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AKATOREITE, A NEW MANGANESE SILICATE FROM EASTERN OTAGO, NEW ZEALAND

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ABSTRACT

The new mineral, akatoreite,[2] is a hydrous manganese aluminosilicate from a manganiferious metachert and carbonate lens on the southeastern margin of the Haast Schist Group, South Island, New Zealand. It occurs as vitreous, orange-brown, massive to radiating twinned columnar aggregates with perfect $\{010\}$ cleavage and imperfect $\{0\bar{1}2\}$ cleavage; $H=6$; $\rho_{\text{meas.}}=3.48$ (± 0.01). Crystals are elongate prismatic a with $\{0kl\}$ predominant and $\{0\bar{2}1\}$ as twin plane.

Akatoreite is triclinic; space group either $P\bar{1}$ or $P1$; a $8.344\pm.0007$, b 10.358 ± 0.0005, c $7.627\pm.0003$ Å, $\alpha=104°29' \pm.3'$, β $93°38'\pm.5'$, γ $103°57'\pm.3'$, $a:b:c=0.8056:1:0.7363$; volume 614.03 ± 0.05 Å^3; $Z=1$; and $\rho_{\text{calc.}}=3.47$. Strongest lines of the indexed powder pattern and visually estimated intensities are, in Å: 9.681 (010) 6, 4.664 $(0\bar{2}1)$ 10, 3.466 $(11\bar{2})$ 5, 3.310 $(1\bar{3}0)$ 9, 3.063 $(\bar{1}\bar{2}2)$ 5, doublet 2.886 and 2.844 $(2\bar{3}1)$ $(\bar{1}\bar{3}1)$ 5, 2.704 $(2\bar{1}2)$ 5, and 2.214 $(\bar{1}41)$ 8.

Optically it is biaxial positive with refractive indices (Na) α 1.698, β 1.704, γ 1.720 all ± 0.001 with $2V=65\frac{1}{2}°$. Extinction angles are $X \wedge \{010\}=58°$, $Y \wedge \{010\}=30°$, $Z \wedge \{010\}=13°$; pleochroic scheme is X = colourless, Y = pale yellow, Z = light canary yellow. Electron microprobe and chemical analyses give SiO_2 36.4, Al_2O_3 8.3, TiO_2 0.03, Fe as FeO 1.0, MgO 0.3, Mn as MnO 47.7, CaO 0.2, and total H_2O 6.21. This results in $(Mn_{8.61}Fe_{0.19}Mg_{0.09}Ca_{0.05})Si_{7.75}Al_{2.09}O_{23.17}(OH)_{8.83}$.

The mineral is named after its only known locality 3 km south of the mouth of Akatore Creek, Eastern Otago, New Zealand.

INTRODUCTION

In 1958, P. Robinson described a manganiferous lens on the east coast of the South Island of New Zealand about 3 kilometers south of the mouth of Akatore Creek and about 32 kilometers southwest of Dunedin. Later H. H. Khoo (unpublished manuscript, 1965) studied the opaque minerals of this deposit and noted an unidentified, fibrous yellow mineral. One of us (A.R.) concentrated enough of the mineral to obtain a diffractogram which was substantiated by later powder photography on hand-picked material. The following optical and X-ray diffraction investigation and electron microprobe analysis indicated a new hydrous manganese aluminosilicate.

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[2] The name akatoreite has been approved by the Commission of New Minerals and New Mineral Names of the International Mineralogical Association. Type material is lodged in the Geology Department, University of Otago, catalogue number O.U. 25686. Type material is also held at the New Zealand Geological Survey, Lower Hutt.

The mineral is named after its only known occurrence just south of Akatore Creek, New Zealand.

OCCURRENCE

The locality is about 3 meters above high tide level, at grid reference S25-389239 as shown on the Dunedin Sheet (First Edition) of the Geological Map of New Zealand 1:250,000 (McKellar, 1966).

