

Pyrochlore and microlite in a pegmatite at Atagoyama, Koriyama City, Fukushima Prefecture, Japan

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Abstract Pyrochlore (oxycalciopyrochlore) and microlite (“hydroxycalciomicrolite”) occur in a pegmatite vein intruded into an ultramafic rock at the Atagoyama quarry, Koriyama City, Fukushima Prefecture, Japan. Pyrochlore and microlite are found as dark brown to amber yellow octahedral crystals or anhedral grains up to 10 mm across. A part of pyrochlore octahedral crystal is often replaced by blackish green clinochlore. The representative chemical analysis for the non-metamict pyrochlore gave Na₂O 2.18, CaO 14.06, Fe₂O₃ 1.32, TiO₂ 10.55, Nb₂O₅ 27.91, Ta₂O₅ 18.22, UO₂ 25.12, H₂O (difference) 0.64, total 100.00 wt%. The empirical formula is: (Ca_{1.14}U_{0.42}Na_{0.32})_{Σ1.88}(Nb_{0.95}Ti_{0.60}Ta_{0.37}Fe_{0.08})_{Σ2}O_{6.00}[O_{0.61}(OH)_{0.32}]_{Σ0.93} on the basis of Nb + Ti + Ta + Fe = 2. It corresponds to oxycalciopyrochlore. The representative chemical analysis for the non-metamict microlite gave Na₂O 0.61, CaO 14.07, Fe₂O₃ 0.95, TiO₂ 5.51, Nb₂O₅ 18.60, Ta₂O₅ 41.48, UO₂ 16.74, H₂O (difference) 2.04, total 100.00 wt%. The empirical formula is: [Ca_{1.23}U_{0.30}(H₂O)_{0.21}Na_{0.10}]_{Σ1.84}(Ta_{0.92}Nb_{0.68}Ti_{0.34}Fe_{0.06})_{Σ2}O_{6.00}[(OH)_{0.69}O_{0.31}]_{Σ1.00} on the basis of Nb + Ti + Ta + Fe = 2. It corresponds to “hydroxycalciomicrolite”, a new member of the microlite group. Almost elements, especially Na and Ca, distinctly decrease in metamict (hydrous) phase of pyrochlore and microlite. The powder X-ray diffraction peaks appear few and broad due to admixed metamict phase. The diffraction pattern are [*d*(Å), (*I*), (*hkl*)]: 5.99(55)(111), 3.14(15)(311), 3.00(100)(222), 2.60(10)(400), 1.838(50)(440) and 1.567(10)(622) for pyrochlore, and [*d*(Å), (*I*), (*hkl*)]: 6.00(50)(111), 2.99(100)(222), 2.59(25)(400), 1.836(20)(440) and 1.570(10)(622) for microlite.

Key words: pyrochlore, microlite, pegmatite, Atagoyama

Introduction

Recently the IMA Commission on New Minerals, Nomenclature and Classification proposed the nomenclature of pyrochlore supergroup minerals (Atencio *et al.*, 2010). According to this nomenclature pyrochlore supergroup is divided in five subgroups as the pyrochlore group, the microlite group, the romèite group, the betafite group and the elsmoreite group. In Japan pyrochlore and microlite subgroup minerals are very rare and only reported from Mitoko, Fukuoka Prefecture (Nagashima and Nagashima, 1960) for pyrochlore, and from Nagatare, Fukuoka Prefecture (Nagashima and Nagashima, 1960) and

Myokenzan, Ibaraki Prefecture (Matsubara *et al.*, 1995) for microlite. But recent study on Mitoko’s pyrochlore revealed it to be oxycalciobetafite (Uehara *et al.*, 2013). About microlite from Japan only exact chemical analysis is reported for Myokenzan’s microlite and it corresponds to fluorocalciomicrolite.

During the mineralogical examination on pegmatite minerals from the Atagoyama quarry, Koriyama City, Fukushima Prefecture, Japan, we have found uranium-rich minerals including pyrochlore, microlite, sklodowskite, and uraninite.

The present paper deals with the occurrence of pyrochlore and microlite and brief discussion on their chemical compositions.

