

Thorium in crandallite-group minerals: an example from a Devonian bauxite deposit, Timan, Russia

L. E. MORDBERG*

Russian Research Geological Institute (VSEGEI), Sredny Pr. 74, St Petersburg 199106, Russia

ABSTRACT

A Th-rich mineral of the crandallite group has been investigated from the weathering profile of the Schugorsk bauxite deposit, Timan, Russia. It occurs within thin (up to 0.5 mm) organic-rich veinlets together with 'leucoxene' in the form of small shapeless grains which vary in size from 1–2 μm to 60–70 μm . Rare grains disseminated among boehmite crystals were also found. Microprobe analyses determined that the ThO_2 content can be as high as 18 wt.%. The mineral composition is intermediate between crandallite $\text{CaAl}_3\text{H}(\text{PO}_4)_2(\text{OH})_6$, goyazite $\text{SrAl}_3\text{H}(\text{PO}_4)_2(\text{OH})_6$, Th-crandallite and svanbergite $\text{SrAl}_3\text{PO}_4\text{SO}_4(\text{OH})_6$ in the beudantite group.

Comparatively high contents of Fe and Si and a very high positive Th and Fe content correlation ($r = +0.98$) suggest that the formula of the hypothetical Th-bearing end-member is $\text{ThFe}_3(\text{PO}_4, \text{SiO}_4)_2(\text{OH})_6$ with Th and Si substituting for REE and P respectively (woodhouseite-type substitution). Another possible substitution is $\text{Th}^{4+} + \text{Ca}^{2+} \rightleftharpoons 2\text{REE}^{3+}$ (florencite-type). A deficiency of cations in the X site can be explained by either the presence of carbon, undetectable by microprobe, in the crystal lattice or a lack of X-site cations due to radiation damage induced by Th. Some excess of cations in the B site (Al and Fe^{3+}) can be explained by the presence of very small boehmite and hematite inclusions on the crandallite grain surfaces. Th-rich crandallite may be the result of alteration of an unidentified silicate mineral from the parent rock with a composition close to the simplified formula $\text{Fe}^{2+}\text{ThSiO}_4(\text{OH})_2$.

KEYWORDS: bauxite, weathering, crandallite, woodhouseite, goyazite, svanbergite, florencite, thorium, Devonian, Timan, Russia.

Introduction

ALUMINOUS phosphates belonging to the crandallite group have been recorded in most known rock types (Dill, 2001). Their simplified formula is $\text{AB}_3(\text{XO}_4)_2(\text{OH})_6\text{H}_{0-1}$. The peculiarities of the crystal lattice allow different elements to occupy the same sites. Thus, the X site can be occupied by P, S, As, Si, C and V; Al and Fe^{3+} usually occur in the B site. The 12-fold A site is shared mainly by divalent Ca, Sr, Ba and Pb, as well as trivalent rare earth elements (REE) or Bi. Van Wambeke (1971) studied a mineral from the Kobokobo pegmatite in the Democratic Republic

of Congo and found it to be a Th-rich crandallite. He observed a deficiency in the A and X sites and explained it by leaching of elements from these sites during weathering.

Gaines *et al.* (1997) distinguish three groups of Al- and Fe-phosphates, namely a crandallite group, a beudantite group and a florencite group. However, the composition of natural species suggests the existence of broad solid solutions among the known end-members (i.e. Mordberg *et al.*, 2001) with typical disorder in the X site (Kolitsch *et al.*, 1999; Huminicki and Hawthorn, 2002). Therefore, in the present paper we refer to minerals of all three groups as 'crandallites'.

Most of the common crandallite group minerals are typical of bauxites and other weathering products (Beneslavsky, 1974; Bardossy, 1982; Dill, 2001). Within the Schugorsk bauxite deposit, crandallites were identified by Likhachev (1993).

* E-mail: leonid_mordberg@vsegi.ru
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Their detailed study shows that they represent solid solutions among crandallite itself, goyazite, plumbogummite, woodhouseite, svanbergite, hinsdallite and florencite (Mordberg *et al.*, 2000, 2001). Depending on their conditions of formation, they may have different *REE* distribution patterns (Mordberg *et al.*, 2000). The present paper is devoted to the study of an unusual Th-rich 'crandallite', which was determined among other crandallites. The location, geology and mineralogy of the deposit were given in previous publications (Mordberg *et al.*, 2000, 2001 and references therein).

