Wernerkrauseite, CaFe³⁺₂Mn⁴⁺O₆: the first nonstoichiometric post-spinel mineral, from Bellerberg volcano, Eifel, Germany

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Abstract: Black prismatic crystals of the new mineral wernerkrauseite, ideally $CaFe^{3+} Mn^{4+}O_6$ [Pnma, a = 9.0548(2), b = 0.0548(2)2.8718(1), c = 10.9908(2) Å; V = 285.80(1) Å³, Z = 8/3, were found in altered xenoliths within alkaline basalts of the Bellerberg volcano, Eifel, Rhineland-Palatinate, Germany. Fluorellestadite, wadalite, andradite-schorlomite, perovskite, gehlenite, magnesioferrite, cuspidine, ettringite-thaumasite, hydrocalumite, jennite, katoite, and portlandite are the main associated minerals. Wernerkrauseite crystals up to 0.5 mm in size show strong submetallic lustre; the streak is black. Wernerkrauseite appears grey in reflected light. Pleochroism is very weak, bireflectance and anisotropy are weak. Reflectance data for the COM wavelengths vary from ~31 % (400 nm) to ~19 % (700 nm). The calculated density is 4.66 g/cm³, microhardness VHN₂₅ is 154(5) kg/mm². Wernerkrauseite is a Ca-deficient structural analogue of harmunite, CaFe₂O₄, and therefore is one of the four known minerals with post-spinel structures. The empirical chemical formula of the holotype wernerkrauseite is $Ca_{0.994}(Fe^{3+}_{1.057}Mn^{4+}_{1.025})$ $Mn^{3+}_{0.878}Mg_{0.030}Al_{0.016})_{\Sigma_{3.006}}O_{6}$. The end-member chemical formula can also be given on the basis of spinel stoichoimetry (Z = 4): $Ca_{2/3}[Fe^{3+}_{4/3}Mn^{4+}_{2/3}]O_4$, which better reflects its non-stoichiometry. The crystal structure was determined using single-crystal Xray diffraction ($R_1 = 0.0233$ for 800 observed reflections [$I > 2\sigma(I)$]). The diffraction pattern shows evidence of short-range ordering of Ca-vacancies. The strongest diffraction lines of the calculated powder diffraction pattern are $[d_{hkl}(I)]$: 2.646 (100), 2.450 (77), 2.748 (62), 4.527 (54), 4.698 (44), 1.818 (43), 2.425 (37), 1.778 (30). Raman spectra of wernerkrauseite were measured and analysed in comparison to the spectra of harmunite and marokite, CaMn₂O₄. Crystallisation of wernerkrauseite took place at temperatures below 850–900°C under high oxygen fugacity. Furthermore, Mn^{4+} -bearing non-stoichiometric harmunite $Ca_{0.862}(Fe^{3+}_{1.719} Mn^{4+}_{0.265}Ti^{4+}_{0.012} Mg_{0.008})_{\Sigma 2.004}O_4$ was found at the same locality, which suggests the existence of a continuous solid solution between wernerkrauseite, harmunite and $Ca_{2/3}Mn^{3+}_{4/3}Mn^{4+}_{2/3}O_4$, described by the formula $Ca_{1-x/2}(Fe^{3+}, Mn^{3+})_{2-x}Mn^{4+}_{x}O_4$, with x ranging from 0 to 2/3.

Key-words: wernerkrauseite; harmunite; new mineral; post-spinel phase; tunnel structure; non-stoichiometry; Raman spectrum; Bellerberg volcano; Eifel; Germany.

Introduction

The new mineral wernerkrauseite, ideally $CaFe^{3+}_{2}Mn^{4+}O_{6}$ (IMA2014-008, *Pnma*, a = 9.0548(2), b = 2.8718(1), c = 10.9908(2) Å; V = 285.80(1) Å³, Z = 8/3) was found in altered xenoliths within basalts of the Bellerberg volcano (Caspar quarry), Ettringen near Mayen, Eifel, Rhineland-Palatinate, Germany. The Bellerberg volcano (50.35°N 7.23°E) is the type locality of more than twenty mineral species (Hentschel, 1987; Blass *et al.*, 2009).

