Sr-Na-REE titanates of the crichtonite group from a fenitized megaxenolith, Khibina alkaline complex, Kola Peninsula, Russia: first occurrence and implications

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Abstract: An extensive, nearly continuous and hitherto unreported solid-solution series is observed in Sr-Na-REE titanates in a fenitized megaxenolith, Khibina alkaline complex, Kola Peninsula, Russia. These titanate minerals, related to crichtonite, landauite and davidite-(Ce,La), may represent potentially new members of the crichtonite group. They display compositional zoning, and are associated with diverse oxide minerals, albite and alkali feldspar. Our compositions (EMP) suggest that the "large cations" (Sr, Na, K, and the rare-earth elements, REE), along with minor Ca, occupy fully the A (M_0) site in their structure; in contrast, Ca enters dominantly the B (M_1) site, probably *via* a coupled substitution of the type $[(Ca^{2+}+Ti^{4+}) = (Zr^{4+}+Fe^{2+})]$. The extensive Na^+-for-Sr^{2+} substitution observed at the A site is coupled with a Ti^{4+}-for-Fe^{2+} substitution at the C (M_3-M_4-M_5) site. The tetrahedral T (M_2) site is dominated by Fe. Among the REE, only the light REE are present in substantial amounts (up to 7.37 wt.% REE_2O_3); they are positively intercorrelated, indicating an ordered distribution at the A site. The incorporation of the REE^{3+}, which probably replace Sr^{2+} and K^+, is controlled by a corresponding decrease in Zr^{4+} (and by relative increase in divalent Mn) at the B site in order to maintain charge balance. The observed presence of up to 1.87 wt.% Cr_2O_3 in the Sr-Na-REE titanate minerals at Khibina indicates that rocks of mafic affinity were the protolith for the mineralized megaxenolith. The high Na contents of these minerals are clearly related to the geochemical environment (*i.e.*, Na-metasomatism). The contrasting association of Cr and Nb (up to 1.06 wt.% Nb_2O_5) in these minerals undoubtedly involves derivation from two different sources. We suggest that the Ti-(Fe)-Nb-REE oxide mineralization formed in the megaxenolith as a result of interaction of a pre-existing mafic rock(s), probably Proterozoic rocks of the Imandra-Varzuga Supergroup, with metasomatizing oxidizing fluids of alkaline affinity.

Key-words: crichtonite, landauite, davidite-(Ce), titanates, oxide minerals, solid solutions, fenites, xenoliths, Ti-(Fe)-Nb-REE mineralization, alkaline rocks, Khibina complex, Kola Peninsula, Russia.

Introduction

We report on a hitherto unreported solid-solution series of Sr-Na-REE-enriched crichtonite-group minerals in a fenitized megaxenolith from the Khibina (or Khibiny) alkaline complex, Kola Peninsula, northwestern Russia. These analytical results imply the existence of new members in this complex group. Our main objectives in this study are (1) to document the extensive solid-solution observed in the Sr-Na-REE titanate minerals related to crichtonite, landauite, davidite-(Ce), and davidite-(La), which expands the known compositional ranges for the crichtonite-type titanates. The presence in this series of Na-dominant members, related to landauite, is also notable. To date, there are a few reported occurrences of landauite, the type locality of which is the Burpala alkaline complex, Baikal

region, Russia (Portnov *et al.*, 1966; Grey & Gatehouse, 1978). (2) To discuss crystallochemical implications on the basis of a total of 1408 (hereafter: $n = 1408$) original wavelength-dispersion electron-microprobe analyses (WDS) of the Sr-Na-REE titanate minerals from Khibina. (3) To contribute to the mineralogy of a fenitized megaxenolith that has already been shown to possess an exotic mineralogy, characterized by the presence of unique species or varieties of minerals, *e.g.*, edgarite [$Fe^{2+}Nb^{3+}{}_2Nb^{4+}S^{2-}{}_6$ or $Fe^{2+}(Nb^{3+},Nb^{4+})_3S^{2-}{}_6$], the first and only natural Nb-rich sulfide (Barkov *et al.*, 2000a), zoned tungstenoan molybdenite (up to 5.8 wt.% W; Barkov *et al.*, 2000b), and the only reported examples of terrestrial sulfides enriched in Ti (up to *ca.* 4 wt.% Ti in pyrrhotite; Barkov *et al.*, 1997). (4) To provide compositional evidence for the precursor of the megaxenolith prior to its intense alteration and fenitization.
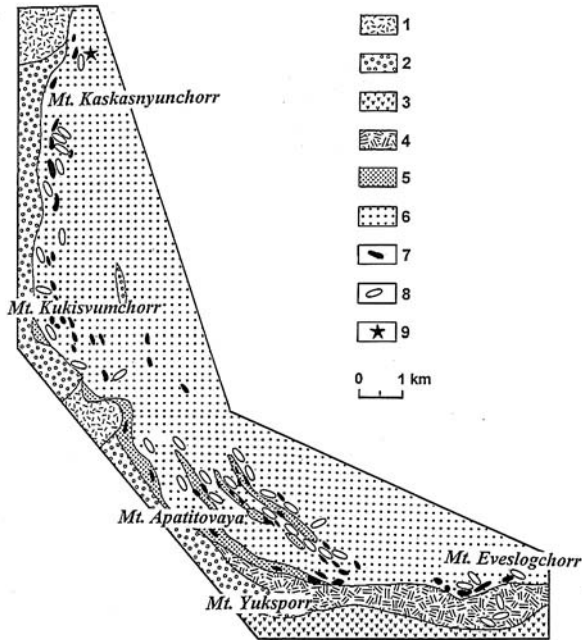
Fig. 1. Schematic geological map showing distribution of bodies of fenitized megaxenoliths in the central part of the Khibina complex. *1*: massive lyavochorrite, *2*: massive rischorrite, *3*: foliated rischorrite, *4*: foliated and recrystallized nepheline syenite, *5*: fine-grained nepheline syenite, *6*: albitized trachytic foyaite, *7*: fenitized megaxenoliths, *8*: pegmatitic alkaline veins (not to scale), and *9*: location of the megaxenolith containing the Sr-Na-REE titanate minerals (this study).

(5) To note the existence of a new type of Ti-Nb-REE oxide mineralization, which may be of economic importance. This mineralization contains minerals of the crichtonite group as the principal ore minerals, and is formed as a result of interaction of a pre-existing mafic rock(s) with metasomatizing oxidizing fluids of alkaline affinity. We note that minerals of the crichtonite group in such ores may contain unusually high levels of the REE, *e.g.*, up to 7.37 wt.% REE_2O_3, as is observed here.

