

## FLUORNATROPYROCHLORE, A NEW PYROCHLORE SUPERGROUP MINERAL FROM THE BOZIGUOER RARE EARTH ELEMENT DEPOSIT, BAICHENG COUNTY, AKESU, XINJIANG, CHINA

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### ABSTRACT

Fluornatropyrochlore is a new pyrochlore supergroup mineral species found in the intrusive alkali granite of the Boziguoer rare earth element deposit in Baicheng County, Akesu, Xinjiang Autonomous Region, China. This new mineral is found to be closely associated with microcline, albite, aegirine, a sodic amphibole, biotite, zircon, rutile, thorite, fluorite, fluocerite-(Ce), columbite-(Fe), xenotime-(Y), astrophyllite, chevkinite-(Ce), and fergusonite-(Y). Fluornatropyrochlore occurs mostly as anhedral crystals, rarely as subhedral grains, with a grain size of 0.02 to 0.25 mm. The color is brownish yellow to reddish orange. Other physical properties are: brittle, translucent to transparent, non-fluorescent, adamantine luster, light yellow streak, with Mohs hardness 4–4½, and calculated density 5.275 g cm<sup>-3</sup>. Fluornatropyrochlore is isotropic,  $n = 2.10(5)$  (589.9 nm). It has a cubic crystal structure, with unit-cell parameters determined using single-crystal X-ray diffraction as:  $a$  10.5053(10) Å,  $V$  1159.4(2) Å<sup>3</sup>,  $Z = 8$ , space group  $Fd\bar{3}m$ . The strongest ten X-ray diffraction (XRD) peaks in the powder XRD pattern are [ $d$  in Å( $hkl$ ): 6.0741(3)(111), 3.0416(100)(222), 2.6280(38)(004), 1.8568(34)(044), 1.5820(15)(226), 1.5148(4)(444), 1.3137(2)(008), 1.2045(3)(266), 1.1726(2)(048), and 1.0712(1)(448)]. Chemical analyses by a combination of electron microprobe, Fourier transform infrared spectroscopy (FTIR), and single crystal-structure refinement give its chemical composition as: Na<sub>2</sub>O 6.80, K<sub>2</sub>O 0.01, CaO 2.01, MgO 0.01, FeO 0.05, SrO 0.03, PbO 16.17, Ce<sub>2</sub>O<sub>3</sub> 4.29, La<sub>2</sub>O<sub>3</sub> 1.65, Nd<sub>2</sub>O<sub>3</sub> 0.41, Y<sub>2</sub>O<sub>3</sub> 0.42, SiO<sub>2</sub> 0.03, TiO<sub>2</sub> 1.36, UO<sub>2</sub> 5.81, Ta<sub>2</sub>O<sub>5</sub> 3.00, Nb<sub>2</sub>O<sub>5</sub> 53.42, F 3.19, Cl 0.02, ThO<sub>2</sub>, Sb<sub>2</sub>O<sub>5</sub> 0.01, ZrO<sub>2</sub> 0.01, MnO 0.04, SnO<sub>2</sub> 0.34, H<sub>2</sub>O not detected, with a sum of 98.21 wt.%. The empirical formula derived from its averaged composition is (Na<sub>1.03</sub>Pb<sub>0.34</sub>Ca<sub>0.17</sub>U<sub>0.10</sub>Th<sub>0.01</sub>Ce<sub>0.12</sub>La<sub>0.05</sub>Y<sub>0.02</sub>Nd<sub>0.01</sub>)<sub>Σ1.85</sub>(Nb<sub>1.88</sub>Ti<sub>0.08</sub>Ta<sub>0.06</sub>Sn<sub>0.01</sub>)<sub>Σ2.03</sub>O<sub>6.21</sub>F<sub>0.79</sub> based on 7 anions per formula unit. The crystal structure was refined to an  $R$  index of 0.053 using *MoKa* X-ray intensity data. Site-scattering refinement analysis shows that the new mineral is characterized by F dominance at the  $Y$  site, Na dominance at the  $A$  site, and Nb dominance at the  $B$  site, based on the overall electroneutrality requirement of the structural formula.

