Natrotitanite, ideally (Na$_{0.5}$Y$_{0.5}$)Ti(SiO$_4$)O, a new mineral from the Verkhnee Espe deposit, Akjailyautas mountains, Eastern Kazakhstan district, Kazakhstan: description and crystal structure

A. V. Stepanov[1], G. K. Bekenova[1], V. L. Levin[1] and F. C. Hawthorne[2],*

[1] Satpaev Institute of Geological Sciences, ul. Kabanbai batyr 69, Almaty 050010, Kazakhstan
[2] Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

ABSTRACT

Natrotitanite, ideally (Na$_{0.5}$Y$_{0.5}$)Ti(SiO$_4$)O, is a new mineral from the Verkhnee Espe rare-element deposit at the northern exo-contact of the Akjailyautas granite massif in the northern part of the Tarbagatai mountain range, Eastern Kazakhstan. Both the mineral and the name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2010-033). Star-shaped aggregates of small short prisms of yellow or yellowish white (Na,Y,*REE*)-bearing titanite rimmed by thin (~2 μm) rims of natrotitanite are embedded in yttrium-bearing fluorite and replace narsarsukite. Associated minerals are microcline, albite, quartz, riebeckite, aegirine, biotite, astrophyllite, rutile, zircon and elpidite. Natrotitanite is milky white to yellowish grey, transparent to translucent, and has a white streak and a vitreous lustre. It shows pale orange cathodoluminescence but does not fluoresce under ultraviolet light. It shows no cleavage or parting, and is brittle; the calculated density is 3.833 g cm^{-3}. The indices of refraction, measured with the Bloss spindle stage for the wavelength 590 nm using a gel filter, are α = 1.904, γ = 2.030, and these values are in accord with the mean refractive index, 1.988, calculated from the Gladstone-Dale relation. Natrotitanite is monoclinic, *C*2/*c*, *a* = 6.5691(2), *b* = 8.6869(3), *c* = 7.0924(2) Å, β = 114.1269(4)º, *V* = 369.4(2) Å^3, *Z* = 4, *a*:*b*:*c* = 0.7562:1: 0.8164. The seven strongest lines in the X-ray powder diffraction pattern [in the order *d* (Å), *I*, (*hkl*)] are as follows: 2.597, 10, (130); 3.248, 8, (11$\bar{2}$); 2.994, 6, (200); 1.641, 4, (330); 4.941, 3, (110); 1.498, 3, (400); 2.273, 3, (11$\bar{3}$). Chemical analysis by electron microprobe gave Nb$_2$O$_5$ 1.28, SiO$_2$ 27.83, TiO$_2$ 35.00, SnO$_2$ 0.57, V$_2$O$_3$ 0.36, Fe$_2$O$_3$ 0.23, Y$_2$O$_3$ 7.87, Ce$_2$O$_3$ 0.83, Sm$_2$O$_3$ 0.26, Gd$_2$O$_3$ 0.46, Tb$_2$O$_3$ 0.17, Dy$_2$O$_3$ 2.45, Ho$_2$O$_3$ 0.16, Er$_2$O$_3$ 2.24, Tm$_2$O$_3$ 0.50, Yb$_2$O$_3$ 2.53, Nd$_2$O$_3$ 0.35, Lu$_2$O$_3$ 0.28, MnO 0.33, CaO 8.16, Na$_2$O 5.55, F 1.52 O≡F −0.64, sum 98.71 wt.%. The resulting empirical formula is (Na$_{0.39}$Ca$_{0.32}$Y$_{0.15}$Dy$_{0.03}$Yb$_{0.03}$Er$_{0.03}$Ce$_{0.01}$Ho$_{0.01}$Tm$_{0.01}$Gd$_{0.01}$Nd$_{0.01}$)$_{\Sigma 1.00}$(Ti$_{0.95}$Nb$_{0.02}$Sn$_{0.01}$Fe$^{3+}_{0.01}$Mn$_{0.01}$V$_{0.01}$)$_{\Sigma 1.01}$Si$_{1.01}$O$_{4.00}$(O$_{0.83}$F$_{0.17}$), calculated on the basis of 3 cations per formula unit. The general formula is written as (Na,Ca,Y,*REE*)TiSiO$_4$(O,F), and the endmember formula is (Na$_{0.5}$Y$_{0.5}$)Ti(SiO$_4$)O.

