

Mianningite, $(\square, \text{Pb}, \text{Ce}, \text{Na})(\text{U}^{4+}, \text{Mn}, \text{U}^{6+})\text{Fe}^{3+}_2(\text{Ti}, \text{Fe}^{3+})_{18}\text{O}_{38}$, a new member of the crichtonite group from Maoniuping REE deposit, Mianning county, southwest Sichuan, China

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Abstract: Mianningite (IMA 2014-072), ideally $(\square, \text{Pb}, \text{Ce}, \text{Na})(\text{U}^{4+}, \text{Mn}, \text{U}^{6+})\text{Fe}^{3+}_2(\text{Ti}, \text{Fe}^{3+})_{18}\text{O}_{38}$, is a new member of the crichtonite group from the Maoniuping REE deposit, Mianning county, Sichuan province, China. It was found in fractures of lamprophyre veins and in the contact between lamprophyre and a later quartz–alkali feldspar syenite dyke with REE mineralization, and is named after its type locality. Associated minerals are microcline, albite, quartz, iron-rich phlogopite, augite, muscovite, calcite, baryte, fluorite, epidote, pyrite, magnetite, hematite, galena, hydroxylapatite, titanite, ilmenite, rutile, garnet-group minerals, zircon, allanite-(Ce), monazite-(Ce), bastnäsite-(Ce), parisite-(Ce), maoniupingite-(Ce), thorite, pyrochlore-group minerals and chlorite. Mianningite occurs as opaque subhedral to euhedral tabular crystals, up to 1–2 mm in size, black in color and streak, and with a submetallic luster. Mianningite is brittle, with a conchoidal fracture. Its average micro-indentation hardness is 83.8 kg/mm² (load 0.2 kg), which is equivalent to ~6 on the Mohs hardness scale. Its measured and calculated densities are 4.62 (8) g/cm³ and 4.77 g/cm³, respectively. Under reflected light, mianningite is grayish white, with no internal reflections. It appears isotropic and exhibits neither birefractance nor pleochroism. The empirical formula, calculated on the basis of 38 O atoms per formula unit (*apfu*), is $[\square_{0.322}(\text{Pb}_{0.215}\text{Ba}_{0.037}\text{Sr}_{0.036}\text{Ca}_{0.010})_{\Sigma 0.298}(\text{Ce}_{0.128}\text{La}_{0.077}\text{Nd}_{0.012})_{\Sigma 0.217}(\text{Na}_{0.127}\text{K}_{0.036})_{\Sigma 0.163}]_{\Sigma 1.000}(\text{U}^{4+}_{0.447}\text{Mn}_{0.293}\text{U}^{6+}_{0.112}\text{Y}_{0.091}\text{Zr}_{0.023}\text{Th}_{0.011})_{\Sigma 0.977}(\text{Fe}^{3+}_{1.224}\text{Fe}^{2+}_{0.243}\text{Mg}_{0.023}\text{P}_{0.008}\text{Si}_{0.006}\square_{0.496})_{\Sigma 2.000}(\text{Ti}_{12.464}\text{Fe}^{3+}_{5.292}\text{V}^{5+}_{0.118}\text{Nb}_{0.083}\text{Al}_{0.026}\text{Cr}^{3+}_{0.017})_{\Sigma 18.000}\text{O}_{38}$. Mianningite is trigonal, belongs to the space group $R\bar{3}$, and has unit-cell parameters $a = 10.3462(5)$ Å, $c = 20.837(2)$ Å, $V = 1931.65$ (20) Å³, and $Z = 3$. The structure was solved ($R_1 = 0.070$) using reflections with $I > 2\sigma(I)$ on a heated crystal; it is isostructural with the other members of the crichtonite group. Mianningite can be considered as the analogue of mapiquiroite with the M0 site preferentially vacant. Its eight strongest X-ray powder-diffraction lines [d in Å(hkl)] are 2.627(100) (125), 2.144 (100) (135), 3.065(75) (025), 2.254 (70) (028), 1.545(60) (336), 2.883(55) (116), 2.476 (55) (027), and 1.705 (55) (146).

Key-words: mianningite; new mineral; Maoniuping REE deposit; crichtonite group; chemical composition; XPS; crystal structure; vacancy; lead uranium iron titanate.

1. Introduction

The Maoniuping deposit is located in Mianning county, Sichuan province, China, and is the third largest REE super-deposit in the world after the Bayan Obo deposit, China, and the Mountain Pass deposit, USA (Yang *et al.*, 2000, 2001). Recently, two new minerals, *i.e.*, maoniupingite-(Ce) (Shen *et al.*, 2005) and hydroxycalcio-pyrochlore (Yang *et al.*, 2014), were discovered in this deposit. More recently, mianningite was also discovered there.

