Mineralogical Magazine, December 2012, Vol. 76(7), pp. 2761–2771

Whiteite-(CaMnMn), $CaMnMn_2Al_2[PO_4]_4(OH)_2{\cdot}8H_2O$, a new mineral from the Hagendorf-Süd granitic pegmatite, Germany

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[*Received 21 June 2012; Accepted 2 October 2012; Associate Editor: Allan Pring*]

ABSTRACT

Whiteite-(CaMnMn), $CaMnMn_2Al_2[PO_4]_4(OH)_2{\cdot}8H_2O$, is a new hydrous phosphate of Ca, Mn and Al, which is closely related to both jahnsite-(CaMnMn) and the minerals of the whiteite group. It is monoclinic, *P*2/*a*, with *a* = 15.02(2), *b* = 6.95(1), *c* =10.13(3) Å, β = 111.6(1)º, *V* = 983.3(6) Å^3, *Z* = 2 (from powder diffraction data) or *a* = 15.020(5), *b* = 6.959(2), *c* = 10.237(3) Å, β = 111.740(4)º, *V* = 984.3(5) Å^3, *Z* = 2 (from single-crystal diffraction data). The mineral was found in the Hagendorf Süd granitic pegmatite (Germany) as small (up to 0.5 mm in size) crystals elongated on *a* and tabular on {010}. The crystals are either simply or polysynthetically twinned on {001}. They crystallize on the walls of voids within altered zwieselite crystals or form coronas (up to 1 mm in diameter) around cubic crystals of uraninite. The mineral is transparent, colourless to pale yellow (depending on $Al-Fe^{3+}$ substitution), with a vitreous lustre and a white streak. The cleavage is perfect on {001}, the fracture is stepped and the Mohs hardness is 3½. In transmitted light, the mineral is colourless; dispersion was not observed. Whiteite-(CaMnMn) is biaxial (+), α = 1.589(2), β = 1.592(2), γ = 1.601(2) (589 nm), $2V_{meas}$ = 60(10)º, $2V_{calc}$ = 60.3º. The optical orientation is *X* = *b*, *Z*^*a* = 5º. The calculated and measured densities are D_{calc} = 2.768 and D_{meas} = 2.70(3) g cm^{-3}, respectively. The mean chemical composition determined by electron microprobe is Na_2O 0.53, MgO 0.88, Al_2O_3 11.66, P_2O_5 34.58, CaO 4.29, MnO 17.32, FeO 8.32, ZnO 2.60 wt.%, with H_2O 19.50 wt.% (determined by the Penfield method), giving a total of 99.68 wt.%. The empirical formula calculated on the basis of four phosphorus atoms per formula unit, with ferric iron calculated to maintain charge balance, is $(Ca_{0.63}Zn_{0.26}Na_{0.14})_{\Sigma 1.03}(Mn_{0.60}Fe^{2+}_{0.40})_{\Sigma 1.00}(Mn_{1.40}Fe^{2+}_{0.37}Mg_{0.18}Fe^{3+}_{0.06})_{\Sigma 2.01}(Al_{1.88}Fe^{3+}_{0.12})_{\Sigma 2.00}[PO_4]_4(OH)_2{\cdot}7.89H_2O$. The simplified formula is $CaMnMn_2Al_2[PO_4]_4(OH)_2{\cdot}8H_2O$. The mineral is easily soluble in 10% HCl at room temperature. The strongest X-ray powder-diffraction lines [listed as *d* in Å (*I*) (*hkl*)] are as follows: 9.443(65)(001), 5.596(25)(011), 4.929(80)(210), 4.719(47)(002), 3.494(46)(400), 2.7958(100)(022). The crystal structure of whiteite-(CaMnMn) was refined for a single crystal twinned on (001) to R_1 = 0.068 on the basis of 5702 unique observed reflections. It is similar to the structures of other members of the whiteite group. The mineral is named for the chemical composition, in accordance with whiteite-group nomenclature.

Keywords: whiteite-(CaMnMn), new mineral, whiteite group, granitic pegmatite, Hagendorf-Süd, Germany.

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DOI: 10.1180/minmag.2012.076.7.09

Introduction

THE Hagendorf granitic pegmatites are a rich source of rare minerals and the type locality for the following ten secondary phosphates: jungite, $Ca_2Zn_4Fe_8(PO_4)_9(OH)_9\cdot16H_2O$; keckite, $CaMn_2Fe_3^{3+}(PO_4)_4(OH)_3\cdot2H_2O$; laueite, $MnFe_2(PO_4)_2(OH)_2\cdot8H_2O$; lehnerite $Mn(UO_2)(PO_4)_2\cdot8H_2O$; nordgauite, $MnAl_2(PO_4)_2(F,OH)_{2.5}\cdot5H_2O$; parascholzite, $CaZn_2(PO_4)_2\cdot2H_2O$; pseudolaueite, $MnFe_2(PO_4)_2(OH)_2\cdot7H_2O$; scholzite, $CaZn_2(PO_4)_2\cdot2H_2O$; strunzite, $MnFe_2(PO_4)_2(OH)_2\cdot6H_2O$; wilhelmvierlingite $CaMnFe^{3+}(PO_4)_2(OH)\cdot2H_2O$. In this paper, we describe the eleventh new phosphate from this locality: whiteite-(CaMnMn), ideally $CaMnMn_2Al_2[PO_4]_4(OH)_2\cdot8H_2O$.

Whiteite-(CaMnMn) is a new member of the jahnsite–whiteite group (Moore and Ito, 1978). The general formula for minerals of this group can be written $XM1M2_2M3_2(PO_4)_4(OH)_2\cdot8H_2O$, where $M3 = Fe^{3+}$ and Al^{3+} (for the jahnsite and whiteite endmembers, respectively); X = Ca, Na, Mn; and the $M1$ and $M2$ sites are occupied by divalent Mn, Fe, Mg and Zn (Grice *et al*., 1989, 1990). In addition to whiteite-(CaMnMn), other members of this group occur at this locality, in some cases as intergrowths or as crystals with zoned compositions (Grey *et al*., 2010).

The whiteite-(CaMnMn)-bearing specimens were collected by Erich Keck in the Cornelia mine open pit. All these specimens consist of altered or decomposed zweieselite–triplite crystals accompanied by numerous secondary phosphates, including two new minerals: nordgauite (Birch *et al*., 2011) and whiteite-(CaMnMn). The mineral was named in accordance with whiteite group nomenclature. Both mineral and mineral name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2011-002). Type material is deposited in the collections of the Mineralogical Museum of St Petersburg State University, Russia under catalogue number 1/19470.