The crystal structure of a composite optically continuous crystal of natrotitanite and (Na, Y)-bearing titanite was mounted on a Bruker D8 three-circle diffractometer equipped with a rotating anode generator (Mo*K*α radiation), a multi-layer optics incident-beam path and an APEX-II CCD detector. The crystal structure was refined in space group *C*2/*c* to a final *R*$_1$ index of 1.8%. Natrotitanite is isostructural with titanite, (Na + Y + *REE*) replacing Ca at the *Ca* site in the titanite structure.

Introduction

TITANITE occurs in a wide variety of rocks as an important accessory mineral and shows extensive compositional variation (Ribbe, 1980). The crystallography (Zachariasen, 1930; Mongiorgi and Riva di Sanseverino, 1968; Higgins and Ribbe, 1976; Speer and Gibbs, 1976; Taylor and Brown, 1976; Oberti *et al.*, 1985, 1991; Hawthorne *et al.*, 1991; Hughes *et al.*, 1997; Liferovich and Mitchell, 2005, 2006) and crystal chemistry (e.g. Černý *et al.*, 1995; Chakhmouradian and Zaitsev, 2002; Chakhmouradian, 2004) of titanite have been studied extensively, and until recently, all minerals were reported as monoclinic with space group symmetries $A2/a$ (for most natural samples) and $P2_1/a$ (for minerals close to endmember composition and synthetic $CaTiSiO_4O$). Recently, Lussier *et al.* (2009) described a triclinic variant of titanite, and suggested that the occurrence of the triclinic structure is driven by substitution of $(Nb + Ta)$ and $(Al + Fe^{3+})$ for Ti^{4+} and subsequent ordering of $(Nb + Ta)$ and $(Al + Fe^{3+})$ at one of the two distinct octahedrally coordinated sites. During continued examination of minerals from the Verkhnee Espe deposit, Kazakhstan (Stepanov and Bekenova, 2009), we came across titanite enriched in Na, Y and *REE*s; further detailed examination showed the presence of a phase with the titanite structure but with Na(Y,*REE*) dominant at the *Ca* site.

The mineral is named natrotitanite after the composition. Both the mineral and the name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2010-033). The holotype specimen of natrotitanite has been deposited in the mineral collection of the Geological Scientific Museum of the Satpaev Institute of Geological Sciences, registration number 3010.

Occurrence

Natrotitanite occurs in the Verkhnee Espe rare-element deposit ($48°03'−48°10'$N $81°26'−81°29'$E), which is spatially related to two small oval outcrops of alkaline granite at the northern exo-contact of the large Akjailyautas granite massif in the northern part of the Tarbagatai mountain range, Eastern Kazakhstan (Stepanov and Bekenova, 2009). These intrusions belong to a belt of alkaline granite dykes that extend 5 km NNE and more than 20 km SSW from these outcrops, and almost coincide with the western exo- and endo-contacts of the Akjailyautas granite massif. The Verkhnee Espe deposit formed during the later stages of the intrusion of the Akjailyautas massif.

Physical properties

Natrotitanite occurs as star-shaped aggregates of small short yellow or yellowish white prisms of (Na,Y,*REE*)-bearing titanite and natrotitanite that replace narsarsukite. The maximum size of individual prisms is 5 mm in length and 1 mm in cross-section. The cores of the prisms are (Na,Y,*REE*)-bearing titanite; natrotitanite forms very thin rims around the (Na,Y,*REE*)-bearing titanite (Fig. 1). A section cut orthogonal to the elongated grains (Fig. 1) shows continuous rims of natrotitanite that average 2 μm in thickness and are separated from (Na,Y,*REE*)-bearing titanite by fairly sharp optical and compositional boundaries (Fig. 2). The composite crystals of (Na,Y,*REE*)-bearing titanite and natrotitanite are
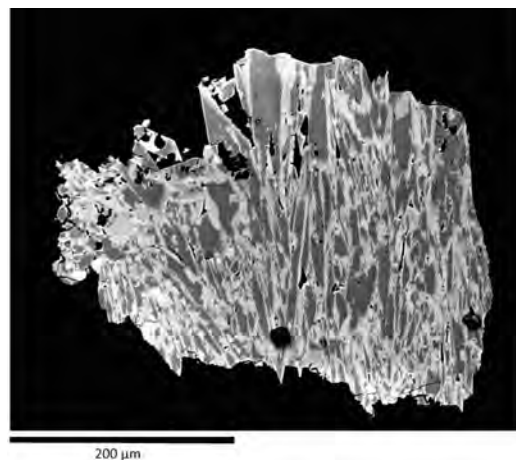

FIG. 1. Backscattered-electron image of an aggregate of wedge-shaped crystals of (Na,Y,*REE*)-bearing titanite (grey) and natrotitanite (white). The polished section is approximately parallel to the direction of elongation of the crystals.

embedded in yttrium-bearing fluorite (Fig. 3). They are associated with microcline, albite, quartz, riebeckite, aegirine, biotite, astrophyllite, rutile, zircon and elpidite.