Since the end of the 1970s, Wei (1979), Zhao *et al.* (1988), and Zhang *et al.* (1995) described davidite, a member of the crichtonite group from the Baozi Hill, near the Maoniuping REE deposit, on the basis of powder X-ray diffraction and wet chemical analysis. About 30 mg of a sample collected nearly 40 years ago by Chen Zhangru has

been used to investigate this mineral. The results of our study indicate that “davidite” from the Baozi Hill should be considered as a new mineral species within the crichtonite group.

The new mineral and its name mianningite have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA CNMNC) (ref. IMA 2014-072). The mineral was named after its type locality, and co-type material has been deposited in the Geological Museum of China (catalog no. M12189).

2. Occurrence

Mianningite was discovered in fractures within lamprophyre veins and the contact zones between lamprophyre and a later quartz–alkali feldspar syenite dyke with REE,

uranium and thorium mineralization in Baozi Hill near the well-known Maoniuping *REE* mine, Mianning county, Sichuan province, China (28°24'20"N, 101°59'3"E). The mineral is associated with microcline, albite, quartz, iron-rich phlogopite, augite, muscovite, calcite, baryte, fluorite, epidote, pyrite, magnetite, hematite, galena, hydroxylapatite, titanite, ilmenite, rutile, garnet-group minerals, zircon, allanite-(Ce), monazite-(Ce), bastnäsite-(Ce), parisite-(Ce), maoniupingite-(Ce) (Shen *et al.*, 2005), thorite, pyrochlore-group minerals and chlorite.

The lamprophyre veins are brownish green and are distributed widely in Baozi Hill. Most of the lamprophyre veins fill the northeast-oriented fractures, and a minority fill the northwest-oriented ones. Their widths are usually 1–1.5 m, with a maximum of 3.4 m. Most of the biotites in lamprophyre are altered to chlorites. Bastnäsite-(Ce) and microcline veins intersect the lamprophyre veins, which commonly include small granitic xenoliths. Mianningite crystals occur dispersed in the lamprophyre groundmass and concentrate predominantly near the bastnäsite-(Ce) and microcline veins. Rare orthobrannerite also exists in the fractures of lamprophyre. The U–Pb age of orthobrannerite is 23 Ma (Wei, 1979). Consequently, the mineralization age of the small intrusions bearing *REEs*, uranium and thorium of the Late Yanshanian epoch should also be young.

3. Physical and optical properties

The new mineral occurs mainly as opaque subhedral to euhedral tabular crystals, black in color and streak, with a submetallic luster (Fig. 1). These properties are similar to those of two other members of the crichtonite group – mapiquiroite (Biagioni *et al.*, 2014) and cleusonite (Wülser *et al.*, 2005). Mianningite crystals are generally 1–2 mm in size, although crystals up to 2 cm in size have been reported (Zhang *et al.*, 1995). Mianningite is brittle and exhibits a conchoidal fracture. Cleavage, parting, and fluorescence have not been observed.

The micro-indentation hardness, as measured under a 0.2 kg load by a Leitz ORTHOLUX-BK micro-indentation hardness tester, ranges from 72.2 to 89.2 kg/mm² with an average of 83.8 kg/mm², which is approximately equivalent to ~6 on Mohs hardness scale. The measured density (4.62(8) g/cm³, as measured by hydrostatic weighing) is lower than the calculated one (4.77 g/cm³, on the basis of the empirical chemical formula, with *Z*=3), possibly owing to the metamict nature of mianningite.

Under reflected light, mianningite is grayish white with no internal reflections. Due to its partial metamict state, the mineral is only very weakly anisotropic, and exhibits neither bireflectance nor pleochroism. The reflectance values in air, calibrated using SiC as the standard, are given in Table 1.

4. Chemical data

A total of 22 chemical spot analyses were carried out on separated and unheated crystals with a JEOL JXA-8100 electron probe micro-analyzer equipped with four wave-



Fig. 1. Photomicrograph of mianningite grains broken from the artificial heavy concentrate.

Table 1. Reflectance values of mianningite in air.

