the thrust produced many fractures and clefts where alpine-type minerals developed.

4.3 Mechanism of titanite formation

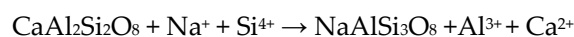
The Ti/Al ratio of the fluid controls the composition of the titanite. These two elements are paradoxically considered relatively insoluble, particularly in aqueous fluids with a low contribution of volatiles (CO₂) identified in the fluid inclusions in quartz. Al is generally regulated by equilibria with aluminosilicates, i.e. the two feldspars (albite-adularia), as shown by the Na/K ratios of alpine fluids from Mont-Blanc [12,17]. Thus, the Na/K ratio around 6.9-6.8 found either by crush-leach technique or LIBS on fluid inclusions indicates an equilibrium with the two alkali feldspars within the 350-400°C range.

The Ti/Al ratio of the fluid is then controlled by the Ti concentration in the fluid, which depends on the rate of alteration of the biotites from the granite and the rate of reincorporation during the formation of the alpine green biotites. In the deformed granite, the

biotite dissolves and releases K, Ti, Fe and Mg according to the following simplified reaction:



All these alterations occur before the titanite is deposited in the presence of stable, newly-formed green biotites. The temperature range is around 400–420°C to keep the biotite stable, not below. What is original in the alpine fissure case is that titanite and green biotites are synchronous. Titanite precipitation in cavities needs calcium, which is available from the albitisation of the anorthite component of granite plagioclases. This dissolution reaction can be written with constant Al or with Al mobility:



The fluids related to quartz growth are aqueous (H₂O is dominant, Cl around 1 mol%, Na (930 ± 90 mmol/kg H₂O), K (135 ± 35 mmol/kg H₂O) Li (30 ± 8 mmol/kg H₂O), Ca (105 ± 25 mmol/kg H₂O), and minimal amounts of CO₂+N₂. In addition, as pCO₂ is relatively low and subsequently carbon is present as bicarbonate in solution under a neutral pH preserving feldspars, no calcite precipitates. Calcite precipitates later in the mineral sequences of the Mont Blanc alpine clefts, probably due to a temperature decrease or fluid mixing [12,17]. The formation of Al-rich titanites with a high CaAlSiO₄-OH component seems favoured by relatively low-temperature conditions [9]. These authors described Al³⁺-rich metamorphic titanites in the metasediments of the Salton Sea geothermal system. There, the Al/Fe ratio of titanites decreases with increasing temperature and depth from 0.3 ± 0.1 pfu in the chlorite-calcite zone (180–320°C) through 0.17 ± 0.05 pfu in the biotite zone (330 ± 10 °C), to 0.12 pfu in the clinopyroxene zone (350 ± 10 °C). In Mont Blanc, titanites crystallised at temperatures around 400 ± 20°C and are also aluminous, low in iron and dominated by OH⁻.

According to [9], titanites are favoured by the degradation of granite biotites, which allows titanite-Al-OH to crystallise. In Mont Blanc, Fe-Mg silicate dissolution in the bleaching zone releases some elements that are then reintegrated into the crystallisation of both titanite and green biotite (Fe, Al, Si). The co-crystallisation of titanite and biotite is, at least in the Courtes example, perfectly demonstrated by textural studies. Suppose sufficient calcium is present in the solution. In that case, titanite can reach oversaturation because the solution is sufficiently loaded with dissolved silica, as shown by the precipitation of abundant quantities of quartz in the alpine fissures, which is synchronous with titanite (last increment of the Q2 quartz stage and small euhedral quartz trapped in titanite). A conceptual model of Ti transfer is shown in Figure 12. When calcium is less abundant, titanium oxides, such as brookite, anatase, and rutile, can form, and all three polymorphs with the formula TiO₂. However, this is not the case in the studied alpine fissures, in contrast with other Alpine massifs such as Oisans, where the lithologies are very different (amphibolites) and anatase is locally abundant.