The crystals are milky white to yellowish grey, transparent to translucent, and have a white streak and a vitreous lustre. They show pale orange cathodoluminescence but do not fluoresce under ultraviolet light. Natrotitanite has no cleavage or parting, and is brittle; Mohs hardness and density could not be determined due to the nature of the sample; the calculated density is 3.833 g cm^{-3}. Optical properties were measured with the Bloss spindle stage for the wavelength 590 nm using a gel filter. The indices of refraction are $\alpha = 1.904$, $\gamma = 2.030$, both ± 0.002; these values are in accord with the mean refractive index of 1.988, calculated from the Gladstone-Dale relation; the calculated birefringence is 0.126. Because of the nature of the crystals (e.g. Fig. 2), we were unable to measure the β refractive index, 2V, optic sign or optical orientation.

Chemical composition

Crystals were analysed using a JEOL JCXA 733 electron microprobe equipped with an EDS INCA ENERGY system and operating in energy-dispersive mode with an accelerating voltage of 25 kV, a specimen current of 25 nA and a beam diameter of 10 μm. The following standards were used: quartz (Si), rutile (Ti), V metal (V),
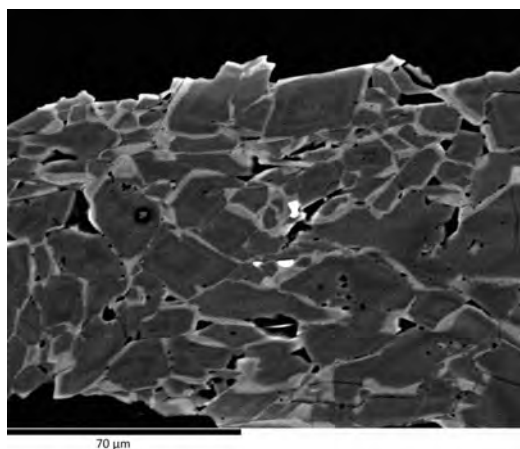

FIG. 2. Backscattered-electron image of an aggregate of (Na,Y,*REE*)-bearing titanite (grey) and natrotitanite (white). The polished section is orthogonal to the direction of elongation of the crystals.

$MnO \cdot Fe_2O_3$ oxide (Mn, Fe), YPO_4 (Y), Nb metal (Nb), Sn metal (Sn), $CePO_4$ (Ce), $SmPO_4$ (Sm), $GdPO_4$ (Gd), $TbPO_4$ (Tb), $DyPO_4$ (Dy), $HoPO_4$ (Ho), $ErPO_4$ (Er), $TmPO_4$ (Tm), $YbPO_4$ (Yb), $NdPO_4$ (Nd), $LuPO_4$ (Lu), $CaSiO_3$ (Ca), albite (Na) and fluorite (F). The chemical composition is given in Table 1. The empirical formula was calculated on the basis of 3 cations per formula unit and is as follows: $(Na_{0.39}Ca_{0.32}Y_{0.15}Dy_{0.03}Yb_{0.03}Er_{0.03}Ce_{0.01}Ho_{0.01}Tm_{0.01}Gd_{0.01}Nd_{0.01})_{\Sigma1.00}(Ti_{0.95}Nb_{0.02}Sn_{0.01}Fe^{3+}_{0.01}Mn_{0.01}V_{0.01})_{\Sigma1.01}Si_{1.01}O_{4.00}(O_{0.83}F_{0.17})$. If we adjust the cations so that they fill the available sites, the resulting formula is nearly neutral (with a residual charge of +0.02) and is as follows: $(Na_{0.39}Ca_{0.32}Y_{0.15}Dy_{0.03}Yb_{0.03}Er_{0.03}Ce_{0.01}Ho_{0.01}Tm_{0.01}Gd_{0.01}Nd_{0.01})_{\Sigma1.00}(Ti_{0.94}Nb_{0.02}Sn_{0.01}Fe^{3+}_{0.01}Mn_{0.01}V_{0.01})_{\Sigma1.00}Si_{1.00}O_{4.00}(O_{0.83}F_{0.17})$.