Occurrence

The Hagendorf-Süd granitic pegmatite No. 25 (49º39′1″N, 12º27′35″E) is one of the largest pegmatites in Europe and is about 150 m in diameter. It has a hood-like concentrically zoned structure (Fig. 1) and is situated in the outermost contact of the Floßenbürg granite massif with the Moldanubian biotite-plagioclase gneisses (Forster *et al*., 1967; Strunz and Forster, 1975). The contact aplitic zone (0.5–8 m thick) consists of fine-grained muscovite, quartz and albite. The quartz-microcline eutectic zone (up to 10 m thick) is composed of hieroglyphic quartz-feldspar intergrowths and large idiomorphic crystals of these minerals.

The internal part of the pegmatite body is occupied by approximately equal volumes of a microcline-perthite, which forms the apical zone (and is up to 100 m thick) and quartz core (which is up to 50 m thick), with a thin albite layer (up to 10 m thick) and numerous local accumulations (nests) of phosphate minerals (up to about 40 m in diameter) in between. The largest accumulations of phosphate minerals are situated on top of the quartz core. A large part of the albite-phosphate zone was mined between 1952 and 1955, producing a considerable number of mineral specimens. All of the whiteite-(CaMnMn)-bearing specimens were collected from the large accumulations of phosphate minerals, which were located at depths between −45 and −85 m.

Primary phosphates in this zone include triphylite, minerals of the zwieselite–triplite series, wolfeite, hagendorfite, sarcopside, scorzalite, graftonite, arrojadite-(NaFe) and fluorapatite. These have been altered and leached by low-temperature oxidizing hydrothermal solutions to produce numerous secondary phosphates including the following species: bassetite, barbosalite, benyacarite, beraunite, childrenite, ferrisicklerite, fluellite, hureaulite, jahnsite-(CaMnMn), koninckite, kryzhanovskite, lipscombite, mitridatite, morinite, paravauxite, phosphophyllite, phosphoferrite, reddingite, rockbridgeite, stewartite, vivianite, whitmoreite, jungite, keckite, laueite, lehnerite nordgauite, parascholzite, pseudolaueite, scholzite, strunzite and wilhelmvierlingite. Associated minerals which are characteristic of this deposit include arsenopyrite, bismuth, bismuthinite, chalcopyrite, columbite-(Fe), covellite, greenockite, hematite, molybdenite, muscovite, pyrite, pyrrhotite, sphalerite, uraninite and zircon (Mücke, 1981; Mücke *et al*., 1990; Grey *et al*., 2010).

Whiteite-(CaMnMn) occurs as druses of small (up to 0.5 mm) tabular crystals (Fig. 2) on the walls of voids (rarely up to several centimetres across but more commonly 0.5–2 mm in size) within brownish orange aggregates of triplite–zwieselite, $(Mn_{1.00}Fe^{2+}_{0.93}Ca_{0.05}Mg_{0.01})_{\Sigma1.99}[P_{1.01}O_4]F$, and fluorapatite, $(Ca_{4.74}Mn_{0.24})_{\Sigma4.98}[P_{3.01}O_{12}]F$. These crystals commonly have

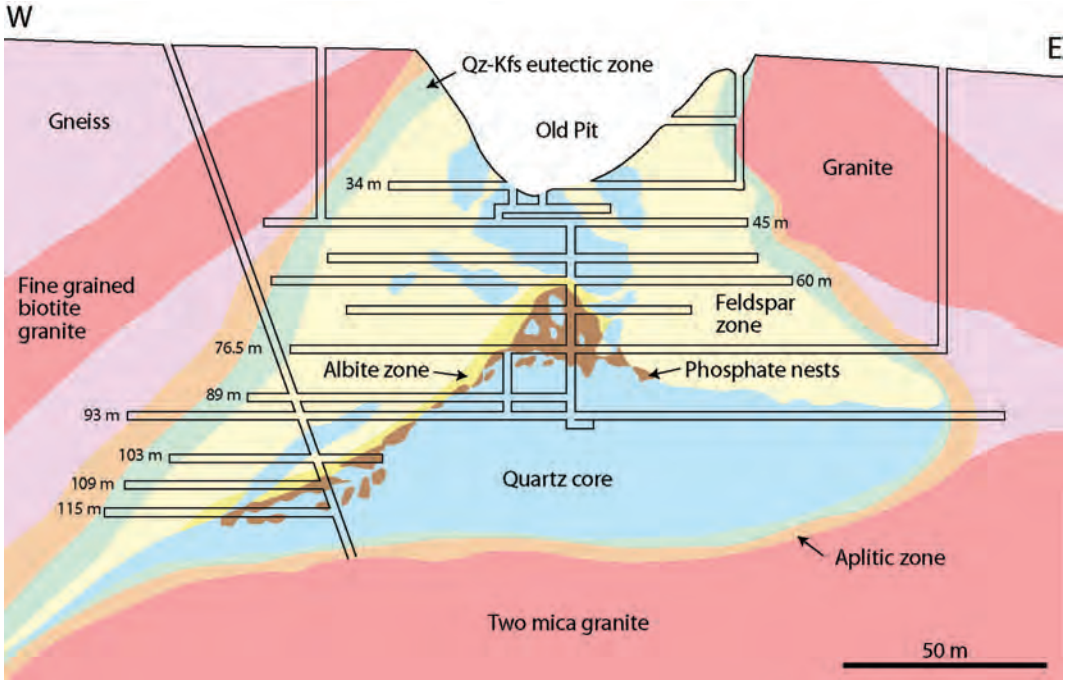

FIG. 1. West–east cross-section of the Hagendorf Süd granitic pegmatite modified from Forster *et al*. (1967).