Material and methods

Samples for the study were taken from drill core during fieldwork. Bulk XRF analyses of powdered samples were used for the estimation of the content of elements which usually associate with crandallite (P, S, Ca, Ba, Sr, Pb and *REE*). Polished sections were prepared from samples enriched in these elements and studied first with the JEOL 5900LV analytical SEM at the Natural History Museum, London. Th-rich crandallite was initially identified quantitatively using this SEM, and subsequently analysed by electron microprobe Cameca SX-100 in the Geological Survey of Germany (BGR). The analytical conditions used for microprobe analyses were 15 kV and 20 nA. In the case of elements for which the contents are close to the detection limit, the following procedure was applied. An average

background value and its standard deviation was calculated. Only the element contents for which the measured peak intensity exceeded the value of the average background plus three standard deviations are listed in Table 1. Only crandallite crystals which were large enough to be sure that no other mineral phase was covered by the beam were analysed.

Results and discussion

Th-rich crandallites were identified within white, high-quality boehmitic bauxite, in the middle of a 100 m thick weathering profile (Fig. 1). Crandallites are spatially associated with organic-enriched veinlets up to 1 mm thick and are frequently accompanied by large amounts of anatase, which also concentrates in the veinlets (Fig. 2). Crandallite mineralization is very finely dispersed (usually <2–3 μm); however, sometimes roundish or elongated crandallite grains occur up to 30–70 μm . Also, disseminated crandallite grains were found among boehmite crystals.

Microprobe analyses of crandallites are given in Table 1. It can be seen, that of the *A*-site elements, Ca (3.40–8.00 wt.%), Sr (1.06–10.02 wt.%) and Th (0.05–18.37 wt.%) are essential. Ba is always present, and small amounts of Pb, Bi and *REE* may appear. Both Al and Fe occur in the *B* site, while the *X* site is shared by P, S and, to a lesser degree, Si. Small amounts of W could be referred to this site as

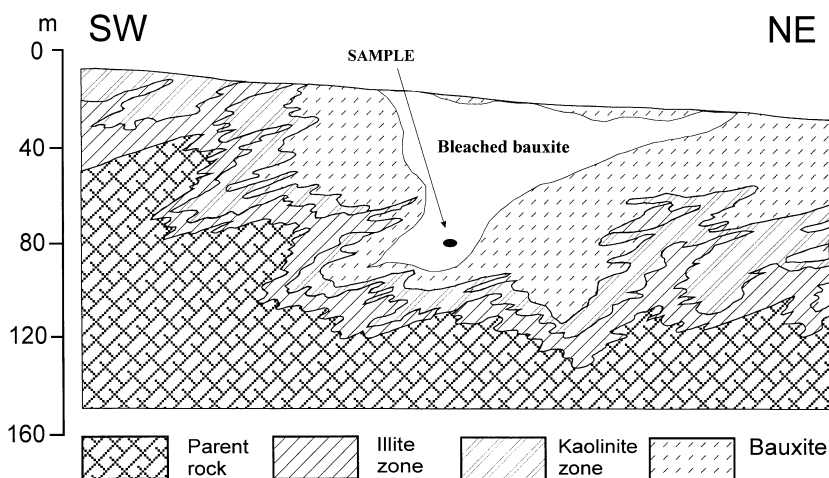


FIG. 1. Geological cross section of the Schugorsk bauxite deposit showing the location of the studied sample. Horizontal and vertical scales are equal.

THORIUM IN CRANDALLITES

TABLE 1. Electron microprobe analyses of Th crandallites (wt.%).