λ (nm)	R_{\max} (%)	R_{\min} (%)	λ (nm)	R_{\max} (%)	R_{\min} (%)
400	18.4	16.4	560	17.7	17.1
420	19.9	18.9	580	17.5	16.9
440	19.8	18.9	589	17.4	16.8
460	19.2	18.5	600	17.3	16.7
470	19.0	18.3	620	17.1	16.5
480	18.8	18.1	640	17.0	16.3
500	18.5	17.9	650	16.9	16.2
520	18.2	17.6	660	16.8	16.1
540	18.0	17.4	680	16.8	16.1
546	17.9	17.4	700	16.5	15.7

Notes: Measurements in air. Silicon carbide (SiC) was used as the standard.

length-dispersive spectrometers, which is housed in the Analytical Laboratory of the Beijing Research Institute of Uranium Geology, Beijing, China. The analytical conditions were as follows: accelerating voltage, 20 kV; beam current, 10 nA; beam size, 2 μ m. The Na-K α , Si-K α , Mg-K α , Y-L α , Al-K α , Sr-L α , and As-L α lines were measured with a TAP crystal; F-K α with an LDE1 crystal; Ti-K α , Fe-K α , V-K α , Cr-K α , Mn-K α , Ce-L α , La-L α , Ta-L α , Nd-K β , and Ba-L α with a LiF crystal; and K-K α , Nb-L α , U-M α , Ca-K α , Pb-M α , P-K α , Cl-K α , Th-M α , Sb-L α , Zr-L α , and Sn-L α with a PETJ crystal. The counting time on the analytical lines, as well as half of this time for background counts on both sides of the peak, was 10 s for each of the analyzed elements. The analytical standards were tugtupite for Na, Al, and Si, sanidine for K, pyrope for Mg, yttrium Al garnet (synthetic) for Y, monazite for Ce, La and Nd, metal uranium for U, bustamite for Ca and Mn, celestine for Sr, galena for Pb, hematite for Fe, ThO₂ (synthetic) for Th, baryte for Ba, apatite for P, benitoite for Ti, KNbO₃ (synthetic) for Nb, zircon for Zr, glass including 59.82% V₂O₅, 31.04% P₂O₅,

Table 2. Chemical data (average of 22 spot analyses) for mianningite, with formula calculated on the basis of 38 oxygen atoms.

Constituent	Wt%	Range	SD	Cations (O=38)
P ₂ O ₅	0.03	0.01–0.08	0.02	0.008
V ₂ O ₅	0.57	0.36–0.88	0.12	0.118
Nb ₂ O ₅	0.59	0.12–1.64	0.36	0.083
SiO ₂	0.02	0.01–0.04	0.01	0.006
TiO ₂	53.12	51.45–54.84	0.94	12.464
ZrO ₂	0.15	0.02–0.33	0.09	0.023
ThO ₂	0.15	0.01–0.39	0.11	0.011
UO ₂ total	8.05	5.75–10.33	1.29	
UO ₂ *	6.44			0.447
UO ₃ *	1.71			0.112
Al ₂ O ₃	0.07	0.01–0.16	0.05	0.026
Cr ₂ O ₃	0.07	0.01–0.16	0.04	0.017
Fe ₂ O ₃ total	28.78	27.42–29.64	0.58	
FeO*	0.93			0.243
Fe ₂ O ₃ *	27.75			6.516
Y ₂ O ₃	0.55	0.08–1.02	0.23	0.091
La ₂ O ₃	0.67	0.26–1.00	0.19	0.077
Ce ₂ O ₃	1.12	0.52–1.50	0.23	0.128
Nd ₂ O ₃	0.11	0.01–0.25	0.08	0.012
MgO	0.05	0.02–0.08	0.02	0.023
CaO	0.03	0.01–0.07	0.02	0.010
MnO	1.11	0.86–1.50	0.15	0.293
SrO	0.20	0.07–0.39	0.06	0.036
BaO	0.30	0.09–0.50	0.12	0.037
PbO	2.56	1.44–3.41	0.47	0.215
Na ₂ O	0.21	0.09–0.36	0.07	0.127
K ₂ O	0.09	0.03–0.23	0.05	0.036
Total	98.60			

* Recalculated on the basis of XPS data.