Pale buff spots, up to 2 cm in diameter, consist of a fine-grained mixture of massive akatoreite and rhodochrosite. Rare sheaves of orange-brown radiating prisms of akatoreite up to 1 cm in length lie in coarsely crystalline rhodochrosite and pyroxmangite. In the exposed sheaves, a few crystal faces, some striated, develop but generally cleavage planes predominate. Accompanying these minerals are minor amounts of rhodonite, spessartine, and quartz; rare prisms up to 1 cm long of heubnerite and cubes of alabandite; and veinlets up to a few millimeters thick of quartz, rhodonite, pyroxmangite, tinzenite, and apatite. Wad, psilomelane, pyrolusite, and todorokite fill veinlets and blacken outcrops.

Pink pods of manganese silicates and carbonates up to a meter in width grade into buff to varicoloured manganiferous metacherts. These compose lenses up to 3 m thick scattered within a felsic metatuff. Associated metavolcanic rocks developed from basic tuffs, breccias, and flows. On the sotheastern margin of the Haast Schist Group, these form distinctive layers up to 50 m thick in an otherwise monotonous sequence of phyllite and metagreywacke. Akatoreite developed during the complex deformation and low grade regional metamorphism of the pumpellyite-actinolite facies (Hashimoto, 1966) which affected this area.

MORPHOLOGY

Akatoreite crystals are elongate prismatic *a* and striated parallel to *a*. Five grains showing partial development of crystal faces were oriented by means of X-rays and the few crystal faces and prominent cleavage indexed by combining two-circle goniometer and X-ray data. The following faces are present: (010), $(0\bar{1}1)$, $(0\bar{4}3)$, $(0\bar{2}1)$, $(0\bar{3}1)$, $(\bar{1}\bar{1}1)$, $(1\bar{3}3)$, with faces in $\{0kl\}$ zone predominant. No grain showed sufficient development of crystal faces to permit calculation of crystallographic elements. The absence of centrosymmetric pairs may be due to either accentric symmetry or poor development of crystal faces. Of the two cleavages only $\{010\}$ develops well in crystal fragments.

PHYSICAL AND OPTICAL PROPERTIES

Prisms of akatoreite are elongate parallel to *a*, cleave well along $\{010\}$ cleavage, but cleave poorly on the imperfect $\{0\bar{1}2\}$ cleavage which shows