Oxide	1/1	2/1	3/1	4/1	5/1	9/1	10/1	13/1	16/1	17/1	18/1	1/2	2/2	5/2	6/2	7/2	8/2	9/2	10/2
CaO	4.68	5.43	5.17	5.40	3.96	4.31	12.12	4.52	4.47	4.54	7.96	5.39	5.07	5.98	4.84	4.89	4.76	3.97	5.26
SrO	8.98	8.53	8.51	9.20	6.36	6.91	1.06	7.24	8.15	8.46	4.30	8.46	10.02	8.73	8.15	9.19	8.15	5.15	9.68
BaO	1.17	1.54	1.54	1.59	0.99	1.23	0.67	1.29	1.23	1.42	1.08	1.77	1.46	1.77	1.37	1.22	1.36	0.85	1.65
La ₂ O ₃	—	—	—	—	—	0.67	0.24	—	—	—	0.97	0.24	—	—	b.d.l.	—	—	b.d.l.	0
Ce ₂ O ₃	0.20	0.22	0.33	0.20	0.39	2.20	0.33	0.18	0.32	0.36	1.89	0.65	0.34	0.26	0.19	0.32	0.20	0.12	0.31
Nd ₂ O ₃	—	—	—	0.14	0.15	0.59	0.21	0.22	0.18	—	0.87	0.42	—	—	—	0.26	—	—	—
Sm ₂ O ₃	b.d.l.	—	—	—	—	0.16	—	b.d.l.	—	—	0.28	—	—	—	b.d.l.	—	—	—	0.09
PbO	—	—	—	b.d.l.	—	7.03	—	b.d.l.	b.d.l.	—	1.12	—	—	0.17	b.d.l.	0.19	—	b.d.l.	—
Bi ₂ O ₃	—	—	—	—	—	—	b.d.l.	—	b.d.l.	—	—	b.d.l.	—	0.12	—	—	—	—	—
ThO ₂	5.50	6.22	7.94	8.00	13.62	1.05	0.05	14.95	10.15	9.13	0.44	5.41	2.94	3.88	11.68	4.54	9.29	18.37	6.32
Al ₂ O ₃	31.39	31.81	25.12	26.88	17.01	35.20	38.24	21.45	22.86	25.11	34.71	32.14	32.18	28.89	23.00	26.74	25.84	14.22	30.92
Fe ₂ O ₃	11.63	15.13	15.31	13.35	27.92	2.01	0.71	21.26	18.49	20.47	2.36	10.67	4.29	8.66	16.79	14.94	19.12	31.81	12.70
SiO ₂	0.80	0.61	0.79	0.85	2.20	0.17	0.11	1.39	0.74	1.22	0.21	0.43	3.34	0.25	0.70	0.40	1.32	2.18	0.97
P ₂ O ₅	16.68	21.26	16.76	16.83	11.69	21.39	31.67	14.94	15.49	16.44	24.88	21.42	21.36	21.98	15.34	18.82	15.86	10.06	18.23
SO ₃	2.42	2.14	1.60	1.86	1.11	3.22	0.02	1.18	1.23	1.77	1.60	2.28	3.61	2.72	1.49	3.22	1.77	0.92	2.35
WO ₃	b.d.l.	—	b.d.l.	0.15	0.20	b.d.l.	—	b.d.l.	—	—	b.d.l.	b.d.l.	—	—	—	—	0.15	—	b.d.l.
ZrO ₂	n.a.	n.a.	n.a.	n.a.	n.a.	b.d.l.	b.d.l.	0.39	—	0.90	b.d.l.	b.d.l.	—	—	b.d.l.	—	1.36	1.77	—
Total	83.45	92.89	83.07	84.45	85.6	86.14	85.43	89.01	83.31	89.82	82.67	89.28	84.61	83.41	83.55	84.73	89.18	89.42	88.39

1/1–18/1 – crandallite grains from organics veinlet; 1/2–10/2 – crandallite grains disseminated in boehmite; n.a. = not analysed; b.d.l. = below detection limit

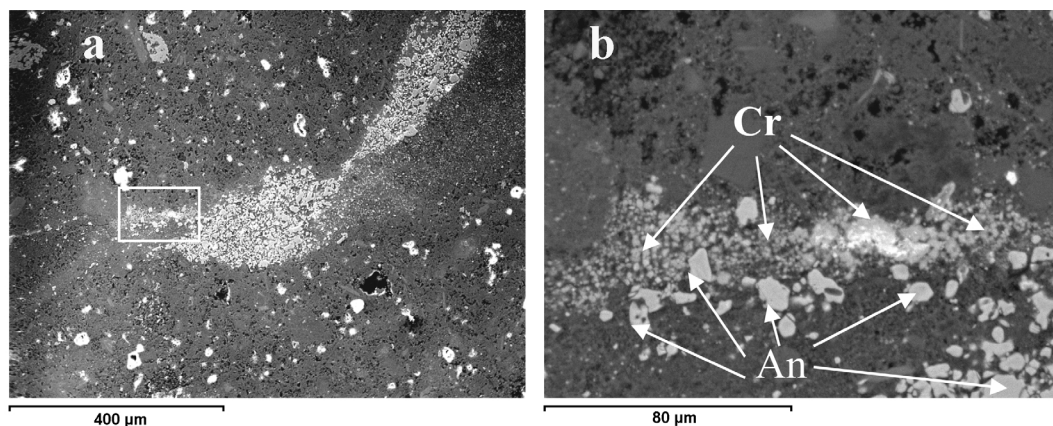
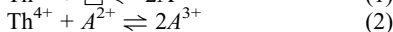
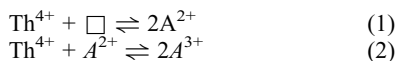


