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KLÖCHITE, $K\square_2(Fe^{2+}Fe^{3+})Zn_3[Si_{12}O_{30}]$, A NEW MILARITE-TYPE MINERAL SPECIES FROM THE KLÖCH VOLCANO, STYRIA, AUSTRIA

HANS-PETER BOJAR§

Department of Mineralogy, Universalmuseum Joanneum, Weinzöttlstraße 16, A–8045 Graz, Austria

FRANZ WALTER AND CHRISTOPH HAUZENBERGER

Institute of Earth Sciences (Mineralogy and Petrology), University of Graz, Universitätsplatz 2, A–8010 Graz, Austria

WALTER POSTL

Department of Mineralogy, Universalmuseum Joanneum, Weinzöttlstraße 16, A–8045 Graz, Austria

ABSTRACT

The new mineral species *klöchite* was found in a SiO_2-rich xenolith from a nepheline basanite quarry at the Klöch volcano, Bad Radkersburg district, Styria, Austria. It forms hexagonal tabular crystals flattened on {001}, with a diameter up to 0.3 mm and a maximal thickness of 0.1 mm. It is associated with sanidine, quartz, diopside, fluoro-richterite, titanite, enstatite, forsterite, ilmenite and mottramite. Klöchite is blue, has a vitreous luster, is devoid of cleavage, and is translucent and non-fluorescent; the calculated density is 3.007 g cm^{-3}. Optically, it is uniaxial negative with ω 1.594(1) and ε 1.590(1) at 589 nm; it is pleochroic with ω deep blue and ε pale yellow. Electron-microprobe analyses gave the composition $(K_{0.78}Na_{0.22})$ $(\square_{1.67}Na_{0.33})$ $(Fe^{3+}{}_{1.19}Fe^{2+}{}_{0.45}Mn_{0.27}Ca_{0.04}Co_{0.02}Ni_{0.01}Mg_{0.01}Ti_{0.01})$ $(\square_{0.25}Zn_{2.63}Fe^{2+}{}_{0.10}Li_{0.02})$ $[Si_{12.00}O_{30.00}]$. Klöchite belongs to the milarite group, space group *P*6/*mcc*, with *a* 10.120(1), *c* 14.298(3) Å, *V* 1268.1(3) Å^3 from single-crystal XRD data at 100 K, and Z = 2. The strongest eight lines in the calculated X-ray powder-diffraction pattern [*d* in Å (I)(*hkl*)] are: 7.149(100)(002), 5.540(43)(102), 4.130(40)(112), 3.736(70)(202), 3.227(67)(211), 2.919(40)(114), 2.770(68)(204) and 2.530(43)(220). From single-crystal X-ray data, the structure has been refined to *R* = 0.023. Klöchite has the typical structural units of the double-ring silicates of the milarite structure-type. Zinc dominates at the *T*2 position with a small vacancy defect at this site, and Fe dominates at the *A* site, which also contains Mn. The *C* site is fully occupied by K and Na, whereas the *B* site (Na) is nearly empty owing to electroneutrality of the chemical formula and the presence of Fe^{3+} at the *A* site, which is indicated from bond-valence calculations. From the structure refinement, the formula $(K_{0.81}Na_{0.19})$ $(\square_{1.83}Na_{0.17})$ $(Fe_{1.74}Mn_{0.26})$ $(\square_{0.21}Zn_{2.79})$ $[Si_{12}O_{30}]$ corresponds well to the ideal end-member formula of klöchite, $K_1\square_2$ $(Fe^{2+}{}_1Fe^{3+}{}_1)$ Zn_3 $[Si_{12}O_{30}]$, with vacancy dominant at the *B* site. Angular distortions at *T*2 and *A* of selected minerals of the milarite group show two separate correlations, for the Be-, B-dominant and Li-, Zn-, and Mg-dominant minerals of this group.

Keywords: klöchite, milarite-type structure, crystal chemistry, angular distortions, Klöch volcano, Styria, Austria.

SOMMAIRE

On a trouvé la nouvelle espèce minérale *klöchite* dans un xénolite riche en SiO_2 dans une carrière de basanite néphélinique au volcan Klöch, district de Bad Radkersburg, en Styrie, Autriche. Elle se présente en tablettes hexagonales applaties sur {001}, avec un diamètre atteignant 0.3 mm et une épaisseur maximale de 0.1 mm. Lui sont associés sanidine, quartz, diopside, fluoro-richterite, titanite, enstatite, forstérite, ilmenite et mottramite. La klöchite est bleue, possède un éclat vitreux, est dépourvue de clivage, et est translucide et non-fluorescente. La densité calculée est 3.007 g cm^{-3}. Optiquement, elle est uniaxe négative, avec ω 1.594(1) et ε 1.590(1) à 589 nm; elle est pléochroïque, avec ω bleu foncé et ε jaune pâle. Les analyses effectuées avec une microsonde électronique ont donné la composition $(K_{0.78}Na_{0.22})$ $(\square_{1.67}Na_{0.33})$ $(Fe^{3+}{}_{1.19}Fe^{2+}{}_{0.45}Mn_{0.27}Ca_{0.04}Co_{0.02}Ni_{0.01}Mg_{0.01}Ti_{0.01})$ $(\square_{0.25}Zn_{2.63}Fe^{2+}{}_{0.10}Li_{0.02})$ $[Si_{12.00}O_{30.00}]$. La klöchite fait partie du groupe de la milarite, groupe spatial *P*6/*mcc*, avec les paramètres *a* 10.120(1), *c* 14.298(3) Å, *V* 1268.1(3) Å^3 mesurés par diffraction X sur monocristal à 100 K, et Z = 2. Les huit raies les plus intenses du spectre de diffraction (méthode des poudres) [*d* en Å (I)(*hkl*)] sont: 7.149(100)(002), 5.540(43)(102), 4.130(40)(112), 3.736(70)(202), 3.227(67)(211), 2.919(40)(114), 2.770(68)(204) et 2.530(43)(220). A partir de données obtenues sur monocristal, nous en avons affiné la structure jusqu'à un résidu *R* de 0.023. La klöchite possède les anneaux doubles