The crystal structure of wernerkrauseite is related to the tunnel structures of CaFe₂O₄ (CF), CaTi₂O₄ (CT), and CaMn₂O₄ (CM), which are considered as post-spinel phases (Irifune *et al.*, 1991; Kirby *et al.*, 1996). Various synthetic compounds with post-spinel structure and the general formula AB_2O_4 are known, where A = Li, Na, Mg, Ca, Sr, Ba, La, Eu, and B = Ti, V, Cr, Mn, Fe, Ru, Rh, Al, Ga, In, Tl, Sc, Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Yb, Lu (Shizuya *et al.*, 2007). So far, only three minerals with post-spinel structure have been described: 1) xieite FeCr₂O₄ [*Bbmm*, a = 9.462(6), b = 9.562(9),

c = 2.916(1) Å] (Chen *et al.*, 2008), 2) marokite CaMn₂O₄ [*Pmab* or $P2_1ab$, a = 9.71(2), b = 10.03(2), c = 3.162(5)Å] (Gaudefroy et al., 1963; Lepicard & Protas, 1966), and 3) harmunite CaFe₂O₄ [*Pnma*; a = 9.2183(3), b = $3.0175(1), c = 10.6934(4) \text{ Å}; V = 297.45(2) \text{ Å}^{3}$ (Galuskina et al., 2014). Xieite is an ultra-high pressure polymorph of chromite, whereas marokite and harmunite are both low-pressure phases. Wernerkrauseite is a Cadeficient analogue of harmunite, therefore its end-member formula can be written as $Ca_{2/3}[Fe^{3+}_{4/3}Mn^{4+}_{2/3}]_{\Sigma 2}O_4$. This also reflects its relation to spinel and highlights its nonstoichiometry. In synthetic CaMn₃O₆ an ordering of Ca-vacancies within the channels is observed, which causes a lowering of its symmetry to monoclinic space group $P2_1/a$ (Hadermann et al., 2006). Yang et al. (2010) studied synthetic phases in the system $Ca_{1-\delta}Fe_{2-x}Mn_xO_4$ with x = 0.44–2 and $\delta \approx$ 0–0.25. All of the reported phases exhibit CF-type structures crystallising in space group Pnma and no evidence of Ca-vacancy ordering was found. The latter system is part of the ternary solid-solution series $CaFe^{3+}_{2}O_{4}-Ca_{2/3}(Mn^{3+},Fe^{3+})_{4/3}Mn^{4+}_{2/3}O_{4}$ in which the highest wernerkrauseite end-member content found reaches 72 mol%.

The new mineral is named in honour of Dr Werner Krause (b. 1949), a chemist with great expertise as a researcher in the chemical industry and a special interest in the crystal chemistry and morphology of secondary minerals. He has discovered and described a considerable number of new minerals, including skorpionite, schlegelite, kapellasite, neustädtelite, schäferite, medenbachite, and several new members of the tsumcorite group. He also dealt with redefinitions (gartrellite, arhbarite) and discreditation (duhamelite) of minerals, and he contributed to the third edition of the Encyclopedia of Minerals (Mandarino project).

Holotype material is deposited in the mineralogical collection of the Museum of Natural History in Bern, Bernastrasse 5, 3005 Bern, Switzerland, catalogue number NMBE 42804.

Experimental procedures

The crystal morphology and chemical composition of wernerkrauseite, harmunite and associated minerals were studied using optical microscopes, analytical electron scanning microscope (Philips XL30 ESEM/EDAX, Faculty of Earth Sciences, University of Silesia), and electron microprobe (CAMECA SX100, Institute of Geochemistry, Mineralogy and Petrology, University of Warsaw). Electron-probe microanalyses (EPMA) of wernerkrauseite and harmunite were performed at 15 kV and 20 nA using the following lines and standards: CaK α , SiK α = wollastonite; AlK α = orthoclase; CrK α = Cr₂O₃; FeK α = hematite; MnK α = rhodochrosite; TiK α = rutile; MgK α = diopside; NaK α = albite.

Raman spectra of wernerkrauseite and harmunite were recorded using a WITec confocal Raman microscope CRM alpha 300 (Jagiellonian Centre for Experimental Therapeutics, Cracow, Poland) equipped with an aircooled solid-state laser, emitting at 488 nm, and a CCD camera operating at -82 °C. The power of the laser at the sample position was 10–20 mW. Some 20–25 scans with an integration time of 10 s and a resolution of 3 cm⁻¹ were collected and averaged. The monochromator of the spectrometer was calibrated using the Raman scattering line of a silicon plate (520.7 cm⁻¹).