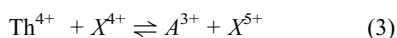
FIG. 2. Backscattered electron images (BSEI) of Th-crandallite mineralization in a boehmitic bauxite: (a) view of organics-rich veinlet filled with anatase. The crandallite-rich area is marked with a rectangle; (b) enlarged rectangle from part a. An – anatase, Cr – Th crandallite.

well. Geochemical maps of elemental distribution in a relatively large crandallite grain surrounded by finely dispersed crystals (Fig. 3) show similarity in their distribution of three essential elements – P, Th and Fe, indicating the existence of a Th-rich mineral phase rather than a mixture of a few minerals.

Formula calculations of crandallite are problematic due to the occupation of *A* and *X* sites by elements which have a different oxidation state. In pure crandallite, charge compensation is achieved by the appearance of an extra proton, which is, according to Blount (1974), shared between two apical oxygen atoms from phosphorus tetrahedra. In gorceixite, the proton is bound to only one of them due to an increase of cell parameters (Radoslovich, 1982). There is no need for the extra proton in woodhouseite or florencite, as either S in the *X* site or REE in the *A* site provide the charge balance (Kato, 1971, 1990). However, these rules refer to endmembers, while in nature, crandallite composition is commonly much more complicated. With Th⁴⁺ going into the *A* site of the crandallite lattice, charge balance can be achieved by the following schemes of isomorphism:



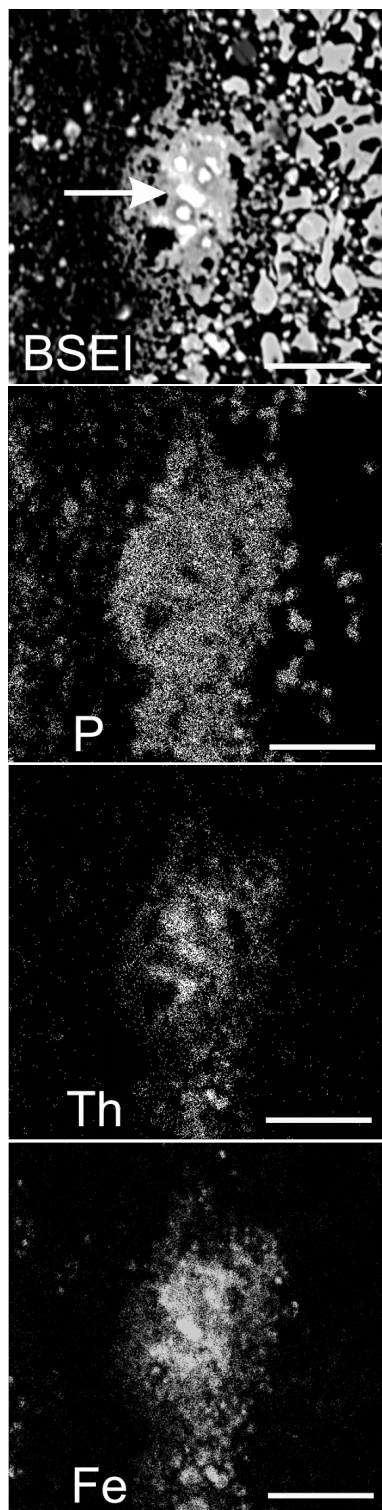
or



The substitution of the first type (1) can be regarded as crandallite-type substitution, since it

requires divalent cations such as Ca or Sr in the *A* site. The second type of substitution (2) can be observed in florencite, e.g. with Th and Ca or Sr substituting for two REE atoms. Thus, it can be referred to as florencite-type. The final case (3) demands complex substitution in the two sites, similar to $\text{Ca}^{2+} + \text{S}^{6+} \rightleftharpoons \text{REE}^{3+} + \text{P}^{5+}$ in woodhouseite. This is a woodhouseite-type substitution, which can occur, for instance, by Si⁴⁺ substituting for P⁵⁺ in the *X* site with REE or Bi in the *A* site. Following the classification of Burt (1989), the substitutions can be considered as substitutions involving cation vacancies (1), simple, within-site substitutions (2) and coupled substitutions involving cations with a tetrahedral second site (3).