§ *E-mail address*: hans-peter.bojar@museum-joanneum.at

de tétraèdres typiques des minéraux du groupe de la milarite. Le zinc est prédominant au site *T*2, avec une légère lacune à cette position, et le Fe prédomine au site *A*, qui contient aussi le Mn. Le site *C* est complet avec K et Na, tandis que le site *B* (Na) est presque vide à cause de l'électroneutralité de la formule chimique et la présence de Fe^{3+} au site *A*, comme l'indique le calcul des valences de liaison. D'après l'affinement de la structure, la formule, $(K_{0.81}Na_{0.19})$ $(\square_{1.83}Na_{0.17})$ $(Fe_{1.74}Mn_{0.26})$ $(\square_{0.21}Zn_{2.79})$ $[Si_{12}O_{30}]$, correspond bien à la formule idéale de la klöchite, $K_1\square_2$ $(Fe^{2+}{}_1Fe^{3+}{}_1)$ Zn_3 $[Si_{12}O_{30}]$, dans laquelle une lacune est dominante au site *B*. Les distorsions angulaires impliquant *T*2 et *A* de minéraux choisis du groupe de la milarite montrent deux corrélations séparées, une pour les minéraux à dominance de Be et B, l'autre pour les minéraux à dominance de Li, Zn, et Mg.

(Traduit par la Rédaction)

Mots-clés: klöchite, structure du type de la milarite, cristallochimie, distorsions angulaires, volcan Klöch, Styrie, Autriche.

Introduction

We present here the description of the new mineral species *klöchite*, including details of its structure. Klöchite was found in the northern part of a nepheline basanite quarry (15°58.0'E, 46°46.5'N) one km north of the village of Klöch, Bad Radkersburg district, Styria, Austria. The Klöch Plio-Pleistocene volcanic massif belongs to the Styrian Basin Volcanic Field. It is the westernmost of several Neogene alkali basaltic to basanitic intracontinental volcanic fields of the Pannonian Basin (Ebner & Sachsenhofer 1995, Seghedi *et al.* 2004). From this area, at Stradner Kogel, Wilhelmsdorf, about 10 km NNW of Klöch, the new milarite-type mineral trattnerite was reported by Postl *et al.* (2004).

Both the mineral and its name were approved by IMA–CNMNC (IMA 2007–054). The holotype material is deposited at the Department of Mineralogy of the Universalmuseum Joanneum in Graz, Austria (mineralogical collection, catalogue number 84.580). Klöchite is named after the well-known location for minerals (Taucher *et al.* 1989) and wine (Lantschbauer & Barwirsch 2008) in Styria.

Appearance and Physical Properties

The nepheline basanite is rich in vesicles and xenoliths. More than 100 minerals have been reported from this location (Taucher *et al.* 1989, Postl *et al.* 1996, 2004, Postl & Bojar 2006). The klöchite-hosting SiO_2-rich xenolith is composed mainly of sanidine, quartz and diopside. Small vesicles in this xenolith commonly host fluoro-richterite, needle-shaped titanite, enstatite, forsterite, ilmenite and the lead–zinc vanadate mottramite. Mottramite is quite common in oxidized zones of Pb–Zn deposits, but scarce in a volcanic environment. Only a few vesicles host the parageneses of klöchite with mottramite, and only two crystals were available for investigations. Klöchite forms hexagonal, tabular blue crystals flattened on {001}, with a diameter of up to 0.3 mm and a maximal thickness of 0.1 mm; two hexagonal prisms, one hexagonal bipyramid and the basal pinacoid are present (Fig. 1). No cleavage was observed. Klöchite is uniaxial negative, ω 1.594(1), ε 1.590(1) at 589 nm, measured on a spindle stage. It is pleochroic, with ω deep blue and ε pale yellow. The mineral has a vitreous luster, is translucent and non-fluorescent. Dispersion was not determined because of the dark color (ω). The Mohs hardness, streak and density were not determined owing to the lack of available crystals. The density calculated from single-crystal unit-cell parameters and the empirical formula is 3.007 g cm^{-3}, and 3.016 g cm^{-3} with the refined structural formula.

Chemical Composition

The chemical characterization of klöchite was done using electron-microbeam analyses and laser-ablation inductively coupled plasma – mass spectrometry (LA–ICP–MS). A JEOL 6310 scanning-electron microscope equipped with energy-dispersive (ED) and wavelength-dispersive (WD) spectrometers was operated with 15 kV and 5 nA, with a beam diameter of ~1 μm. As standards, we have used: WD: Na (kaersutite), ED: Si, K (K-feldspar), Mn (rhodonite), Fe (kaersutite), Zn (gahnite). The PHI-RHO-Z software (Pouchou & Pichoir 1987) was used for data reduction.

The concentration of trace elements was determined by LA–ICP–MS (laser-ablation unit: New Wave UP 213; ICP–MS: Agilent 7500, ICP-quadrupole MS at the Department of Chemistry, Faculty of Science, Karl–Franzens University, Graz). Material was ablated by using a 213 nm laser pulsed at 5 Hz, 40 μm spot size and 85% laser power, which corresponds to an energy of ~7 J/cm^2. Helium was used as carrier gas at ~1.2 L/min flow, and the data were acquired in time-resolved mode. The standard glass NIST610 was routinely analyzed for standardization and drift correction. The standard glasses NIST612 and BCR–2 were analyzed as unknowns and could be reproduced within 10% relative error. The concentration of SiO_2 was used as the internal standard. Three spots were measured on polished crystals of klöchite that had been previously used for electron-microbeam analyses.