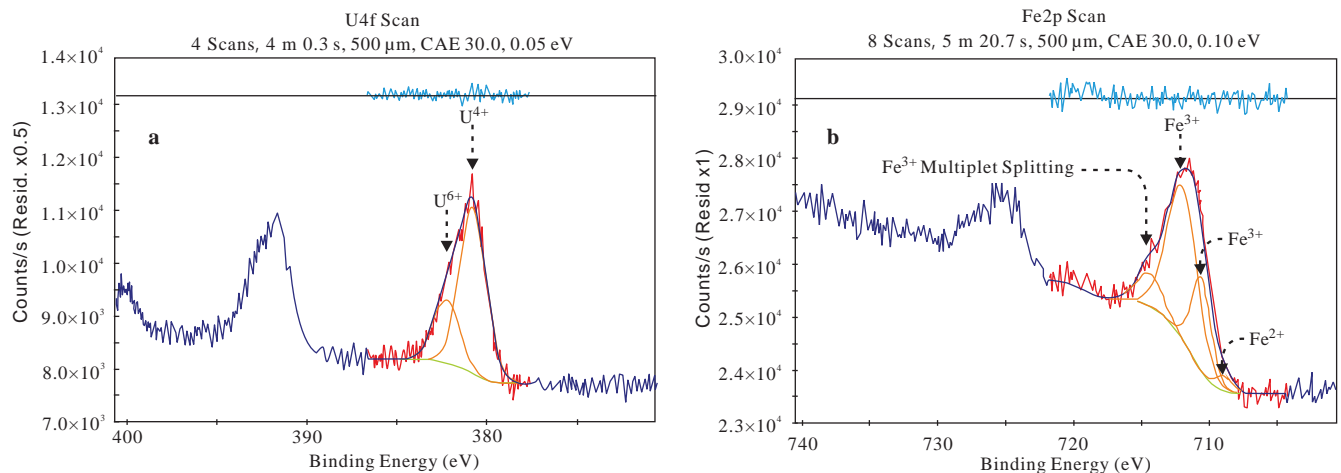


Fig. 2. X-ray photoelectron spectrum of U⁴⁺ and U⁶⁺ (a) and Fe²⁺ and Fe³⁺ (b) for mianningite.

and 10.12% K₂O for V, and Cr₂O₃ (synthetic) for Cr. The ZAF routine was applied for data correction. The analytical data are given in Table 2.

Wülser *et al.* (2005) verified that X-ray photoelectron spectroscopy (XPS) measurements can represent the bulk oxidation state of cleusonite. Accordingly, we used XPS to determine the relative amounts of Fe²⁺ versus Fe³⁺ and U⁴⁺ versus U⁶⁺. The analytical equipment comprised a Thermo ESCALAB 250Xi, with an Al K α X-ray source operated at 200 W at the Institute of Chemistry of the

Chinese Academy of Sciences, Beijing, China. Several selected mineral particles were ground with an agate mortar to 200 mesh, and the ground powders were spread on double-sided adhesive tape (1 × 1 cm in size) for the XPS measurements. The analytical diameter was about 500 μ m. Finally, the valence states of Fe and U were identified according to the different electron binding energies, and the analytical data were fitted using Thermo Advantage software (Fig. 2) to calculate the percentages of Fe²⁺, Fe³⁺, U⁴⁺ and U⁶⁺ (Table 3).

Table 3. X-ray photoelectron spectroscopy (XPS) data for mianningite.

Element	Uranium			Iron		
Envelope		U4f ^{7/2}			Fe2p ^{3/2}	
Oxidation state	U ⁴⁺		U ⁶⁺		Fe ³⁺	Fe ²⁺
Binding energy (eV)	380.77		382.25	711.93	710.51	708.87
Atomic (%)	0.12		0.03	0.63	0.18	0.03
% of total area	80.0		20.0		96.4	3.6

Table 4. X-ray powder diffraction data (*d* in Å) for annealed mianningite (most intense diffraction lines in bold).

<i>d</i> _{meas}	<i>d</i> _{calc}	<i>I</i> / <i>I</i> ₀	<i>hkl</i>	<i>d</i> _{meas}	<i>d</i> _{calc}	<i>I</i> / <i>I</i> ₀	<i>hkl</i>	<i>d</i> _{meas}	<i>d</i> _{calc}	<i>I</i> / <i>I</i> ₀	<i>hkl</i>
6.840	6.799	5	012	1.704	1.705	55	146	1.071	1.072	5	274
4.168	4.152	30	113	1.651	1.655	35	1.2.11	1.040	1.041	15	1.6.13
3.416	3.399	30	024	1.599	1.598	5	1.3.10	1.010	1.010	5	278
3.065	3.054	75	025	1.545	1.545	60	336	0.981	0.982	1.5	4.5.11
2.883	2.886	55	116	1.506	1.508	5	1.3.11	0.963	0.965	3	0.8.11
2.627	2.630	100	125	1.438	1.436	50	250	0.941	0.942	5	286
2.476	2.482	55	027	1.371	1.373	45	066	0.902	0.903	5	1.7.15
2.254	2.254	70	028	1.342	1.343	15	1.1.15	0.886	0.886	10	0.7.17
2.144	2.136	100	135	1.247	1.244	5	074	0.859	0.859	5	388
1.975	1.974	40	045	1.210	1.211	5	168	0.844	0.844	5	482
1.913	1.913	15	234	1.159	1.159	10	0.0.18	0.831	0.831	2	0.1.25
1.801	1.799	20	138	1.127	1.127	5	0.4.16	0.799	0.799	5	2.6.20