Background information

The naturally occurring members of the crichtonite group were previously classified on the basis of the nature of the dominant "large cation" occupying the *A* (or M_0) site in "$AM_{21}(O,OH)_{38}$": crichtonite (Sr), loveringite (Ca), landauite (Na), davidite-(Ce), davidite-(La), mathiasite (K), lindsleyite (Ba), and senaite (Pb). The "*M*-site" cations are Ti, Fe, Zr, V, Mn, Mg, Cr, U, and Zn (Grey *et al.*, 1976; Grey & Gatehouse, 1978; Gatehouse *et al.*, 1978, 1979, 1983; Campbell & Kelly, 1978; Haggerty, 1983; Haggerty *et al.*, 1983; Foord & Sharp, 1984; Peterson & Grey, 1995). The structure of these complex titanates is trigonal or pseudotrigonal, and is based on a 9-layer close-packed anion lattice, with the *A*-site cations occupying an anion site, and the "*M*-site" cations ordered into 19 octahedral and 2 tetrahedral sites per unit cell. The "*M* site" is composite, and

actually comprises several sites of distinct size, from large M_1, intermediate (M_3, M_4, and M_5), to small (M_2). Orlandi *et al.* (1997) have described a new member: dessauite, $(Sr,Pb)(Y,U)(Ti,Fe^{3+})_{20}O_{38}$, and suggested a revised $ABC_{18}T_2O_{38}$ formula for the crichtonite group, where *B*, *C*, and *T* correspond to large, intermediate, and small *M*-cation sites, respectively. Additionally, there are two recently discovered members of this group: cleusonite, $(Pb,Sr)(U^{4+},U^{6+})(Fe^{2+},Zn)_2(Ti,Fe^{2+},Fe^{3+})_{18}(O,OH)_{38}$, from Nendaz Valley, Switzerland (Wülser *et al.*, 2003), and gramaccioliite-(Y), $(Pb,Sr)(Y,Mn)Fe_2(Ti,Fe)_{18}O_{38}$, from Stura Valley, Italy (Orlandi *et al.*, 2004). Interestingly, a new structural sub-unit, consistent with the "$M_{20}O_{39}$" formula, has been reported for an unusual senaite enriched in U, the *A* site of which is occupied by O (Armbruster & Kunz, 1990).

The geology, mineralogy and occurrence of Sr-Na-REE titanate minerals at Khibina

The Khibina alkaline complex is a large (1327 km²) concentrically zoned intrusion of Devonian age, located at the contact of Archean granite gneisses with Proterozoic volcanic-sedimentary complexes (Zak *et al.*, 1972; Galakhov, 1975; Kramm *et al.*, 1993). The alkaline rocks of the complex are associated with apatite-nepheline rocks, carbonatites, and hornfelsic and fenitic rocks at the outer contact. In addition, heterogeneous megaxenoliths of diverse fenites are scattered along a ~20-km-long sector near the center of the Khibina complex, in the outer part of the "Albitized Trachytic Nepheline Syenite (Foyaite) Unit" (Men'shikov, 1978; Barkov *et al.*, 2000a).