The mean element-concentration from 10 analyses, the range of values and trace-element contents are given in Table 1. On the basis of the X-ray data, klöchite is a member of the milarite group; therefore, the empirical formula is based on 30 atoms per formula unit. If all the iron is assumed to be divalent, the calculated formula coefficient for silicon is 12.26 atoms per formula unit

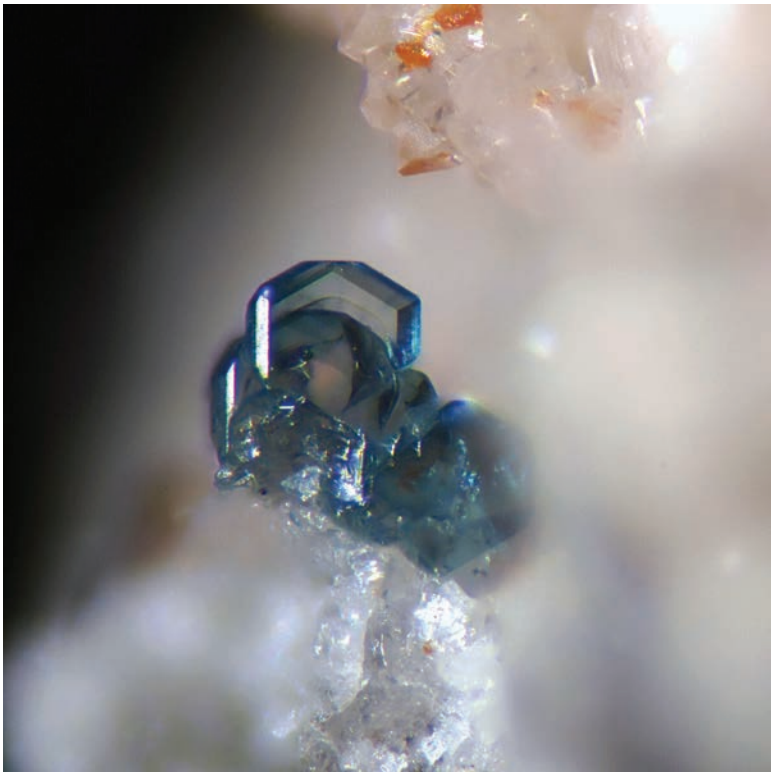

FIG. 1. Image of blue crystals of klöchite in parageneses with orange mottramite, sanidine and quartz. Field of view 1.5 mm across. Photo: W. Trattner.

(*apfu*), which is too high for the double ring complex. If all iron is assumed as trivalent, the result for silicon is too low (11.91 *apfu*). Only a mixed valence for iron gives the ideal value of 12.00 *apfu* for silicon in the double ring complex (Table 1): $(K_{0.78}Na_{0.22})$ $(\square_{1.67}Na_{0.33})$ $(Fe^{3+}{}_{1.19}Fe^{2+}{}_{0.45}Mn_{0.27}Ca_{0.04}Co_{0.02}Ni_{0.01}Mg_{0.01}Ti_{0.01})$ $(\square_{0.25}Zn_{2.63}Fe^{2+}{}_{0.10}Li_{0.02})$ $[Si_{12.00}O_{30.00}]$. All formula calculations result in a significant vacancy at the *B* site and a small vacancy at the *T2* site. The simplified chemical formula is: $K\square_2$ $(Fe^{2+}Fe^{3+})$ Zn_3 $[Si_{12}O_{30}]$, which requires K_2O 4.05, FeO 6.17, Fe_2O_3 6.86, ZnO 20.97 and SiO_2 61.95%.

X-RAY CRYSTALLOGRAPHY

X-ray powder diffraction

No experimental powder X-ray diffraction was performed because insufficient sample is available. Therefore, a simulated powder-diffraction pattern of klöchite for Bragg–Brentano geometry (Cu*K*α radiation, λ = 1.5405 Å) using the parameters of the single-crystal refinement is presented in Figure 2, and the calculated values are listed in Table 2.

X-ray structure determination

For the structure analysis, the crystal was mounted onto the tip of a glass fiber, and data collection was performed with a Bruker–AXS SMART APEX CCD diffractometer using graphite-monochromated Mo*K*α radiation (λ = 0.71073 Å). The data were reduced to F_o^2 and corrected for absorption effects with SAINT (Bruker–AXS 2003) and SADABS (Sheldrick 1998), respectively. The structure of klöchite was refined using the software SHELX–97 (Sheldrick 1997). Bond-valences were calculated using the software VALENCE (Brown 1996) with the parameters of Brese & O´Keeffe (1991).

Systematic absences and the intensity statistics favor the space group *P*6/*mcc*. Only one non-significant reflection violates the conditions of this space group, and no inconsistent equivalents were recorded during data processing. The structure refinement was started with the positional parameters of the milarite-group mineral darapiosite (Ferraris *et al.* 1999) and with the site labeling according to Forbes *et al.* (1972). In the first step, the *T*1, *T*2, *A* and *C* sites were set to a full occupancy with Si, Zn, Fe + Mn and K, respectively.

TABLE 1. KLÖCHITE: CHEMICAL COMPOSITION AND CALCULATED FORMULA COEFFICIENTS

	average	range		1	2	3
Na wt.%	1.09	0.88 - 1.51	Li_2O wt%	0.03	0.03	0.03
Si	29.29	28.84 - 29.55	Na_2O	1.47	1.47	1.47
K	2.64	2.53 - 2.67	MgO	0.04	0.04	0.04
Mn	1.31	1.22 - 1.39	SiO_2	62.66	62.66	62.66
Fe	8.46	7.89 - 8.79	K_2O	3.18	3.18	3.18
Zn	14.91	14.16 - 15.81	CaO	0.25	0.25	0.25
			TiO_2	0.05	0.05	0.05
Li ppm	151	117 - 169	MnO	1.69	1.69	1.69
Be	5	4 - 5	FeO	10.88	-	3.46
Mg	233	171 - 341	Fe_2O_3	-	12.09	8.25
Al	116	83 - 135	CoO	0.16	0.16	0.16
Ca	1821	1186 - 2843	NiO	0.08	0.08	0.08
Ti	325	300 - 366	ZnO	18.56	18.56	18.56
V	17	12 - 21				
Cr	1		sum	99.05	100.26	99.88
Co	1259	1131 - 1391				
Ni	653	581 - 736	Li *apfu*	0.03	0.02	0.02
Cu	4	2 - 5	Na	0.56	0.54	0.55
Rb	157	152 - 164	Mg	0.01	0.01	0.01
Sr	<1		Si	12.23	11.88	12.00
Y	<1		K	0.79	0.77	0.78
Zr	7	6 - 8	Ca	0.05	0.05	0.04
Nb	1		Ti	0.01	0.01	0.01
Ba	3	1 - 4	Mn	0.28	0.27	0.27
			Fe^{2+}	1.78	-	0.55
			Fe^{3+}	-	1.73	1.19
			Co	0.03	0.02	0.02
			Ni	0.01	0.01	0.01
			Zn	2.68	2.60	2.63

Concentrations of the major elements were measured by electron-microbeam analyses. Concentrations of the trace elements were established by laser-ablation ICP–MS. 1: Iron assumed to be divalent, 2: iron assumed to be trivalent, 3: mixed valence of iron assuming that there are 12 atoms of Si per formula unit. The formula is based on 30 atoms of oxygen per formula unit. Number of analyses: ten for the major elements, and three for the trace elements. An average and the range are shown.