Taking into account the results of the electron-microprobe analyses as well as the XPS data, the empirical formula of mianningite (with rounding errors) can be written as $[\square_{0.322}\text{Pb}_{0.215}\text{Ba}_{0.037}\text{Sr}_{0.036}\text{Ca}_{0.010}]_{\Sigma 0.298}(\text{Ce}_{0.128}\text{La}_{0.077}\text{Nd}_{0.012})_{\Sigma 0.217}(\text{Na}_{0.127}\text{K}_{0.036})_{\Sigma 0.163}]_{\Sigma 1.000}(\text{U}^{4+}_{0.447}\text{Mn}_{0.293}\text{U}^{6+}_{0.112}\text{Y}_{0.091}\text{Zr}_{0.023}\text{Th}_{0.011})_{\Sigma 0.977}(\text{Fe}^{3+}_{1.224}\text{Fe}^{2+}_{0.243}\text{Mg}_{0.023}\text{P}_{0.008}\text{Si}_{0.006}\square_{0.496})_{\Sigma 2.000}(\text{Ti}_{12.464}\text{Fe}^{3+}_{5.292}\text{V}^{5+}_{0.118}\text{Nb}_{0.083}\text{Al}_{0.026}\text{Cr}^{3+}_{0.017})_{\Sigma 18.000}\text{O}_{38}$, which agrees with the general formula $\text{ABC}_{18}\text{T}_2\text{O}_{38}$ (Orlandi *et al.*, 1997).

5. Annealing, X-ray diffraction, and crystal structure

The unheated crystals of mianningite were partially metamict, showing a poor X-ray powder diffraction pattern. This partially metamict feature is identical to nearly half of the crichtonite-group species, such as cleusonite (Wülser *et al.*, 2005), davidite-(La) and davidite-(Ce) (Gatehouse *et al.*, 1979), dessauite-(Y) (Orlandi *et al.*, 1997), loveringite (Gatehouse *et al.*, 1978), and mapiquiroite (Biagioni *et al.*, 2014), probably as a result of radiation damage due to the presence of uranium. However, their recrystallization can be promoted by annealing. Taking this information into account, mianningite was annealed in N₂ for 4 h at 1000 °C and then cooled to room temperature at the rate of 10 °C/h. Fortunately, we discovered a single crystal within the recrystallized mianningite, and determined its X-ray powder pattern using the single-crystal repeat-rotation diffraction method (Li *et al.*, 2005). The X-ray powder diffraction pattern was integrated using GADDS software

(Häming, 2000). The mianningite powder data are given in Table 4. The eight strongest X-ray powder diffraction lines [*d* in Å (*I*/*I*₀) (*hkl*)] are 2.627 (100) (125), 2.144 (100) (135), 3.065(75) (025), 2.254 (70) (028), 1.545(60) (336), 2.883 (55) (116), 2.476 (55) (027), and 1.705 (55) (146). These data are similar to those of other crichtonite-group members.

The single-crystal X-ray diffraction experiment was conducted on the annealed crystal of the same metamict grain using a Bruker Smart APEX CCD diffractometer equipped with a normal focus, 2.4 kW sealed X-ray tube source operating at 45 kV and 35 mA, with a graphite monochromator. A hemisphere of intensity data was collected at room temperature in 1265 frames with ω scans (frame width 0.30° and an exposure time of 10 s per frame). A total of 6041 reflections were collected in a range between 4.94° and 66.90°. The data were corrected for polarization, Lorentz, and absorption using the Bruker program SADABS (Sheldrick, 1996). The crystal structure model was solved through direct methods, and refined by full-matrix least-squares using SHELXTL PC package (Sheldrick, 2008). One or two main elements were assigned to each site. According to the chemical data, we fixed 0.34 Pb + 0.34 Ce in the M0 site, 0.93 Fe + 0.07 Ti in the M3 site, and 1.0 Ti in the M4 and M5 sites (Table 6). Uranium and Mn were assigned to the M1 site and Fe to the M2 site for free refinement. The higher maximum and minimum heights in the final difference Fourier synthesis (14.74 and -6.01 e/Å³, respectively) may indicate the occurrence of four additional sites (M6–M9) with low occupancies, which also exist in some species of the crichtonite group, such as U-rich senaite (Armbruster &

Table 5. Crystal data, data-collection information, and structure refinement details for mianningite.

