

Colinowensite, $\text{BaCuSi}_2\text{O}_6$, a new mineral from the Kalahari Manganese Field, South Africa and new data on wesselsite, $\text{SrCuSi}_4\text{O}_{10}$

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ABSTRACT

A new silicate, colinowensite, $\text{BaCuSi}_2\text{O}_6$, has been found in the Wessels mine, Kalahari Manganese Field, South Africa. It is associated with effenbergerite, wesselsite, lavinskyite, scottyite, diegogattaite, as well as with pectolite, quartz, aegirine, richterite, minerals of the garnet group and a number of different manganese and iron oxides, especially hausmannite and hematite. The mineral was named for the mineral collector and finder of the new species, Colin R. Owens, of Somerset West, South Africa. Colinowensite is brittle, with uneven fracture, and the estimated Mohs hardness is ~ 4 . It occurs as subhedral crystals $< 100 \mu\text{m}$ in size. The forms $\{100\}$ and $\{110\}$ are observed while $\{001\}$ is always present in cleavage plates. The calculated density is 4.236 g cm^{-3} . It is the natural analogue of the synthetic pigment referred to as Chinese or Han purple, which is found on artifacts from ancient and imperial China. The mineral is of dark blue to purple colour, with a purple streak, and is uniaxial (–), with $\omega = 1.740 (20)$, $\epsilon = 1.735 (20)$ (420 nm) and $\omega = 1.745 (20)$, $\epsilon = 1.730 (20)$ (650 nm). The lustre is vitreous and no fluorescence is observed under either shortwave or longwave ultraviolet radiation. A very strong pleochroism occurs from purple along the c axis to blue in a perpendicular direction. Colinowensite is not soluble in acids except HF. Electron microprobe analyses gave an average composition (wt.%) of CuO 22.53, BaO 43.43 and SiO_2 34.04 yielding the empirical formula (based on 6 O a. p.f.u.) $\text{BaCuSi}_2\text{O}_6$. The new mineral is tetragonal, space group $I4_1/acd$ with $Z = 16$, and $a = 9.967(1)$, $c = 22.290(2)$ Å. Colinowensite is a cyclosilicate with $[\text{Si}_4\text{O}_{12}]^{8-}$ 4-membered single rings, arranged in sheets parallel to (001). The structure is further characterized by CuO_4 squares sharing corners with four neighbouring silicate rings within a sheet. Ba^{2+} cations are bonded to ten O atoms in irregular coordination. Average Si–O, Cu–O and Ba–O bond lengths are 1.619, 1.934 and 2.943 Å, respectively. Colinowensite belongs to subdivision 9. CE of the Strunz Mineralogical Tables. In addition, based on single-crystal X-ray work, new structural data for wesselsite of chemical composition $\text{Sr}_{0.9}\text{Ba}_{0.1}\text{CuSi}_4\text{O}_{10}$ are provided.

KEYWORDS: Colinowensite, $\text{BaCuSi}_2\text{O}_6$, new mineral, Wessels Mine, Kalahari Manganese Field, South Africa, wesselsite, $\text{SrCuSi}_4\text{O}_{10}$.

Introduction

THE Kalahari Manganese Field, South Africa, is well known for the occurrence of a large number of mineral species. A comprehensive description of the so far 161 minerals – 19 of which having their type locality in the region – is given by Cairncross

and Beukes (2013). Over the last two decades, the mineralogy of this deposit has been subject to several studies at our Institute, resulting in the description of the new mineral species effenbergerite, $\text{BaCuSi}_4\text{O}_{10}$ (Giester and Rieck, 1994), wesselsite, $\text{SrCuSi}_4\text{O}_{10}$ (Giester and Rieck, 1996) and cairncrossite, $\text{Sr}_2\text{Ca}_{7-x}\text{Na}_{2x}(\text{Si}_4\text{O}_{10})_4(\text{OH})_2 \cdot (\text{H}_2\text{O})_{15-x}$ (with $x \sim 0-1$) (Giester *et al.*, 2016).