The calculation of the crandallite formula is based on the assumption that the total number of oxygen atoms is 14. However, depending on the presence of an extra proton, the real statistical average number of oxygen atoms which are bound to cations may vary from 10.5 (a case of sharing an oxygen atom with a proton) to 11, and actually occur within this range. Thus, for formula calculations, an assumption should be made concerning the number of cations. Four possibilities can be considered: (1) the number of all cations is six; (2) the number of *A*-site cations is one; (3) the number of *B*-site cations is three; and (4) the number of *X*-site cations is two. Calculations have been made for all these assumptions. The assumption *X* = 2 gives a strong excess in both *A* and *B* sites, while the assumption *B* = 3 gives a corresponding



deficiency in both *A* and *X* sites. Also, a comparison of the analyses obtained in this study with published analyses of various “crandallites” (Nriagu, 1984) shows that the total of Al and Fe is somewhat higher than usual. Similar results were obtained using the assumption that the total number of cations is six, and for the assumption $A = 1$. Table 2 presents the data calculated for six total cations. It can be seen from the table that low-Th crandallites are closer to stoichiometry, while crandallite which contains more Th has poor stoichiometry. An excess of cations in the *B* site is typical, as well as a lack of cations in the *X* site. The former can be explained by the presence of nm-scale inclusions of boehmite and hematite. As for the *X* site in crandallite, this site is usually fully occupied. It is suggested that carbon may be present in the site, as organics surround the crandallite grains. However, the microprobe study was unable to prove this. Another suggestion is the removal of the *X*-site cations due to long-term radiation damage by Th.

The substitution (1) seems to be restricted, since no obvious deficiency is observed in the *A* site. The substitution (3) obviously occurs, as all the analyses show the presence of Si. However, the formula coefficient of Si is usually smaller than that of Th, and Ca and Sr dominate in the *A* site. This points to substitution (2) as the most likely to occur in the lattice.

Correlation analysis of element contents in crandallite (Fig. 4) illustrated a very strong positive correlation between Th and Fe ($R = +0.98$), as well as a very high negative correlation between Th and Al. The Fe and Al contents correlate negatively, which is understandable since they both occupy the same site. Also, of the two cations prevailing in the *A* site, Sr shows a positive correlation with S and a negative correlation with Ca, while the latter correlates with S negatively. This points indirectly to the existence of svanbergite-type cells (Sr in the *A* site and disordered P and S in the *X* site) and a florencite-type substitution (2) for Th and Ca.

FIG. 3. BSE image of a Th-crandallite grain and geochemical maps of elemental distribution. The arrow indicates an inclusion, probably the remnant of a Th-rich mineral from the parent rock. Roundish bright spots are points of microprobe analyses. The distribution of Th is not quite even, but follows the distribution of P and Fe. Scalebar: 50 μm .

TABLE 2. Formula coefficients (the number of cations is 6).