X-ray powder diffraction

The powder-diffraction pattern (Table 2) was recorded with Fe$K\alpha$ radiation using a Debye-Scherrer camera with a diameter of 57.3 mm.

TABLE 1. Chemical composition of natrotitanite.

Constituent	Mean (wt.%)	Range
SiO_2	27.83(9)	27.41−28.40
TiO_2	35.00(14)	34.01−35.62
V_2O_3	0.36(7)	0.15−0.98
MnO	0.33(4)	0.11−0.50
Fe_2O_3	0.23(3)	0.11−0.39
Y_2O_3	7.87(8)	7.25−8.14
Nb_2O_5	1.28(8)	0.95−1.72
SnO_2	0.57(4)	0.37−0.75
Ce_2O_3	0.83(8)	0.51−1.30
Sm_2O_3	0.26(6)	0.00−0.57
Gd_2O_3	0.46(6)	0.08−0.76
Tb_2O_3	0.17(7)	0.00−0.59
Dy_2O_3	2.45(7)	2.12−2.77
Ho_2O_3	0.58(10)	0.16−1.13
Er_2O_3	2.24(10)	1.77−2.71
Tm_2O_3	0.50(9)	0.02−1.03
Yb_2O_3	2.53(10)	1.96−3.08
Nd_2O_3	0.35(7)	0.00−0.64
Lu_2O_3	0.28(9)	0.00−0.86
CaO	8.16(8)	7.75−8.64
Na_2O	5.55(9)	5.08−6.00
F	1.52(14)	0.77−2.24
$O \equiv F$	−0.64	
Total	98.71	

TABLE 2. X-ray powder-diffraction data for zoned crystals of (Na,Y,*REE*)-bearing titanite and natrotitanite.

I	$d_{obs.}$ (Å)	$d_{calc.}$ (Å)	h k l
3	4.941*	4.923	1 1 0
8	3.248*	3.243	1 1 $\bar{2}$
6	2.994*	2.996	2 0 0
<1	2.824	2.848	2 0 $\bar{2}$
10	2.597*	2.595	1 3 0
1	2.362	2.364	1 1 2
3	2.273	2.271	1 1 $\bar{3}$
<1	2.151	2.159	0 4 0
2	2.067*	2.067	3 1 $\bar{2}$
1	1.925	1.928	0 2 3
2d**	1.795*	1.795	0 4 2
<1		1.752	2 4 0
	1.750	1.749	2 0 $\bar{4}$
1		1.714	1 1 $\bar{4}$
	1.714	1.712	3 3 $\bar{2}$
4	1.641*	1.641	3 3 0
1	1.557	1.551	2 4 $\bar{3}$
3	1.498*	1.498	4 0 0
1	1.416	1.415	4 2 0
1	1.346	1.343	2 2 $\bar{5}$5

* Used for calculating unit-cell parameters.
** The abbreviation d is diffuse.

Refinement of the unit-cell parameters gave the following values: $a = 6.557(2)$, $b = 8.636(4)$, $c = 7.071(5)$ Å, $\beta = 113.95(3)°$, $V = 365.9(3)$ Å^3.

Crystal structure: X-ray data collection and structure refinement

A single chemically zoned crystal measuring $40 \times 80 \times 80$ μm was mounted on a Bruker D8 three-circle diffractometer equipped with a rotating-anode generator (Mo*K*α radiation), multi-layer optics and an APEX-II CCD detector. Reflection intensities were collected using a frame width of 0.2°, a frame time of 2 s and a crystal-to-detector distance of 5 cm. A total of 6478 reflections was collected to 60°2θ. Absorption corrections were done using the program *SADABS* (Sheldrick, 2008). The data were corrected for Lorentz, polarization and background effects, averaged and reduced to structure factors, resulting in 537 unique reflections of which 534 have $F_o > 4\sigma F$. The structure was refined in the space group $C2/c$ to an R_1 value of 1.84%. Cell dimensions and details of the data collection and structure refinement are given in Table 3, final atom parameters in Table 4 and selected interatomic distances in Table 5. The refined site-scattering values (Hawthorne *et al.*, 1995) for the *Ca* and *Ti* sites are as follows: *Ca*: 22.91(8), *Ti*: 22.30(8) e.p.f.u. (electrons per formula unit). Analogous values from the empirical formula given above are as follows: *Ca*: 25.84, *Ti*: 22.75 e.p.f.u. Of course, we do not expect agreement between the refined site-scattering value for the *Ca* site and the corresponding effective site-scattering indicated by the empirical formula. The X-ray intensity data were collected from a zoned crystal of (Na,Y,*REE*)-bearing titanite and natrotitanite, and hence the refined site-scattering value for the *Ca* site represents a mixture of values for natrotitanite and (Na,Y,*REE*)-bearing titanite (cf. Figs 1−3), whereas the corresponding effective site-scattering indicated by the empirical formula represents natrotitanite alone. A table of structure factors has been deposited with the Principal Editor of *Mineralogical Magazine* and is available at www.minersoc.org/pages/e_journals/dep_mat.html.