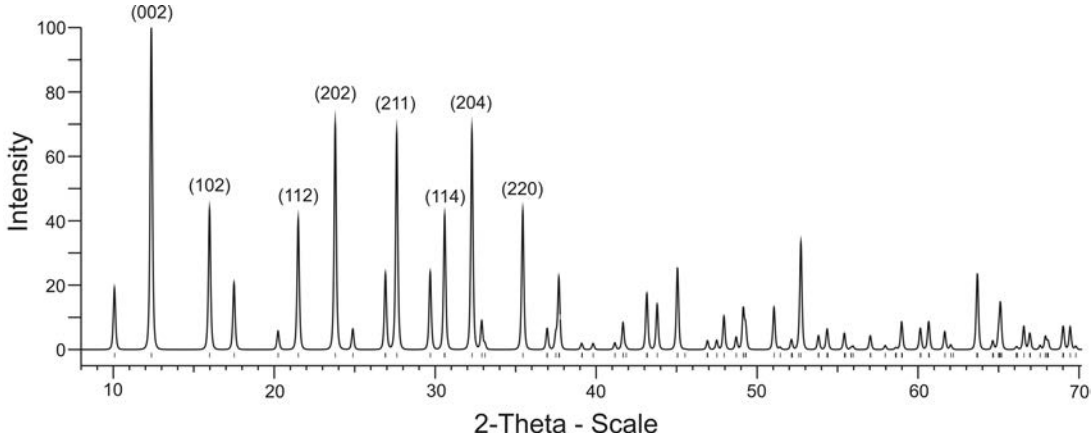

FIG. 2. Simulated powder X-ray-diffraction pattern of klöchite in a Bragg–Brentano geometry and with Cu*K*α radiation using the parameters of the single-crystal refinement. The strongest eight reflections are indexed.

Subsequent refinements of the site occupancies resulted in 93(1)% Zn for *T*2. The refined scattering power for this site is too low for a full occupancy by heavy elements like Zn and Fe. Apart from Si, no elements with Z ≤ 14 were detected from chemical analyses in significant amounts for a constrained full occupancy at *T*2 (Li 117–169, Be 4–5, Mg 171–341, Al 83–135 ppm). Therefore, a vacancy of 7% results for the site-occupancy refinement of *T*2. Subsequent difference-Fourier maps gave an indication that the *B* site is nearly empty [8(2)% Na] and the *C* site is almost fully occupied by K, complemented by Na to a full occupancy [81(3)% K, 19(3)% Na]. The final refinement converged to R_1 = 2.28% (wR_2 = 6.74%), and the minimum and maximum on the final difference-Fourier map was –0.31 and 0.41 eÅ^{-3}, from the *A* and O2 site, respectively. On the basis of these results, the refined structural formula for klöchite can be given as $(K_{0.81}Na_{0.19})$ $(\square_{1.83}Na_{0.17})$ $(Fe_{1.74}Mn_{0.26})$ $(\square_{0.21}Zn_{2.79})$ $[Si_{12}O_{30}]$, which is in good agreement with the results of the chemical analyses.

Further details relevant to the data collection and selected refinement data for klöchite are given in Table 3. Refined positional and displacement parameters are given in Table 4, and selected interatomic distances and angles in Table 5. A table of structure factors and a cif file are available from the Depository of Unpublished Data on the Mineralogical Association of Canada website [document Klöchite CM49_1115)

TABLE 2. X-RAY POWDER DATA FOR KLÖCHITE

h	*k*	*l*	d_{calc}	I_{calc}	*h*	*k*	*l*	d_{calc}	I_{calc}
1	0	0	8.764	19	4	1	0	1.9124	3
0	**0**	**2**	**7.149**	**100**	4	1	1	1.8956	10
1	**0**	**2**	**5.540**	**43**	4	0	4	1.8680	4
1	1	0	5.060	20	3	1	5	1.8520	11
2	0	0	4.382	6	4	1	2	1.8475	4
1	**1**	**2**	**4.130**	**40**	3	0	6	1.8465	3
2	**0**	**2**	**3.736**	**70**	0	0	8	1.7872	13
0	0	4	3.5745	6	5	0	0	1.7528	3
1	0	4	3.3097	23	2	2	6	1.7346	33
2	**1**	**1**	**3.2270**	**67**	3	1	6	1.7016	3
2	1	2	3.0055	24	3	3	0	1.6866	3
1	**1**	**4**	**2.9195**	**40**	4	1	4	1.6863	3
2	**0**	**4**	**2.7698**	**68**	4	2	0	1.6562	5
2	1	3	2.7200	9	4	2	2	1.6135	3
2	**2**	**0**	**2.5299**	**43**	5	1	1	1.5646	7
2	1	4	2.4296	5	5	1	2	1.5372	4
3	1	1	2.3963	4	3	2	6	1.5367	3
2	2	2	2.3850	21	3	3	4	1.5253	7
3	1	2	2.3013	2	3	0	8	1.5245	2
3	1	3	2.1653	8	4	2	4	1.5027	6
4	0	2	2.0948	13	6	0	0	1.4607	4
2	0	6	2.0934	5	2	2	8	1.4597	21
2	2	4	2.0650	14	5	1	4	1.4406	2
3	2	0	2.0106	7	4	3	1	1.4335	2
3	1	4	2.0100	18	6	0	2	1.4311	13
2	1	6	1.9344	3	5	2	0	1.4033	7

The pattern was calculated with parameters from the structure refinement (intensities calculated for Cu*K*α radiation).