Occurrence

The Atagoyama quarry is located at Takanokura, Nakata Town, Koriyama City, Fukushima Prefecture about 6 km SE of Koriyama station of JR Tohoku line (37°21'59"N, 140°25'55"E). At the quarry are observed contact metamorphosed ultramafic rocks due to intrusion of Crataceous granite and its pegmatite veins. The ultramafic rocks are included as blocks in amphibolite and gneiss along the western margin of Abukuma metamorphic belt (*e.g.* Yashima *et al.*, 1981). Matsubara (1996) has described the minerals in the contact metamorphosed ultramafic rocks.

In February of 2012 a new pegmatite vein came out from an open pit (Fig. 1). The pegmatite vein is 1 to 2 m wide and dips north. Major constituents of the pegmatite are quartz, albite, K-feldspar, muscovite, biotite, almandine, and schorl. We recognized such minor constituents as zircon, rutile, monazite-(Ce), columbite-(Fe), fergusonite-(Y) (or beta-fergusonite-(Y)), throgumite, pyrochlore, microlite, sklodowskite and uraninite. Sometimes clinocllore replace schorl and pyrochlore.

The pyrochlore and microlite are found as dark brown to amber yellow octahedral crystal or anhedral grain less than 5 mm across (Figs. 2 & 3).



Fig. 1. The mode of occurrence of a pegmatite (white) intruded into ultramafic rock (dark greenish gray) at the open pit of the Atagoyama quarry. Width of pegmatite: approximately 1.5 m.

Also a part of the crystal appears in dark green color, which is replaced by clinocllore. Almost crystals and anhedral grains of pyrochlore and microlite change to metamict phase.

X-ray Crystallography

The powder X-ray diffraction patterns of pyrochlore and microlite were obtained by using a Gandolfi camera, 114.6 mm in diameter, employing Ni-filtered Cu- $K\alpha$ radiation. The diffraction patterns of pyrochlore and microlite appear few and broad due to admixed metamict phase (Table 1; Figs. 4 & 5).

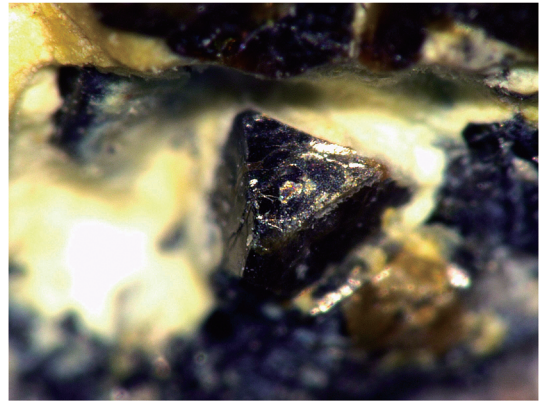


Fig. 2. Microphotograph of octahedral crystal of pyrochlore. Crystal size: approximately 5 mm of dimension.

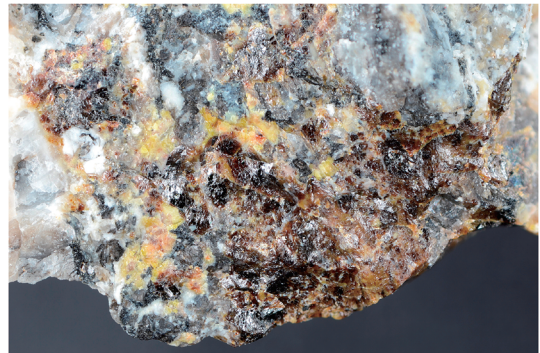


Fig. 3. Microphotograph of microlite aggregate showing slightly remnant of crystal form. Field view: approximately 5×3.5 mm.

Table 1. Powder X-ray diffraction data for pyrochlore and microlite.

<i>hkl</i>	1		2		3		4		5	
	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>
1 1 1	5.99	40	5.98	25	5.99	10	6.00	50	6.03	30
2 2 0			3.72	<1					3.696	2
3 1 1	3.14	20	3.13	20	3.13	6			3.153	24
2 2 2	3.00	100	3.00	100	2.995	100	2.99	100	3.017	100
4 0 0	2.60	10	2.60	20	2.594	16	2.59	20	2.611	21
3 3 1									2.396	4
4 2 2			2.12	1						
5 1 1			2.00	10	1.996	6			2.009	9
4 4 0	1.838	40	1.838	60	1.8338	40	1.836	25	1.845	25
5 3 1			1.761	5					1.765	5
6 2 0			1.645	1						
5 3 3			1.588	5					1.592	3
6 2 2	1.567	20	1.568	50	1.5637	30	1.570	15	1.573	13
4 4 4			1.502	15	1.4968	8			1.506	4
7 1 1			1.457	5					1.462	2
7 3 1			1.357	10	1.3500	2			1.359	3
8 0 0			1.304	10	1.2961	4			1.305	2