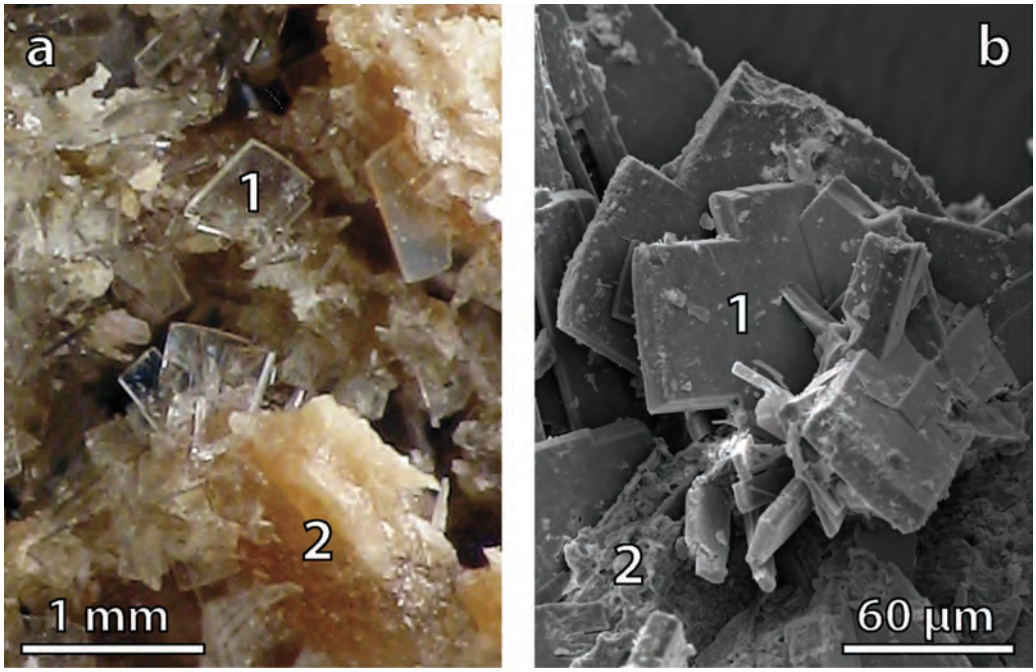

FIG. 2. Colourless, tabular crystals of whiteite-(CaMnMn) (1, up to 0.5 mm) in a void within leached triplite (2), from the Hagendorf Süd granitic pegmatite; (*a*) photo and (*b*) SEM image.

complex chemical zonation, with Al-rich cores and between 1 and 4 marginal zones enriched in Fe^{3+} (Fig. 3*a*). Fibrous nordgauite, $(Mn_{0.77}Mg_{0.14}Ca_{0.05}Fe^{2+}_{0.04})_{\Sigma 1.00}(Al_{2.04}Fe^{3+}_{0.02})_{\Sigma 2.06}[P_{2.00}O_8](F,OH)_{2.18}\cdot 5.5H_2O$; a Mn-analogue of montgomeryite, $(Ca_{3.92}Mn_{0.04}Zn_{0.04})_{\Sigma 4.00}(Mn_{0.69}Mg_{0.21}Fe^{2+}_{0.10})_{\Sigma 1.00}(Al_{3.76}Fe^{3+}_{0.24})_{\Sigma 4.00}(P_6O_{24})(OH)_{4.00}\cdot 15H_2O$; cuboctahedral crystals of uraninite, $(U_{0.96}Pb_{0.07})_{1.03}O_2$; and tabular grains of columbite-(Fe), $(Fe_{0.76}Mn_{0.29})_{\Sigma 1.05}(Nb_{1.81}Ta_{0.12}Ti_{0.06})_{\Sigma 1.99}O_6$; commonly occur in intimate association with whiteite-(CaMnMn).

Compositionally zoned crystals of whiteite-(CaMnMn) commonly form coronas (up to 1 mm in diameter) around crystals of uraninite; they are associated with nordgauite, koninckite, $(Fe^{3+}_{0.92}Mn_{0.03}Al_{0.01}Na_{0.01})_{\Sigma 0.97}[P_{1.00}O_{3.94}]\cdot 3.2H_2O$, and jahnsite-(CaMnMn), $(Ca_{0.76}Zn_{0.25})_{\Sigma 1.01}(Mn_{0.72}Fe^{2+}_{0.20})_{\Sigma 0.92}(Mn_{1.22}Fe^{2+}_{0.36}Fe^{3+}_{0.25}Mg_{0.13})_{\Sigma 1.96}(Fe^{3+}_{1.42}Al_{0.58})_{\Sigma 2.00}[PO_4]_4(OH)_2\cdot 9.0H_2O$ (Fig. 3*b*).

Morphology, physical and optical properties

Whiteite-(CaMnMn) forms bar-shaped crystals elongated along [100] and tabular on {010}. The crystals are either simply or polysynthetically twinned on {001}, with dominant pinacoidal {100}, {010}, {001} and {$\bar{1}$01} faces; the {100} pinacoid is usually rounded. The *a*:*b*:*c* ratio calculated from the unit-cell parameters is 2.161:1:1.458 (on the basis of powder diffraction data). Cleavage is perfect on (001). The mineral is brittle and has a stepped fracture. The Mohs hardness is ~3½. The density determined by the float–sink method in Clerici solution is 2.70(3) g cm^{-3}. This value is in good agreement with the calculated density of 2.768 g cm^{-3} (using the cell from powder data).

Macroscopically, whiteite-(CaMnMn) is colourless to pale yellow, depending on its Fe^{3+} content, and has a vitreous lustre. The mineral is transparent, with a white streak. It is biaxial positive, with refractive indices α = 1.589(2), β = 1.592(2), γ = 1.601(2) (589 nm); $2V_{meas}$ =