Single-crystal X-ray diffraction data of wernerkrauseite were collected using a Bruker APEX II SMART system (Institute of Geological Sciences, University of Bern). Experimental details are listed in Table 1. Data were processed using SAINT (Bruker, 2011), and an empirical absorption correction was applied using SADABS (Bruker, 2011). The crystal structure was solved with direct methods (SIR97, Altomare *et al.*, 1999) and subsequently refined using neutral-atom scattering factors with the program SHELX97 (Sheldrick, 2008). Both octahedral sites were modelled using Mn and Fe with (fixed) site occupancy factors (s.o.f.) of 0.665 and 0.335, respectively, to match the Mn/Fe ratio revealed by electron-microprobe analysis. Further details of the refinement can be found in Table 1. Structural parameters are listed in Table 2 (atomic

Table 1. Data collection and structure refinement details for wernerkrauseite.

Crystal data	
Chemical formula	Ca _{0.99} Fe _{0.98} Mn _{2.02} O ₆
Crystal system	orthorhombic
Space group	Pnma
Unit-cell dimensions	a = 9.0548(2) Å
	b = 2.8718(1) Å
	c = 10.9908(2) Å
Volume	285.80(1) Å ³
Density (calculated)	4.674 g/cm ³
Ζ	8/3
Intensity measurement	
Crystal shape	plate
Crystal size	$80 imes 40 imes 15 \ \mu m$
Diffractometer	APEX II SMART
X-ray radiation	Mo $K\alpha$ $\lambda = 0.71073$ Å
X-ray power	50 kV, 30 mA
Monochromator	graphite
Temperature	293(2) K
Time per frame	30 s
Max. θ	38.31°
Index ranges	$-15 \le h \le 12$,
	$-4 \le k \le 4$,
	$-12 \le l \le 19$
No. of measured reflections	4410
No. of unique reflections	898
No. of observed reflections $[I > 2\sigma(I)]$	800
Refinement of structure	
No. of parameter used	47
R _{int}	0.0209
R_{δ}	0.0217
$R_1 \left[I > 2\sigma(I) \right]$	0.0233
R_1 , all data	0.0288
wR_2 (on F^2)	0.0522
Goof	1.093
Largest diff. peak and hole	0.88 / and -1.538 e A

	x	У	Z	sof	$U_{ m eq}$
Cal	0.25655(8)	0.8201(4)	0.16285(7)	0.325(1)	0.0113(4)
Mn1	0.56433(4)	0.25	0.61257(3)	0.665Mn + 0.335Fe	0.01222(8)
Mn2	0.08442(3)	0.25	0.40066(3)	0.665Mn + 0.335Fe	0.00873(7)
01	0.29435(16)	0.25	0.34793(13)	1	0.0114(3)
O2	0.38422(16)	0.25	0.01975(13)	1	0.0116(3)
O3	0.47133(16)	0.25	0.79534(14)	1	0.0128(3)
O4	0.07316(16)	0.25	0.07956(15)	1	0.0135(3)

Table 2. Atom coordinates and equivalent isotropic atomic displacement parameters (Å²) of wernerkrauseite.

coordinates) and Table S1 (anisotropic displacement parameters; freely available online as Supplementary Material linked to this article on the GSW website of the journal: http://eurjmin.geoscienceworld.org/).

Occurrence, description and chemistry

Wernerkrauseite was found in samples of altered xenoliths within alkaline basalts of the Bellerberg volcano (Fig. 1A). The xenolith samples are represented by a light, strongly altered rock with widespread development of low-temperature minerals such as ettringite–thaumasite, hydrocalumite, jennite, katoite, portlandite, *etc*. The matrix of lowtemperature minerals contains relict grains of a hightemperature mineral association: bright-blue Cl-bearing fluorellestadite, yellow wadalite, brownish andradite–schorlomite, perovskite and, rarely, pink reinhardbraunsite. Furthermore, kerimasite, lakargiite, gehlenite, magnesioferrite, cuspidine and rankinite were identified. Pavlovskyite $Ca_8(SiO_4)_2(Si_3O_{10})$, and rusinovite $Ca_{10}(Si_2O_7)_3Cl_2$ were found at this locality for the first time.

Wernerkrauseite forms black, elongated, prismatic and acicular crystals up to 0.5 mm in length with rhombic cross-section and characteristic striation parallel to the direction of crystal elongation (Fig. 1). The crystals exhibit forms such as {210},{110}, {010}, {011}, and{111}. No twinning is observed, whereas parallel crystal intergrowths are typical. Wernerkrauseite also forms aggregates with



Fig. 1. (A) black (steel-grey) long prismatic wernerkrauseite crystals in altered xenolith, photograph of Fred Kruijen; (B) wernerkrauseite crystals in a groundmass of hydrosilicates (jennite-like), ettringite with relics of fluorellestadite, the crystal magnified in Fig. 1C is shown in frame; (C) grey colour of wernerkrauseite in reflected light, orientations of crystals at reflectivity measurements are shown by double-ended arrows (see Fig. S1 in Supplementary Material); (D) long-prismatic wernerkrauseite crystal. Wkr – wernerkrauseite, Prv – perovskite, Mgf – magnesioferrite, Ell – fluorellestadite, Etr – ettringite–thaumasite, Hsi – Ca-hydrosilicates.