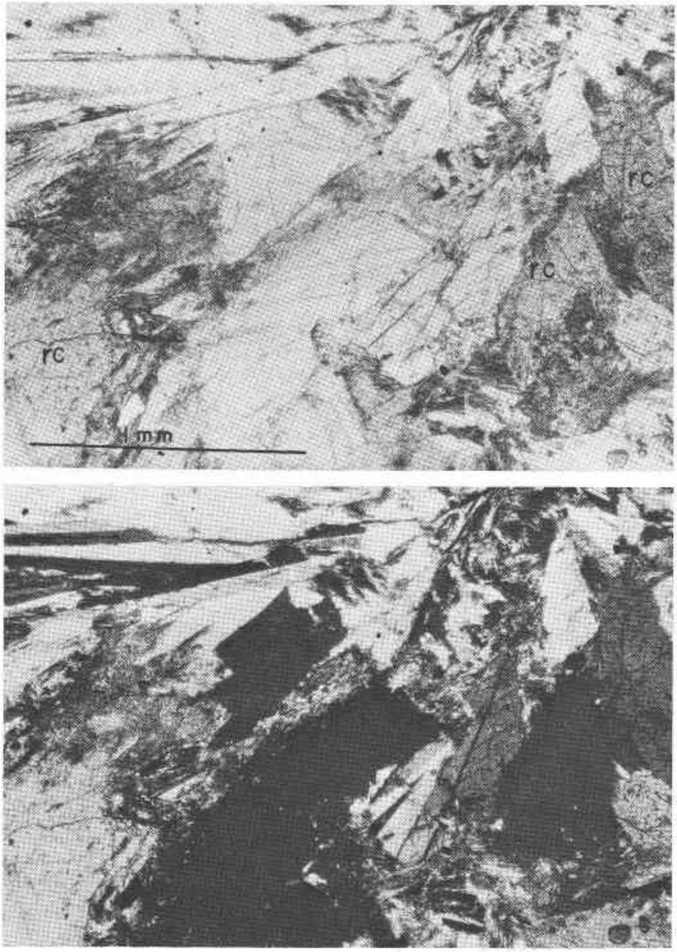

FIG. 1. Photomicrographs of twinned akatoreite showing prismatic habit, cut parallel to *a* upper left and perpendicular to *a* middle, set in a rhodochrosite (*rc*) matrix.
(a) Akatoreite white and rhodochrosite light grey. Plane light.
(b) Normal twinning is ubiquitous and intersecting cleavages show in twinned grain right of centre. Crossed nicols.

only in thin section (Figure 1). Akatoreite ranges in color from yellow-orange to orange-brown, and fine inclusions of rhodochrosite commonly dull the otherwise vitreous luster. The mineral has a hardness of 6 and a specific gravity of 3.48 (± 0.01) determined by centrifuging in Clerici solution of known specific gravity.

The refractive indices, measured in sodium light, and pleochroic scheme are $\alpha = 1.698$ (colorless), $\beta = 1.704$ (pale yellow), and $\gamma = 1.720$

(light canary yellow), all ±0.001. The mean index of refraction calculated by the Gladstone and Dale Rule (Larsen and Berman, 1934, p. 31) is 1.724 compared to the mean measured index of 1.707. Birefringence is 0.022 and the optic axial angle is (+) $65\frac{1}{2}^\circ$ measured conoscopically on the universal stage under optimum conditions suggested by Munro (1963). This value compares to (+) $63\frac{1}{2}^\circ$ calculated from refractive index data and lies within the limits of error of the refractive indices. In thin section akatoreite commonly show lamellar normal twins with 2 to 6 individuals per grain. Universal-stage measurement of the angular relationships of twin plane to cleavage and optical directions indicate the twin plane is $\{0\bar{2}1\}$ and the normal twin test (Emmons and Gates, 1939, p. 579) gives the twin axis as $\perp\{0\bar{2}1\}$.

The optical orientation of akatoreite was determined on the same crystal used for investigation of unit cell parameters. The two-circle goniometer was used with a petrographic microscope as a spindle stage (Wilcox, 1959). Conoscopic work on a crystal oriented by means of X-rays yielded the following information substantiated by universal-stage measurements:

	ϕ	ρ	*Extinction Angles*
X	114°	58°	$X\wedge\{010\}=58^\circ$
Y	253°	41°	$Y\wedge\{010\}=30^\circ$
Z	6°	68°	$Z\wedge\{010\}=13^\circ$

An upper hemisphere stereographic projection indicates the relationship of optical and crystallographic elements (Figure 2). In Table 1, the physical and optical properties of akatoreite are compared with those of the compositionally similar but physically and optically different minerals bementite and caryopilite.

CHEMICAL ANALYSIS

Duplicate electron microprobe analyses by B. E. Evans and one of us (P.B.R.) gave similar results (Table 2) within the assumed limits of error of an ARL electron microprobe analyser. Conditions of analysis were as follows: 10-kV accelerating potential, 0.025-μA sample current, 5–10 μm beam diameter, and a 48-second counting time on each location. Total water was determined with a Perkin-Elmer 240 C-H-N analyser after fusing the sample at 900°C. Qualitative trace element analysis was carried out by J. M. Rooke using an emission spectrographic technique (Rooke and Fisher, 1962).

Akatoreite contains two elements, iron and manganese, that may occur in more than one valency state. It was impossible to determine the oxidation state of the iron and manganese with the very small amounts of material available. Both are assumed to be in the divalent state on the evidence that significant amounts of trivalent cations would increase the analysis total well above 100 percent, and substantially increase the mean refractive index. The pale colour of the mineral and the moderate pleochroism suggest that trivalent manganese is not an important constituent.