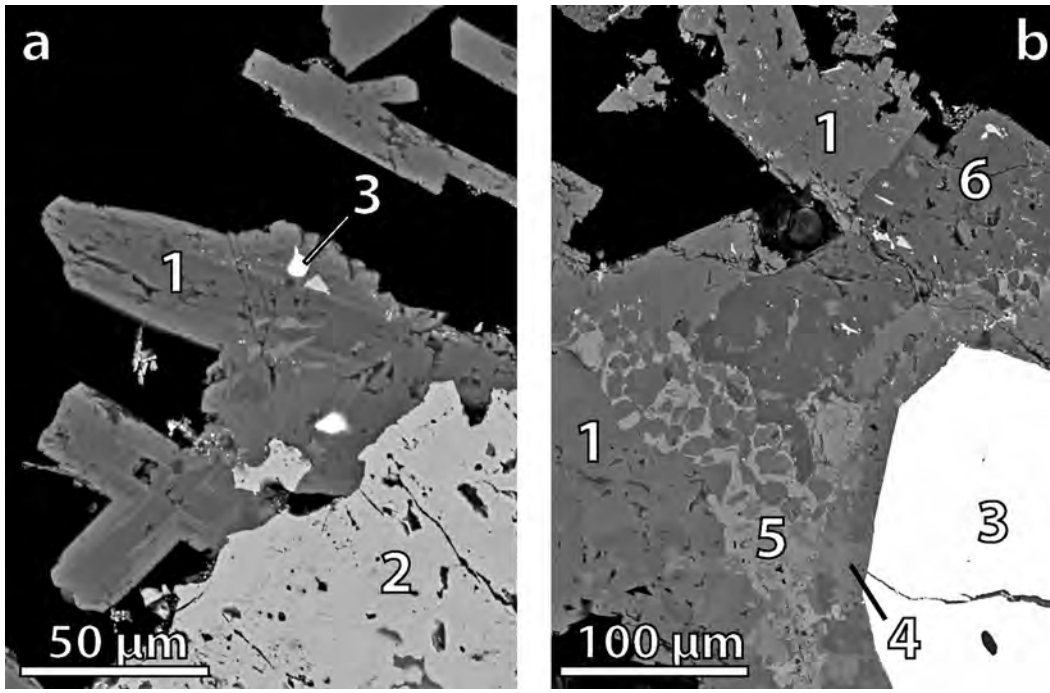

FIG. 3. Back-scattered electron images of whiteite-(CaMnMn) (1), intergrowths with triplite (2), uraninite (3), koninckite (4), jahnsite-(CaMnMn) (5) and nordgauite (6).

TABLE 1. Chemical composition of whiteite-(CaMnMn).

Constituent	Mean (wt.%)	Range	SD
Na_2O	0.53	0.00–1.03	0.29
MgO	0.88	0.56–1.41	0.22
Al_2O_3	11.66	7.78–13.32	1.71
P_2O_5	34.58	33.84–35.14	0.47
CaO	4.29	3.68–4.90	0.43
MnO	17.32	15.21–18.93	1.07
FeO	8.32	5.87–13.71	2.01
ZnO	2.60	1.74–4.14	0.72
H_2O	19.50		
Total	99.68		

60(10)º, $2V_{calc}$ = 60.3º. The optical orientation is $X = b$, $Z \wedge a$ = 5º. In transmitted light, the mineral is colourless, without dispersion or pleochroism. A Gladstone–Dale calculation provides a compatibility index of 0.035, which is regarded as excellent (Mandarino, 1981).

Chemical composition

The chemical composition of whiteite-(CaMnMn) was determined by wavelength-dispersive spectrometry on a Cameca MS-46 electron microprobe (Geological Institute, Kola Science Centre, Russian Academy of Sciences, Apatity) operating at 20 kV, 20–30 nA, with a 10 μm beam diameter. The standards used were lorenzenite (Na), pyrope (Mg, Al), fluorapatite (P, Ca), hematite (Fe), synthetic $MnCO_3$ (Mn) and ZnO (Zn). The H_2O content was determined by the Penfield method (Sandell, 1951) on purified material. The absence of carbon and fluorine was confirmed by energy-dispersive spectrometry using a Röntec spectrometer on a LEO 1450 scanning electron microscope. Table 1 provides mean analytical results for 13 different crystals (5–6 analyses per crystal).

TABLE 2. Crystallographic data and refinement parameters for whiteite-(CaMnMn).

Crystal data	
Chemical formula	$Mn_{2.96}Al_{1.85}Ca_{0.93}Fe_{0.16}Zn_{0.07}Mg_{0.04}(PO_4)_4(OH)_2(H_2O)_8$
Temperature (K)	293
Radiation, wavelength (Å)	Mo$K\alpha$, 0.71073
Crystal system	monoclinic
Space group	*P2/a*
Unit-cell dimensions *a*, *b*, *c* (Å), β (º)	15.020(5), 6.959(2), 10.137(3), 111.740(4)
Unit-cell volume (Å^3)	984.3(5)
Z	2
Calculated density (g cm^{-3})	2.77
Absorption coefficient (mm^{-1})	2.86
Crystal size (mm)	0.01 × 0.03 × 0.01
Data collection	
θ range	10.24–28.50º
h, *k*, *l* ranges	–19 → 20, –9 → 9, –13 → 13
Total reflections collected	15,029
Unique reflections (R_{int})	10,207 (0.222)
Unique reflections $F > 4\sigma(F)$	5702
Structure refinement	
Refinement method	Full-matrix least-squares on F^2
Weighting coefficients *a*, *b*	0.0000, 3.8858
Extinction coefficient	0.0000(5)
Data/restraints/parameters	10,207/6/180
R_1 [$F > 4\sigma(F)$], wR_2 [$F > 4\sigma(F)$],	0.0679, 0.1321
R_1 all, wR_2 all	0.1382, 0.1690
Goodness-of-fit on F^2	1.032
Largest diff. peak and hole, e Å^{-3}	1.382, −1.151

TABLE 3. Atom coordinates, site-occupancy factors, bond-valence sums and displacement parameters (Å^2) of atoms in the structure of whiteite-(CaMnMn).

Site	SOF†	BVS*	*x*/*a*	*y*/*b*	*z*/*c*	U_{iso}
X	$Ca_{0.93(2)}Zn_{0.07(2)}$	2.26	¼	0.9757(3)	0	0.0216(8)
*M*1	$Mn_{0.99(2)}Mg_{0.01(2)}$	2.14	¼	0.4788(2)	0	0.0185(6)
*M*2a	$Mn_{0.97(2)}Mg_{0.03(2)}$	1.70	½	0	½	0.0156(6)
*M*2b	Mn	2.22	¼	0.49571(14)	½	0.0167(6)
*M*3a	$Al_{0.87(2)}Fe_{0.13(2)}$	2.84	0	0	0	0.0125(11)
*M*3b	$Al_{0.97(2)}Fe_{0.03(2)}$	2.84	0	½	0	0.0135(12)
P1	P	4.85	0.17754(10)	0.25640(16)	0.18605(12)	0.0153(3)
P2	P	4.93	0.07970(10)	0.74922(15)	0.80459(11)	0.0121(3)
O1	O	1.84	0.2686(3)	0.2298(7)	0.1494(4)	0.0336(12)
O2	O	1.75	0.2016(4)	0.2839(6)	0.3424(4)	0.0218(9)
O3	O	1.89	0.1174(4)	0.0786(5)	0.1357(5)	0.0434(14)
O4	O	1.84	0.1317(3)	0.4351(5)	0.0961(4)	0.0242(9)
O5	O	1.88	0.1890(3)	0.7085(6)	0.8560(4)	0.0318(11)
O6	O	1.69	0.0456(4)	0.7738(5)	0.6450(3)	0.0206(10)
O7	O	1.85	0.0709(4)	0.9340(5)	0.8817(4)	0.0341(12)
O8	O	1.72	0.0279(3)	0.5817(5)	0.8423(4)	0.0276(9)
O9	OH	0.95	0.0206(3)	0.7508(5)	0.0798(3)	0.0126(5)
O10	H_2O	0.29	0.2200(5)	0.7290(6)	0.3391(4)	0.0358(13)
O11	H_2O	0.34	0.4496(5)	0.2205(6)	0.3388(4)	0.0364(14)
O12	H_2O	0.37	0.6353(4)	0.9975(5)	0.4773(8)	0.0354(16)
O13	H_2O	0.37	0.3940(4)	0.5121(6)	0.5099(8)	0.0311(12)