The Sr-Na-REE titanate minerals of the crichtonite group are associated with one of these unusual bodies of fenitized megaxenoliths, which is *ca.* 0.2 km across and in sharp contact with the host foyaite (Fig. 1). Locally, these titanate minerals are essential or principal oxides of a complex Ti-Fe-rich oxide mineralization, which is semi-massive to massive and contains up to 80 vol.% oxides. A wide variety of minerals is observed in various parts of this heterogeneous megaxenolith, which is fine-grained to pegmatitic and contains: perthitic alkali feldspar, discrete albite, nepheline, analcime, andalusite, corundum, topaz, phlogopite, quartz, rutile, various crichtonite-type phases, ferroan freudenbergite, titanite, manganoan ilmenite, Na-rich phases related to loparite-(Ce), neighborite, monazite-(Ce), and fluorite. Typically, the alkali feldspar has a sodic bulk-composition [$Ab_{56-69}Or_{27-42}An_{1-4}$], and consists of cryptoperthitic intergrowths, as revealed by powder-XRD scans. A phlogopite grain is nearly free of Fe and unusually rich in F (*ca.* 6 wt.%; Barkov *et al.*, 1997), although varieties richer in Fe are also observed. The following base-metal sulfides are present in the megaxenolith: pyrrhotite, marcasite (both Ti-V-rich and Ti-V-free), chalcopyrite (Ti-V-free); ferroan alabandite (6.0-7.7 wt.% Fe), and an unusual wurtzite (*2H* polytype) enriched in Mn and Fe in almost equal proportions (27 and 26 mol.% MnS and FeS, respectively). Also present are microspheroids of a
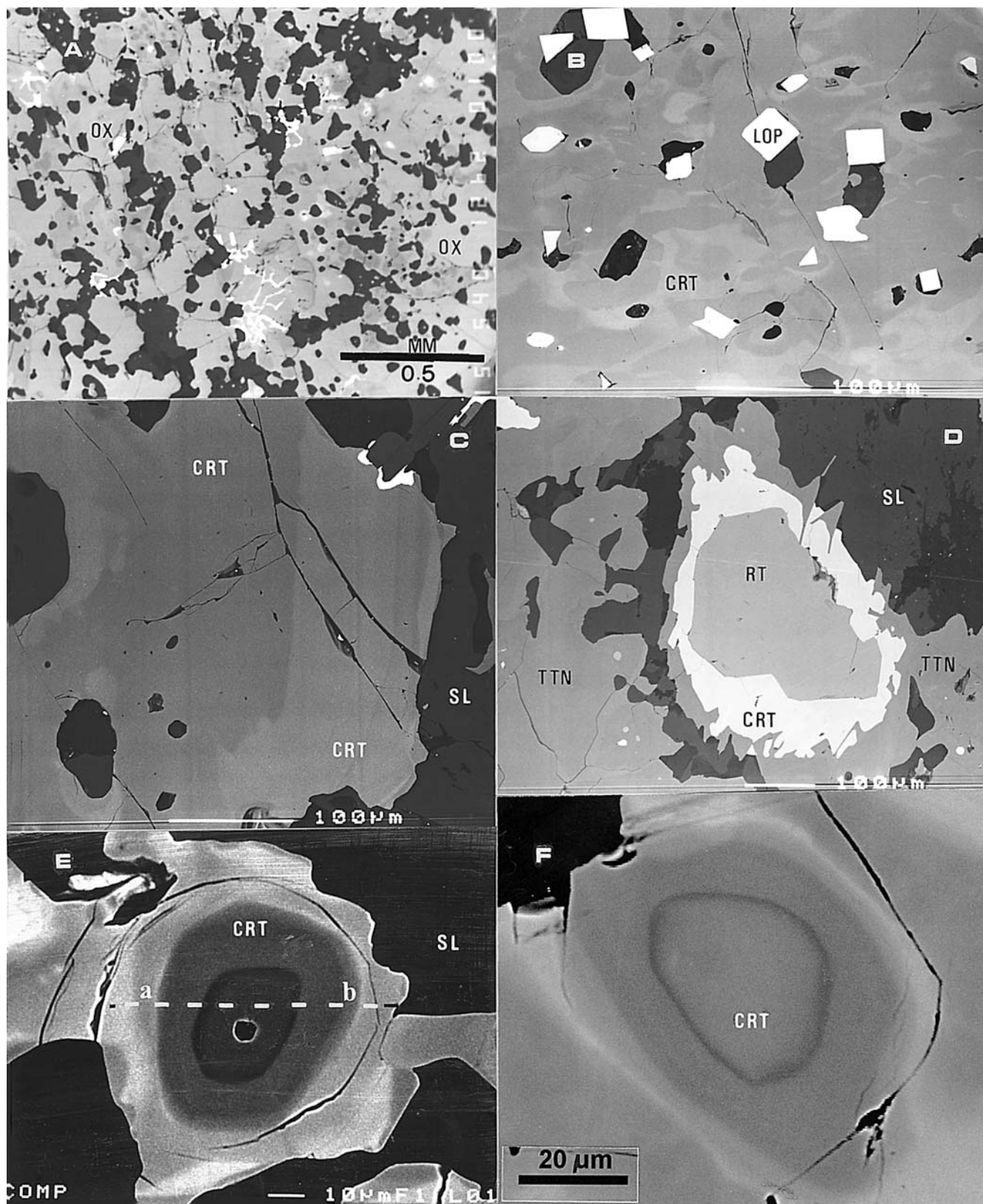
Fig. 2. A: Texture of oxide ore (OX, grey: dominantly the Sr-Na-REE minerals of the crichtonite group) from a fenitized megaxenolith in the Khibina complex. B–F: Patterns of zoning and textural relationships of the Sr-Na-REE minerals of the crichtonite group (CRT) with associated minerals: Na-REE-rich members of the perovskite group, enriched in loparite (LOP, white), rutile (RT), titanite (TTN) and silicate minerals (SL, dark gray to black: alkali feldspar and albite). Back-scattered electron images. The dashed line (*ab*; Fig. 2E) shows the location of a detailed electron-microprobe profile.
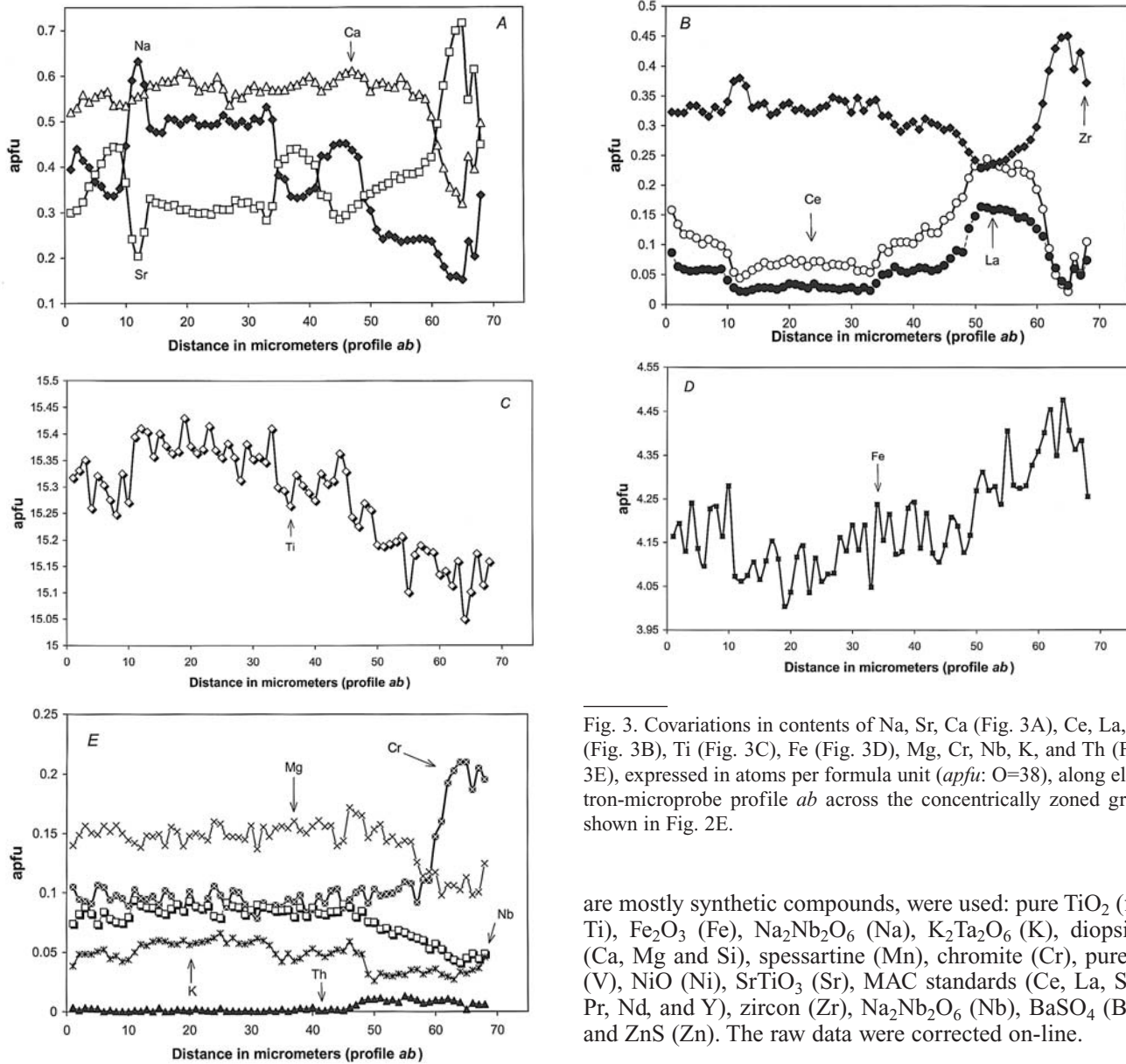
Fig. 3. Covariations in contents of Na, Sr, Ca (Fig. 3A), Ce, La, Zr (Fig. 3B), Ti (Fig. 3C), Fe (Fig. 3D), Mg, Cr, Nb, K, and Th (Fig. 3E), expressed in atoms per formula unit (*apfu*: O=38), along electron-microprobe profile *ab* across the concentrically zoned grain shown in Fig. 2E.

are mostly synthetic compounds, were used: pure TiO_2 (for Ti), Fe_2O_3 (Fe), $Na_2Nb_2O_6$ (Na), $K_2Ta_2O_6$ (K), diopside (Ca, Mg and Si), spessartine (Mn), chromite (Cr), pure V (V), NiO (Ni), $SrTiO_3$ (Sr), MAC standards (Ce, La, Sm, Pr, Nd, and Y), zircon (Zr), $Na_2Nb_2O_6$ (Nb), $BaSO_4$ (Ba), and ZnS (Zn). The raw data were corrected on-line.