TABLE 3. Miscellaneous information for natrotitanite-(Na,Y,*REE*)-bearing-titanite.

a (Å)	6.5691(2)	Crystal size (μm)	$40 \times 80 \times 80$
b (Å)	8.6869(3)	Radiation/monochromator	Mo*K*α/Graphite
c (Å)	7.0924(2)	No. of reflections	6478
V (Å^3)	369.4(2)	No. unique reflections	537
β (°)	114.1269(4)	No. $|F_o| > 4\sigma(|F|)$	534
Space group	$C2/c$	R_{merge}%	0.81
Z	4	R_{obs}%	1.84
		wR_{obs}%	4.86

$R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$
$wR = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.0182P)^2 + 0.94P]$ where $P = (Max(F_o^2, 0) + 2F_c^2)/3$

TABLE 4. Atom positions and displacement parameters ($Å^2$) for natrotitanite-(Na,Y,*REE*)-bearing titanite.

| Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Ca	0	0.16960(5)	¾	0.0085(2)	0.0078(2)	0.0267(3)	0	−0.00015(16)	0	0.01673(16)
Ti	0	½	0	0.0081(2)	0.0100(2)	0.0154(2)	0.00346(13)	0.0331(16)	−0.00018(12)	0.01164(17)
Si	0	0.18221(7)	¼	0.0065(3)	0.0075(3)	0.0092(3)	0	0.0032(2)	0	0.00775(17)
O(1)	0	0.57186(18)	¼	0.0135(7)	0.0094(7)	0.0083(6)	0	0.0049(5)	0	0.0102(3)
O(2)	0.18651(18)	0.06603(13)	0.40948(17)	0.0082(5)	0.0135(5)	0.0131(5)	0.0028(4)	0.0026(4)	0.0017(4)	0.0121(3)
O(3)	0.10171(19)	0.28936(13)	0.11898(18)	0.0128(5)	0.0100(5)	0.0173(6)	0.0037(4)	0.0091(4)	0.0015(4)	0.0124(3)
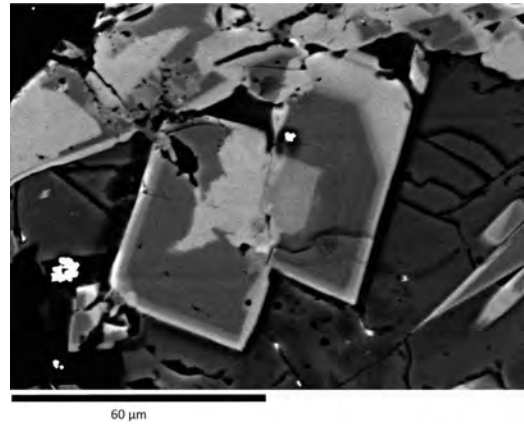
FIG. 3. Backscattered-electron image of an intergrowth of two crystals (in centre) of (Na,Y,*REE*)-bearing titanite (grey) and natrotitanite (white) in Y-bearing fluorite (dark-grey), all of which have replaced narsarsukite.