**Keywords:** Fluornatropyrochlore, new mineral, pyrochlore supergroup, electron microprobe data, single-crystal X-ray diffraction, Boziguoer rare earth element deposit, Baicheng County, Akesu, Xinjiang, China.

### INTRODUCTION

After searching the mineral data base, no minerals with a crystal structure similar to fluornatropyrochlore

as defined in this study were found in the lists of published unnamed minerals (Smith & Nickel 2007). Atencio *et al.* (2010) noted that fluornatropyrochlore was studied by P.M. Kartashov, but the data remain

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unpublished. The status of this mineral prior to this study was a possible new species (Christy & Atencio 2013). This study is the first full description of a natural occurrence of fluornatropyrochlore, discovered in the Boziguoer rare earth element deposit, Baicheng County, Akesu, Xinjiang Autonomous Region, China. A combination of polarizing microscopy, electron-microprobe, X-ray diffraction, and FTIR techniques were employed to determine its petrographic properties, chemical composition, spectral properties, and crystal structure. The new species and mineral name have been approved by the International Mineralogical Association Commission on New Minerals and Mineral Names, Nomenclature and Classification (CNMNC) (IMA 2013-056). Holotype materials, including the polished thin section used for microprobe analyses, the single crystal used for crystal structure analysis, and a macro-crystal of fluornatropyrochlore, have been deposited in the Geological Museum of China, Beijing, China, and added into the collection catalog with the sample number M12183.

#### OCCURRENCE AND ASSOCIATED MINERALS

Fluornatropyrochlore was found in the alkaline intrusive rocks (Type-A granitoids) of the Boziguoer rare earth element deposit, Baicheng County, Akesu, Xinjiang, China, about 43 km north of Baicheng County City (42°13'14"N 81°54'29"E), Xinjiang Autonomous Region, China. The alkaline intrusive rocks occur as an EW-trending bedding invasion into the Silurian marble of the Qiongkushitai Formation (Chen *et al.* 2002, Liu *et al.* 2004); the igneous intrusion played an important role in Nb-Ta mineralization and contributed to the high content of rubidium, uranium, thorium, zirconium, and rare earth elements (Xu *et al.* 2010). The intrusive body may be divided into two mining districts (eastern and western) which formed at different times. The petrographic and mineralogical characteristics of the alkaline intrusive rocks have been well documented in previous studies (Liu *et al.* 2012, Yin *et al.* 2013). The Boziguoer Type-A granitoid is a Nb, Ta, and rare earth element-rich plutonic rock (Shao *et al.* 2011).

There are different mineral parageneses in the two mine areas. As accessory minerals, xenotime-(Y), chevkinite-(Ce), and fergusonite-(Y) are mainly found in aegirine granite in the western mining area, and thorite and columbite-(Fe) are mainly found in a biotite adamellite in the eastern mining area. However, fluornatropyrochlore, together with astrophyllite, zircon, fluorite, fluocerite-(Ce), and monazite, are commonly found in both of the mining areas. Other common minerals are microcline, albite, anorthite, quartz, aegirine, a sodic amphibole, biotite, rutile, fluorite, and niobite. Fluornatropyrochlore mainly occurs in a niobium-tantalum-rich alkali-syenite deposit.

#### PHYSICAL AND OPTICAL PROPERTIES

The fluornatropyrochlore crystals are mostly allotriomorphic, however in rare cases they also occur as sub-hedral grains, with sizes ranging from 0.02 to 0.25 mm (Fig. 1). The mineral is brownish yellow to reddish orange in color with a light yellow streak, translucent to transparent with adamantine luster, and it does not fluoresce under ultraviolet light. No cleavage or parting were observed. With a Mohs hardness of 4–4½, fluornatropyrochlore is brittle with a conchoidal fracture. The calculated density of this new mineral, based on the empirical formula and single-crystal unit-cell parameters, is 5.275 g/cm<sup>3</sup>. Optical properties were measured at a wavelength 589.9 nm using a GEM-A REF0006 refractometer. Fluornatropyrochlore appears to be isotropic with a refractive index  $n = 2.10(5)$ . Based on the calculated density and measured refractive index, the compatibility index [ $1 - (K_p/K_C)$ ] is 0.015, which corresponds to the “superior” category (Mandarino 1981).