Site	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
X	0.0293(14)	0.0082(8)	0.0230(11)	0	0.0046(10)	0
*M*1	0.0300(11)	0.0111(7)	0.0149(8)	0	0.0088(7)	0
*M*2a	0.0300(11)	0.0111(7)	0.0149(8)	0	0.0088(7)	0
*M*2b	0.0158(11)	0.0122(7)	0.0177(7)	−0.0068(4)	0.0049(10)	0.0007(4)
*M*3a	0.0164(11)	0.0153(8)	0.0190(7)	0	0.0073(10)	0
*M*3b	0.0209(19)	0.0071(14)	0.0090(14)	0.0021(6)	0.0050(12)	−0.0003(7)
P1	0.012(2)	0.0105(16)	0.0210(18)	0.0023(7)	0.0091(15)	0.0014(8)
P2	0.0151(8)	0.0116(6)	0.0165(6)	−0.0018(4)	0.0029(5)	0.0014(5)
O1	0.0178(8)	0.0073(6)	0.0124(6)	0.0014(4)	0.0070(5)	0.0029(5)
O2	0.027(3)	0.047(2)	0.031(2)	0.009(2)	0.0158(18)	0.016(2)
O3	0.025(2)	0.0218(17)	0.020(2)	−0.008(2)	0.0092(16)	−0.003(2)
O4	0.053(3)	0.0077(16)	0.041(3)	0.0004(16)	−0.016(2)	−0.006(2)
O5	0.025(2)	0.0142(16)	0.0281(19)	0.0043(14)	0.0036(16)	0.002(2)
O6	0.025(3)	0.038(2)	0.027(2)	0.0060(18)	0.0037(17)	0.007(2)
O7	0.027(3)	0.0210(17)	0.0102(15)	0.0008(13)	0.0021(16)	−0.001(2)
O8	0.067(4)	0.0085(16)	0.040(2)	0.0002(15)	0.036(2)	−0.000(2)
O9	0.051(3)	0.0106(16)	0.028(2)	−0.003(1)	0.0226(19)	−0.002(2)
O10	0.0141(9)	0.0062(8)	0.0153(9)	−0.0003(8)	0.0031(8)	−0.0001(7)
O11	0.048(3)	0.024(2)	0.029(2)	0.0017(18)	0.006(2)	0.005(3)
O12	0.039(3)	0.024(2)	0.025(2)	−0.002(2)	−0.013(2)	−0.006(2)
O13	0.023(3)	0.030(2)	0.059(4)	−0.012(2)	0.022(3)	−0.006(2)

† The abbreviation SOF is site occupancy factor.

* The bond valence sums are calculated using bond-valence parameters taken from Brese and O'Keeffe (1991).

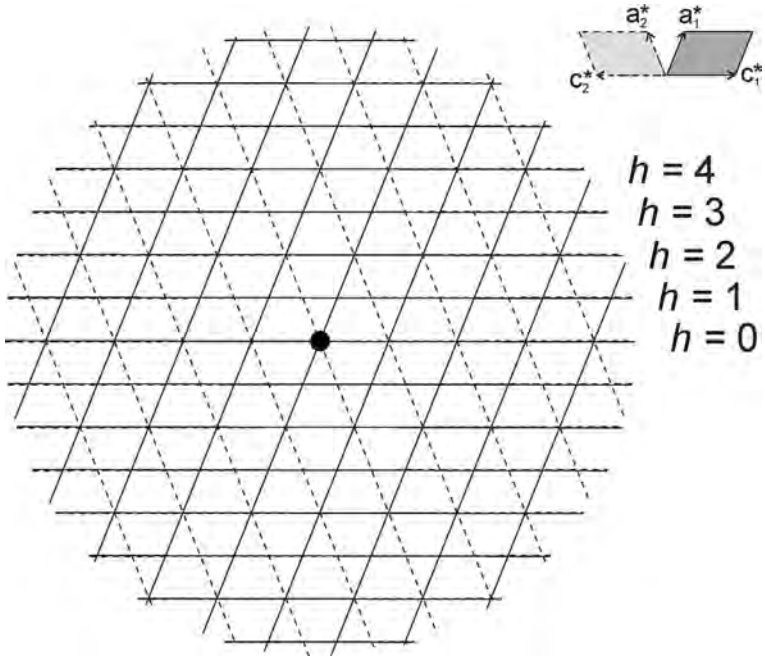

FIG. 4. The overlap of the reciprocal lattices of two twin components of a crystal of whiteite-(CaMnMn) related by the (001) plane.

Taking into account the results of the single-crystal X-ray diffraction study, the empirical formula (based on P = 4 a.p.f.u., with ferric iron calculated to maintain charge balance) is

TABLE 4. Selected interatomic distances (Å) in the structure of whiteite-(CaMnMn).