Zoning in the Sr-Na-REE titanate minerals of the crichtonite group at Khibina

The Sr-Na-REE titanate minerals are closely associated with rutile, ferroan freudenbergite (with up to 0.45 wt.% Nb_2O_5), titanite, manganoan ilmenite, Na-REE-rich members of the perovskite group, alkali feldspar and albite (Fig. 2A-F). Using back-scattered electron imaging (BSE), various patterns of compositional zoning were observed, as a reflection of the difference in mean atomic number, primarily due to variations in Na and Sr, and corresponding variations in Ti and Fe (Fig. 2A-F). The following types of zoning are observed in these Sr-Na-REE titanate minerals: (1) "irregular" zoning (most common), with zones of varying size and composition, which are distributed rather chaotically (*e.g.*, Fig. 2B); (2) growth-related zoning, with individual zones that are generally subparallel to the grain

graphite-like material up to 0.5 mm in diameter, which occur sporadically in association with edgarite and Ti-, V-, Mn-, and W-rich sulfides formed under reducing conditions (Barkov *et al.*, 1997, 2000a, b).

Analytical method

The Sr-Na-REE titanate minerals from the Khibina complex were analyzed in wavelength-dispersion spectrometry mode (WDS) using a JEOL JXA-8900 electron microprobe operated at 15 kV and 30 nA. A finely focused beam (< 2 μm) was applied in all cases. The $K\alpha$ X-ray line was used for Ti, Fe, Na, K, Ca, Mn, Mg, Cr, V, Ni, and Si. The $L\alpha$ line was used for Sr, Ce, La, Zr, Nb, Y, Ba, and Zn. The $L\beta$ line was used for Nd, Pr and Sm. The $M\alpha$ line was used for Pb and Th. The following set of standards, which

Table 1. Representative compositions of the Sr-Na-REE titanate minerals of the crichtonite group from a fenitized megaxenolith, Khibina alkaline complex, Kola Peninsula, Russia.

Nb_2O_5	ZrO_2	ThO_2	TiO_2	Cr_2O_3	V_2O_3	Ce_2O_3	La_2O_3	Nd_2O_3	Pr_2O_3	Sm_2O_3	FeO	MnO	MgO	CaO	SrO	PbO	ZnO	NiO	Na_2O	K_2O	Total
0.44	1.58	n.d.	70.50	0.40	0.48	0.19	0.14	n.d	n.d	n.d	17.00	1.56	0.38	2.47	2.85	0.08	0.21	0.00	0.56	0.15	99.00
0.18	3.41	n.d.	68.69	0.46	0.41	0.25	0.20	n.d	n.d	n.d	18.10	1.27	0.63	1.59	3.76	0.36	n.d	0.05	0.30	0.15	99.81
0.21	3.34	n.d.	69.31	0.61	0.39	0.30	0.24	n.d	0.11	n.d	17.55	1.32	0.66	1.53	3.53	0.35	0.05	n.d	0.38	0.15	100.03
0.25	3.25	0.08	69.51	0.79	0.47	0.34	0.38	0.13	n.d	n.d	18.24	0.35	0.60	1.50	3.36	0.09	0.04	n.d	0.45	0.15	99.98
0.40	3.67	n.d.	70.03	0.49	0.45	0.29	0.13	n.d	n.d	n.d	17.54	1.24	0.58	1.49	1.62	0.13	n.d	0.04	0.95	0.18	99.23
0.53	3.65	n.d.	71.54	0.50	0.49	0.18	n.d	n.d	n.d	n.d	17.31	1.58	0.40	1.51	0.11	n.d	0.11	n.d	1.53	n.d	99.44
0.72	2.37	n.d.	72.18	0.41	0.35	0.46	0.17	n.d	n.d	n.d	17.13	1.61	0.34	2.00	1.24	0.09	0.17	n.d	1.04	0.15	100.43
0.62	2.01	0.17	67.89	0.44	0.42	2.03	1.01	0.22	0.18	n.d	17.80	1.71	0.33	1.56	1.85	n.d	0.15	n.d	0.58	0.09	99.06
0.73	3.46	n.d.	71.46	0.33	0.47	0.25	0.09	n.d	n.d	n.d	17.44	1.51	0.50	1.70	0.38	n.d	0.09	n.d	1.26	0.16	99.83
0.33	3.99	0.11	68.68	0.28	0.48	0.78	0.73	0.23	n.d	n.d	18.45	0.58	0.71	1.30	1.70	n.d	n.d	n.d	0.66	0.19	99.20
0.78	0.98	0.34	68.01	0.48	0.42	2.90	2.11	0.43	0.13	0.10	17.87	1.69	0.36	1.70	1.87	n.d	0.19	0.06	0.37	0.05	100.84

Note: Results of WDS electron-microprobe analyses (in wt.%; JEOL JXA-8900 microprobe); n.d. is not detected.

Table 2. Structural formulae of the Sr-Na-REE titanate minerals of the crichtonite group from the Khibina complex.