The amount of titanite precipitated (mm in size in some cavities) is very low compared to the mass of Ti released during the granite bleaching, which occurs all around the cavities and along faults. If an altered rock volume of 10 cm of bleaching is considered on a meter square, the weight of released Ti (if 100% is leached) is 780 g TiO₂. Considering titanite density of 3.5 g/cm³, this weight corresponds to 222 cm³ of titanite, e.g. 16000 grains of titanites of millimetric size (2x1x1mm), thus more than 100 hundred times the amount of observed titanite in the exceptional cases. That means that the efficiency of reprecipitation of Ti is less than one %, and Ti is mobile in altering fluids, contrary to

what is generally assumed in mass balance calculations [14]. However, some Ti released is also precipitated in green biotites with a TiO₂ content between 0.8 and 1.3%.

4.4 Origin of Nb, Y and REE in titanite

The main carrier of Nb, Y, and REE in granite is allanite, the most abundant accessory mineral. However, allanite is most often altered to epidote in the vicinity of alpine fissures, which may have resulted in the release of these elements in fluid phases. The allanite to epidote conversion has also been described along shear zones in the Mont Blanc massif [14]. Allanite is the main carrier that can explain the concentrations of Nb (20-30 ppm), Y (30-45 ppm) or REE (sum around 150 ppm) in the Mont Blanc granite [14].

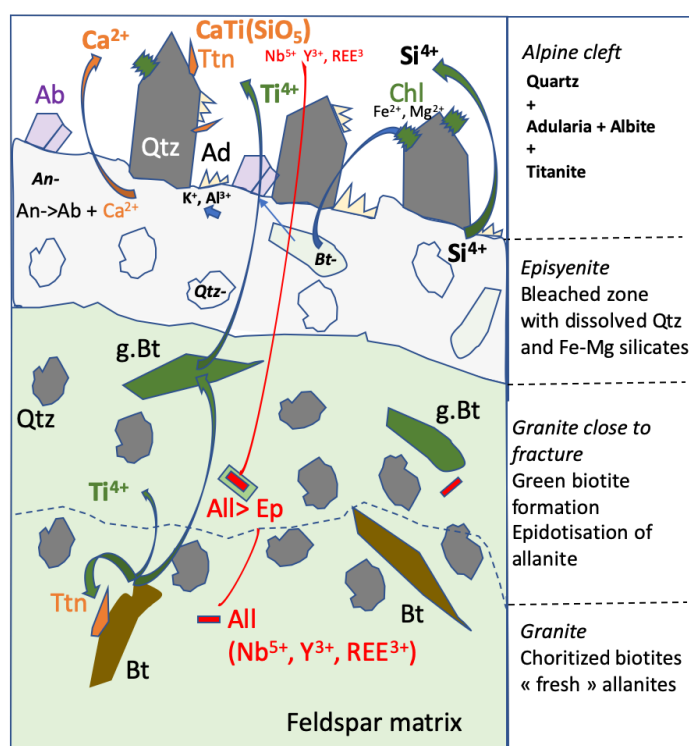


Figure 12. Conceptual model of titanite formation: titanium is released by the dissolution of ferromagnesian silicates in the bleaching band (episyenite), whereas quartz is also unstable and completely dissolved. Titanites crystallise in the paragenesis Qtz₂ + albite + adularia with green biotites. Trace elements (Nb, Y, REE) are liberated both from the bleached zones and alteration of the granite allanite and their alteration secondary mineral phases. Ab: albite, An: anorthite, Ad: adularia, Ttn; titanite, Chl: chlorite, Qtz: quartz, Bt: biotite, g. Bt: green biotite, All: allanite, Ep: epidote.