#### CHEMICAL COMPOSITION

In order to determine the chemical composition of the new mineral, a JEOL JXA-8100M electron microprobe at the Institute of Geology and Geophysics, Chinese Academy of Sciences was employed using the following operating conditions: wavelength-dispersive mode, excitation voltage 20 kV, specimen current 10 nA, peak-count time 20 s, background-count time 10 s, and 2 µm beam diameter. The analyzing standards and crystals used for the calibration of the microprobe analyses are given in Table 1. The microprobe data were calibrated and corrected using a ZAF-type correction procedure and 10 microprobe analyses from two single grains are given in Table 1. BaO, Al<sub>2</sub>O<sub>3</sub>, and P<sub>2</sub>O<sub>5</sub> were found to be below the detection limit of 0.01 wt.%. The empirical formula was calculated on the basis of 7 anions per formula unit (*apfu*),



Fig. 1. Crystals of fluornatropyrochlore up to 0.25 mm in size.

TABLE 1. ELECTRON MICROPROBE DATA OF FLUORNATOPYROCHLORE

Constituent	wt. %	Range	SD	EMP standard
Na <sub>2</sub> O	6.80	3.33–9.30	1.57	albite
K <sub>2</sub> O	0.01	0.00–0.04	0.01	sanidine
CaO	2.01	1.69–2.22	0.16	CaSiO <sub>3</sub>
MgO	0.01	0.00–0.05	0.02	almandine
FeO	0.05	0.00–0.15	0.05	Synth-Fe
SrO	0.03	0.00–0.11	0.04	celestine
PbO	16.17	14.75–18.77	1.19	PbCrO <sub>4</sub>
Ce <sub>2</sub> O <sub>3</sub>	4.29	3.76–5.41	0.49	monazite
La <sub>2</sub> O <sub>3</sub>	1.65	1.37–1.93	0.17	monazite
Nd <sub>2</sub> O <sub>3</sub>	0.41	0.00–0.62	0.18	monazite
Y <sub>2</sub> O <sub>3</sub>	0.42	0.17–0.67	0.16	Y <sub>3</sub> Al <sub>5</sub> O <sub>12</sub>
SiO <sub>2</sub>	0.03	0.00–0.09	0.03	tuhualite
TiO <sub>2</sub>	1.36	0.72–1.91	0.33	rutile
UO <sub>2</sub>	5.81	4.21–7.36	1.01	Metal U
Ta <sub>2</sub> O <sub>5</sub>	3.00	1.33–4.00	1.03	tantalite-(Mn)
Nb <sub>2</sub> O <sub>5</sub>	53.42	51.71–56.16	1.43	monazite
F	3.19	2.33–4.12	0.64	fluorapatite
Cl	0.02	0.00–0.06	0.02	tuhualite
ThO <sub>2</sub>	0.48	0.13–1.41	0.39	ThO <sub>2</sub>
Sb <sub>2</sub> O <sub>5</sub>	0.01	0.00–0.07	0.02	Sb <sub>2</sub> Te <sub>3</sub>
ZrO <sub>2</sub>	0.01	0.00–0.13	0.04	ZrO <sub>2</sub>
MnO	0.04	0.00–0.11	0.05	MnSiO <sub>3</sub>
SnO <sub>2</sub>	0.34	0.23–0.41	0.06	SnO <sub>2</sub>
O = F, Cl	–1.35			
Total	98.21			

as indicated by crystal-structure solution and refinement (see later sections), giving a formula of (Na<sub>1.03</sub>Pb<sub>0.34</sub>Ca<sub>0.17</sub>U<sub>0.10</sub>Th<sub>0.01</sub>Ce<sub>0.12</sub>La<sub>0.05</sub>Y<sub>0.02</sub>Nd<sub>0.01</sub>)<sub>Σ1.85</sub>(Nb<sub>1.88</sub>Ti<sub>0.08</sub>Ta<sub>0.06</sub>Sn<sub>0.01</sub>)<sub>Σ2.03</sub>O<sub>6.21</sub>F<sub>0.79</sub>, which can be grouped and consolidated and further simplified to (Na, Pb, Ca, REE, U)<sub>2</sub>Nb<sub>2</sub>O<sub>6</sub>F.