A (M_0)	B (M_1)	C (M_3–M_4–M_5)	T (M_2)
$(Sr_{0.48}Na_{0.31}Ca_{0.10}K_{0.06}Ce_{0.02}La_{0.02}Pb_{0.01})_{S1.00}$	$(Ca_{0.67}Mn_{0.38}Zr_{0.22})_{S1.27}$	$(Ti_{15.43}Fe_{2.14}Mg_{0.16}V_{0.11}Cr_{0.09}Nb_{0.06})_{S17.99}$	$(Fe_{2.0}Zn_{0.04})$
$(Sr_{0.64}Na_{0.17}K_{0.06}Ca_{0.05}Ce_{0.03}Pb_{0.03}La_{0.02})_{S1.00}$	$(Zr_{0.49}Ca_{0.45}Mn_{0.31})_{S1.25}$	$(Ti_{15.13}Fe_{2.43}Mg_{0.27}Cr_{0.11}V_{0.10}Nb_{0.02})_{S18.06}$	$Fe_{2.0}$
$(Sr_{0.60}Na_{0.21}K_{0.06}Ca_{0.03}Ce_{0.03}Pb_{0.03}La_{0.03}Pr_{0.01})_{S1.00}$	$(Zr_{0.47}Ca_{0.45}Mn_{0.32})_{S1.24}$	$(Ti_{15.19}Fe_{2.28}Mg_{0.29}Cr_{0.14}V_{0.09}Nb_{0.03})_{S18.02}$	$(Fe_{2.0}Zn_{0.01})$
$(Sr_{0.57}Na_{0.26}K_{0.06}Ce_{0.04}La_{0.04}Nd_{0.01}Pb_{0.01})_{S0.99}$	$(Ca_{0.47}Zr_{0.46}Mn_{0.09})_{S1.02}$	$(Ti_{15.21}Fe_{2.44}Mg_{0.26}Cr_{0.18}V_{0.11}Nb_{0.03})_{S18.23}$	$(Fe_{2.0}Zn_{0.01})$
$(Na_{0.54}Sr_{0.27}K_{0.07}Ca_{0.07}Ce_{0.03}La_{0.01}Pb_{0.01})_{S1.00}$	$(Zr_{0.52}Ca_{0.39}Mn_{0.31})_{S1.22}$	$(Ti_{15.28}Fe_{2.25}Mg_{0.25}Cr_{0.11}V_{0.11}Nb_{0.05})_{S18.05}$	$Fe_{2.0}$
$(Na_{0.85}Ca_{0.10}Sr_{0.02}Ce_{0.02}K_{0.01})_{S1.00}$	$(Zr_{0.51}Mn_{0.38}Ca_{0.36})_{S1.25}$	$(Ti_{15.40}Fe_{2.14}Mg_{0.17}Cr_{0.11}V_{0.11}Nb_{0.07})_{S18.00}$	$(Fe_{2.0}Zn_{0.02})$
$(Na_{0.57}Sr_{0.20}Ca_{0.09}K_{0.06}Ce_{0.05}La_{0.02}Pb_{0.01})_{S1.00}$	$(Ca_{0.52}Mn_{0.39}Zr_{0.33})_{S1.24}$	$(Ti_{15.48}Fe_{2.08}Mg_{0.14}Cr_{0.09}Nb_{0.09}V_{0.08})_{S17.96}$	$(Fe_{2.0}Zn_{0.04})$
$(Na_{0.33}Sr_{0.32}Ce_{0.22}La_{0.11}K_{0.03}Nd_{0.02}Pr_{0.02}Th_{0.01})_{S1.06}$	$(Ca_{0.50}Mn_{0.43}Zr_{0.29})_{S1.22}$	$(Ti_{15.15}Fe_{2.42}Mg_{0.15}Cr_{0.10}Nb_{0.08}V_{0.10})_{S18.00}$	$(Fe_{2.0}Zn_{0.03})$
$(Na_{0.70}Ca_{0.13}Sr_{0.06}K_{0.06}Ce_{0.03}La_{0.01}Nd_{0.01})_{S1.00}$	$(Zr_{0.48}Ca_{0.39}Mn_{0.36})_{S1.23}$	$(Ti_{15.36}Fe_{2.17}Mg_{0.21}V_{0.11}Nb_{0.09}Cr_{0.07})_{S18.01}$	$(Fe_{2.0}Zn_{0.02})$
$(Na_{0.37}Sr_{0.29}Ca_{0.08}Ce_{0.08}La_{0.08}K_{0.07}Nd_{0.02}Th_{0.01})_{S1.00}$	$(Zr_{0.57}Ca_{0.33}Mn_{0.14})_{S1.04}$	$(Ti_{15.15}Fe_{2.52}Mg_{0.31}V_{0.11}Cr_{0.07}Nb_{0.04})_{S18.20}$	$Fe_{2.0}$
$(Sr_{0.32}Ce_{0.31}La_{0.23}Na_{0.21}Nd_{0.05}K_{0.02}Th_{0.02}Sm_{0.01}Pr_{0.01})_{S1.18}$	$(Ca_{0.54}Mn_{0.42}Zr_{0.14})_{S1.10}$	$(Ti_{15.08}Fe_{2.41}Mg_{0.16}Cr_{0.11}V_{0.10}Nb_{0.10})_{S17.96}$	$(Fe_{2.0}Zn_{0.04})$

edges (Fig. 2C), and (3) concentric zoning, which is combined with the cryptic zoning, with individual zones that are developed around a mineral inclusion located in the center. For example, the zoned grain shown on Fig. 2E contains a central inclusion of a K-Mg-Fe-rich silicate. A micro-inclusion of titanite was observed in the center of another concentrically zoned grain exhibiting the same type of zoning. These micro-inclusions could be the nucleus of crystallization of the zoned grains. Concentric cracks are present in these grains, and the observed zones tend to become BSE-brighter outward (Fig. 2E). In some cases, concentric zones are developed without a central inclusion, as is shown in Fig. 2F.

Zoned intergrowths involving the Sr-Na-REE titanate minerals are also observed; these minerals mantle rutile (Fig. 2D) or occur as a partial rim around ferroan freudenbergite, and are mantled by manganoan ilmenite. These observations argue for the late deposition of the crichtonite-type phases at an advanced stage of fenitization. Note that the concentrically zoned grain (Fig. 2E) displays a cryptic zoning, which is revealed only by detailed electron-microprobe analyses (Fig. 3A-E).