Recently, two samples from the Wessels Mine, provided by the mineral collector C.R. Owen, were found to contain small grains of a mineral phase

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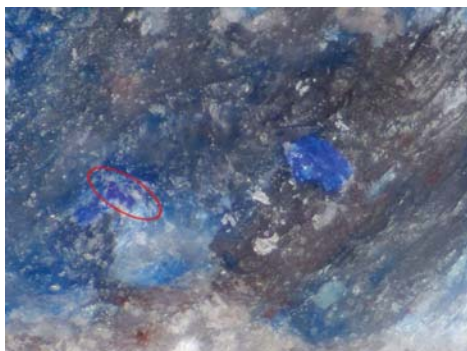


FIG. 1. Dark blue (with a purplish sheen) colinowensite (marked red) with bright blue effenbergerite and blue-green scottycite with pectolite in a matrix of sugilite, braunite and hausmannite.



FIG. 2. Hand specimen of blue wesselsite. Field of view = 8 cm.

that – while being similar in some respects – differed in their physical appearance from gillespite-group minerals effenbergerite/wesselsite also present on the specimens (Fig. 1). Energy-dispersive X-ray spectroscopy (EDX) analyses and preliminary single-crystal X-ray diffraction (XRD) analyses revealed the first occurrence of the synthetically well-known compound $\text{BaCuSi}_2\text{O}_6$. In the literature three different space groups have been proposed for synthetic $\text{BaCuSi}_2\text{O}_6$. The first description of the crystal structure was presented by Finger *et al.* (1989) who suggested $I4m2$ ($Z = 4$, $a = 7.042(3)$, $c = 11.133(3)$ Å). The same authors alternatively proposed $I4/mmm$ but considered this solution worse because of large displacement parameters for the oxygen atoms. Basically the same centrosymmetric solution was reported by Janczak and Kubiak (1992). Finally, a further, improved structure model was proposed by Sparta and Roth (2004) for $\text{BaCuSi}_2\text{O}_6$ at room temperature with a larger unit cell in space group $I4_1/acd$ with $Z = 16$ and $a = 10.009(2)$, $c = 22.467(6)$ Å. This unit cell is characterized by a rotation of 45° along the c axis resulting in a lattice parameter $a = a_{(\text{Finger})} \times \sqrt{2}$ and by $c = c_{(\text{Finger})} \times 2$. Our investigations on colinowensite as well as recent studies on the synthetic pigment $\text{BaCuSi}_2\text{O}_6$ (Chen *et al.*, 2014) confirmed the cell choice, space group and crystal structure at ambient conditions presented by Sparta and Roth (2004). These authors have also shown that $\text{BaCuSi}_2\text{O}_6$ undergoes a phase transition at high temperature (610 K) when superstructure reflections disappear and a structure model in space group $I4/mmm$ with $Z = 4$ is obtained. The mineral is named for Colin

R. Owens, Somerset West, South Africa (born in Rusape, Zimbabwe, on January 6th, 1937), who brought the specimens to our attention and provided the samples for deposition. The mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA 2012-060, Rieck, 2013). Type material is deposited in the collection of the Institut für Mineralogie und Kristallographie, University of Vienna, Austria, catalogue number HS13.097.

In late 2011 and in Spring 2012 two spectacular finds of wesselsite, $\text{SrCuSi}_4\text{O}_{10}$ (Fig. 2), were made in the Wessels Mine (C.R. Owen, pers. comm.) and the material started to become obtainable on the market by early 2012 through some South African mineral dealers. One of the authors (B.R.) was contacted by Mr Owen with samples to characterize the minerals of the wesselsite–effenbergerite solid solution. The results of these analyses encouraged us to complete the description of wesselsite as well as to compare structural details with those of the synthetic analogues. Thus, a high-quality X-ray structure refinement of single crystals taken from the new material is also included in the present study. Wesselsite belongs to the gillespite type of compounds, a group of minerals and synthetic representatives of general formula $AB\text{Si}_4\text{O}_{10}$ with $A = \text{Ca, Sr, Ba}$ and $B = \text{Cr, Fe, Cu}$. The crystal structure type was first described by Pabst (1943, 1959). Structure refinements on synthetic $\text{SrCuSi}_4\text{O}_{10}$ were done by Rietveld analysis of neutron powder diffraction data (Chakoumakos *et al.*, 1993; Knight *et al.*, 2010). The first description of wesselsite (Giester and Rieck, 1996), had been based on powder XRD data due to the lack of appropriate single crystals. From EDX analyses of 111 samples it was evident that a solid

solution series between wesselsite and effenbergerite exists with substitutions of Sr by Ba up to 50 mol.%. Studies of synthetic $\text{Sr}_{1-x}\text{Ba}_x\text{CuSi}_4\text{O}_{10}$ members (Knight and Henderson, 2007; Knight *et al.*, 2010) proved complete miscibility in the wesselsite–effenbergerite solid solution series.