The differences in the REE spectra of the titanites from the two localities may be due to primary accessory source minerals in the granite having different rare-earth availability or to selective trapping by other minerals. For example, when epidote forms at the expense of allanite, it can trap some of the elements released when the allanite dissolves. Allanites being dissolved or replaced release trace elements that can be incorporated first in the epidote as an in situ alteration product of allanite and then by titanite or other phases, such as described in shear zones by [14]. The local partition between allanite and epidote or others such as Y-bearing phases such as aeschynite ((Y, Ca, Fe, Th)(Ti, Nb)₂(O, OH)₆), or thombartite (Y₄(Si, H₄)₄O_{12-x}(OH)_{4+2x}) described by [14] may explain the local availability of REE(Y) and the differences in concentration levels in titanite. In addition, some titanites co-grow with biotite (Courtes), while others do not incorporate biotite

493 crystals during their growth. The presence or absence of biotites may reveal differences
494 in the characteristics of the percolating fluids, particularly whether fluids are oversatu-
495 rated or not with respect to biotites. Other differences may concern their rate of disequi-
496 librium with REE-Y-Nb source minerals.

497 5. Conclusions

498 - Euhedral titanites from several alpine fissures on Mont Blanc, particularly
499 those of Périades and Courtes, provide some essential information about element trans-
500 fers related to the development of alpine fissures in Mont Blanc massif.

501 - Titanites crystallised at the end of the crystallisation of the principal quartz in
502 the alpine fissures (Qtz2 stage) and are synchronous with the crystallisation of green
503 biotites and albite, around $400 \pm 20^\circ\text{C}$.

504 - As they predate the deposition of chlorites, titanites mark the transition be-
505 tween the biotite and chlorite stability domains in the Mont Blanc massif.

506 - The titanites are rich in Al. OH dominates the OH-F site, as fluorine remains
507 relatively low or is absent, such as in the Courtes sample. They are thus quite different
508 from magmatic titanites characterised by high Fe and F contents.

509 - Titanites show a wide range of concentrations of trace elements such as Nb, Y,
510 Zr, Sn, and REE. Although some sectorial zoning could explain differences in the distri-
511 bution of concentrations, these elements are generally positively correlated. No simple
512 relation could be established with the titanite structure, as most Raman spectra display
513 remarkable similarities apart from two bands at 603 and 881 cm^{-1} with varying intensities.

514 - The granite allanite, partly destabilised into epidote, is the most likely source of
515 Nb, Y, Zr, Sn and REE. Titanites are characterised by rare-earth spectra enriched in HREE
516 and show variations in LREE depending on the location in the Mont Blanc massif. They
517 are, therefore, excellent markers of element transfer in medium-temperature retrograde
518 metamorphism for elements generally considered relatively immobile, such as Ti, Zr, and
519 Nb.
520
521
522

523 **Author Contributions:** Conceptualisation, M.C.; methodology, M.C.; software, C.P.; investigation,
524 M.C.; resources, M.C; data curation, C.P.; writing—original draft preparation, M.C.; writ-
525 ing—review and editing, M.C.; funding acquisition, M.C. All authors have read and agreed to the
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538

Appendix A

Table 1. Chemical compositions with the structural formulas of analysed titanites.