	Eifel, Germany						Jabel Harmun, Palestine			
	Wernerkrauseite		Harmunite		Magnesioferrite	Harmunite				
	mean 9	s.d.	range	mean 6	s.d.	range	mean 3	mean 13	s.d.	range
TiO ₂				0.44	0.09	0.34-0.56	0.35	0.15	0.08	0.07-0.31
Al_2O_3	0.27	0.09	0.15-0.43				3.33	0.36	0.07	0.26-0.45
Cr_2O_3							0.40	0.38	0.09	0.20-0.52
Fe ₂ O ₃	27.97	1.37	25.98-31.35	65.29	2.40	62.86-67.88	73.93	71.94	0.35	71.36-72.56
MnO ₂ *	29.52	0.22	29.18-29.91	10.95	1.59	8.59-13.09				
Mn ₂ O ₃ *	22.97	1.37	19.78-24.76				0.63			
MnO*							2.13			
MgO	0.40	0.08	0.26-0.53	0.15	0.03	0.12-0.18	19.10	0.06	0.02	0.04-0.09
CaO	18.48	0.18	18.09-18.67	22.99	0.87	21.78-24.21	0.40	26.15	0.14	25.80-26.31
Total	99.61			99.81			100.31	99.04		
Calculated	d: \bullet on 4 O and \bullet	on 6 O								
Ca	0.663*/0.994*			0.862*			0.014	1.013*		
Mg							0.935			
Mn ²⁺							0.059			
A site	0.663/0.994			0.862			1.008	1.013		
Fe ³⁺	0.705/1.057			1.719			1.828	1.957		
Mn^{4+}	0.683/1.025			0.265						
Mn ³⁺	0.585/0.878						0.016			
Mg	0.020/0.030			0.008				0.003		
Al	0.011/0.016						0.129	0.015		
Cr ³⁺							0.010			
Ti ⁴⁺				0.012			0.009	0.004		
B site	2.004/3.006			2.004			1.992	1.979		

Table 3. Electron-microprobe analyses of wernerkrauseite, harmunite and magnesioferrite from altered xenoliths of the Eifel, Germany, and of harmunite from pyrometamorphic larnite rocks of the Jabel Harmun, Palestinian Autonomy (wt.%).

Footnote: * - calculated on charge balance.

magnesioferrite and perovskite (Fig. 1C). Black wernerkrauseite crystals show strong submetallic lustre; the streak is black. The microhardness (VHN, load 25 g, average of 12 measurements) was determined to 154(5) kg mm⁻², which corresponds to a Mohs hardness of 3. The mineral does not show cleavage and exhibits uneven fracture. Based on the empirical formula (Table 3) the calculated density is 4.66 g cm⁻³. Wernerkrauseite appears grey in reflected light (Fig. 1C), there are no internal reflections, pleochroism is very weak, bireflectance and anisotropy are weak. Reflectance values (Zeiss SiC 182 standard in air) are given in Table 4. Reflectance spectra are shown in

Table 4. Reflectance data (%) for wernerkrauseite.

$R_{\rm max.}/R_{\rm min}$	λ/nm	$R_{\rm max.}/R_{\rm min}$	λ/nm
31.4/21.4	400	25.5/19.0	560
30.8/20.9	420	25.1/19.1	580
29.7/20.5	440	25.0/19.1	589 (COM)
28.6/20.0	460	24.8/19.1	600
28.1/19.8	470 (COM)	24.6/19.1	620
27.6/19.6	480	24.4/19.1	640
26.8/19.3	500	24.3/19.0	650 (COM)
26.2/19.1	520	24.2/19.0	660
25.8/19.0	540	24.1/18.9	680
25.7/19.0	546 (COM)	23.9/18.8	700

Fig. S1, freely available as Supplementray Material linked to this article on the GSW website of the journal: http://eurjmin.geoscienceworld.org/.