Compositional variations

The compositional data (WDS; n = 1408) have been obtained on numerous grains of the Sr-Na-REE titanate minerals, either along electron-microprobe profiles or as individual point-analyses. These data gave the following average contents and ranges (in wt.%), TiO_2 68.39 (64.66–73.28), ZrO_2 2.55 (0.74–4.71), FeO 17.53 (15.49–19.15), MnO 1.43 (0.28–2.23), MgO 0.47 (n.d.–0.78), ZnO 0.12 (n.d.–0.36), Cr_2O_3 0.52 (0.25–1.87), SrO 2.49 (n.d.–4.28), CaO 1.58 (0.90–2.53), BaO n.d. (n.d.–0.28), NiO n.d. (n.d.–0.07), PbO 0.10 (n.d.–0.47), K_2O 0.13 (n.d.–0.31), Na_2O 0.53 (n.d.–1.56), V_2O_3 0.46 (0.32–0.60), Ce_2O_3 0.98 (n.d.–3.99), La_2O_3 0.80 (n.d.–3.22), Nd_2O_3 0.16 (n.d.–0.60), Sm_2O_3 n.d. (n.d.–0.35), Pr_2O_3 n.d. (n.d.–0.40), Y_2O_3 n.d., Nb_2O_5 0.42 (0.12–1.06), ThO_2 0.13 (n.d.–0.99), where n.d. is not detected, and total 98.89. The corresponding ranges in atoms per formula unit (*apfu*; O = 38) are the following: Ti 14.81–15.65, Zr 0.11–0.66, Fe 3.86–4.76, Mn 0.07–0.56, Mg 0–0.34, Zn 0–0.08, Cr 0.06–0.45, Sr 0–0.75, Ca 0.29–0.80, Ni 0–0.02, Pb 0–0.04, K 0–0.11, Na 0–0.87, V 0.08–0.14, Ce 0–0.43, La 0–0.36, Nd 0–0.06, Sm < 0.05, Pr < 0.05, Nb 0–0.14, and Th 0-0.07. The contents of (Sr + Na + Ca + K + REE + Pb + Th), which are commonly assumed to be the *A*-site cations in the crichtonite group, vary from 1.12 to 1.85 *apfu*, whereas the contents of the other cations (Ti + Fe +Zr + Mn + Mg + Cr + V + Nb + Zn + Ni) vary from 20.50 to 21.11 *apfu*, showing a small excess in cations relative to ideal $ABC_{18}T_2O_{38}$. The representative compositions and structural formulae, based on 38 oxygen atoms, are listed in Tables 1 and 2.
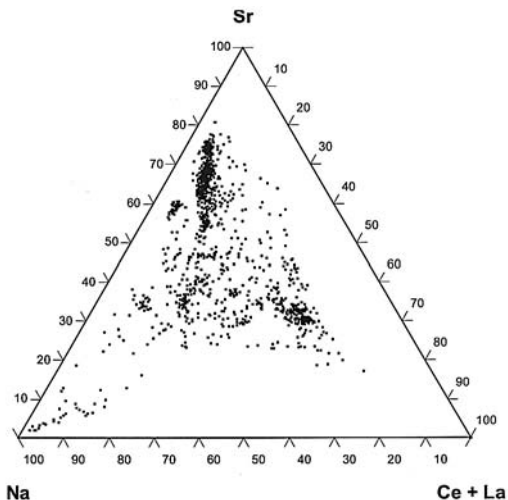
Fig. 4. Compositions of the Sr-Na-REE minerals of the crichtonite group from the fenitized megaxenolith, Khibina complex, in the Na–Sr–(Ce+La) compositional space (atomic proportions). Results of a total of 1408 electron-microprobe analyses (WDS; this study) are plotted.

Comparison with crichtonite-type titanates from other localities

There are important compositional differences between the Sr-Na-REE-enriched crichtonite-type minerals at Khibina and related titanates described in the literature. The minerals investigated here display an extensive Na-for-Sr substitution (Fig. 4), and Pb and Ba are generally lacking in their compositions. In contrast, crichtonite-type titanates from other localities are commonly enriched in Pb, such as the Pb-(Mn-Ba-Y)-rich crichtonite from Dauphiné, France (Grey et al., 1976), from Minas Gerais, Brazil (Foord et al., 1994), from various localities in the Swiss Alps (Stalder & Bühler, 1987), cleusonite from Nendaz Valley, Switzerland (Wülser et al., 2003), and gramaccioliite-(Y) from Stura Valley, Italy (Orlandi et al., 2004).

The Khibina titanates are also poor in V, with low to moderate Mn contents (Tables 1, 2). These characteristics contrast with those of crichtonite rich in V from the Deadhorse Creek diatreme complex, Ontario, Canada (Platt & Mitchell, 1996), with Mn-rich varieties of crichtonite from kimberlite breccias (Filippov, 1987) and from nepheline syenite pegmatites at Pegmatite Peak, Montana, USA (Chakhmouradian & Mitchell, 1999). Minerals of the crichtonite series enriched in K, Ba, Ca, REE and extremely rich in Cr (up to 16 wt.% Cr_2O_3) occur as xenocrysts in the Jagersfontein kimberlite, South Africa (Haggerty, 1983) and in mantle-derived peridotite xenoliths associated with kimberlite (Jones & Ekambaram, 1985). Members of the davidite-loveringite series, rich in V and Cr, have been reported from an albite felsite, Norway (Olerud, 1988). Crichtonite enriched in Ca, Ba (or Pb), REE, and Cr occurs as inclusions in garnet in crustal and mantle xenoliths (Varlamov et al., 1995) and from the

Garnet Ridge, Arizona, USA (Wang et al., 1999). Landauite from the Burpala alkaline complex, Baikal region, Russia, has the composition $Na[MnZn_2(Ti,Fe)_6Ti_{12}]O_{38}$ (Grey & Gatehouse, 1978). Recently, landauite has been reported from dikes of peralkaline alkali syenite at Katzenbuckel, Germany (Stahle et al., 2002).

Various crichtonite-group minerals were previously reported to contain the light REE and heavy REE, and to be depleted in the intermediate REE (Haggerty, 1983; Green & Pearson, 1987; Foord et al., 1994). Our compositional data for the crichtonite-type Sr-Na-REE minerals at Khibina show a relative enrichment only in the light REE (Tables 1, 2), consistent with the findings of Jones & Ekambaram (1985).

The presence of elevated contents of Cr and Mg in these titanates at Khibina is especially noteworthy (Tables 1, 2). Levels of these elements are comparable to those observed in loveringite from various mafic-ultramafic layered complexes (Campbell & Kelly, 1978; Tarkian & Mutanen, 1987; Lorand et al., 1987; Barkov et al., 1996), and from the Bracco ophiolitic complex, Italy (Cabella & Gazzotti, 1997).

Discussion

Crystallochemical implications

Na, Sr and Ca are the dominant "large cations" in the observed series of the crichtonite-type phases from Khibina. If Ca is assigned to the A site, compositions of this series would correspond to formulae that are strongly "nonstoichiometric" relative to $ABC_{18}T_2O_{38}$, with a dominance of Ca over Sr and Na at the A site in many cases. Thus, in contrast to most of compositions reported in the literature, our data suggest the preferential incorporation of Ca at the B site, not the A site (Tables 1, 2). This assignment is consistent with the element correlations, which clearly indicate that the crystallochemical behavior of Ca in the observed series is strongly distinct from that shown by the other "large cations": Na, Sr, and the REE. Thus, in spite of the high contents of Ca (Table 1), loveringite is an insignificant end-member component in this series. Such behavior of Ca is unusual, although it is known that the Ca content of the loveringite-type titanates may exceed the ideal value of 1 apfu, e.g., in synthetic "$Ca_2Zn_4Ti_{16}O_{38}$", isostructural with crichtonite, one of the two Ca atoms occupies the A site, whereas the other atom of Ca occupies the B site (Gatehouse & Grey, 1983). Also, synthetic loveringite obtained under reducing conditions contains from 1.1 to 1.7 Ca apfu, and the Ca in excess of 1 apfu is ordered at the large octahedral site B (M_1) (Peterson et al., 1998). It is also noteworthy that all Ca (0.29 apfu) enters the B site, not the A site, in mathiasite (Gatehouse et al., 1983).