Results and Discussion

The structure of klöchite is isotypic with that of milarite, with the general structural formula $^{[12]}C$ $^{[9]}B_2$ $^{[6]}A_2$ $^{[4]}T2_3$ $[^{[4]}T1_{12}O_{30}]$. The basic structural unit, $[T1_{12}O_{30}]$, is built by double six-membered rings of corner-linked *T*1 tetrahedra. The $[T1_{12}O_{30}]$ units are stacked along [001] and build channels along the **c** axis. The twelve-coordinated *C* site is situated at the center of the channel between two $[T1_{12}O_{30}]$ units (Fig. 3a). The *T*2 tetrahedra and *A* octahedra are on the same plane, parallel to (001), arranged in groups of three *T*2 tetrahedra around one *A* octahedron giving $AT2_3$ units (Fig. 3b). These connect the $[T1_{12}O_{30}]$ units by sharing corners along [001]. The *B* site is located in the voids between three $[T1_{12}O_{30}]$ units at the same *x*, *y* coordinates as the *A* site but with *z* (0, ½) at the mirror plane.

With the publication of the paper on friedrichbeckeite (Lengauer *et al.* 2009), structure refinements of 21 mineral species with a milarite-type structure have been reported. The *c*:*a* ratio of minerals of the milarite group shows a bimodal distribution controlled by the size of the cation at the *A* site. Klöchite, with *c*:*a* = 1.413, fits well with the majority of the milarite-group minerals, which belong to the first subgroup with a mean *c*:*a* ratio of 1.41(1) (Lengauer *et al.* 2009).

The chemical variation in the milarite-type minerals is generally caused by the different elements substituting in the $AT2_3$ units; the charge balance is compensated by substitutions at the *B* site and, in a few examples, also at the *C* site (*e.g.*, trattnerite, Postl *et al.* 2004). Dusmatovite (Sokolova & Pautov 1995), shibkovite (Sokolova *et al.* 1999) and darapiosite (Ferraris *et al.* 1999) are milarite-type minerals with Zn at the *T*2 site. They show a range of the *T*2–O3 distances (d_{T2}) from 1.959 Å to 1.976 Å for shibkovite (*T*2 = Zn_3) and darapiosite (*T*2 = $Li_{1.54}Zn_{1.15}Fe^{2+}_{0.31}$), respectively. In klöchite, *T*2–O3 is equal to 1.957 Å ($\square_{0.21}Zn_{2.79}$), and fits well with the normal Zn–O bond lengths for Zn atoms in tetrahedral

TABLE 3. KLÖCKITE: CRYSTAL DATA, DATA-COLLECTION INFORMATION AND DETAILS CONCERNING THE REFINEMENT

a (Å)	10.120(1)	Total reflections / rejected	10093/1555
c (Å)	14.298(3)	Unique reflections	451
V (Å^3)	1268.1(3)	Unique $\lvert F_o\rvert > 4\sigma F_o$	449
Space group	*P*6/*mcc*	R_{merge}	0.057
Z	2	Refined parameters, *p*	44
D_{calc} (g cm^{-3})	3.016	Goodness of fit, *S*	1.056
Crystal size	0.06 × 0.08 ×	R_1 ($\lvert F_o\rvert > 4\sigma F_o$)	0.0228
(mm)	0.15	R_1 (all data)	0.0231
F_{000}	1126.1	wR_2 (all data)	0.0674
μ (cm^{-1})	45.5	Largest diff. peak	0.41
Radiation	Mo*K*α	hole (eÅ^{-3})	-0.31
Temperature (K)	100	Transmission ratio	
θ_{max} (°)	26.20	T_{min} / T_{max}	0.767

Note: $R_1 = \Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \Sigma\lvert F_o\rvert$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0427P)^2 + 3.00P]$, where $P = (\max(F_o^2,0) + 2F_c^2) / 3$; $S = \{\Sigma[w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$, where *n* is the number of reflections, and *p* is the number of refined parameters.

TABLE 4. FRACTIONAL COORDINATES, EQUIVALENT ISOTROPIC-DISPLACEMENT PARAMETERS, SITE OCCUPANCIES AND ANISOTROPIC DISPLACEMENT PARAMETERS OF ATOMS IN KLÖCHITE

Site	Atom	CN	MW	*x*	*y*	*z*	U_{eq}	sof	Occ.
C	K	[12]	2 a	0	0	¼	0.013(1)	0.067(3)	0.81(3)[a]
	Na							0.016(3)	0.19(3)[a]
B	Na	[9]	4 d	⅓	⅔	0	0.03*	0.014(2)	0.08(2)
A	Fe	[6]	4 c	⅓	⅔	¼	0.0063(3)	0.145	0.87
	Mn							0.022	0.13
*T*2	Zn	[4]	6 f	½	0	¼	0.0081(3)	0.232(1)	0.93(1)
*T*1	Si	[4]	24 m	0.11653(8)	0.35251(8)	0.10978(5)	0.0079(2)	1	1
O1	O	[3]	12 l	0.1303(3)	0.3911(3)	0	0.0135(6)	0.5	1
O2	O	[3]	24 m	0.2211(2)	0.2773(2)	0.1354(1)	0.0146(5)	1	1
O3	O	[4]	24 m	0.1586(2)	0.4993(2)	0.1720(1)	0.0103(4)	1	1

Site	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C	0.014(1)	0.014(1)	0.010(1)	0	0	0.0069(5)
A	0.0071(3)	0.0071(3)	0.0047(4)	0	0	0.0035(2)
*T*2	0.0096(4)	0.0074(4)	0.0064(4)	0	0	0.0037(2)
*T*1	0.0084(4)	0.0107(4)	0.0048(4)	-0.0006(3)	-0.0003(2)	0.0049(3)
O1	0.016(1)	0.020(1)	0.005(1)	0	0	0.009(1)
O2	0.018(1)	0.020(1)	0.0103(9)	-0.0011(7)	-0.0017(7)	0.0135(9)
O3	0.0119(9)	0.0116(9)	0.0081(9)	-0.0005(7)	0.0001(7)	0.0063(7)

CN: coordination number; M: site multiplicity; W: Wyckoff letter; U_{eq}: equivalent isotropic displacement factor according to Fischer & Tillmanns (1988); sof: site-occupancy factor; Occ.: site-occupancy values; *U_{iso}: constrained in refinement; [a] sum constrained to 1.0.