The holotype wernerkrauseite is characterized by a relatively uniform composition (Table 3). The chemical formula, calculated from the average of nine analyses on the basis of 6 and 4 oxygen atoms, is $Ca_{0.994}(Fe^{3+}_{1.057})$ the main compositional variations of wernerkrauseite can be accounted for by the $Fe^{3+} \leftrightarrow Mn^{3+}$ substitution (Table 4). During the study of mayenite-supergroup minerals in a fluorellestadite xenolith from the same locality (sample courtesy Bernd Ternes), Mn⁴⁺-bearing harmunite was found (Galuskin et al., 2013), for which composition and Raman spectrum are reported here in Table 3 and Fig. 2, respectively. This harmunite is a non-stoichiometric phase as it contains ~ 40 mol% of wernerkrauseite endmember: $(Ca_{0.862} \square_{\sim 0.138})_{\Sigma \sim 1} (Fe^{3+}_{1.719} Mn^{4+}_{0.265} Ti^{4+}_{0.012})$ $Mg_{0.008})_{\Sigma 2.004}O_4.$

X-ray powder diffraction data for wernerkrauseite could not be measured, therefore we present a calculated powder pattern (Cu $K\alpha$ radiation, Debye-Scherrer geometry), based on the obtained structure model (Table S2 in Supplementary Material).



Fig. 2. Raman spectra and back-scattered electron images of the minerals showing where Raman spectra were obtained: (A) holotype wernekrauseite, (B) holotype harmunite, (C) nonstoichiometric Mn⁴⁺-bearing harmunite, (D) marokite (R060829; Downs, 2006). Wkr-wernerkrauseite, May-chlormayenite, Elt-eltyubyuite, Lrn - larnite, Hrm - harmunite, Mgf - magnesioferrite, Ell fluorellestadite.

Crystal structure

Wernerkrauseite can be described as a Ca-deficient analogue of harmunite, CaFe₂O₄ (*Pnma*, a = 9.2183(3), b = 3.0175(1), c = 10.6934(4) Å), with the post-spinel structure type (Yamanaka et al., 2008; Galuskina et al., 2014). The structure of both minerals is built from rutile-type chains of two types of edge-sharing Fe and/or MnO₆ octahedra. Between these two slightly different chains tunnels are formed, which host the Ca sites (Fig. 3; Hadermann et al., 2006; Yang et al., 2010; Galuskina et al., 2014). Marokite, CaMn₂O₄ (*Pmab* or $P2_1ab$, a = 9.71(2), b =10.03(2), c = 3.162(5) Å), belongs to the post-spinel structures, in which rutile-type chains are built by only one type of octahedron (Fig. 3; Gaudefroy et al., 1963; Giesber et al., 2001). Unlike harmunite and marokite with four fully occupied Ca sites per unit cell, in wernerkrauseite only 1/3 of eight Ca sites are occupied in the structural tunnels (Fig. 3). The doubled number of Ca sites arises from splitting of the standard Ca site of harmunite. The split positions are 0.403(2) Å apart. Only one of two adjacent sites can be locally occupied, indicating the disordered nature of this mineral.

Wernerkrauseite - nonstoichiometric post-spinel mineral

The Fe³⁺, Mn³⁺ and Mn⁴⁺ ions occupy two different octahedral sites in wernerkrauseite, Mn1 and Mn2. It may be assumed that Mn^{4+} will favour Mn^2 with shorter distances, Mn2-O = 1.96 Å, in comparison with Mn1-O =2.02 Å (Table 5). This is also reflected by bond valence sum (BVS) calculations (Brown & Altermatt, 1985). The Mn1 site shows a BVS of ca. 3.1 valence unit (v.u.) for the trivalent species [Fe³⁺: 3.093(4), and Mn³⁺: 3.102(4)], calculated for Mn⁴⁺ the BVS is 3.044(4) v.u. The *Mn*2 site exhibits considerable higher BVS of 3.543(5), 3.553(5), and 3.486(4) v.u. for Fe³⁺, Mn³⁺, and Mn⁴⁺, respectively. Thus, the general crystal-chemical formula of wernerkrauseite can be represented as $Ca(R^{3+},Mn^{4+})_{1.5}(Mn^{4+},R^{3+})_{1.5}O_6$, where $R^{3+} = Fe^{3+}$ or Mn^{3+} . We are not able to pinpoint a detailed occupational scheme of octahedral sites due to the close ionic radii and scattering factors of Fe³⁺ and Mn³⁺. All available data indicate that the Mn^{2+} replacing Ca [BVS: 2.220(3) v.u.] is very low. We propose to use the simplified crystal-chemical formula $Ca(R^{3+}_{2}Mn^{4+})O_{6}$ with the combined octahedral Mn1 and Mn2 sites and with double site occupation. In wernerkrauseite $Fe^{3+} > Mn^{3+}$, what defines its end-member formula as $CaFe^{3+}_2Mn^{4+}O_6$. No natural phase with $Mn^{3+} > Fe^{3+}$ and with formula $CaMn^{3+}_2Mn^{4+}O_6$ is known, but there is a synthetic phase, the formula of which is usually written as CaMn₃O₆ (Hadermann et al., 2006).