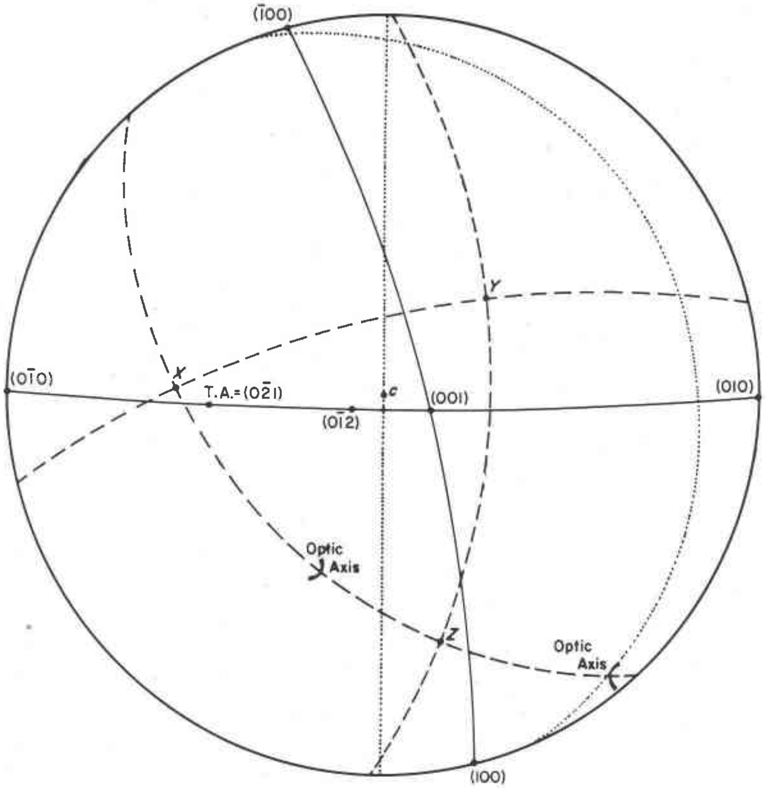

FIG. 2. Upper hemisphere stereographic projection showing optical orientation of akatoreite.

These analytical data, the measured specific gravity, and the unit cell volume suggest a cell content and formula of:

$$(Mn_{8.61}Fe_{0.19}Mg_{0.09}Ca_{0.05})Si_{7.75}Al_{2.09}O_{23.17}(OH)_{8.83}.$$

Based solely on chemical data, akatoreite, bementite, and particularly caryopilite are similar. The significant differences are lower H_2O and MgO content, and higher Al_2O_3 of akatoreite.

TABLE 1. PHYSICAL, OPTICAL AND UNIT CELL DATA FOR AKATOREITE COMPARED WITH THOSE OF BEMENTITE AND CARYOPILITE[a]