Occurrence and paragenesis

The two samples (2 cm × 2 cm × 2 cm and 2 cm × 3 cm × 5 cm in size) containing colinowensite originate from the central-eastern orebody of the Wessels Mine, located in the Kalahari Manganese Field, Northern Cape Province, South Africa. Both specimens contain a subset of the typical paragenesis of barium-, strontium- and copper-bearing minerals (effenbergerite; wesselsite; lavinskyite, $\text{K}(\text{LiCu})\text{Cu}_6(\text{Si}_4\text{O}_{11})_2(\text{OH})_4$ Yang *et al.* 2014; scottiyite, $\text{BaCu}_2\text{Si}_2\text{O}_7$ Yang *et al.* 2013; diegogataite, $\text{Na}_2\text{CaCu}_2\text{Si}_8\text{O}_{20}\cdot\text{H}_2\text{O}$ Rumsey *et al.* 2013) in close association with Cu-, Ba- and Sr-bearing pectolite, quartz, aegirine, richterite, minerals of the garnet group and a number of different manganese and iron oxides, hausmannite and hematite being dominant. Abundant members of the effenbergerite–wesselsite solid solution series are present in both specimens. However, the chemistry of these minerals differs significantly between the two specimens; crystals on the smaller specimen are commonly close to a composition of $\text{Ef}_{80}\text{We}_{20}$ while those on the other specimen often yielded $\text{Ef}_5\text{We}_{95}$, indicating a different locality within an orebody characterized by local geochemical effects with respect to the Ba- and Sr-distribution. The formation of different Ba/Sr mineral species is a result of phase stability in the micro-environments that developed during the Wessels event (J. Gutzmer, pers. comm., 2012). We note that sugilite, which is generally found in the same paragenesis, is almost completely absent on these specimens.

Physical and optical properties

Crystals of colinowensite are subhedral with maximum dimensions of 100 μm × 100 μm × 50 μm while most do not exceed 50 μm in any direction. Rarely the forms {100} and {110} are observed while {001} is always present on cleavages plates. Cleavage is very good, but less perfect than for effenbergerite. Colinowensite is brittle, with an uneven fracture, and an estimated Mohs hardness of ~4. The density was established by micropycnometry to be 4.20(5) g cm^{-3} , which is in surprisingly good

agreement with the calculated value of 4.236 g cm^{-3} based on the idealized chemical formula and lattice parameters. The largest crystals appear dark blue while those smaller than 40 μm are distinctively purple; the streak is purple. Because of its intense colour, the synthetic pigment, known as Chinese or Han purple, was used in ancient and imperial China from the Western Zhou period (1045 – 771 BC) until the end of the Han dynasty (206 BC – 220 AD) (Berke, 2007; Liu *et al.*, 2007; Chen *et al.*, 2014; Xia *et al.*, 2014). Colinowensite shows very intense absorption in the range 450 – 620 nm, rendering the samples almost opaque. Optical measurements in this range lack any confidence. Below and above this range they are, although difficult, feasible, albeit with a relatively large estimated error. Colinowensite is uniaxial (–) negative, with $\omega = 1.740$ (20), $\epsilon = 1.735(20)$ (420 nm) and $\omega = 1.745$ (20), $\epsilon = 1.730(20)$ (650 nm), determined on a spindle stage. The lustre is vitreous and no fluorescence was observed under either shortwave or longwave ultraviolet radiation. Very strong pleochroism from purple (RGB 224,1,245, measured as the average pixel colour as detected by the sensor of a NIKON D7000 camera) along the *c* axis, to blue (RGB 22,0,82) in the perpendicular direction is noted. Chen *et al.* (2014) characterized the synthetic pigment $\text{BaCuSi}_2\text{O}_6$ by powder XRD techniques, infrared spectroscopy, X-ray photoelectron spectroscopy, energy dispersive spectroscopy, luminance and magnetic measurements. Calculation of the Gladstone–Dale relationship using the constants of Mandarino (1981) yields good (–0.058 for 420 nm) and fair (–0.061 for 650 nm) compatibility. These suboptimal results are explained by the optical behaviour of colinowensite.