1: Pyrochlore, Atagoyama (this study). 2: Pyrochlore, British Columbia, Canada (ICDD 13-254)

3: Pyrochlore, heated, Quebec, Canada (ICDD 17-747)

4: Microlite, Atagoyama (this study). 5: Microlite, Myokenzan, Ibaraki, Japan (ICDD 48-1873)

Chemical Composition

Chemical analyses of pyrochlore and microlite were carried out using an INCA Oxford energy dispersive X-ray spectrometer installed in JSM-6610 SEM. The standard materials used were NaCl for Na, wollastonite for Ca, Ti for Ti, FeS₂ for Fe, Nb for Nb, Ta for Ta, Th for Th and UO₂ for U, respectively. No other elements were observed in the EPMA analyses. Table 2 shows the representative results for pyrochlore and its hydrous (probably intense metamict) phase. The representative results for microlite and its hydrous (probably intense metamict) phase are demonstrated in Table 3. F was under detected limit by using this spectrometer and also WDS (JOEL JXA8230) in the present pyrochlore and microlite. If it is presumed that the difference from 100 wt% in non-metamict pyrochlore (1 in Table 2) and microlite (1 in Table 3) are H₂O, the empirical formulae of pyrochlore and microlite are (Ca_{1.14}U_{0.42}Na_{0.32})_{Σ1.88}(Nb_{0.95}Ti_{0.60}Ta_{0.37}Fe_{0.08})_{Σ2}O_{6.00}[O_{0.61}(OH)_{0.32}]_{Σ0.93} and [Ca_{1.23}U_{0.30}(H₂O)_{0.21}Na_{0.10}]_{Σ1.84}(Ta_{0.92}Nb_{0.68}Ti_{0.34}Fe_{0.06})_{Σ2}O_{6.00}[(OH)_{0.69}O_{0.31}]_{Σ1.00} on the basis of Nb + Ti + Ta + Fe = 2, respectively. According to the nomenclature of the pyro-

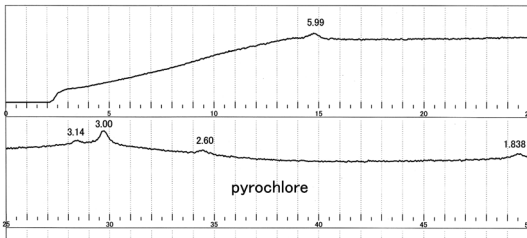


Fig. 4. X-ray diffraction chart of pyrochlore by using a Gandolfi camera.

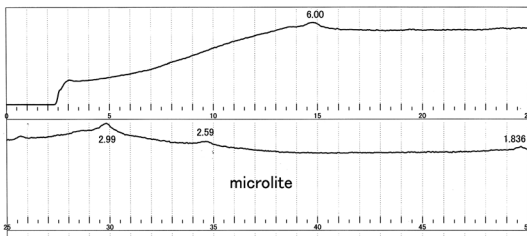


Fig. 5. X-ray diffraction chart of microlite by using a Gandolfi camera.

Table 2. The representative chemical compositions of pyrochlore.

	1	2	3	4	5
Na ₂ O	2.18	2.15	0.12	0	0
CaO	14.06	13.92	6.57	6.58	5.74
UO ₂	25.12	24.87	24.40	24.15	23.94
TiO ₂	10.55	10.44	9.56	9.48	10.12
Fe ₂ O ₃	1.32	1.30	1.42	1.35	1.20
Nb ₂ O ₅	27.91	27.62	26.70	27.39	26.98
Ta ₂ O ₅	18.22	18.03	19.06	17.52	17.86
(H ₂ O)	0.64	1.67	12.17	13.53	14.16
Total	100.00	100.00	100.00	100.00	100.00
Ta + Nb + Ti + Fe = 2					
Na	0.33	0.32	0.02	0	0
Ca	1.11	1.14	0.55	0.56	0.48
U	0.41	0.42	0.43	0.43	0.42
Σ	1.85	1.88	1.00	0.99	0.90
Ti	0.60	0.60	0.56	0.57	0.60
Fe	0.07	0.07	0.09	0.08	0.07
Nb	0.95	0.95	0.94	0.98	0.95
Ta	0.38	0.38	0.41	0.37	0.38
Σ	2	2	2	2	2

Table 3. The representative chemical compositions of microlite.