	Akatoreite	Bementite	Caryopilite
Composition	$(MnFeMgCa)_9Si_{7.75}Al_{2.09}O_{23.2}(OH)_{8.8}$	$Mn_5Si_4O_{10}(OH)_6$	$Mn_{6-x}Si_4O_{10}(OH)_{8-2x}$
System	Triclinic	Orthorhombic	Monoclinic (?)
Habit	Massive to prismatic, elongate along *a*	Prismatic	Massive to platy, elongate along *b*
Cleavage	$\{010\}$ excellent $\{0\bar{1}2\}$ imperfect	3 pinacoids with different perfection	$\{001\}$ perfect
Hardness	6	5.5	3–4
Refractive indices	α 1.698±0.001	1.624	1.603−1.608
	β 1.704±0.001	1.650	1.632−1.633
	γ 1.720±0.001	1.650	1.632−1.633
Birefringence	0.022	0.026	0.029−0.025
Optic sign, $2V$	(+) $65\frac{1}{2}°$	(−) near 0°	(−) near 0°
Optical orientation	$X\wedge\{010\}=58°$ $Y\wedge\{010\}=30°$ $Z\wedge\{010\}=13°$	*X* normal to best cleavage	*X* normal to cleavage
Pleochroism	*X* colourless		
	Y pale yellow	yellowish	
	Z light canary yellow		
References	This report	König (1887) Palache (1910)	Hamberg (1889) Flink (1917) Pardee *et al.* (1921) Larsen (1925)
Cell dimensions	*a* 8.344±0.0007 Å	14.5	5.65
	b 10.358±0.0005 Å	17.5	$\sqrt{3}a=9.78$
	c 7.627±0.0003 Å	7.28×4=29	7.50
	α 104°29′±.3′	90°00′	90°00′
	β 93°38′±.5′	90°00′	104.5°
	γ 103°57′±.3′	90°00′	90°00′
Volume of cell	614.03±.05 Å^3	7359[b]	400.2[b]
Cell content	1	18[b]	1[b]
G(meas)	3.48±.01	2.98	2.83−2.91
G(calc)	3.47	3.06[b]	2.97[b]
Space Group	$P\bar{1}$ or $P1$	$P2_12_12_1$	not determined
References	This report	Kato (1963)	Kato (1963)

[a] Nomenclature accords with Kato's recommendations (1963) and the synonym of ektropite (ectropite) for caryopilite (Fleischer, 1964).

[b] Calculated from published data.

X-RAY CRYSTALLOGRAPHY

Approximate unit-cell parameters were obtained from six upper-layer and three quartz-calibrated normal beam Weissenberg patterns for the three principal zones of one crystal fragment. Weissenberg patterns of three other grains substantiated, in whole or part, these parameters. Combining these unrefined data with those from powder photographs taken on a 114.59 mm diameter Debye-Scherrer camera, permitted unambiguous indexing of some powder reflections. Use of these reflections in a Fortran IV computer program (Appleman, Handwerker, and Evans, 1963) gave a least squares refinement of unit cell parameters based on low 2θ reflections. The refined parameters were used in a Fortran IV computer program (Eggleton pers. comm.) to generate all possible reflections and spacings. Numerous reiterations and checking of Weissenberg patterns for intensities of all possible reflections resulted in a least squares refinement of unit cell parameters based on 77 unambiguously indexed reflections. Lack of suitable single crystal patterns resulted in a further 22 suggested but unchecked indexings. These unchecked reflections were not used in the refinement of unit cell parameters.

TABLE 2. ANALYSES OF AKATOREITE, BEMENTITE AND CARYOPILITE

	Akatoreite	Bementite	Caryopilite
SiO_2	36.4%	38.36%	36.16%
Al_2O_3	8.3	0.96	0.35
TiO_2	0.03		
Fe_2O_3		0.71	1.33
FeO	1.0[a]	4.94	
MnO	47.7[b]	39.22	46.46
MgO	0.3	3.35	4.80
CaO	0.2	0.62	0.28
ZnO		2.93	
Total H_2O	6.21[c]	8.61	9.81
TOTAL	100.1[d]	99.70	99.85

Akatoreite: Electron microprobe analysis by B. E. Evans

[a] Total Fe as FeO

[b] Total Mn as MnO

[c] Duplicate determination. Microchemical Laboratory, University of Otago.

[d] Includes trace amounts of sodium, boron, chromium, nickel, copper, and vanadium Analyst: J. M. Rooke.

Bementite: Franklin Furnace, New Jersey. Analyst: Steiger, Pardee *et al.*, 1921.

Caryopilite: Analysis includes PbO = 0.37%, alkalies = 0.20% and Cl = 0.09%, Pajsberg, Sweden. Analyst: A. Hamberg (1889).