X–O1	2.277(5) 2 ×	*M*3b–O3	1.871(4) 2 ×
X–O5	2.332(4) 2 ×	*M*3b–O9	1.890(3) 2 ×
X–O7	2.524(5) 2 ×	*M*3b–O7	1.931(4) 2 ×
X–O3	2.899(6) 2 ×	**<*M*3b–O>**	**1.897**
<*X*–O>	**2.509**		
		*M*3a–O8	1.884(4) 2 ×
*M*1–O5	2.130(4) 2 ×	*M*3a–O9	1.900(3) 2 ×
*M*1–O1	2.250(4) 2 ×	*M*3a–O4	1.907(4) 2 ×
*M*1–O4	2.342(4) 2 ×	**<*M*3a–O>**	**1.897**
<*M*1–O>	**2.240**		
		P1–O2	1.501(4)
*M*2a–O6	2.089(4) 2 ×	P1–O3	1.506(4)
*M*2a–O12	2.129(6) 2 ×	P1–O4	1.545(4)
*M*2a–O11	2.164(4) 2 ×	P1–O1	1.556(5)
<*M*2a–O>	**2.128**	**<P1–O>**	**1.528**
*M*2b–O2	2.096(4) 2 ×	P2–O6	1.515(4)
*M*2b–O13	2.131(5) 2 ×	P2–O8	1.527(4)
*M*2b–O10	2.226(4) 2 ×	P2–O7	1.536(4)
<*M*2b–O>	**2.151**	P2–O5	1.553(4)
		<P2–O>	**1.533**

$(Ca_{0.63}Zn_{0.26}Na_{0.14})_{\Sigma 1.03}(Mn_{0.60}Fe^{2+}_{0.40})_{\Sigma 1.00}(Mn_{1.40}Fe^{2+}_{0.37}Mg_{0.18}Fe^{3+}_{0.06})_{\Sigma 2.01}(Al_{1.88}Fe^{3+}_{0.12})_{\Sigma 2.00}[PO_4]_4(OH)_2{\cdot}7.89H_2O$. The simplified formula of whiteite-(CaMnMn) is $CaMnMn_2Al_2[PO_4]_4(OH)_2{\cdot}8H_2O$.

Grey *et al*. (2010) noted that fluorine is a common impurity in primary Fe^{3+}-poor whiteite (up to 0.68 wt.% and 0.29 a.p.f.u. of fluorine), whereas comparatively late-stage Fe^{3+}-rich whiteite and jahnsite are fluorine free. The mineral is easily soluble in 10% HCl at room temperature.

Crystal structure

Experimental

A transparent platy crystal of whiteite-(CaMnMn) was investigated using a Bruker Smart Apex II diffractometer at the Department of Crystallography, St Petersburg State University, Russia. More than a hemisphere of X-ray diffraction data (θ_{max} = 28.50º) with frame widths of 0.5º in ω and 45 s counting times for each frame was collected at room temperature using Mo*K*α radiation. None of the crystals that were examined produced high quality diffraction data. The intensity data were integrated and corrected for absorption using an empirical laminar model in the Bruker programs *APEX* and *XPREP*. The observed systematic absences are consistent with space group *P*2/*c*, but this was transformed to space group *P*2/*a* for consistency with previous structural refinements of jahnsite- and whiteite-group minerals (Moore and Araki, 1974; Kampf *et al*., 2008) (Table 2). The structure was refined to R_1 = 0.157 on the basis of F^2 for all unique data using atom coordinates from Kampf *et al*. (2008). Examination of reciprocal space (Fig. 4) indicated that the crystals of whiteite-(CaMnMn) were invariably twinned. Grey *et al*. (2010) studied crystal from the same locality and proposed that twinning was probably due to 180º rotation about [100] with {001} as the twin plane. The unit cells of the two twinned components are related by the matrix [−1 0 −0.5 / 0 1 0 / 0 0 1], which results in an exact overlap of reflections with $h = 2n$. Diffraction data collected were transformed into a HKLF5 reflection file by means of the program *HKLF5* (Bolte, 2004). The use of the twinning model significantly improved the refinement parameters and the structure refined to R_1 = 0.068 on the basis of 5702 unique observed reflections in the θ range 10.24−28.50º. No diffraction intensities were recorded for θ values of less than 10º. The R_{int} value given in Table 2 is very high (0.222) and is reported for the dataset before the effect of twinning was taken into account (the *HKLF5* program did not account for the effects of twinning upon the dataset). The *SHELX* program package was used for all structural calculations (Sheldrick, 2008). The final model included all atom positions, a refinable weighting scheme of

TABLE 5. X-ray powder diffraction data for whiteite-(CaMnMn).

I_{rel}	d_{obs} (Å)	d_{calc} (Å)	*h k l*
65	**9.443**	9.417	0 0 1
7	6.947	6.954	0 1 0
12	6.154	6.224	1 1 0
25	**5.596**	5.594	0 1 1
80	**4.929**	4.926	2 1 0
47	**4.719**	4.708	0 0 2
23	3.954	3.962	2 1 1
		3.956	$\bar{2}$ 1 2
10	3.767	3.754	$\bar{4}$ 0 1
46	**3.494**	3.489	4 0 0
3	3.273	3.270	-1 2 1
5	3.134	3.139	0 0 3
9	3.019	3.032	2 1 2
21	2.9334	2.9381	4 0 1
		2.9321	$\bar{4}$ 0 3
100	**2.7958**	2.7970	0 2 2
2	2.6107	2.5906	5 1 0
12	2.5512	2.5508	$\bar{4}$ 2 1
4	2.4647	2.4630	4 2 0
7	2.4022	2.4104	$\bar{4}$ 0 4
		2.4055	
19	2.3362	2.3370	$\bar{6}$ 1 1
		2.3359	$\bar{6}$ 1 2
3	2.2010	2.2061	6 1 0
		2.2033	$\bar{6}$ 1 3
		2.1998	0 3 2
4	2.0823	2.0891	2 3 1
		2.0882	$\bar{2}$ 3 2
12	2.0176	2.0198	$\bar{6}$ 2 1
24	**1.9790**	1.9810	4 2 2
		1.9782	$\bar{4}$ 2 4
24	**1.9508**	1.9494	0 2 4
9	1.9120	1.9097	2 3 2
15	1.8780	1.8769	$\bar{8}$ 0 2
13	1.7363	1.7385	0 4 0
4	1.6337	1.6309	0 4 2
20	1.5578	1.5594	8 2 0

The eight strongest lines are listed in bold.

TABLE 6. Comparative data for whiteite-(CaMnMn), whiteite-(CaMnMg) and jahnsite-(CaMnMn).