Different crystallographic orientations in work on titanite

The crystal structure of titanite was originally solved in space group *C2/c* (Zachariasen, 1930) but much of the ensuing work on this mineral (or the equivalent synthetic compound) has involved space groups *A2/a* or *P2₁/a*. We have chosen (here and elsewhere, e.g. Hawthorne *et al.*, 1991) to use the *C2/c* orientation for the titanite cell for the following reason. The principal feature of the titanite structure is the [TiO_4O] chain that is decorated by (SiO_4) tetrahedra that cross-link to other [TiO_4O] chains to produce the [$CaTiSiO_4O$] framework. We may write the [TiO_4O] chain in a more general way as [$M\varphi_5$] where M is an octahedrally coordinated cation and φ are unspecified anions. The [$M\varphi_5$] chain is a prominent motif in many mineral structures. Moore (1970) produced his classic work on the [$M\varphi_5$] chain in minerals and possible stereo-isomerism involving the decorating tetrahedra. Subsequent work showed the importance of this generalized chain in both rare (e.g. jahnsite, Moore and Araki, 1974; sinkankasite, Burns and Hawthorne, 1995) and common phosphates (e.g. amblygonite−montebraseite, Groat *et al.*, 1990), and in a wide variety of other structures (e.g. sulfates: slavikite, Süsse, 1975; kieserite, Hawthorne *et al.* 1987; tellurites: teinite, Zemann and Zemann, 1962; chalcomenite, Robinson *et al.*, 1992). It is common practice in

TABLE 5. Selected interatomic distances (Å) in natrotitanite-(Na,Y,*REE*)-bearing-titanite.

Si−O(2)	1.633(1)	×2	*Ca*−O(1)	2.246(16)	
Si−O(3)	1.638(2)	×2	*Ca*−O(2)	2.416(12)	×2
<*Si*−O>	1.636		*Ca*−O(3)	2.418(11)	×2
			Ca−O(3)	2.636(12)	×2
Ti−O(1)	1.8798(5)	×2	<*Ca*−O>	2.455	
Ti−O(2)	1.975(1)	×2			
Ti−O(3)	2.011(1)	×2			
<*Ti*−O>	1.955				

crystal structures based on chain units to orient the chain parallel to the c axis; this has the advantage that the structure can be recognized from the repeat distance in that direction, and also facilitates comparison of structures with similar motifs. Therefore we orient natrotitanite and titanite in the same way as other [Mφ5] structures.

Natrotitanite and its relation to titanite

It was not possible to obtain a crystal that consisted entirely of natrotitanite and we therefore collected diffraction data on zoned crystals of (Na,Y,*REE*)-bearing titanite and natrotitanite. The two species are optically continuous in transmitted plane-polarized and cross-polarized light, and the single-crystal data and powder-diffraction patterns are completely compatible with a single coherent and continuous structure, indicating that both species in the zoned crystals have the titanite structure.

The empirical formula was calculated on the basis of 3 cations per formula unit (p.f.u.) because (1) the crystal-structure refinement indicates that all cation sites are completely occupied, and
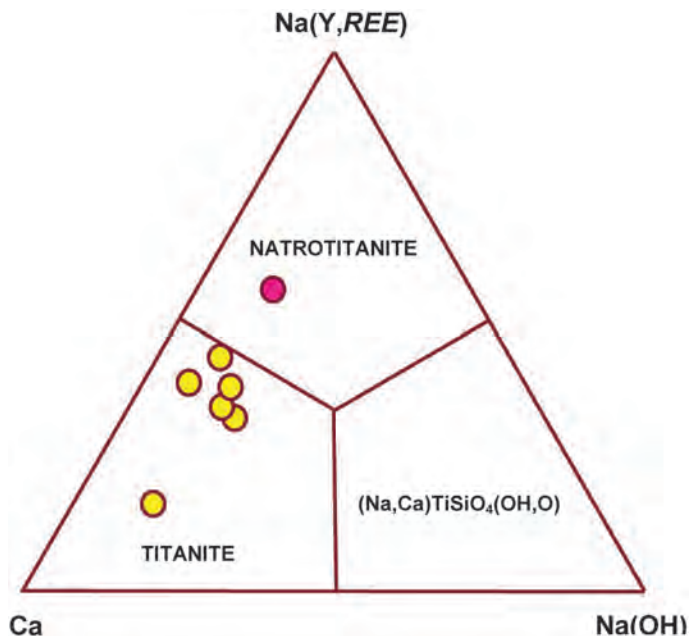

FIG. 4. Triangular diagram showing the composition fields of titanite, natrotitanite and un-named (Na,Ca)Ti(SiO$_4$)(F,O); the composition of holotype natrotitanite is shown by the red circle; the compositions of (Na,Y,*REE*)-bearing titanite are shown as yellow circles.