Table 3. X-ray Powder Data of Akatoreite Compared with those of Bementite and Caryopilite

Akatoreite				Bementite			Caryopilite		
hkl	*d*, Å(calc.)	*d*, Å(obs.)	*I*	*hkl*	*d*, Å	*I*	*hkl*	*d*, Å	*I*
010	9.668	9.681	60						
$01\bar{1}$	6.802	6.792	20	004	7.25	90	001	7.31	100
$11\bar{1}$	5.031	5.027	30						
$0\bar{2}1$	4.664	4.665	100	310	4.60	2			
				230[a]	4.60	2			
				131[a]	4.40	2			
				320[a]	4.06	3			
				311[a]	3.97	4			
002	3.660	3.662	20	400[a]	3.66	100			
021	3.605	3.603	40	008[a]	3.58	90	002	3.63	80
$11\bar{2}$	3.466	3.466	50	510[a]	3.43	9			
				150	3.43	9			
$21\bar{1}$	3.366	3.363	40						
$1\bar{3}0$	3.311	3.310	90	420	3.30	6			
030	3.223	3.224	30						
012	3.149	3.143	10						
$\bar{1}22$	3.061	3.063	50	250	3.09	5			
				430[a]	3.01	2			
$2\bar{3}0$	2.920	2.917	10						
$2\bar{3}1$	2.867	2.866	50						
$\bar{1}31$	2.848	2.844		350	2.823	4			
$1\bar{3}\bar{1}$	2.788	2.791	30				130	2.797	40
							$20\bar{1}$	2.797	40
$2\bar{1}2$	2.710	2.704	50	520	2.722	4			
$1\bar{2}\bar{2}$	2.661	2.660	20						
$\bar{3}01$	2.627	2.626	20						
022	2.596	2.599	20						
$1\bar{4}1$	2.570	2.573	20						
202	2.543	2.543	5				131	2.508	70
							$20\bar{2}$		
$02\bar{3}$	2.467	2.468	30						
$11\bar{3}$	2.467	2.468		152[a]	2.436	14			
$1\bar{1}3$	2.373	2.373	10						
$\bar{2}40$	2.367	2.366							
131	2.365	2.366							
							132[a]	2.308	20
							201[a]		
$3\bar{1}\bar{2}$	2.276	2.278	5						
$\bar{1}13$	2.253	2.253	5						
103	2.254	2.253							
230	2.239	2.237	20						
$\bar{1}41$	2.212	2.214	80		2.212	2			
$23\bar{2}$	2.183	2.184	10						

TABLS 3.—(*Continued*)

Akatoreite				Bementite			Caryopilite		
hkl	*d*, Å(calc.)	*d*, Å(obs.)	*I*	*hkl*	*d*, Å *I*	*I*	*hkl*	*d*, Å	*I*
$2\bar{4}\bar{1}$	2.136	2.135	10	280	2.113	7			
$3\bar{3}2$	2.088	2.089		532^a	2.099	6	132^a		
$3\bar{4}1$	2.086	2.089	10				$20\bar{3}$	2.103	20
				506					
$2\bar{3}3$	2.031	2.030	30	362^a	2.053	2			
400	2.007	2.008	20						
023	1.9719	1.9728					$13\bar{3}^a$		
203	1.9729	1.9728	10				202^a	1.973	10
$4\bar{2}1$	1.9711	1.9728							
050	1.9336	1.9324	5						
$3\bar{1}\bar{3}$	1.8877	1.8854	10						
$\bar{4}02$	1.8663	1.8664		660					
$\bar{1}42$	1.8670	1.8664	10	642^a	1.859	2			
				632^a	1.852	2			
$33\bar{2}$	1.8289	1.8296	10	00.16	1.828	4			
$\bar{3}\bar{2}3$	1.8115	1.8108					310^a		
213	1.8121	1.8108	5				$31\bar{2}^a$	1.800	10
$21\bar{4}$	1.7728	1.7728	20						
				820^a					
				580^a	1.759	2			
$42\bar{1}$	1.7376	1.7365	5						
							133		
							$20\bar{4}$	1.728	10
$04\bar{4}$	1.7004	1.7015	5						
$33\bar{3}$	1.6770	1.6776	20						
$\bar{1}60$	1.6677	1.6683							
142	1.6675	1.6683	40						
$23\bar{4}$	1.6456	1.6449					$33\bar{1}$		
$25\bar{1}$	1.6460	1.6449	20		1.639	2	060	1.634	20
114	1.6211	1.6205	20		1.621	2			
133	1.6150	1.6139	20						
500	1.6054	1.6046	5						
$25\bar{2}$*	1.5909	1.5904	20						
$53\bar{1}$*	1.5825	1.5819	20						
$\bar{2}43$	1.5573	1.5570	30						
501	1.5266	1.5270	5						
242*	1.5031	1.5019	20						
341	1.4806	1.4806	5		1.478	2			
$43\bar{3}$	1.4566	1.4558	20						
$52\bar{1}$	1.4432	1.4424							
$35\bar{2}$*	1.4429	1.4424	10						
$\bar{1}70$	1.4260	1.4260	10						
$14\bar{5}$	1.4095	1.4105							
$1\bar{1}\bar{5}$	1.4112	1.4105	30						