	1	2	3
Na ₂ O	0.61	0.59	0
CaO	14.07	14.24	4.95
UO ₂	16.74	15.51	15.56
ThO ₂	0	0.19	0.04
TiO ₂	5.51	4.98	5.23
Fe ₂ O ₃	0.95	0.81	0.78
Nb ₂ O ₅	18.60	18.09	18.23
Ta ₂ O ₅	41.48	41.66	39.75
(H ₂ O)	2.04	3.41	15.47
Total	100.00	100.00	100.00
Ta + Nb + Ti + Fe = 2			
Na	0.10	0.10	0
Ca	1.23	1.27	0.45
U	0.30	0.28	0.29
Th	0	0	0
Σ	1.63	1.64	0.74
Ti	0.34	0.32	0.34
Fe	0.06	0.05	0.04
Nb	0.68	0.68	0.70
Ta	0.92	0.95	0.92
Σ	2	2	2

chlore supergroup minerals (Atencio *et al.*, 2010) the present pyrochlore corresponds to oxycalcipyrochlore, and the microlite corresponds to “hydroxycalciumicrolite”. The “hydroxycalciumicrolite”, however, does not appear as a valid spe-

Table 4. The representative chemical compositions of columbite-(Fe) and fergusonite-(Y) (or fergusonite-beta-(Y)).

	1	2	3
MgO	0.63	0.56	
CaO			1.58
MnO	6.57	6.69	
FeO	10.55	11.13	
UO ₂			5.09
ThO ₂			0.31
Sc ₂ O ₃	1.69	1.38	
Y ₂ O ₃			28.46
Nd ₂ O ₃			0.51
Sm ₂ O ₃			1.39
Gd ₂ O ₃			1.76
Dy ₂ O ₃			3.09
Er ₂ O ₃			1.04
Yb ₂ O ₃			3.79
Lu ₂ O ₃			1.01
TiO ₂	2.38	2.35	
Nb ₂ O ₅	68.82	68.84	45.20
Ta ₂ O ₅	9.01	9.18	4.44
Total	99.66	100.13	97.67
O = 6		O = 4	
Mg	0.05	0.05	
Ca			0.08
Mn	0.32	0.32	
Fe	0.50	0.53	
U			0.05
Th			0
Sc	0.08	0.07	
Y			0.70
Nd			0.01
Sm			0.02
Gd			0.03
Dy			0.05
Er			0.01
Yb			0.05
Lu			0.01
Σ	0.95	0.97	1.01
Ti	0.10	0.10	
Nb	1.78	1.78	0.94
Ta	0.14	0.14	0.06
Σ	2.02	2.02	1.00

1 & 2: columbite-(Fe)
3: fergusonite-(Y) or beta-fergusonite-(Y)

cies in the table of the present members of the microlite group. We need further study especially on quantitative analysis for H₂O content to establish the “hydroxycalciumicrolite” as a new mineral.

The representative chemical compositions of columbite-(Fe) in association with pyrochlore and fergusonite-(Y) (or fergusonite-beta-(Y)) in association with microlite are demonstrated in Table 4.

Discussion

The present pyrochlore and microlite include possibly much H₂O as well as metamict state. Na₂O and CaO distinctly decrease as increasing H₂O, but the constituents of other elements do not vary (Fig. 6). The tone of BEI photographs indicate mainly H₂O contents, that is, light fields show high Na₂O and CaO but low H₂O (Figs. 7 & 8). In Fig. 7 sklodowskite is observed as minute flakes around crystal rims and along cracks of crystals (bright field). The chemical compositions of the present pyrochlore and microlite are

plotted in Ta–Nb–Ti diagram (Fig. 9). According to the diagram, we understand the distinct trend from Ta-rich phase to Nb- and Ti-rich phase or the reverse trend.