TABLE 5. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN KLÖCHITE

C–O2	x 12	3.047(2)	*T*1 –O3	1.596(2)
			–O1	1.606(1)
B–O1	x 3	2.504(3)	–O2	1.623(2)
B–O3	x 6	3.008(2)	–O2	1.624(2)
			mean	1.612
A–O3	x 6	2.060(2)		
			O1–O2	2.641(3)
O3–O3	x 3	2.755(3)	O1–O2	2.650(3)
O3–O3	x 3	2.892(3)	O1–O3	2.649(2)
O3–O3	x 6	3.000(3)	O2–O2	2.569(2)
			O2–O3	2.673(3)
O3–*A*–O3	x 3	83.9(1)	O2–O3	2.610(3)
O3–*A*–O3	x 3	89.2(1)		
O3–*A*–O3	x 6	93.5(1)	O2–*T*1–O2	104.6(1)
O3–*A*–O3	x 3	176.4(1)	O1–*T*1–O2	109.7(1)
			O2–*T*1–O3	108.3(1)
*T*2–O3	x 4	1.957(2)	O1–*T*1–O2	110.3(1)
			O2–*T*1–O3	112.2(1)
O3–O3	x 2	2.755(3)	O1–*T*1–O3	111.6(1)
O3–O3	x 2	3.217(3)	mean	109.5
O3–O3	x 2	3.564(3)		
			*T*1–O1–*T*1	155.4(2)
O3–*T*2–O3	x 2	89.5(1)	*T*1–O2–*T*1	151.6(1)
O3–*T*2–O3	x 2	110.6(1)	*T*1–O3–*T*2	118.9(1)
O3–*T*2–O3	x 2	131.1(1)	*T*1–O3–*A*	141.9(1)
			*T*2–O3–*A*	93.3(1)

coordination. There are also shorter ^{IV}Zn–O distances. In the crystal structure of $K_2ZnSi_2O_6$ (Hogrefe & Czank 1995), the Zn–O distances in the tetrahedra are 1.926 Å (×2) and 1.962 Å (×2); the median value is 1.944 Å.

The mean <*T*1–O> distance of 1.612 Å for klöchite indicates a *T*1 site fully occupied with Si, which was also found for shibkovite (1.613 Å), dusmatovite (1.613 Å) and darapiosite (1.614 Å).

The *A*–O3 distances (d_A) in klöchite are significantly shorter ($A = Fe_{1.74}Mn_{0.26}$, $d_A = 2.060$ Å, $d_A : d_{T2} = 1.05$) than in shibkovite ($A = Ca_{1.26}Mn_{0.40}Na_{0.34}$, $d_A = 2.300$ Å, $d_A : d_{T2} = 1.17$), which belongs, with c:a = 1.351, to the second subgroup of milarite-type minerals, with a mean c:a ratio of 1.32(2) (Lengauer *et al.* 2009). Dusmatovite ($d_A = 2.120$ Å, $d_A : d_{T2} = 1.08$) and darapiosite ($d_A = 2.151$ Å, $d_A : d_{T2} = 1.09$) belong to the first subgroup, with c:a = 1.399 and 1.394, respectively, and they have longer *A*–O3 distances than in klöchite. For the milarite group, Armbruster & Oberhänsli (1988) demonstrated the positive correlation that exists between the length of a and the length of the edge (O3–O3) shared between *T*2 and *A*. This is also confirmed by the values for klöchite (2.755, 10.120), dusmatovite (2.832, 10.218), darapiosite (2.869, 10.262) and shibkovite (2.973, 10.502) (O3–O3, a both in Å). Application of the equation $a = 5.610 + 1.59d_{A–O3} + 0.63d_{T2–O3}$ reported by Armbruster & Oberhänsli (1988) to klöchite results in $a = 10.118$ Å and agrees well with the experimental value, $a = 10.120$ Å.

The linear function $\langle A–O\rangle = 1.311 + 1.066 \langle r_A\rangle$ for milarite-group minerals (Hawthorne *et al.* 1991) yields the *A*–O3 distance with the aggregate radius of the octahedrally coordinated cations at the *A* site. For klöchite

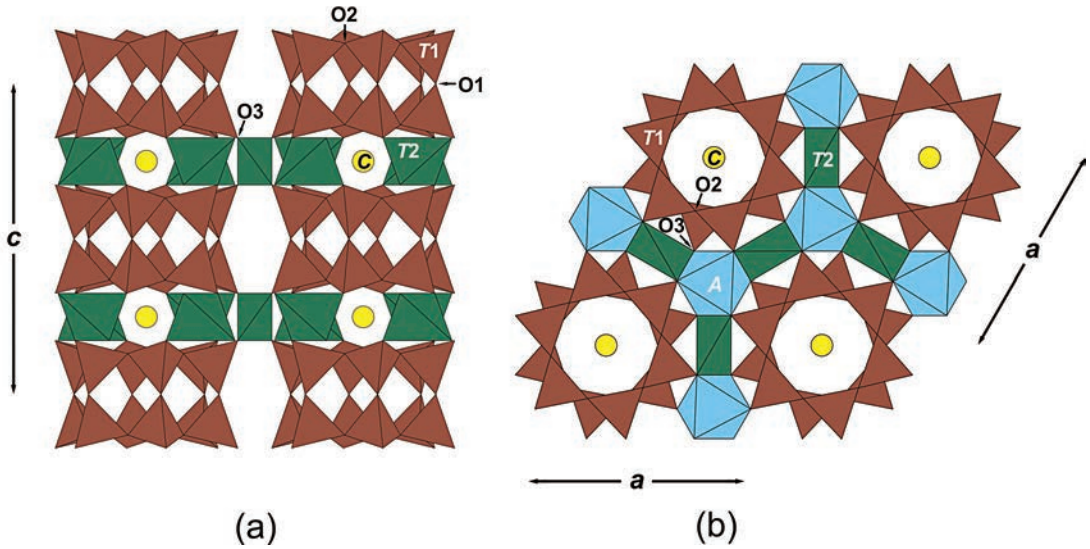

FIG. 3. Projections of the structure of klöchite: (a) along [$\bar{1}$10], the *A* octahedron has been omitted for clarity; (b) along [001]. In both projections, the empty *B* site is omitted.