In addition, Fourier transform infrared spectroscopy (FTIR) analysis of fluornatopyrochlore shows the total absence of bands of O–H stretching vibrations (2900–3700 cm<sup>-1</sup>) and H–O–H bending vibrations of H<sub>2</sub>O molecules (1640 and 1620 cm<sup>-1</sup>) in the sample studied (Fig. 2), with only a single peak at ~931 cm<sup>-1</sup>.

## X-RAY CRYSTALLOGRAPHY RESULTS

### Powder X-ray data

The powder X-ray diffraction (XRD) pattern of fluornatopyrochlore was acquired using a Bruker AXS SMART APEX single-crystal diffractometer equipped with a Charge-Coupled Device (CCD) detector followed the method as described by Li *et al.* (2005) at the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences (Beijing). Powder XRD data acquired with graphite monochromatized MoK $\alpha$  X-radiation

( $\lambda = 0.71073\text{\AA}$ ) are listed in Table 2. XRD peak intensities were measured with an automated densitometer and the pattern was indexed on the basis of the powder spectra calculated from the results of the crystal structural study (see below). The indexed powder diffraction data and estimated standard deviation for the observed *d*-values for this mineral are also listed in Table 2. The 10 strongest lines of the X-ray powder-diffraction pattern [*d* in  $\text{\AA}(I)(hkl)$ ] are: 6.0741(3) (111), 3.0416(100)(222), 2.6280(38)(004), 1.8568(34) (044), 1.5820(15)(226), 1.5148(4)(444), 1.3137(2)(008), 1.2045(3)(266), 1.1726(2)(048), and 1.0712(1)(448).

### Single-crystal X-ray results and structure refinement

A single-crystal X-ray diffraction analysis was also performed, using the same diffractometer as above, to determine the crystal structural of fluornatopyrochlore, with operating conditions of 45 kV and 35 mA. A hemisphere of single-crystal XRD data was collected using graphite-monochromatized MoK $\alpha$  ( $\lambda = 0.71073\text{\AA}$ ) radiation and frame widths of 0.3° in  $\omega$ , with 10 s per frame exposure time. The data were collected at room temperature. The crystal structure was then derived by direct analytical methods, and the structure refinement was conducted using the SHELXTL PC (Bruker AXS Inc.) package. A subset

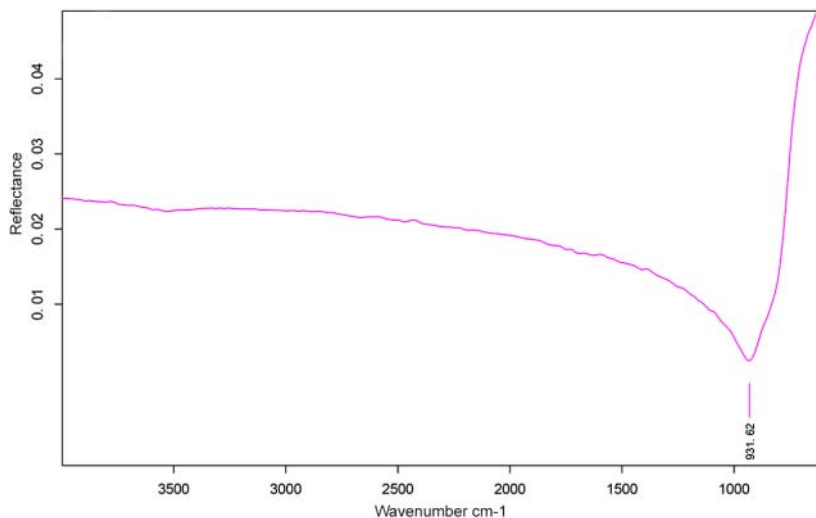


FIG. 2. The IR spectrum of fluornatropyrochlore.