The present microlite includes relatively lower Na₂O and UO₂ than the present pyrochlore in A site constituents (Fig. 6). The A site hosts mainly Na, Ca, Sr, Pb, Sn, Sb, Y, U, and H₂O, and these are one of the important factors to decide species name (Atencio *et al.*, 2010). Therefore, we need to analyze exact H₂O content by the method except EPMA. But, if we can know exact H₂O content, there is another problem. It is necessary to clear that H₂O in the analyzed microlite (1 in Table 3) is due to original composition or subse-

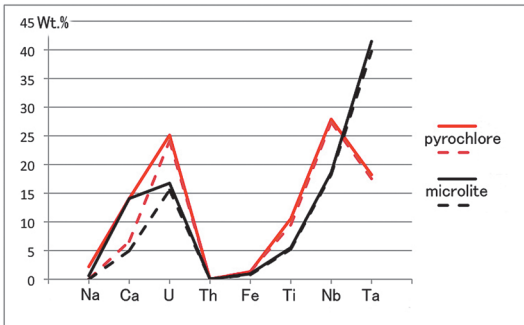


Fig. 6. Comparison of compositions between low-H₂O (solid line) and high-H₂O (dotted line) in pyrochlore (red) and microlite (black).

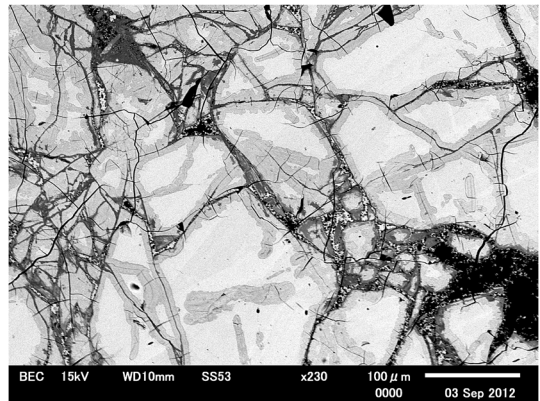


Fig. 8. Back-scattered image of microlite. Along cracks low-Na₂O and CaO but high-H₂O fields (slightly dark) are observed.

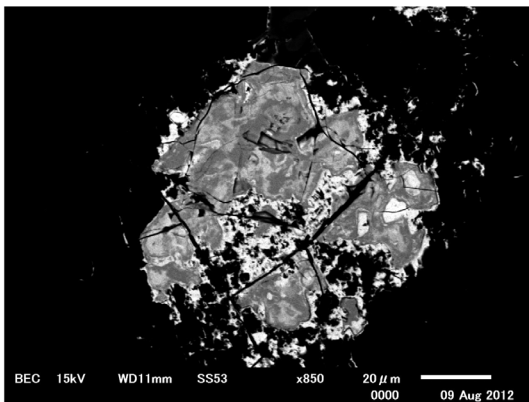


Fig. 7. Back-scattered image of pyrochlore. High-Na₂O and CaO but low-H₂O fields (light) and low-Na₂O and CaO but high-H₂O fields (dark) are observed. Minute flakes around crystal rim and along cracks of crystal (bright) are sklodowskite.

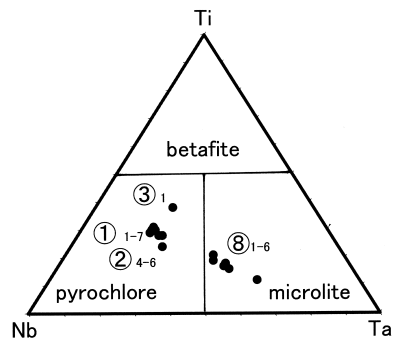


Fig. 9. Ta–Nb–Ti diagram of pyrochlore and microlite from Atagoyama. ①, ②, ③, ⑧: Sample number, 1, 1–6, 1–7, 4–6: analysed area.

quent hydrous replacement. Of these two cases, the microlite including H₂O as the original composition has possibility of a new mineral.

Consequently, we recognized the pyrochlore from Atagoyama to be oxycalciopyrochlore as the first occurrence in Japan and we proposed the microlite from Atagoyama to be tentatively “hydroxycalciummicrolite”.

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