Mineral	Whiteite-(CaMnMn) (this study)	Whiteite-(CaMnMg) (Grice *et al*., 1989)	Jahnsite-(CaMnMn) (Grice *et al*., 1990)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	P2/*a*	*P*2/*a*	*P*2/*a*
a (Å)	15.02	14.84	14.88
b (Å)	6.95	6.98	7.15
c (Å)	10.13	10.11	9.97
β (º)	111.6	112.6	109.8
Z	2	2	2
Strongest lines in	9.443 (65)	9.31 (100)	9.40 (100)
powder pattern: *d* (*I*)	5.596 (25)	4.85 (50)	5.74 (20)
	4.929 (80)	3. 51 (50)	5.02 (20)
	4.719 (47)	3.256 (40)	4.971 (20)
	3.494 (46)	2.953 (50)	4.704 (30)
	2.7958 (100)	2.790 (80)	2.870 (80)
Density (g cm^{-3})	2.77	2.63	2.78
Mohs hardness	3½	3½	4
Colour	colourless to pale yellow	yellow to pink	brownish yellow
Opt. character	biaxial (+)	biaxial (+)	biaxial (−)
α	1.589	1.580	1.643
β	1.592	1.584	1.659
γ	1.601	1.591	1.671
2V (º)	60	81	80
Orientation	$X = b$, $Z \wedge a = 5^{\circ}$	$Y = b$, $Z \wedge c = 15^{\circ}$	$Z = b$, $X \wedge c = 20^{\circ}$
Dispersion	none observed	none observed	none observed
Pleochroism	none observed	*X* = mauve	*X* = pale yellow−green
		Y = light mauve	*Y* = brown−green
		Z = colourless	*Z* = yellow−green
Habit	bar-shaped crystals elongated along [100] and flattened on (010)	canoe-shaped crystals	crystals flattened on {001}
Cleavage	{001} perfect	{001} poor	{001} poor

the structure factors and anisotropic-displacement parameters for all atoms (hydrogen atoms were not located). Anisotropic refinement of the O9 atom resulted in physically unrealistic displacement parameters, and restraints were imposed to obtain a positive-definite behaviour. The final atom coordinates, site occupancy factors, bond-valence sums and displacement parameters are listed in Table 3; selected interatomic distances are listed in Table 4. The bond-valence sums are in agreement with previous results on the structures of whiteite- and jahnsite-group minerals. A crystallographic information file and a list of observed and calculated structure factors has been deposited with *Mineralogical Magazine* and is available at http://www.minersoc.org/pages/e_journals/dep_mat_mm.html.

X-ray powder diffraction

The X-ray powder diffraction pattern of whiteite-(CaMnMn) was obtained using a STOE IPDS II instrument (in Gandolfi mode using Mo*K*α radiation) operating at 40 kV and 30 mA (Table 5). Unit-cell parameters determined from powder patterns are as follows: $a = 15.02(2)$, $b = 6.95(1)$, $c = 10.13(3)$ Å, $\beta = 111.6(1)^{\circ}$ with $V = 983.3(6)$ Å^3 and $Z = 2$, which are in good agreement with the single-crystal data (Table 2).

Discussion

Whiteite-(CaMnMn) is isotypic with other whiteite- and jahnsite-group minerals (Moore and Araki, 1974; Kampf *et al*. 2008). Its crystal structure is essentially the same as that refined by

Grey *et al*. (2010) for a crystal with a similar composition from the same locality. The *X* site is 8-coordinate; its occupancy was refined to $Ca_{0.93}Zn_{0.07}$. Grey *et al*. (2010) indicated that the refined number of electrons in the *X* site "...is matched with 0.73Ca + 0.37Zn", which is clearly a misprint (the proper assignment being 0.73Ca + 0.27Zn). The crystal studied by Grey *et al*. (2010) was, therefore, richer in Zn than the crystal described in this text. Site-occupancies for the octahedral sites (*M*1, *M*2a, *M*2b, *M*3a and *M*3b) are in general agreement with those obtained by Grey *et al*. (2010), except that the Mn scattering curve was used for the refinement of the *M*1, *M*2a and *M*2b sites in this report, whereas Grey *et al*. (2010) used the Fe scattering curve.

Figure 5 shows the basic features of the atomic arrangement in whiteite-(CaMnMn). The structure can be described as based upon chains of *trans*-corner-sharing $M3aO_6$ and $M3bO_6$ octa-