Besides the Bragg reflections, which are explained by the given unit cell, the diffraction pattern of wernerkrauseite shows additional weak diffuse features. These diffuse intensities can be seen, for example, in the reciprocal space sections 0kl and hk0 (Fig. 4). They are located between the lattice nodes in layers with $k = n \pm \frac{1}{3}$. In sections parallel to **b*** these features show up as short lines (*e.g.* Fig. 4). Sections perpendicular to \mathbf{b}^* , such as h.2/3.l and h.5/3.lreveal that these features have the shape of two-dimensional blobs.

The position and shape of the diffuse intensities reveals that the underlying short-range order is caused by onedimensional features, exhibiting a tripled periodicity



Fig. 3. Low-pressure minerals with post-spinel structure, projection perpendicular to the tunnel direction (different octahedral sites marked with different colours, Ca sites drawn in orange): (A) marokite (Zouari *et al.*, 2003), (B) harmunite (Galuskina *et al.*, 2014), (C) wernerkrauseite; (D) Ca sites in tunnels coordinated by O (red balls): I – marokite, II – harmunite, III – wernerkrauseite with Ca sites doubling with 1/3 occupation, IV – monoclinic synthetic CaMn₃O₆ with Ca sites ordering (Hadermann *et al.*, 2006).

compared to the lattice, which corresponds to Ca-vacancy ordering in the tunnels. Correlation between neighbouring channels may create local superstructures. Ca-vacancy and charge ordering has been observed in another Ca-deficient CF-type structure: CaMn₃O₆ (Hadermann et al., 2006) exhibits a long-range ordered monoclinic superstructure $[P2_1/a, a = 10.6940(3), b = 11.3258(3), c = 8.4881(2)$ Å, $\beta = 122.358(2)^{\circ}$]. The monoclinic superstructure reflections of CaMn₃O₆ (Hadermann et al., 2006) can be indexed with a q-vector of $(2/3\mathbf{a}_{0}^{*} + 1/3\mathbf{c}_{0}^{*})$ [orthorhombic subcell $a_0 = 9.07$, $b_0 = 11.3$, $c_0 = 2.83$ Å in *Pnam*setting as in Hadermann et al. (2006)]. Transformed to the *Pnma*-setting used here the q-vector would be $(2/3a^* + 1/2)$ 3b*). However, using this vector the diffuse blobs cannot be indexed, as for example the features in 0kl are not accounted for. This reveals that the observed (shortrange) order in wernerkrauseite does not correspond to the superstructure in CaMn₃O₆. A possible q-vector to 'index' the diffuse blobs would be $(1/3b^* + c^*)$, which also results in a monoclinic superstructure. The monoclinic direction, however, is different than in $CaMn_3O_6$. Further investigation of the short-range order in wernerkrauseite will be subject of a future study.

Raman investigation

The vibration modes of the Raman spectrum of wernerkrauseite were interpreted by analogy with the Raman spectra of marokite and harmunite (Fig. 2; Kolev *et al.*, 2003; Wang *et al.*, 2003; Galuskina *et al.*, 2014). Observed Raman bands of wernerkrauseite are (cm⁻¹): ~1300 and 1239 [combination first-order phonons Ag (622) × 2]; 670, 622, 558 (Ag); 495 (B2g/Ag); 408 and 332 (Ag/B1g/B3g); 294 (Ag); 169 (Ag/B2g); 117 (Ag).

The Raman spectrum of wernerkrauseite is significantly distinct from the spectra of harmunite and marokite owing to the occurrence of one strong broad band centred at about 620 cm⁻¹ (Fig. 2). In marokite structure there is only one type of heavily deformed octahedra $(Mn^{3+}O_6)^{9-}$ centred by

Table 5. Selected bond lengths (\AA) in the structure of wernerkrauseite.