(2) we do not have an analysis for H_2O. When the site populations were adjusted to complete occupancy, the net charge of the formula calculated on the basis of 3 cations and 5 O^{2-} anions is ~+0.02, with a small amount of monovalent anion(s) present in the crystal, in accord with the small amount of F indicated by the chemical analysis (Table 1). As we shall see next, the conclusion is also compatible with the cation occupancy of the Ca site. The occupancies of the sites as derived from the empirical formula are as follows: $Ca = (Na_{0.39}Ca_{0.32}Y_{0.15}REE_{0.14})$, $Y \approx Ti$, $Si = Si$, anions $= O_4$ and $[O_{0.83}F_{0.17}]$. It is apparent that the substitutions primarily involve the Ca site with a small amount of anion substitution (F for O):

$$^{Ca}Na + {}^{Ca}(Y,REE) \rightarrow {}^{Ca}Ca + {}^{Ca}Ca \qquad (1)$$
$$^{Ca}Na + F \rightarrow {}^{Ca}Ca + O \qquad (2)$$
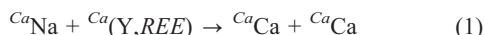
Starting with the endmember titanite composition, $CaTi(SiO_4)O$, complete replacement of Ca by Na + (Y,REE) via substitution [1] gives the composition $(Na_{0.5}Y_{0.5})Ti(SiO_4)O$, which is in accord with the criteria for an endmember defined by Hawthorne (2002), in particular, the criterion that one site may be occupied by two species (cation or anion) when required by the constraint of electroneutrality. The composition of natrotitanite is shown in terms of its principal endmember compositions in Fig. 4. The incorporation of slightly heavier cations (on average) at the Ca site is reflected in the slightly higher refined site-scattering value (22.9 e.p.f.u.) relative to that of Ca (20 e.p.f.u.) in ideal titanite. For the compositions of (Na,Y,REE)-bearing titanite and natrotitanite (Fig. 4), it is apparent that the content of the $NaTi(SiO_4)F$ component is fairly constant at ~10%, and variation in chemical composition in these crystals involves variation of the titanite and natrotitanite components.

Acknowledgements

References

Burns, P.C. and Hawthorne, F.C. (1995) The crystal structure of sinkankasite, a complex heteropolyhedral sheet mineral. *American Mineralogist*, **80**, 620−627.

Černý, P., Novak, M. and Chapman, R. (1995) The Al(Nb,Ta)Ti$_{-2}$ substitution in titanite: the emergence of a new species? *Mineralogy and Petrology*, **52**, 61−73.

Chakhmouradian, A.R. (2004) Crystal chemistry and paragenesis of compositionally-unique (Al-, Fe-, Nb-, and Zr-rich) titanite from Afrikanda, Russia. *American Mineralogist*, **89**, 1752−1762.

Chakhmouradian, A.R. and Zaitsev, A.N. (2002) Calcite−amphibole−clinopyroxene from the Afrikanda Complex, Kola Peninsula, Russia: mineralogy and a possible link to carbonatites III. Silicate minerals. *The Canadian Mineralogist*, **40**, 1347−1374.

Groat, L.A., Raudsepp, M., Hawthorne, F.C., Ercit, T.S., Sherriff, B.L. and Hartman, J.S. (1990) The amblygonite−montebrasite series: characterization by single-crystal structure refinement, infrared spectroscopy and multinuclear MAS-NMR spectroscopy. *American Mineralogist*, **75**, 992−1008.

Hawthorne, F.C. (2002) The use of end-member charge-arrangements in defining new mineral species and heterovalent substitutions in complex minerals. *The Canadian Mineralogist*, **40**, 699−710.

Hawthorne, F.C., Groat, L.A., Raudsepp, M. and Ercit, T.S. (1987) Kieserite, $Mg(SO_4)(H_2O)$, a titanite-group mineral. *Neues Jahrbuch für Mineralogie Abhandlungen*, **157**, 121−132.

Hawthorne, F.C, Groat, L.A., Raudsepp, M., Ball, N.A., Kimata, M., Spike, F.D., Gaba, R., Halden, N.M., Lumpkin, G.R., Ewing, R.C., Greegor, R.B., Lytle, F.W., Ercit, T.S., Rossman, G.R., Wicks, F.J., Ramik, R.A., Sherriff, B.L., Fleet, M.E. and McCammon, C. (1991) Alpha-decay damage in titanite. *American Mineralogist*, **76**, 370−396.