TABLE 2. X-RAY POWDER DIFFRACTION DATA FOR FLUORNATROPYROCHLORE

<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> <sub>obs</sub>	<i>d</i> <sub>calc</sub>	<i>I</i> / <i>I</i> <sub>0</sub>
1	1	1	<b>6.0741</b>	<b>6.0652</b>	<b>3</b>
2	2	2	<b>3.0416</b>	<b>3.0326</b>	<b>100</b>
0	0	4	<b>2.6280</b>	<b>15.553</b>	<b>38</b>
0	4	4	<b>1.8568</b>	<b>1.8571</b>	<b>34</b>
2	2	6	<b>1.5820</b>	<b>1.5837</b>	<b>15</b>
4	4	4	<b>1.5148</b>	<b>1.5163</b>	<b>4</b>
0	0	8	<b>1.3137</b>	<b>1.3132</b>	<b>2</b>
2	6	6	<b>1.2045</b>	<b>1.2050</b>	<b>3</b>
0	4	8	1.1726	1.1745	2
4	4	8	1.0712	1.0722	1

of reflections accounting for nearly half of the total number of reflections was identified and found to obey a single orientation matrix and gave a cubic unit cell with *a* 10.5053(10), *V* 1159.4(2) Å<sup>3</sup>, *Z* = 8, which gives space group *Fd* $\bar{3}$ *m*. The structure refinement was performed with anisotropic-displacement

parameters for all atoms. The final conventional *R*<sub>1</sub> factor [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.053. Atomic coordinates and anisotropic displacement parameters, as well as selected bond distances and angles, are given in Tables 3, 4, and 5. Observed and calculated structure-factors tables may be obtained from the Depository of Unpublished Data on the MAC web site [document Brontesite CM53-3\_10.3749/canmin.1500007].

## DISCUSSION

Chemical compositions, X-ray diffraction, crystal structure, and ion-occupied sites are all important factors for mineral identification and classification. As a new member of the pyrochlore supergroup as identified in this study, fluornatropyrochlore occurs in a niobium-tantalum-rich alkali-syenite type deposit and differs from all known species of the pyrochlore supergroup minerals. The general formula of the pyrochlore supergroup minerals is *A*<sub>2-*m*</sub>*B*<sub>2</sub>*X*<sub>6-*w*</sub>*Y*<sub>1-*n*</sub>, where *m* = 0 to 1.7, *w* = 0 to 0.7, *n* = 0 to 1 (Lumpkin & Ewing 1995). Two prefixes in pyrochlore-supergroup species names are required

TABLE 3. FINAL ATOM COORDINATES FOR FLUORNATROPYROCHLORE

Atom	Occ.	Occ.	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Na1	16c	0.763	1/4	1/2	3/4
Pb1	16c	0.237	1/4	1/2	3/4
Nb1	16d		0	1/2	0
O1	48f		1/8	5/8	0.9333(10)
F1	8a		3/8	3/8	7/8

TABLE 4. ANISOTROPIC DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ ) FOR FLUORNATROPYROCHLORE

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Na1	0.0303(11)	0.0303(11)	0.0303(11)	0.0010(8)	-0.0010(8)	0.0010(8)
Pb1	0.0303(11)	0.0303(11)	0.0303(11)	0.0010(8)	-0.0010(8)	0.0010(8)
Nb1	0.0182(5)	0.0182(5)	0.0182(5)	-0.0021(4)	-0.0021(4)	-0.0021(4)
O1	0.024(3)	0.024(3)	0.028(5)	-0.010(4)	0.00000	0.00000
F1	0.056(8)	0.056(8)	0.056(8)	0.00000	0.00000	0.00000

 TABLE 5. SELECTED GEOMETRIC PARAMETERS ( $\text{\AA}$ ,  $^\circ$ )

Na1-F1	2.2745(2)	Nb1-O1	1.985(4)
Na1-O1	2.675(8)		
F1-Na1-O1	98.71(16)	Nb1-O1-Na1	104.72(1)

according to Atencio *et al.* (2010); the first prefix indicates the dominant species of the dominant valence at the *Y* sites, and the second prefix indicates the dominant species of the dominant valency at the *A* site. In this particular case, the *Y* site is dominated by F and the *A* site is dominated by Na. In addition, the *B* site is dominated by Nb.