Atom	-atom		Distance
Mn1	-04	$\times 2$	1.935(1)
	-01	$\times 2$	1.972(1)
	-03		2.178(2)
	-04		2.113(2)
		mean	2.018
Mn2	-03	$\times 2$	1.912(1)
	02	$\times 2$	1.964(1)
	01		1.987(2)
	02		2.013(2)
		mean	1.959
Cal	-O4		2.263(2)
	02		2.310(2)
	-01		2.404(2)
	-04		2.505(2)
	-03		2.515(2)
	-03		2.534(2)
	-O2		2.548(2)
	-01		2.634(1)
		mean	2.464
Ca1–Ca1			0.403(2)



Fig. 4. Reconstructed reciprocal space sections 0kl and hk0, showing weak diffuse features in layers with $k = n \pm 1/3$. The used intensity scale enhances weak intensities, diffuse features are much less intense (*ca.* 20 counts) than the Bragg spots (*ca.* 10^4).

Jahn-Teller cation with four bonds ≈ 1.9 Å and two bonds ≈ 2.4 Å (Giesber *et al.*, 2001). The Mn³⁺–O stretching vibrations of marokite and its synthetic analogue are related to two strong bands near 630 cm⁻¹ and 612 cm⁻¹ with pronounced orientation effect (Fig. 2; Wang *et al.*, 2003; Downs, 2006; Ivanov *et al.*, 2014). These two bands in the Raman spectra of synthetic marokite are replaced by one broad band at high temperature (Ivanov *et al.*, 2014) or high pressure (Wang *et al.*, 2003). The shape of these Raman spectra resembles the wernerkrauseite spectrum. The maximum of the broad band is shifted towards higher wavenumbers at increasing pressure and lower wavenumbers upon heating, which indicates a weakening of the Jahn-Teller effect.

Harmunite, $CaFe_2O_4$, isostructural with wernerkrauseite, has two types of $(Fe^{3+}O_6)^{9-}$ octahedra (Galuskina *et al.*, 2014). The Raman spectrum of the harmunite holotype, of near-end-member composition, is characterized by sharp bands which can be well assigned to stretching, tilting, bending and also rotating modes (Fig. 2). The shape of the Raman spectrum is grossly changed in the case of Mn^{4+} -bearing harmunite from Eifel, with about 40 mol% of wernerkrauseite end-member (Table 3). In this case the intensity of tilting, bending, and rotation modes is lowered and one broad asymmetric band related to stretching vibrations centred at about 590 cm⁻¹ appears (Fig. 2).

On the wernerkrauseite spectrum as well as on the Mn⁴⁺-bearing harmunite spectrum there is one broad band (Fig. 2). In the structure of wernerkrauseite there are three types of octahedral population: $(Fe^{3+}O_6)^{9-}$, $(Mn^{3+}O_6)^{9-}$ and $(Mn^{4+}O_6)^{8-}$, which can distribute in the two structural sites Mn1 and Mn2. As shown by the singlecrystal study, $Fe^{3+}(+Mn^{3+})$ is predominant in *Mn*1, and Mn^{4+} in *Mn*2. The ionic radii of Fe³⁺ (0.645 Å) and Mn³⁺ (0.645 Å) are identical and differ from Mn⁴⁺ radius (0.53 Å, Shannon, 1976). The relatively smaller Mn⁴⁺ ion at octahedral sites of wernerkrauseite should cause a shift of the Mn⁴⁺–O stretching vibrations band towards higher frequency (band at 670 cm^{-1} ?) and broadening of the band (Fig. 2). The interpretation of Raman data is complicated by the fact that, in wernerkrauseite, a part of the octahedra, occupied by Mn³⁺, is deformed (Jahn-Teller effect), and a part of the octahedra is coordinated by Cavacancies in channel sites. It is assumed that in the synthetic Mn^{3+} -analogue of wernerkrauseite $(Mn^{4+}O_6)^{8-}$ octahedra are associated with Ca-vacancies (Hadermann et al., 2006). Generally, it may be concluded that the Raman spectrum of wernerkrauseite with the one broad band centred at about 620 cm^{-1} underlines the disorder character of the structure, related to random distribution of three cations Mn^{4+} , Mn^{3+} , Fe^{3+} over two octahedral sites, where Mn³⁺O₆ octahedra are deformed due to of Jahn-Teller effect.

Discussion

Despite the fact that wernerkrauseite exhibits some shortrange order related to the Ca-vacancies, its average structure can be considered as a disordered 1/3 substructure of synthetic CaMn₃O₆. Using a similar chemical formula (based on 6 oxygen atoms) results in a non-integer value of Z = 8/3. This formula does not reflect its relation to the post-spinel minerals. Transformation into the typical postspinel formula (Z = 4) results in $(Ca_{2/3} \Box_{1/3})_{\Sigma 1}[(Fe^{3+}, Mn^{3+})_{4/3}Mn^{4+}_{2/3}]_{\Sigma 2}O_4$.