Hawthorne, F.C, Ungaretti, L. and Oberti, R. (1995) Site populations in minerals: terminology and presentation of results of crystal-structure refinement. *The Canadian Mineralogist*, **33**, 907−911.

Higgins, J.B. and Ribbe, P.H. (1976) The crystal chemistry and space groups of natural and synthetic titanites. *American Mineralogist*, **61**, 878−888.

Hughes, J.M., Bloodaxe, E.S., Hanchar, J.M. and Foord, E.E. (1997) Incorporation of rare earth elements in titanite: stabilization of the A2/a dimorph by creation of antiphase boundaries. *American Mineralogist*, **82**, 512−516.

Liferovich, R.P. and Mitchell, R.H. (2005) Composition and paragenesis of Na-, Nb- and Zr-bearing titanite from Khibina, Russia, and crystal-structure data for synthetic analogues. *The Canadian Mineralogist*, **43**, 795−812.

Liferovich, R.P. and Mitchell, R.H. (2006) Tantalum-bearing titanite: synthesis and crystal structure data. *Physics and Chemistry of Minerals*, **33**, 73−83.

Lussier, A.J., Cooper, M.A., Hawthorne, F.C. and Kristiansen, R. (2009) Triclinic titanite from the Heftetjern granitic pegmatite, Tørdal, southern Norway. *Mineralogical Magazine*, **73**, 709−722.

Mongiorgi, R. and Riva di Sanseverino, L.R. (1968) A reconsideration of the structure of titanite, $CaTiOSiO_4$. *Mineralogica et Petrographica Acta*, **14**, 123−141.

Moore, P.B. (1970) Structural hierarchies among minerals containing octahedrally coordinating oxygen. *Neues Jahrbuch für Mineralogie Monatshefte*, **1970**, 163−173.

Moore, P.B. and Araki, T. (1974) Jahnsite, $CaMn^{2+}Mg_2(H_2O)_8Fe_2^{3+}(OH)_2[PO_4]_4$: a novel stereo-isomerism of ligands about octahedral corner-sharing chains. *American Mineralogist*, **59**, 964−973.

Oberti, R., Rossi, G. and Smith, D.C. (1985) X-ray crystal structure refinement studies of the TiO ↔ Al(OH,F) exchange in high-aluminum sphenes. *Terra Cognita*, **5**, 428 (abstract).

Oberti, R. Smith, D.C., Rossi, G. and Caucia, F. (1991) The crystal-chemistry of high-aluminium titanites. *European Journal of Mineralogy*, **3**, 777−792.

Ribbe, P.H. (1980) Titanite. Pp. 137−154 in: *Orthosilicates* (P.H. Ribbe, editor). Reviews in Mineralogy, **5**. Mineralogical Society of America, Washington DC.

Robinson, P.D., Sen Gupta, P.K., Swihart, G.H. and Houk, L. (1992) Crystal structure, H positions, and the Se lone pair of synthetic chalcomenite, $Cu(H_2O)_2(SeO_3)$. *American Mineralogist*, **77**, 834−838.

Sheldrick, G.M. (2008) A short history of *SHELX*. *Acta Crystallographica*, **A64**, 112−122.

Speer, J.A. and Gibbs, G.V. (1976) The crystal structure of synthetic titanite, $CaTiOSiO_4$, and the domain textures of natural titanites. *American Mineralogist*, **61**, 238−247.

Stepanov, A.V. and Bekenova, G.K. (2009) Brief description of the Verkhnee Espe rare-element deposit. Proceedings of an international conference on geology, mineralogy and future trends of mineral resources development. Almaty, Kazakhstan, 248−258.

Süsse, P. (1975) Structure and crystal chemistry of slavikite, $NaMg_2Fe_5(SO_4)_7(OH)_6 \cdot 33H_2O$. *Neues Jahrbuch für Mineralogie Monatshefte*, **1975**, 27−40.

Taylor, M. and Brown, G.E. (1976) High-temperature structural study of the $P21/a \rightleftarrows A2/a$ phase transitions in synthetic titanite, $CaTiSiO_5$. *American Mineralogist*, **61**, 435−447.

Zachariasen, W.H. (1930) The crystal structure of titanite. *Zeitschrift für Kristallographie*, **73**, 7−17.

Zemann, A. and Zemann, J. (1962) Die Kristallstruktur von Teinit. Ein Beispiel für die Korrektur einer chemischen Formel auf Grund der strukturbestimmung. *Acta Crystallographica*, **15**, 698−702.