	1/1	2/1	3/1	4/1	5/1	9/1	10/1	13/1	16/1	17/1	18/1	1/2	2/2	3/2	4/2	5/2	6/2	7/2	8/2	9/2
Ca	0.40	0.43	0.47	0.48	0.39	0.36	0.90	0.42	0.42	0.39	0.65	0.43	0.42	0.49	0.51	0.46	0.42	0.41	0.39	0.43
Sr	0.42	0.36	0.42	0.45	0.34	0.31	0.04	0.36	0.41	0.39	0.19	0.37	0.44	0.42	0.40	0.42	0.43	0.38	0.28	0.43
Ba	0.04	0.04	0.05	0.05	0.04	0.04	0.02	0.04	0.04	0.04	0.03	0.05	0.04	0.04	0.06	0.05	0.04	0.04	0.03	0.05
REE	0.01	0.01	0.02	0.01	0.02	0.10	0.02	0.01	0.02	0.02	0.11	0.04	0.02	0.01	0.01	0.01	0.02	0.01	<0.01	0.02
Pb	<0.01	<0.01	<0.01	<0.01	<0.01	0.15	<0.01	<0.01	<0.01	<0.01	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Bi	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Th	0.10	0.10	0.15	0.15	0.28	0.02	<0.01	0.29	0.20	0.17	0.01	0.09	0.05	0.03	0.07	0.23	0.08	0.17	0.39	0.11
A	0.97	0.95	1.12	1.14	1.07	0.98	0.98	1.13	1.10	1.01	1.01	0.99	0.98	1.00	1.06	1.17	1.00	1.02	1.09	1.04
Fe	0.70	0.83	0.98	0.84	1.92	0.12	0.04	1.38	1.22	1.24	0.14	0.60	0.25	0.14	0.52	1.12	0.91	1.16	2.21	0.73
Al	2.98	2.74	2.52	2.64	1.83	3.25	3.11	2.18	2.36	2.38	3.12	2.85	2.90	2.97	2.72	2.39	2.55	2.45	1.55	2.80
B	3.68	3.57	3.50	3.48	3.75	3.37	3.14	3.55	3.58	3.61	3.25	3.46	3.15	3.11	3.24	3.51	3.45	3.61	3.75	3.54
Si	0.06	0.04	0.07	0.07	0.20	0.01	0.01	0.12	0.06	0.10	0.02	0.03	0.26	0.21	0.02	0.06	0.03	0.11	0.20	0.07
P	1.14	1.32	1.21	1.19	0.90	1.42	1.85	1.09	1.15	1.12	1.60	1.37	1.38	1.47	1.49	1.15	1.29	1.08	0.79	1.19
S	0.15	0.12	0.10	0.12	0.08	0.19	<0.01	0.08	0.08	0.11	0.09	0.13	0.21	0.19	0.16	0.10	0.20	0.11	0.06	0.14
V	<0.01	<0.01	<0.01	<0.01	0.01	0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01
W	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Zr	<0.01	<0.01	<0.01	<0.01	<0.01	0.02	0.02	0.03	0.02	0.05	0.02	0.02	0.02	0.02	0.02	0.01	0.02	0.07	0.09	0.02
X	1.35	1.48	1.38	1.38	1.19	1.65	1.88	1.32	1.32	1.37	1.73	1.55	1.87	1.89	1.69	1.33	1.54	1.37	1.15	1.42

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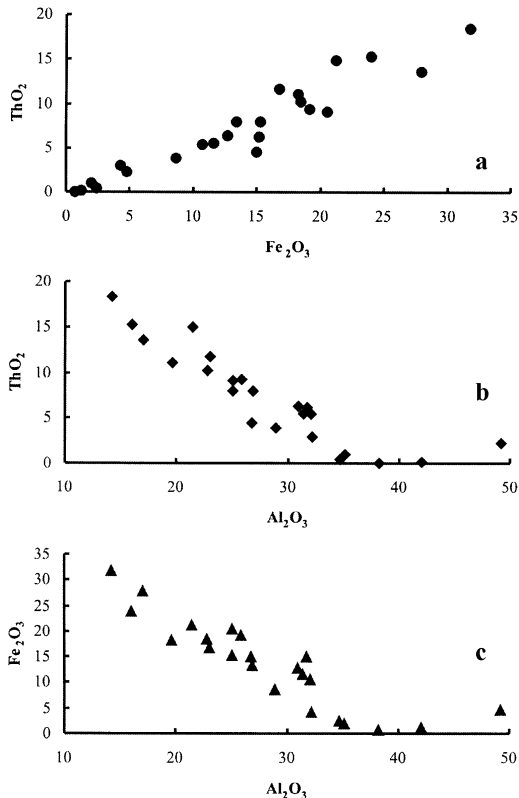


FIG. 4. Correlation plots of oxide concentrations in Th-crandallite: (a) ThO₂ vs. Fe₂O₃; (b) ThO₂ vs. Al₂O₃; (c) Fe₂O₃ vs. Al₂O₃.