Wernerkrauseite and harmunite form a solid solution with the common formula $Ca_{1-x/2}Fe^{3+}{}_{2-x}Mn^{4+}{}_{x}O_{4}$, where x = 0 corresponds to harmunite ($CaFe^{3+}{}_{2}O_{4}$), and x = 2/3 represents wernerkrauseite ($Ca_{2/3}Fe^{3+}{}_{4/3}Mn^{4+}{}_{2/3}O_{4}$). The main substitution mechanisms are $1/2Ca^{2+} + Fe^{3+} \rightarrow \Box + Mn^{4+}$ [harmunite \rightarrow wernerkrauseite] and $Fe^{3+} \rightarrow Mn^{3+}$ [wernerkrauseite $Ca_{2/3}Fe^{3+}{}_{4/3}Mn^{4+}{}_{2/3}O_{4} \rightarrow$ potentially new mineral $Ca_{2/3}Mn^{3+}{}_{4/3}Mn^{4+}{}_{2/3}O_{4}$]. The holotype harmunite from Palestinian Autonomy corresponds to the iron end-member with x = 0 in the proposed solid-solution

series, $CaFe_2O_4$ (Galuskina *et al.*, 2014), and the holotype wernerkrauseite is very close to the formula ~ $CaFe^{3+}Mn^{3+}Mn^{4+}O_6$ (Table 3), containing 44 mol% of the $CaMn^{3+}_2Mn^{4+}O_6$ end-member and 53 mol% of $CaFe^{3+}_2Mn^{4+}O_6$, the wernerkrauseite end-member. The existence of a solid solution between harmunite and wernerkrauseite is confirmed by the fact that Mn^{4+} -bearing harmunite was found in xenoliths from the Eifel. The chemical composition was determined as $Ca_{0.862}Fe^{3+}_{1.719}Mn^{4+}_{0.265}Ti^{4+}_{0.012}Mg_{0.008}O_4$ (Table 3, Fig. 2C), which contains ~ 40 mol% of the $Ca_{2/3}Fe^{3+}_{4/3}Mn^{4+}_{2/3}O_4$ end-member.

Formation of wernerkrauseite and harmunite is connected with high-calcium pyrometamorphic rocks occurring as xenoliths in basaltoids (Southern Ossetia and Germany) or combustion rocks (Hatrurim Complex, Israel and Palestine Autonomy). The formation of such rocks takes place in the field of the sanidinite facies at temperatures higher than 1000 °C and low pressures, from a few kilobars up to atmospheric conditions (Grapes, 2006; Galuskin et al., 2013; Galuskina et al., 2014). Crystallisation of these minerals took place at high oxygen fugacity, as shown by the absence of Fe^{2+} and the association with magnesioferrite. Investigations of the Ca-Mn-O system show that CaMn₃O₆ crystallises below 925 °C and at high MnO_x/ CaO ratios of ca. 2 to7 (Longo & Horowitz, 1977; White et al., 2008). Repeated heating of synthetic CaMn₃O₆ to temperatures close to its crystallisation temperature under oxygen atmosphere leads to the decomposition of this phase. Minerals of the wernerkrauseite-harmunite series in xenoliths from the Eifel crystallise after magnesioferrite, overgrowing and partially substituting it. Magnesioferrite usually exhibits low Mn contents (Table 3) and plays a dual role in wernerkrauseite formation. On the one side, mass crystallisation of magnesioferrite causes an increase of the Mn/Fe ratio and, on the other side, magnesioferrite is a source of Fe³⁺ for later wernerkrauseite crystallisation. The high Fe³⁺ content in wernerkrauseite probably extends its field of stability in comparison of its Mnanalogue. Magnesioferrite crystallises at an early, prograde stage of xenoliths reaction, whereas wernerkrauseite is a late-stage mineral formed during retrograde metamorphism. The temperature of wernerkrauseite crystallisation probably was not higher than 850–900 °C and its formation occurred at redox conditions higher than the magnetite-hematite buffer (Grapes, 2006).

Acknowledgements: The authors are grateful to Thomas Armbruster, Christian Chopin and to anonymous reviewers for their constructive remarks, which allowed us to improve the manuscript. The work was partly supported by the National Science Centre (NCN) of Poland, grants no. DEC-2012/05/B/ST10/00514 and 2013/11/B/ST10/00272. The harmunite-bearing specimen from Eifel was kindly provided by Bernd Ternes (Mayen).

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Received 25 June 2015

Modified version received 23 September 2015 Accepted 5 November 2015