<i>Crystal data</i>	
Structural formula	$(\square_{0.32}, \text{Pb}_{0.34}, \text{Ce}_{0.34})(\text{U}^{4+}_{0.56}, \text{Mn}_{0.44})\text{Fe}^{3+}_{1.44} (\text{Ti}, \text{Fe}^{3+})_{18}\text{O}_{38}$
Crystal size	0.21 mm × 0.18 mm × 0.07 mm
Space group	$R\bar{3}$
Z	3
Unit-cell parameters	$a = 10.3462(5) \text{ \AA}$, $c = 20.837(2) \text{ \AA}$, $V = 1931.65(20) \text{ \AA}^3$
Density (calculated)	4.767 g/cm ³
<i>Data collection</i>	
Radiation, wavelength	Mo K α , $\lambda = 0.71073 \text{ \AA}$
Measured reflections	6041
Independent reflections	1630
Independent reflections with $I > 2\sigma(I)$	1594
R_{int}	0.036
θ_{min} , θ_{max}	2.47°, 33.45°
Index range	$-15 \leq h \leq 11$, $-16 \leq k \leq 15$, $-32 \leq l \leq 30$
<i>Refinement</i>	
Refinement method	Full matrix least squares on F^2
Data/restraints/parameters	1630/0/89
Goodness-of-fit on F^2	1.053
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.070$, $wR_2 = 0.19$
R indices (all data)	$R_1 = 0.071$, $wR_2 = 0.19$
Extinction coefficient	0.0020(3)
Largest diff. peak and hole	14.74 and -6.01 e/\AA^3

Table 6. Site coordinates, multiplicity and Wyckoff symbol, occupancies, atom fractional coordinates and equivalent isotropic displacement parameters (\AA^2) for mianningite.

Site	Wyck.	Occupancies	x	y	z	U_{eq}
M0	3a	$\square_{0.32}\text{Pb}_{0.34}\text{Ce}_{0.34}$	0	0	0	0.029(1)
M1	3b	$\text{U}_{0.56}\text{Mn}_{0.44}$	1/3	-1/3	1/6	0.004
M2	6c	$\text{Fe}_{0.72}\square_{0.28}$	2/3	1/3	0.02431(10)	0.003
M3	18f	$\text{Fe}_{0.93}\text{Ti}_{0.07}$	0.48299(12)	0.29630(13)	0.16878(5)	0.012(1)
M4	18f	$\text{Ti}_{1.00}$	0.40921(13)	-0.01269(14)	0.06561(6)	0.009(1)
M5	18f	$\text{Ti}_{1.00}$	0.33589(14)	0.08535(13)	-0.05811(6)	0.009(1)
O1	18f		0.2757(6)	-0.2007(6)	0.1033(3)	0.011(1)
O2	18f		0.2351(6)	-0.0641(6)	0.0071(3)	0.012(1)
O3	18f		0.1700(6)	0.0429(6)	-0.1089(3)	0.012(1)
O4	18f		0.4091(6)	-0.0255(6)	-0.1065(3)	0.011(1)
O5	18f		0.5193(6)	0.1353(6)	-0.0028(2)	0.010(1)
O6	18f		0.3670(6)	0.1068(6)	0.1168(3)	0.011(1)
O7	6c		2/3	1/3	0.1184(4)	0.010(1)

Kunz, 1990), dessauite (Orlandi *et al.*, 1997), mapiquiroite (Biagioni *et al.*, 2014), and almeidaite (Menezes *et al.*, 2015). Nevertheless, assignment of Fe to these additional sites did not improve the refinement significantly. Consequently, we left them out in the structural refinement as done by Orlandi *et al.* (2004).

Details of the crystal data, data collection, and crystal structure refinement of the treated crystal are shown in Table 5. Multiplicity and Wyckoff letters, occupancies, fractional atom coordinates and equivalent isotropic displacement parameters are given in Table 6, selected bond distances are listed in Table 7. The anisotropic displacement parameters are listed in Table S1, freely

available online as Supplementary Material linked to this article on the GSW website of the journal, <http://eurjmin.geoscienceworld.org/>.