From the point of view of ionic radii, Sr fits the *A* site of crandallite or woodhouseite much better than Ca (Schwab *et al.*, 1990, 1993). The ionic radius of tetravalent Th is smaller, but its ionic potential is higher, and this can play a stabilizing role, as was already shown for trivalent light rare earth elements (*LREE*) (Schwab *et al.*, 1993). Thus, both the large Sr ionic radius and the large Th valence may be factors which stabilize the crystal lattice. Such observations allow the proposal of the existence of a solid solution in which Th-rich crandallite has a formula



where $0 < X < 1$ and $1 < Y < 2$. However, a mineral of such composition has not yet been formally described.

Van Wambeke (1971) studied a mineral from Kobokobo pegmatite in Democratic Republic of

Congo and found it to be a Th-rich crandallite. He observed a deficiency in the *A* and *X* sites and explained it by leaching of Ca, Sr, Ba and Pb from the *A* site and replacement of PO₄ tetrahedra with an H₄O₄ group in the *X* site due to the weathering process. This explanation has not yet been confirmed. Unlike the observations of Van Wambeke, in the present case the *A* site seems to be filled completely without any deficiency. The lack of *X*-site elements can also be explained by the damage caused by the natural Th radioactivity, similar to the process which takes place in Th- or U-rich zircons.

The source of P for crandallite formation was apatite from the parent rock, while dolomite provided Sr and Ca (Mordberg *et al.*, 2000). Thorium mineralization was also observed in the parent rock. A Th mineral was discovered which has a composition corresponding to the simplified formula Fe²⁺ThSiO₄(OH)₂ (Mordberg *et al.*, 2001); however, such a mineral does not appear to have been formally characterized. From back-scattered electron images of the mineral (Fig. 5), it can be seen that it is surrounded by Fe oxide minerals and sometimes by pyrite. It seems very likely that Th-crandallite was formed *in situ* as a result of metasomatic replacement of that mineral, since Th is known to be an element of restricted mobility in the weathering environment.

Conclusions

The first occurrence of Th-rich crandallite formed in a supergene environment is reported. The formula coefficient of Th attains 0.39, and it is always less than that of Ca and Sr together. This suggests that the crystal lattice may be of florencite type with a possible isomorphism scheme $2\text{REE} \rightleftharpoons \text{Th}^{4+} + \text{Ca}^{2+}$, and it is Sr which stabilizes the crystal lattice. A certain 'woodhouseite-type' substitution such as $\text{Th}^{2+} + \text{Si}^{4+} \rightleftharpoons \text{REE}^{3+} + \text{P}^{5+}$ also took place.

It is expected that Th-rich crandallites of complicated compositions containing elements such as Ba, Sr and Pb, may be found in other localities, especially in weathering profiles over alkaline rocks, although the appearance of pure Th-crandallite seems to be unlikely.

The possibility of strong Th accumulation in the *A* site of crandallite could increase the importance of crandallite-group minerals with respect to the problem of capturing nuclear elements and their fission products in a waste disposal environment.

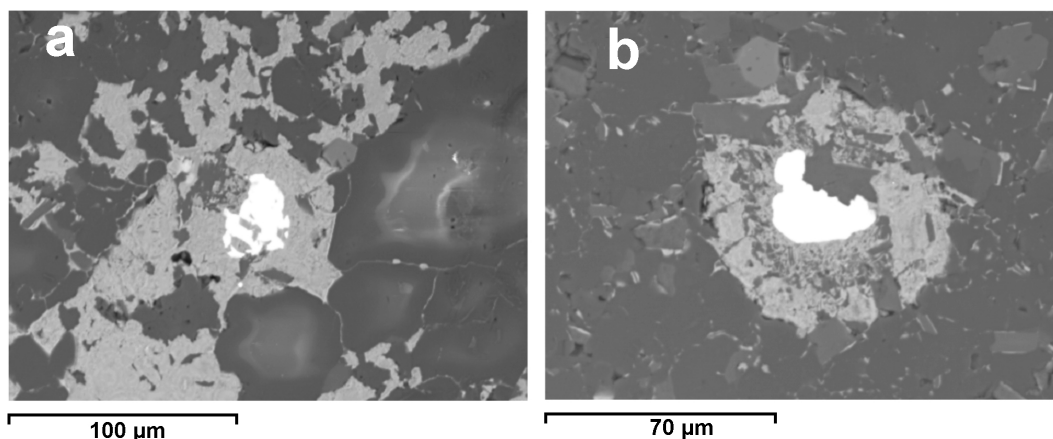


FIG. 5. BSE images of an unidentified Th mineral from the parent rock (bright) surrounded by Fe oxides (grey) in carbonate and feldspar matrix (dark).