TABLE 3.—(*Continued*)

Akatoreite				Bementite			Caryopilite		
hkl	*d*, Å(calc.)	*d*, Å(obs.)	*I*	*hkl*	*d*, Å	*I*	*hkl*	*d*, Å	*I*
252*	1.3268	1.3276							
3$\bar{6}$4*	1.3269	1.3276	10						
17$\bar{3}$	1.3135	1.3139							
2$\bar{5}$5*	1.3145	1.3139	10						
5$\bar{5}\bar{2}$*	1.3004	1.3008	10						
07$\bar{4}$	1.2846	1.2846							
2$\bar{8}$2*	1.2848	1.2846	10						
02$\bar{6}$	1.2683	1.2679	20						
5$\bar{2}\bar{4}$*	1.2568	1.2568	20						
21$\bar{6}$	1.2328	1.2333							
22$\bar{6}$*	1.2334	1.2333	5						
45$\bar{4}$*	1.1745	1.1747							
62$\bar{3}$*	1.1748	1.1747	5						
4$\bar{7}$4*	1.1671	1.1669	10						
$\bar{4}$35	1.1506	1.1504							
2$\bar{4}\bar{5}$*	1.1510	1.1504	5						
163	1.1452	1.1455	5						
25$\bar{6}$*	1.1295	1.1291	10						
4$\bar{7}\bar{3}$*	1.0800	1.0797	10						
63$\bar{4}$	$\alpha_1$1.0682	1.0676	20						
$\bar{2}$91	$\alpha_1$1.0632	1.0633							
21$\bar{7}$	$\alpha_1$1.0637	1.0633	20						
17$\bar{6}$	$\alpha_1$1.0498	1.0493							
44$\bar{6}$*	$\alpha_1$1.0497	1.0493	10						
6$\bar{2}\bar{5}$*	$\alpha_1$1.0377	1.0378	10						
19$\bar{4}$	$\alpha_1$1.0283	1.0283	30						
2$\bar{9}\bar{2}$	$\alpha_1$0.99933	0.99931	20						

Akatoreite: *d* (obs.) as measured on film corrected for shrinkage from 114.59 mm diameter Debye-Scherrer camera with manganese filtered Fe radiation exposed in spot position. Intensities are visually estimated. Reflections marked with an asterisk were not used in least squares refinement of unit cell parameters.

Bementite: Data from Kato (1963) who indicated indexing was tentative.

Caryopilite: Data from Kato (1963)

[a] Least squares analysis indicates these values are not consistent with published unit cell parameters of bementite and caryopilite.

For comparison, the powder data for bementite and caryopilite (Table 3) emphasize the distinctness of akatoreite from bementite and caryopilite.

ACKNOWLEDGEMENTS

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