Mianningite has a similar structure to other members of the crichtonite group, comprising nine layers of close-packed octahedra M1 and M3–5 and tetrahedra M2, which contains a large 12-coordinate M0 site. Small cations occupy the voids of 19 octahedra and 2 tetrahedra (Fig. 3). Large cations (Pb, Ce, La, Na) partially occupy the 12-coordinate M0 site, leaving it 32.2% vacant. The U, Mn, and Y ions are located in the octahedral M1 site. The tetrahedral M2 site is occupied by Fe^{3+} , while the M3–5 sites host Ti and Fe^{3+} .

Table 7. Main cation-oxygen distances (Å) for mianningite.

Cation	Oxygen	Distance (Å)
M0	O3LX 6	2.767(6)
M0	O2LX 6	2.827(2)
M1	O1LX 6	2.192(4)
M2	O7	1.961(9)
M2	O5LX 3	1.928(6)
M3	O6 ^{xiii}	1.934(6)
M3	O4 ⁱⁱ	1.970(6)
M3	O3 ^{xiv}	1.969(4)
M3	O6	2.026(5)
M3	O3 ^{xv}	2.094(6)
M3	O7	2.033(4)
M4	O6	1.843(7)
M4	O2	2.014(6)
M4	O1	1.903(5)
M4	O5	1.982(5)
M4	O4 ^{xvi}	1.916(7)
M4	O5 ^{xvi}	2.193(7)
M5	O3	1.872(6)
M5	O4	1.943(7)
M5	O2 ⁱⁱⁱ	2.065(6)
M5	O1 ⁱⁱⁱ	2.004(5)
M5	O2	1.927(6)
M5	O5	2.053(6)

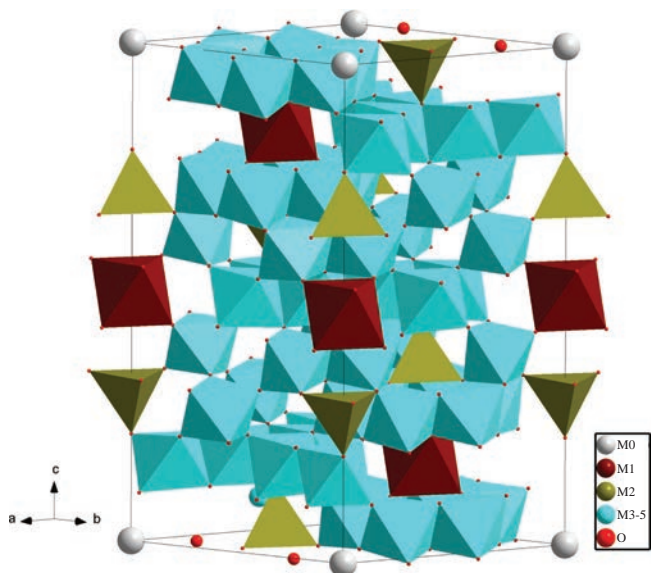


Fig. 3. Crystal structure of mianningite as seen down [110].

6. Review of the crichtonite group

The crichtonite group includes a series of complex titanium and iron oxides with the general chemical formula initially given as $AM_{21}O_{38}$ (Grey & Lloyd, 1976; Grey *et al.*, 1976; Grey & Gatehouse, 1978; Gatehouse *et al.*, 1979; Kelly *et al.*, 1979; Haggerty *et al.*, 1983), where A = large cations (Ca, REE, Pb, Sr, Na, K) and M = small cations (Ti, Fe, Mn, Zn). Orlandi *et al.* (1997) modified the formula for $^{XII}A^{VI}B^{VI}C_{18}^{IV}T_2O_{38}$, in which A = Ba, K, Pb, Sr, La, Ce, Ca, Na; B = Mn, Y, U, Fe, Zr, Sc; C = Ti, Fe³⁺, Cr, Nb, V⁵⁺,

Table 8. Crichtonite-group minerals and their characteristic site population.