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References

- Bárdossy, Gy. (1982) *Karst Bauxites. Bauxite Deposits on Carbonate Rocks*. Elsevier, Amsterdam, 441 pp.
- Beneslavsky, S.I. (1974) *Mineralogy of Bauxites*, 2nd edition. Nedra, Moscow, 133 pp. (in Russian).
- Blount, A.M. (1974) The crystal structure of crandallite. *American Mineralogist*, **59**, 41–47.
- Burt, D.M. (1989) Compositional and phase relations among rare earth minerals. Pp. 259–308 in: *Geochemistry and Mineralogy of Rare Earth Elements* (B.R. Lipin and G.R. McKay, editors). Reviews in Mineralogy, **21**. Mineralogical Society of America, Washington, D.C.
- Dill, H.G. (2001) The geology of aluminium phosphates and sulphates of the alunite group minerals: a review. *Earth-Science Reviews*, **53**, 35–93.
- Gaines, R.V., Skinner, H.C.W., Foord, E.E. and Mason, B. (1997) *Dana's New Mineralogy: The System of Mineralogy of James Dwight Dana and Edward Salisbury Dana*, 8th edition. J. Wiley & Sons, New York, 1819 pp.
- Huminicki, D.M.C. and Hawthorne, F.C. (2002) The crystal chemistry of the phosphate minerals. Pp. 123–254. in: *Phosphates – Geochemical, Geobiological and Materials Importance* (M.L. Kohn, J. Rakovan and J.M. Hughes, editors). Reviews in Mineralogy & Geochemistry, **48**. Mineralogical Society of America, Washington, D.C.
- Kato, T. (1971) The crystal structures of goyazite and woodhouseite. *Neues Jahrbuch für Mineralogie Monatshefte*, 241–247.
- Kato, T. (1990) The crystal structure of florencite. *Neues Jahrbuch für Mineralogie Monatshefte*, 227–231.
- Kolitsch, U., Tiekling, E.R.T., Slade, P.G., Taylor, M.R. and Pring, A. (1999) Hinsdallite and plumbogummite, their atomic arrangements and disordered lead sites. *European Journal of Mineralogy*, **11**, 513–520.
- Likhachev, V.V. (1993) *Rare-metal Bauxite-bearing Weathering Crust of the Middle Timan*. Komi Nauchnu zentr UrO RAN, Syktyvkar, Russia, 224 pp. (in Russian).
- Mordberg, L.E., Stanley, C.J. and Germann, K. (2000) Rare earth element anomalies in crandallite group minerals from the Schugorsk bauxite deposit, Timan, Russia. *European Journal of Mineralogy*, **12**, 1229–1243.
- Mordberg, L.E., Stanley, C.J. and Germann, K. (2001) Mineralogy and geochemistry of trace elements in bauxites: the Devonian Timan deposit, Russia. *Mineralogical Magazine*, **65**, 81–101.
- Nriagu, J.O. (1984) Phosphate Minerals: their properties and general mode of occurrence. Pp. 1–136 in: *Phosphate Minerals* (J.O. Nriagu and P.B. Moore, editors). Springer-Verlag, Berlin.

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- Radoslovich, E.W. (1982) Refinement of gorceixite structure in Cm. *Neues Jahrbuch für Mineralogie Monatshefte*, 446–464.
- Schwab, R.G., Götz, C., Herold, H. and Oliveira, N.P. de (1990) Compounds of crandallite type: Synthesis and properties of pure Rare Earth Element-phosphates. *Neues Jahrbuch für Mineralogie Monatshefte*, 241–254.
- Schwab, R.G., Götz, C., Herold, H. and Oliveira, N.P. de (1993) Compounds of crandallite type: Thermodynamics properties of Ca-, Sr-, Ba-, Pb-, La-, Ce- to Gd-phosphates and -arsenates. *Neues Jahrbuch für Mineralogie Monatshefte*, 551–568.
- Van Wambeke, L. (1971) The problem of cation deficiencies in some phosphates due to alteration processes. *American Mineralogist*, **56**, 1366–1384.
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