The crichtonite-type phases at Khibina contain a wide variety of elements (Tables 1, 2), whose apparent charges vary from +1 to +5: Na, K (+), Sr, Ca, Pb, Fe, Mn, Mg, Zn (2+), Ce, La, Nd, Pr, Sm, Cr, V (3+), Ti, Zr, Th (4+), and Nb (5+). This assumption leads to a value of 76.08 positive

charges per unit cell, calculated for the mean composition (for $n = 1408$), which is consistent with the electroneutrality requirements. The mean contents of Ti^{4+} and Fe^{2+} are *ca.* 15 and 4 *apfu*, respectively. It is known that Ti is generally Ti^{4+} in various crichtonite-type titanates, and even loveringite, formed under strongly reducing conditions of synthesis, mostly contains Ti^{4+} and only subordinate Ti^{3+} (Peterson *et al.*, 1998).

The representative formulae for the crichtonite-type phases from Khibina are listed in Table 2. They are consistent with the revised formula of the crichtonite group: $ABC_{18}T_2O_{38}$, where T cations are in tetrahedral coordination in the M_2 site, B and C cations have octahedral coordination, and B cations are located in the larger, high-symmetry M_1 site, and C cations are located in the smaller M_3, M_4, and M_5 sites (Orlandi *et al.*, 1997). The revised formula indicates that all cations, not only the A-site cations, should be taken into consideration in the mineral nomenclature of this group, in agreement with principles of the CNMMN, IMA. Thus, the crichtonite-type phases from Khibina appear to have the following (generalized) formulae (Table 2): $(Sr,Na,K,REE)(Ca,Zr,Mn)(Ti,Fe)_{18}Fe_2O_{38}$ (1); $(Sr,Na,K,REE)(Zr,Ca,Mn)(Ti,Fe)_{18}Fe_2O_{38}$ (2); $(Na,Sr,K,REE)(Ca,Zr,Mn)(Ti,Fe)_{18}Fe_2O_{38}$ (3); and $(Na,Sr,K,REE)(Zr,Ca,Mn)(Ti,Fe)_{18}Fe_2O_{38}$ (4). Note that on the basis of the dominant cation present at the B (M_1) site, formulae 1 and 2 probably correspond to Ca- or Zr-dominant variants of crichtonite, which, in the type locality, displays a dominance of Mn at the B site (*e.g.*, Orlandi *et al.*, 1997). Similarly, formulae 3 and 4 probably correspond to Ca- or Zr-dominant variants (also unnamed) of landauite. It should be noted that, in landauite from the type locality, Mn occupies fully the B site and Zn, not Fe, occupies the T (M_2) site (Grey & Gatehouse, 1978).

The existence of an extensive substitution of Na^+ for Sr^{2+} at the A (M_0) site of the crichtonite-type minerals at Khibina is evident from our dataset ($R = -0.75$; Fig. 3A, 4). This substitution is coupled with a Ti^{4+}-for-Fe^{2+} substitution in the C (M_3-M_4-M_5) site in order to maintain charge balance, consistent with the R of -0.90 between the contents of Ti and Fe. Also, the existence of these substitutions is demonstrated conclusively by the observations made in the concentrically zoned grain (Fig. 3A-D). An important role of Ti^{4+} (and its Fe^{2+} counterpart) in charge compensation is also displayed by the observed positive correlations of Ti with the elements having lower valences: Na^+, K^+ and Ca^{2+} ($R = 0.61$, 0.51 and 0.53), and its negative correlations with Ce^{3+}, La^{3+} and Th^{4+} ($R = -0.45$, -0.51 and -0.51), having higher valences. This tendency can be also seen in the behavior of minor Nb^{5+}, which is sympathetically correlated with Na^+ ($R = 0.50$) and antipathetically with Cr^{3+} (-0.58) and Sr^{2+} (-0.54). The crystallochemical behavior of Fe^{2+} is opposite to that shown by Ti, as is evident in the observed anticorrelations of Fe with Na^+, K^+ and Ca^{2+} and positive correlations with Ce^{3+}, La^{3+} and Th^{4+}. The amounts of Ca covary with Ti ($R = 0.53$) and are negatively correlated with Zr and Fe ($R = -0.56$ and -0.57). Thus, Ca could be incorporated in the B (M_1) site *via* a coupled substitution of the type: $(Ca^{2+}+Ti^{4+}) = (Zr^{4+}+Fe^{2+})$.
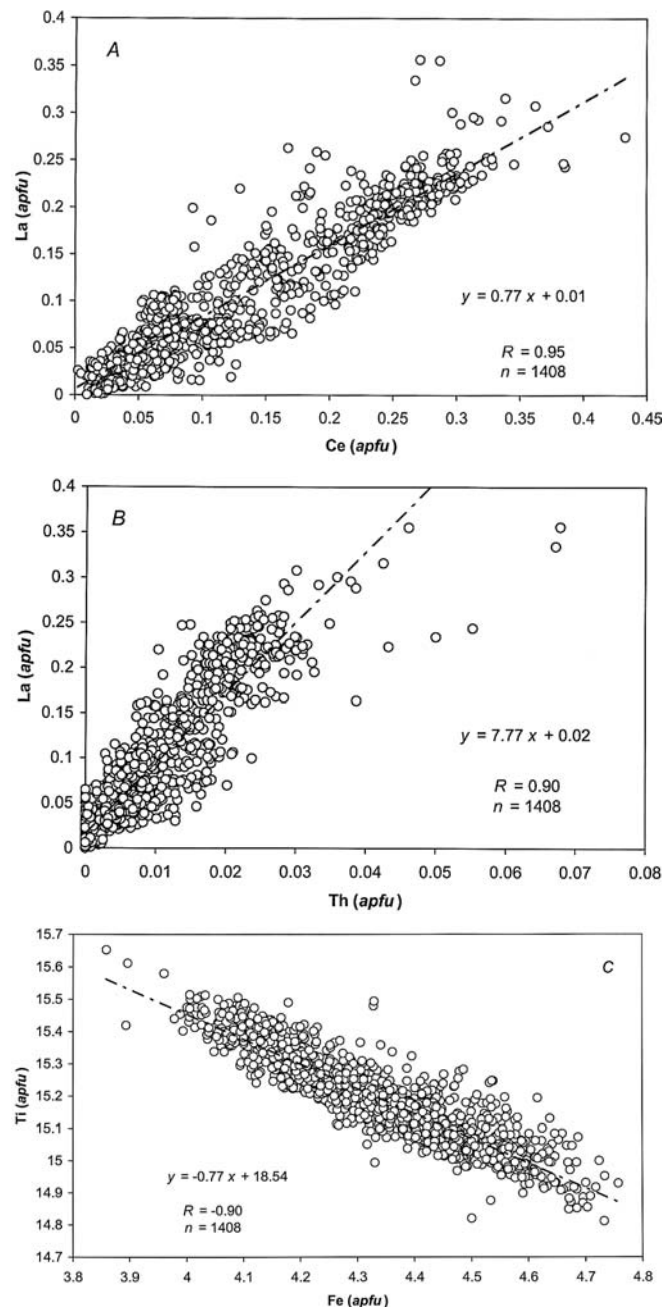