Mineral*	M0	M1	M3-5	M2	Reference
Mianningite	□	U ⁴⁺	Ti	Fe ³⁺	This study
Almeidaite	Pb	Mn	Ti	Zn	(1)
Cleusonite	Pb	U ⁴⁺	Ti	Fe ²⁺	(2)
Crichtonite	Sr	Mn	Ti	Fe	(3)
Davidite-(Ce)	Ce	Y	Ti	Fe ³⁺	(4)
Davidite-(La)	La	Y	Ti	Fe ³⁺	(4)
Dessauite-(Y)	Sr	Y	Ti	Fe ³⁺	(5)
Gramaccioliite-(Y)	Pb	Y	Ti	Fe	(6)
Landauite	Na	Mn	Ti	Zn	(7)
Lindsleyite	Ba	Zr	Ti	Mg	(8), (9)
Loveringite	Ca	Zr	Ti	Mg	(10)
Mapiquiroite	Sr	U	Ti	Fe ³⁺	(11)
Mathiasite	K	Zr	Ti	Mg	(8), (9)
Paseroite	Pb	Mn ²⁺	V ⁵⁺	Mn	(12)
Senaite	Pb	Mn	Ti	Fe	(13)

* The space group of the crichtonite-group minerals is $R\bar{3}$; (1) Menezes *et al.*, 2015; (2) Wülser *et al.*, 2005; (3) Grey *et al.*, 1976; (4) Gatehouse *et al.*, 1979; (5) Orlandi *et al.*, 1997; (6) Orlandi *et al.*, 2004; (7) Grey & Gatehouse, 1978; (8) Haggerty *et al.*, 1983; (9) Zhang *et al.*, 1988; (10) Gatehouse *et al.*, 1978; (11) Biagioni *et al.*, 2014; (12) Mills *et al.*, 2012; (13) Grey & Lloyd, 1976.

Mn³⁺, Al; and T = Fe, Mn, Mg, Zn (Mills *et al.*, 2012; Menezes *et al.*, 2015), and the Roman numerals represent the coordination numbers. Meanwhile, a few oxygen atoms may be substituted by hydroxyl and F (Wülser *et al.*, 2004). The cation sites are denoted as follows: A = M0, B = M1, C = M3–M5 (sometimes including M6–M9), and T = M2. The different crichtonite-group minerals are defined using not only the A cations but also all cation sites according to their various chemical compositions. As a result, in addition to the early defined species, such as crichtonite (Grey *et al.*, 1976), senaite (Grey & Lloyd, 1976), landauite (Grey & Gatehouse, 1978), loveringite (Gatehouse *et al.*, 1978), davidite-(Ce) and davidite-(La) (Gatehouse *et al.*, 1979), and lindsleyite and mathiasite (Haggerty *et al.*, 1983; Zhang *et al.*, 1988), several new crichtonite members have been approved by IMA CNMNC (Table 8) thus far, namely dessauite-(Y) (Orlandi *et al.*, 1997), gramaccioliite-(Y) (Orlandi *et al.*, 2004), cleusonite (Wülser *et al.*, 2005), paseroite (Mills *et al.*, 2012), mapiquiroite (Biagioni *et al.*, 2014), almeidaite (Menezes *et al.*, 2015), and mianningite.

Mianningite is the fifteenth member of the crichtonite group. The total number of cations in its M0 site is 0.678 [(0.215 Pb + 0.037 Ba + 0.036 Sr + 0.010 Ca) + (0.128 Ce + 0.077 La + 0.012 Nd) + (0.127 Na + 0.036 K)], leaving 0.322 vacancy. In other words, the amount of vacancy in the M0 site is greater than that of any other cation, and even greater than any total of homovalent elements in this site. According to “the dominant-valency rule” (Hatert & Burke, 2008), mianningite might be the first vacancy-dominant analogue in the M0 site of the crichtonite group. More precisely, it is the vacancy-dominant analogue of mapiquiroite (Biagioni *et al.*, 2014). Dragila (1990) named a mineral with the formula (□, Pb, Ca)UF₂²⁺(Ti, Fe³⁺)₆Ti₁₂O₃₈ ‘romanite’ and considered that it belongs to the davidite

group. Wülser *et al.* (2005) classified it as cleusonite. In any case, this mineral was not submitted to the CNMNC (previously the CNMMN) prior to publication and cannot be considered to be a valid species of the crichtonite group. According to its cation occupancies, only the valence of Fe on the M2 site differs from that of mianningite, and it can be seen as the Fe²⁺ analogue of mianningite, although this is not verified as yet.

7. Discussion

Wülser *et al.* (2004) proposed that the formation of the crichtonite-group minerals was related to their geological environments and was probably controlled by five factors. They divided the crichtonites into two genetic groups based on their genesis, namely magmatism (\pm metasomatism) and metamorphism. Mianningite should be classified into the magmatic group consisting of five subgroups and corresponds to the davidite subgroup, which forms in granodiorite, granite, alkali-granite and syenite pegmatites. There are currently two species [davidite-(La) and davidite-(Ce)] in this sub-group, and mianningite should be considered as the third, characterized by the dominance of vacancy in the M0 site.

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