Wt. %	Al ₂ O ₃	SiO ₂	CaO	TiO ₂	Fe ₂ O ₃	Y ₂ O ₃	Nb ₂ O ₃	ZrO ₂	F	total
Périades	1,22	30,06	28,58	38,56	0,17	0,78	1,16	0,31	0,00	100,99
Périades	1,24	30,49	28,41	38,38	0,16	0,75	1,29	0,26	0,00	101,12
Périades	1,25	30,41	28,42	38,24	0,14	0,86	1,36	0,26	0,00	101,07
Périades	1,30	30,26	27,97	37,93	0,22	0,81	1,62	0,22	0,00	100,53
Périades	1,13	31,25	28,34	39,71	0,13	0,99	0,75	0,00	0,00	102,42
Périades	1,36	30,45	28,37	37,65	0,30	0,78	1,83	0,30	0,00	101,31
Périades	1,44	30,23	28,16	37,55	0,28	0,76	1,85	0,28	0,00	100,80
Périades	1,47	30,11	28,52	37,73	0,30	0,93	1,60	0,20	0,00	101,13
Périades	1,45	29,79	28,11	37,66	0,26	0,84	1,66	0,21	0,00	100,21
Périades	1,57	30,04	28,08	37,91	0,03	0,92	1,76	0,05	0,00	100,39
Périades	1,54	30,18	28,46	37,56	0,20	0,82	1,84	0,19	0,00	100,97
Périades	1,55	29,96	28,52	37,23	0,11	0,77	2,13	0,23	0,00	100,60
Périades	1,54	30,25	28,39	37,26	0,27	0,75	2,25	0,18	0,00	101,13
Périades	1,58	30,48	28,43	38,30	0,16	0,78	1,64	0,07	0,00	101,58
Périades	1,70	30,25	28,56	37,88	0,33	0,71	1,72	0,07	0,00	101,52
Périades	1,73	30,54	28,59	38,68	0,07	0,28	0,42	0,07	0,00	100,44
Périades	1,53	30,12	28,32	37,52	0,11	0,75	1,99	0,30	0,00	100,74
Périades	1,52	30,25	28,46	38,26	0,20	0,82	1,40	0,34	0,00	101,43
Périades	1,47	30,48	28,58	38,41	0,30	0,79	1,26	0,25	0,00	101,81
Périades	1,22	30,25	28,55	38,69	0,21	0,76	0,82	0,17	0,00	100,86
Courtes	2,84	30,47	29,51	37,35	0,73	0,00	0,00	0,00	0,49	102,05
Courtes	2,83	30,67	29,53	37,14	0,58	0,00	0,00	0,00	0,50	101,77
Courtes	3,25	30,73	29,39	36,59	0,61	0,00	0,08	0,01	0,62	101,83
Courtes	3,57	30,80	29,48	36,47	0,62	0,00	0,00	0,00	0,67	102,17
Courtes	3,38	30,58	29,62	36,81	0,60	0,00	0,04	0,05	0,53	102,15
Courtes	3,36	30,68	29,40	36,41	0,57	0,00	0,00	0,00	0,52	101,45
Courtes	3,32	30,26	29,15	36,44	0,66	0,00	0,01	0,07	0,55	101,05
Courtes	3,14	29,98	29,25	36,69	0,63	0,00	0,00	0,08	0,52	100,86
Courtes	3,07	30,86	29,65	37,20	0,44	0,00	0,00	0,00	0,54	102,16
Courtes	3,22	30,75	29,39	37,03	0,49	0,00	0,00	0,06	0,52	101,90
Courtes	3,48	31,05	29,22	35,94	0,76	0,00	0,00	0,00	1,23	102,36
Courtes	3,60	31,27	28,86	35,31	0,81	0,00	0,00	0,00	0,82	101,40
Courtes	3,17	31,11	29,13	36,45	0,48	0,00	0,00	0,00	0,84	101,61
Charlet Straton	4,04	30,06	26,21	29,67	0,00	0,00	0,00	0,00	0,00	89,98
Charlet Straton	2,96	25,58	27,32	33,89	0,00	0,00	0,00	0,00	0,00	89,75
Charlet Straton	5,50	33,89	24,63	31,05	0,00	0,00	0,00	0,00	0,00	95,07
Charlet Straton	5,91	30,96	31,10	32,02	0,00	0,00	0,00	0,00	0,00	99,99
Charlet Straton	3,49	28,85	30,51	37,15	0,00	0,00	0,00	0,00	0,00	100,00
Petites Jorasses	8,26	33,64	27,24	26,74	0,00	0,00	0,00	0,00	0,00	97,41
Petites Jorasses	6,72	32,97	28,66	31,65	0,00	0,00	0,00	0,00	0,00	100,00
Aiguille du Tour	7,66	33,53	29,44	29,37	0,00	0,00	0,00	0,00	0,00	100,00

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