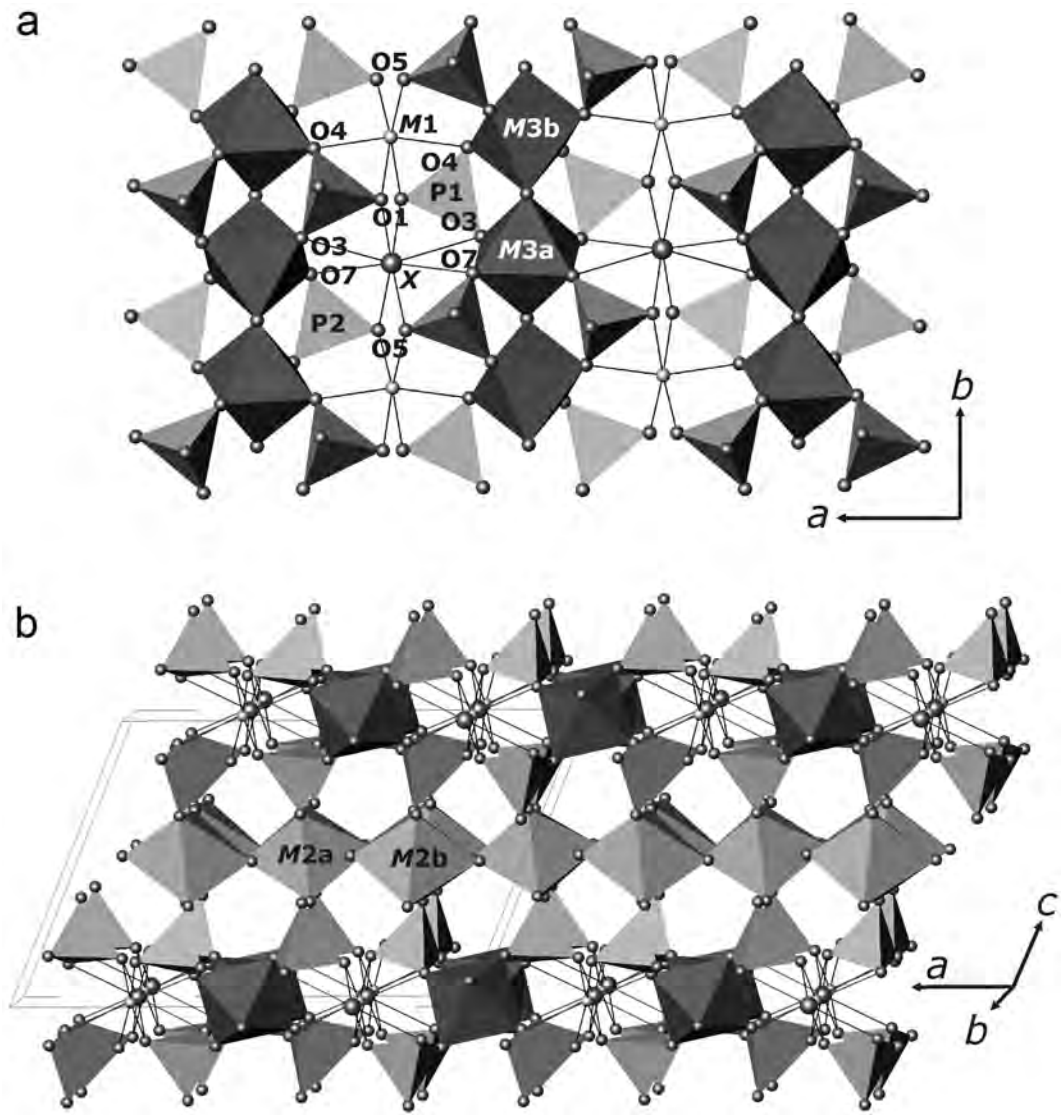

FIG. 5. (*a*) Layer of corner-sharing chains of AlO_6 octahedra, PO_4 tetrahedra and Ca^{2+} and Mn^{2+} cations and (*b*) projection of the structure of whiteite-(CaMnMn).

hedra decorated by PO_4 tetrahedra. The resulting $[(Al,Fe)(OH))(PO_4)_2]$ chains are linked via Ca^{2+} (*X* site) and Mn^{2+} (*M*1 site) cations into layers parallel to (001) (Fig. 5*a*). The layers are linked via $[Mn^{2+}O_2(H_2O)_4]$ octahedra into a three-dimensional structure (Fig. 5*b*).

The crystal-chemical formula for whiteite-(CaMnMn) (Table 2) is in general agreement with the results of the microprobe analyses, taking into account that the Mn scattering factor was used to account for both Mn and Fe.

Whiteite-(CaMnMn) and the other associated phosphates form as a result of the alteration of triplite and fluorapatite by low-temperature acidic Al-rich hydrothermal solutions according to the following reaction:

$$2Mn_2PO_4F + Ca_5P_3O_{12}F + 17H_2O + 5H_3PO_4 + 6AlO_2 + 3H_2 \rightarrow$$
triplite fluorapatite hydrothermal solution

$$CaMn_3Al_2P_4O_{16}(OH)_2{\cdot}8H_2O + Ca_4MnAl_4P_6O_{24}(OH)_4{\cdot}15H_2O + 3HF$$
whiteite-(CaMnMn) nordgauite

This reaction is autocatalytic as one of its products, HF, causes further dissolution of primary aluminosilicates and fluorine-bearing phosphates. We believe this is one of the main reasons for the large chemical and structural diversity of secondary phosphates within the Hagendorf-Süd granitic pegmatite.

Acknowledgements

We are grateful to Joel Grice and Ian Grey for their insightful reviews; S.V.K. and A.P.Ch. were supported in this work by the Russian Federal Grant-in-Aid Program 'Cadres' (state contract 16.740.11.0490).

References

Birch, W.D., Grey, I.E., Mills, S.J., Pring, A., Bougerol, C., Ribaldi-Tunnicliffe, A., Wilson, N.C. and Keck, E. (2011) Nordgauite, $MnAl_2(PO_4)_2(F,OH)_2{\cdot}5H_2O$, a new mineral from the Hagendorf-Süd pegmatite, Bavaria, Germany: description and crystal structure. *Mineralogical Magazine*, **75**, 269–278.

Bolte, M. (2004) *TWINLAW* and *HKLF5*: two programs for the handling of non-merohedral twins. *Journal of Applied Crystallography*, **37**, 162–165.

Brese, N.E. and O'Keeffe, M. (1991) Bond-valence parameters for solids. *Acta Crystallographica*, **B47**, 192–197.

Forster, A., Strunz, H. and Tennyson, Ch. (1967) Die Pegmatite des Oberpfälzer Waldes, insbesondere der Pegmatit von Hagendorf-Süd. *Aufschluss*, **16**, 137–198.

Grey, I.E., Mumme, W.G., Neville, S.M., Wilson, N.C. and Birch, W.D. (2010) Jahnsite–whiteite solid solutions and associated minerals in the phosphate pegmatite at Hagendorf-Süd, Bavaria, Germany. *Mineralogical Magazine*, **74**, 969–978.

Grice, J.D., Dunn, P.J. and Ramik, R.A. (1989) Whiteite-(CaMnMg), a new mineral species from the Tip Top pegmatite, Custer, South Dakota. *The Canadian Mineralogist*, **27**, 699–702.

Grice, J.D., Dunn, P.J. and Ramik, R.A. (1990) Jahnsite-(CaMnMn), a new member of the whiteite group from Mangualde, Beira, Portugal. *American Mineralogist*, **75**, 401–404.

Kampf, A.R., Steele, I.M. and Loomis, T.A. (2008) Jahnsite-(NaFeMg), a new mineral from the Tip Top mine, Custer County, South Dakota: description and crystal structure. *American Mineralogist*, **93**, 940–945.

Mandarino, J.A. (1981) The Gladstone–Dale relationship. IV. The compatibility concept and its application. *The Canadian Mineralogist*, **19**, 441–450.

Moore, P.B. and Araki, T. (1974) Jahnsite, $CaMnMg_2(H_2O)_8Fe_2(OH)_2(PO_4)_4$. A novel stereoisomerism of ligands about octahedral corner-chains. *American Mineralogist*, **59**, 964–973.

Moore, P.B. and Ito, J. (1978) I. Whiteite, a new species, and a proposed nomenclature for the jahnsite–whiteite complex series. II. New data on xanthoxenite. III. Salmonsite discredited. *Mineralogical Magazine*, **42**, 309–323.

Mücke, A. (1981) The parageneses of the phosphate minerals of the Hagendorf pegmatite – a general view. *Chemie der Erde*, **40**, 217–234.

Mücke, A., Keck, E. and Haase, J. (1990) Die genetische Entwicklung des Pegmetits von Hagendorf-Süd/Oberpfalz. *Aufschluss*, **41**, 33–51.

Sandell, E.B. (1951) Micro determination of water by the Penfield method. *Microchimica Acta*, **38**, 487–491.

Sheldrick, G.M. (2008) A short history of *SHELX*. *Acta Crystallographica*, **A64**, 112–122.

Strunz, H. and Forster, A. (1975) Der Pegmatit von Hagendorf-Süd. *Aufschluss*, **26**, 329–339.