Fig. 5. Correlations of La *versus* Ce (Fig. 5A), Th *versus* La (Fig. 5B), and Fe *versus* Ti (Fig. 5C), in *apfu*: O = 38, in compositions of the Sr-Na-REE minerals of the crichtonite group from the Khibina complex. Results of a total of 1408 electron-microprobe analyses (WDS method; this study) are plotted.

High contents of the light REE (up to 7.4 wt.% REE_2O_3) are observed (Tables 1, 2). In terms of atomic proportions, the contents of (Ce+La) may exceed 50 % of total content of the "large cations" at the A site (Fig. 5A), classifying these compositions as davidite-dominated members of the solid-solution series. The REE are positively intercorrelated, and the La-Ce correlation is especially strong ($R = 0.95$: Fig. 5A), indicating the existence of

geochemical relationships and the ordered distribution of the REE at the *A* site. Both Ce^{3+} and La^{3+} display negative correlations with Sr^{2+} (R = -0.46 and -0.39) and with K^+ (-0.66 and -0.62), and the REE thus probably replace Sr and K at the *A* site. In addition, minor amounts of Th^{4+} are positively correlated with REE, with the R of 0.90 for La *versus* Th (Fig. 5B). The incorporation of REE is controlled by Zr^{4+}, which is consistent with the observed negative correlations between Zr and Ce (R = -0.62), Zr and La (-0.58), and Zr and Nd (-0.53). Also, Fig. 3B demonstrates the existence of strong relationships between La and Ce, and between these elements and Zr in the concentrically zoned grain. In terms of the entire dataset, Zr exhibits negative correlations with Th (R = -0.52), Mn (-0.60) and Zn (-0.56). All these observations suggest that the REE^{3+} (and minor Th^{4+}) likely replace Sr^{2+} and K^+ at the *A* site, and this substitution is controlled by the corresponding decrease in levels of Zr^{4+} at the *B* site, which is probably replaced by divalent cations (Mn and minor Zn) in order to maintain charge balance.

Genetic implications

The unusual fenitic assemblages at Khibina appear to have developed at the expense of roof pendants, composed of rocks of unknown composition, which foundered into a late batch of silica-undersaturated felsic magma to form the megaxenolithic bodies (Barkov *et al.*, 2000a). The Na-metasomatism affected both the mineralized megaxenolith and the host "albitized" unit of the complex. Presumably, the oxidizing alkali fluids transformed the original rock(s) into an albite- perthite-(nepheline) assemblage and controlled the deposition and distribution of the Ti-Nb-REE-rich oxide mineralization (minerals of the crichtonite group, rutile, ferroan freudenbergite, titanite, manganoan ilmenite, and minerals of the perovskite group).

The observed Na-rich compositions of the crichtonite-type phases (Tables 1, 2) and associated oxide (freudenbergite and Na-REE-rich minerals of the perovskite group) and silicate minerals (albite and perthite) are clearly related to the environment of high Na activity, associated with the intense Na-metasomatism in the "albitized" area of the Khibina complex.

The zoning observed in minerals of the crichtonite group (Fig. 2B-F) is inferred to be metasomatic in origin, reflecting significant variations in activities of Na and Sr in the fluid medium during crystallization. The absence of cross-cutting relationships and of evidence for dissolution of earlier concentric zones in the zoned grains (Fig. 2E, F) is consistent with the deposition from a single batch of fluid, which changed (evolved) in composition progressively with crystallization, rather than with multiple metasomatic events. The formation of these concentrically zoned grains presumably requires that the microsystem remained closed for a sufficient period of time to permit evolution of the fluid and to precipitate the narrow concentric zones. A change in volume during the formation could have resulted in the appearance of concentric cracks conformable to the zoning (Fig. 2E). These textural observations argue for a late-stage deposition of the crichtonite-type phases, which locally postdated the deposition of the associated rutile (Fig. 2D), freudenbergite or titanite.

Our compositional data reveal the surprising presence of elevated levels of Cr (up to 1.87 wt.% Cr_2O_3) and up to 0.78 wt.% MgO in the crichtonite-type phases at Khibina. Typically, mineral associations of the Khibina complex are totally devoid of Cr. The reported occurrences of Cr-rich phases are few in this complex: chromite in xenoliths of mafic-ultramafic rocks and picritic diatremes (Galakhov, 1975), eskolaite in a fenitized xenolith (Shlyukova, 1986), and magnesiochromite and a Cr-rich spinel in dike rocks (Arzamastsev *et al.*, 1988).

On the basis of the observed Cr-rich compositions of the crichtonite-type phases, we suggest that rocks of mafic affinity are probably the protolith for the mineralized megaxenolith and related xenolithic bodies. Indeed, various mafic rocks of Proterozoic age, both (meta)-volcanic and igneous, are common at the southern and southwestern contacts of the Khibina complex with the Proterozoic Imandra-Varzuga Supergroup, including layered bodies of the Imandra complex. Thus, large fragments of mafic rocks of Proterozoic age may have foundered into the silica-undersaturated felsic magma of the Devonian Khibina complex to form the megaxenolithic (and subsequently fenitized) bodies. The association of Cr and Nb (Tables 1, 2), which are geochemically distinct, is observed in the Sr-Na-REE minerals of the crichtonite group at Khibina, and reflects two different sources for these elements. The Cr was presumably scavenged from a mafic precursor of the fenitized megaxenolith, whereas Nb was mobilized, transported and introduced by a metasomatic fluid from alkaline rocks of the Khibina complex during fenitization.

After the main event of fenitization, at a very late or final stage of metasomatism, the association of edgarite $FeNb_3S_6$, containing reduced Nb, and of the Ti-, V-, Mn-, and W-rich sulfides formed on a local scale in this megaxenolith, from a highly reduced, subalkaline S-C-H-rich fluid that may well have remobilized Nb and the other lithophile elements as a result of destabilization of the oxide minerals (Barkov *et al.*, 1997, 2000a, b).

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