($A = Fe_{1.74}Mn_{0.26}$), two extreme values are possible: for all Fe = Fe^{2+}: <*A*–O> = 2.15 Å (<r_A> = 0.79), and for all Fe = Fe^{3+}: <*A*–O> = 2.02 Å (<r_A> = 0.67). From bond-valence calculations for klöchite, the value obtained for the *A* site is 2.54, which indicates that about 50% of the site occupancy is a cation of valence 3+. Taking this into account (A: $Fe^{3+}_{1.00}$ $Fe^{2+}_{0.74}Mn^{2+}_{0.26}$), <*A*–O> is inferred to be 2.078 Å (<r_A> = 0.72), which is in good agreement with the refined *A*–O3 distance of 2.060 Å. A perfect agreement of the *A*–O3 distances is calculated for klöchite with <*A*–O> = 2.060 Å (<r_A> = 0.72) using the equation from Cooper *et al*. (1999), <*A*–O> = 1.411 + 0.901 <r_A>.

The octahedron and tetrahedron in the $AT2_3$ units show the characteristic distortion coupled with a significant reduction in the length of the shared O3–O3 edges. In klöchite, the deviations from the ideal value, 109.47°, of the O3–T2–O3 angles are in the range 89.5–131.1°, and O3–O3 is reduced to 2.755 Å.

Armbruster & Oberhänsli (1988) reported a negative correlation of the angular distortion in *A* and *T*2: sugilite and brannockite have large *T*2 tetrahedra, which show a strong angular distortion, and these tetrahedra are connected to very weak distorted *A* octahedra. In Table 6, angular distortion indices (DI) of *A*, *T*2, *T*1 and the ratio ($d_A : d_{T2}$) of the bond lengths *A*–O3 and *T*2–O3 are calculated for the Li-, Zn-, Be- and B-bearing minerals of the milarite group. Values for trattnerite, merrihueite and roedderite are given for comparison. The distortion indices (DI) for the tetrahedron (*T*) and the octahedron (*A*) are calculated using the equations reported by Baur (1974): DI(O–*T*–O) = [$\Sigma|(O - T–O)_i - (O–T–O)_m|$] / 6(O–*T*–O)$_m$ and DI(O–*A*–O) = [$\Sigma|(O–A–O)_i - (O–A–O)_m|$] / 12(O–*A*–O)$_m$; i = 1 → 6 for the tetrahedron angles and i = 1 → 12 for the octahedron angles, m is the mean value of (O–*T*–O) and (O–*A*–O), respectively. In Figure 4, two separate negative correlations are visible for DI(O–*T*2–O) and DI(O–*A*–O): in the first group (Be and B at *T*2), a strong negative linear correlation exists from poudretteite, spanning milarite, oftedalite and almarudite to friedrichbeckeite; DI(O–*A*–O) = 0.221 – 1.096DI(O–*T*2–O), with R^2 = 0.999. Poudretteite has an almost undistorted *T*2 tetrahedron coupled with a strongly distorted *A* octahedron; friedrichbeckeite shows nearly equal distortions for *A* and *T*2. The values for $d_A : d_{T2}$ decrease from poudretteite (1.62) to friedrichbeckeite (1.24), respectively.

Klöchite is a member of the second group, with almost undistorted *A* octahedra and strongly distorted *T*2 tetrahedra, from sugilite to dusmatovite. Shibkovite shows nearly equal distortions for *A* and *T*2 like friedrichbeckeite, but with smaller values. The distortion values for merrihueite, roedderite and trattnerite also fit with the second group, with almost undistorted *A* octahedra; DI(O–*A*–O) = 0.125 – 0.666DI(O–*T*2–O), with R^2 = 0.937 .

Hawthorne *et al*. (1991) reported in their Figure 13 two separate correlations for the variation in <*A*–O> as a function of constituent-cation radius <r> at the *A* site. Small cations at the *A* site show a different correlation than the larger ones, with a constituent-cation radius exceeding 0.7 Å. This is also evident in the correlation

TABLE 6. SELECTED MINERALS OF THE MILARITE GROUP, WITH THE MAIN OCCUPANTS OF THE SITES *A* AND *T*2, THE RATIO d_A:d_{T2} OF THE DISTANCES FOR *A*–O3 AND *T*2–O3, AND ANGULAR DISTORTION INDICES FOR *A*, *T*2 AND *T*1*

	$^{[6]}A$	$^{[4]}T2$	$d_A : d_{T2}$	DI (O-*A*-O)	DI (O-*T*2-O)	DI (O-*T*1-O)
Shibkovite [1]	**Ca**, Mn, Na	**Zn**	1.17	0.071	0.088	0.018
Dusmatovite [2]	**Mn**, Y, Zr	**Zn**, Li	1.08	0.042	0.117	0.017
Darapiosite [3]	**Mn**, Zr, Y	**Li**, Zn, Fe	1.09	0.039	0.118	0.019
Sogdianite [4]	**Zr**, Ti, Fe	**Li**	1.07	0.040	0.124	0.016
Klöchite [5]	**Fe**, Mn	**Zn**	1.05	0.039	0.126	0.018
Brannockite [6]	**Sn**	**Li**	1.05	0.036	0.138	0.017
Sugilite [6]	**Fe**, Al	**Li**	1.00	0.025	0.151	0.025
Merrihueite [7]	**Mg**, Fe	**Mg**, Fe	1.08	0.047	0.119	0.017
Roedderite [8]	**Mg**, Fe	**Mg**, Fe	1.07	0.043	0.121	0.018
Trattnerite [9]	**Fe**, Mg	**Mg**, Fe	1.05	0.042	0.132	0.012
Poudretteite [10]	**Na**	**B**	1.62	0.196	0.024	0.016
Milarite [11]	**Ca**	**Be**, Al	1.42	0.165	0.049	0.016
Oftedalite [12]	**Sc**, Ca, Mn	**Be**	1.36	0.141	0.073	0.016
Almarudite [13]	**Mn**, Fe, Mg	**Be**, Al	1.29	0.122	0.092	0.017
Friedrichbeckeite [14]	**Mg**, Mn, Fe	**Be**, Mg	1.24	0.103	0.107	0.019

References: [1] Sokolova *et al.* (1999), [2] Sokolova & Pautov (1995), [3] Ferraris *et al.* (1999), [4] Cooper *et al.* (1999), [5] this study, [6] Armbruster & Oberhänsli (1988), [7] Dodd *et al.* (1965), [8] Armbruster (1989), [9] Postl *et al.* (2004), [10] Grice *et al.* (1987), [11] Hawthorne *et al.* (1991), sample 36, [12] Cooper *et al.* (2006), [13] Mihajlović *et al.* (2004), [14] Lengauer *et al.* (2009). * Calculated using the equations reported by Baur (1974).