The crystal structure of fluornatropyrochlore is characterized by edge-shared  $[\text{NdO}_6]$  octahedra forming a chain along the  $[110]$  direction, whilst a corner-shared  $[\text{NdO}_6]$  octahedra forms a three-dimensional cage, with Na atoms occupying the center of the cage formed by six O and two F, and edge-shares  $[\text{NdO}_6]$  octahedra and  $[\text{NaO}_6\text{F}_2]$  cubic polyhedra as shown in Figure 3. The Na and Nb cations occupy the  $16c$  and  $16d$  sites respectively, whilst O and F occupy the  $48f$  and  $8a$  sites, respectively (see Table 3). The Nb cation is surrounded by six O atoms in an octahedron and the Na cation is in a cubic polyhedron formed by two F and six O atoms. The six O atoms form a puckered hexagonal ring, while two F atoms are probably in linear coordination. The F-Na-F angle

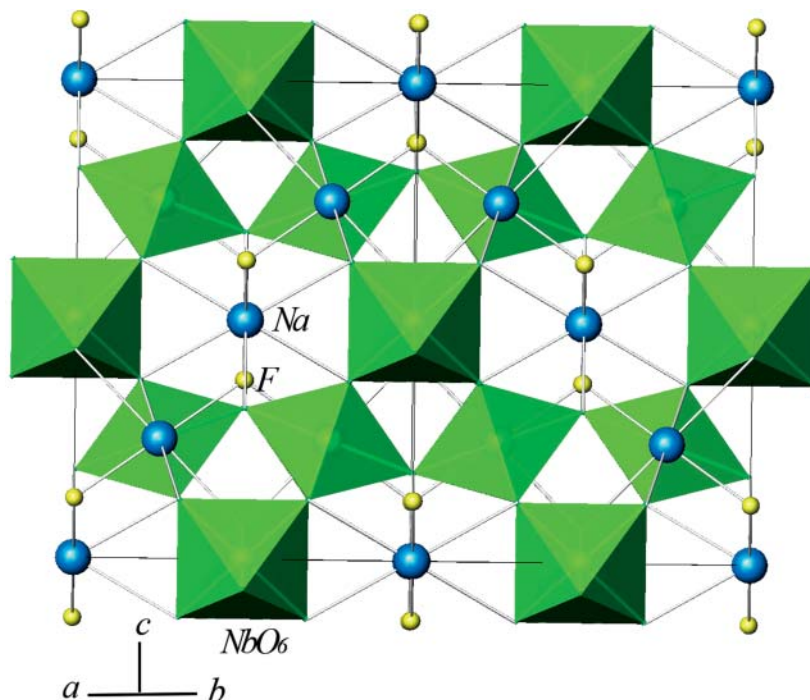


FIG. 3. The crystal structure of fluornatropyrochlore.

appears to be 180°. The Na–O and Na–F bond distances are different.

#### ACKNOWLEDGMENTS

Financial support for this study was provided by a NSF grant of China (Grant No. 41172052) and the Institute of Mineral Resources, Chinese Academy of Geological Sciences (Grant No. 3-4-2011-166-A). This manuscript has been improved by constructive comments from two referees, Dr. Daniel Atencio and Dr. Wei Sun as well as the Editor, Yuanming Pan. This manuscript has also benefited from the comments and suggestions of Dr. Zhongsheng Li of the Commonwealth Scientific and Industrial Research Organization, Australia.

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Received January 11, 2015, revised manuscript accepted June 3, 2015.