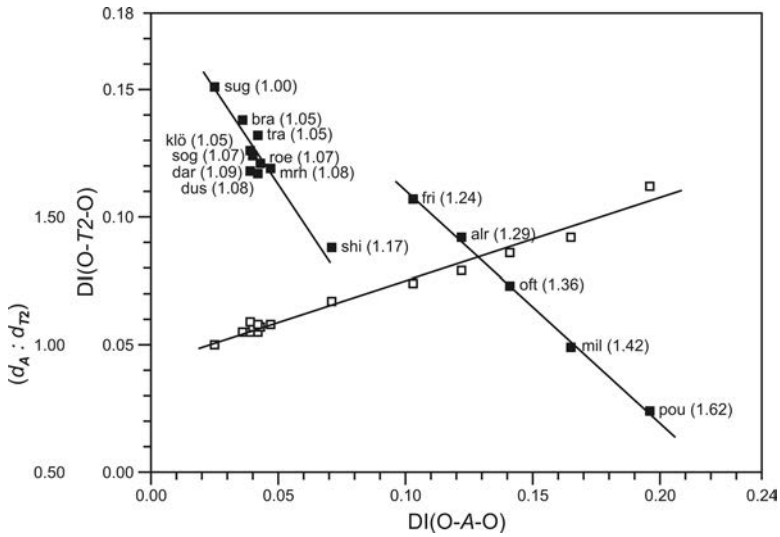

FIG. 4. Angular distortions for *A* and *T*2 plotted with the distortion indices DI(O–*A*–O) *versus* DI(O–*T*2–O) (full squares) for shibkovite (shi: Sokolova *et al.* 1999), dusmatovite (dus: Sokolova & Pautov 1995), darapiosite (dar: Ferraris *et al.* 1999), sogdianite (sog: Cooper *et al.* 1999), klöchite (klö: this study), brannockite (bra) and sugilite (sug: Armbruster & Oberhänsli 1988), merrihueite (mrh: Dodd *et al.* 1965), roedderite (roe: Armbruster 1989), trattnerite (tra: Postl *et al.* 2004), poudretteite (pou: Grice *et al.* 1987), milarite (mil: Hawthorne *et al.* 1991, sample 36), oftedalite (oft: Cooper *et al.* 2006), almarudite (alr: Mihajlović *et al.* 2004), friedrichbeckeite (fri: Lengauer *et al.* 2009). Two separate negative correlations for DI(O–*A*–O) *versus* DI(O–*T*2–O) are visible. Open squares show the positive linear correlation for DI(O–*A*–O) *versus* $d_A : d_{T2}$ (values in brackets) for selected minerals of the milarite group.

of the angular distortions in *T*2 and *A* compared with the ratio $d_A : d_{T2}$ in this study. In addition, there is a positive linear correlation between the angular distortion for *A* and the ratio of $d_A : d_{T2}$ for all milarite-type minerals plotted in Figure 4: DI(O–*A*–O) = –0.284 + 0.307($d_A : d_{T2}$), with $R^2 = 0.989$. Values for $d_A : d_{T2}$ close to 1.0 indicate almost undistorted *A* octahedra, whereas values from 1.17 (shibkovite) to 1.62 (poudretteite) show a significant increase in the distortion of the octahedron.

Except for trattnerite and sugilite, the angular distortion for the *T*1 tetrahedron is in a restricted range between 0.016 and 0.019, and no correlation with the distortion of *A* and *T*2 is obvious (Table 6). One of the reasons for the angular distortions in *T*1 is the size of the cation at the *C* site, which connects the double-ring unit along **c** (Winter *et al*. 1995). The small value of DI(O–*T*1–O) for trattnerite, 0.012, is also caused by the vacancy at the *C* site, *C*–O2 = 3.123 Å, a distance that is too long if K occupies *C*. Sugilite shows the shortest *C*–O2 distance (2.994 Å) for K at the *C* site, and the largest angular distortion for *T*1, DI(O–*T*1–O) (0.025) of the milarite-group minerals. The values for klöchite, *C*–O2 = 3.047 and DI(O–*T*1–O) = 0.018, are in the range for milarite-group minerals with K at the *C* site.

Bond-valence sums were calculated for the cations and anions in klöchite taking into account the refined mixed occupancies of the *A* and *C* sites, and the partial occupancy of the *B* and *T*2 sites. The values obtained are 0.90 (*C*), 0.05 (*B*), 2.54 (*A*), 1.88 (*T*2), 4.13 (*T*1), 2.11 (O1), 2.08 (O2) and 1.98 (O3) valence units (*vu*). The value for the *B* site indicates a nearly empty site, as a fully occupied *B* site would result in an oversaturated O1 site. For the *T*2 site, the expected value for a divalent cation and a site vacancy of 7% is 1.86 *vu*. The low site-vacancy at *T*2 is also confirmed by the calculated valence-sum of 1.88 *vu*. A somewhat high value for *T*1 is also reported by Lengauer *et al*. (2009) for friedrichbeckeite (4.18 *vu*). The value for *A* (2.54 *vu*) in klöchite indicates the presence of a mixed valence, 2+ and 3+, at this site, already discussed in connection with the refined and calculated *A*–O3 distance, 2.060 Å.

In accordance to the site occupancies and the bond-valence considerations and following Hawthorne (2002) for the definition of an end-member formula, the formula for klöchite is $K_1 \square_2 (Fe^{2+}{}_1Fe^{3+}{}_1) Zn_3 [Si_{12}O_{30}]$ for the *C*, *B*, *A*, *T*2 and *T*1 sites, respectively. Klöchite can be considered as the Fe-analogue of dusmatovite, $K_1 (\square_1Na_1) Mn^{2+}{}_2 Zn_3 [Si_{12}O_{30}]$ or shibkovite, $K_1 (\square_1K_1) Ca_2 Zn_3 [Si_{12}O_{30}]$.

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