Chemical composition

The chemical composition of colinowensite was established with an automated JEOL JXA-8230 SuperProbe with five integrated dual-crystal wavelength dispersive spectrometers and an energy dispersive detector. The measurements (20 kV, 20 nA, ~6 μm beam diameter) were taken on five fragments, four spots each, at the Austrian Armed Forces ChemLab, as well as the CID (Laboratory of the Criminal Investigation Department of the Ministry of Interior, Austria). Colinowensite is stoichiometrically pure with no minor elements >100 ppm present. Probe standards used were CuO , BaSO_4 and SiO_2 . The results (wt.%) are CuO 22.53 (22.09–22.98), BaO 43.43 (42.58–44.29) and SiO_2 34.04 (33.71–34.37). This yields the empirical formula (based on 6 O atoms per

TABLE 1. Crystal data and details of the intensity measurement and structure refinement for colinowensite and wesselsite.

Crystal Data	colinowensite	wesselsite
Formula	BaCuSi ₂ O ₆	Sr _{0.9} Ba _{0.1} CuSi ₄ O ₁₀
Space group	<i>I</i> 4 ₁ / <i>acd</i>	<i>P</i> 4/ <i>mcc</i>
<i>a</i> (Å)	9.967(1)	7.374(1)
<i>c</i> (Å)	22.290(2)	15.636(2)
<i>V</i> (Å ³)	2214.3(5)	850.2(3)
<i>Z</i>	16	4
ρ _{calc} (g cm ⁻³)	4.236	3.347
X-ray radiation	MoKα	MoKα
Absorption coefficient, μ (mm ⁻¹)	11.3	9.22
Data collection and Refinement		
Unique data	1751	1345
Data with <i>F</i> _o > 4σ(<i>F</i> _o)	1379	989
No. variables	48	41
<i>R</i> ₁ [for <i>F</i> _o > 4σ(<i>F</i> _o)]	0.021	0.056
<i>wR</i> ₂ [for all <i>F</i> _o ²]	0.051	0.091
<i>a</i> , <i>b</i> ¹	0.021, 4.15	0.0086, 7.28
Δρ _{min/max} (e Å ⁻³)	-1.03 / 1.14	-1.52 / 2.24

$$R_1 = \Sigma F_o - F_c / \Sigma F_o; wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}; w = 1/[\sigma^2(F_o^2) + (a \times P)^2 + b \times P]; P = \{[\max \text{ of } (0 \text{ or } F_o^2)] + 2F_c^2\} / 3.$$

formula unit) Ba_{1.00}Cu_{1.00}Si_{2.00}O₆ or BaCuSi₂O₆. Colinowensite is not soluble in acids except HF. The investigated sample of wesselsite was analysed and the empirical formula is Sr_{0.90}Ba_{0.10}Cu_{1.00}Si_{4.00}O₁₀. Calcium contents like those found in some crystals in previous work (Giester and Rieck, 1996) were not detected.

X-ray crystallography

Selected crystal fragments of colinowensite and wesselsite were studied on a Bruker APEXII diffractometer equipped with a CCD area detector and an Incoatec Microfocus Source IμS (30 W, multilayer mirror, MoKα radiation). Several sets of phi- and omega-scans with 2° scanwidths were measured up to 80°2θ (full sphere) at room temperature at crystal-detector distances of 35 mm (colinowensite) and 30 mm (wesselsite). The sample of colinowensite turned out to consist of several intergrown fragments with random orientation, but the intensities of the major component could be integrated satisfactorily. Absorption was corrected by evaluation of multi-scans. The atom coordinates given by Sparta and Roth (2004) and by Giester and Rieck (1994) were taken as starting sets for colinowensite and wesselsite, respectively. Refinements by full-matrix least-squares techniques on *F*² were performed with the program *SHELXL-97* (Sheldrick, 2008). Anisotropic displacement

parameters for all atoms were applied. A compilation of crystal data and details of measurements and refinements are given in Table 1. Final structure parameters are listed in Table 2 and selected interatomic bond distances and angles in Table 3.

The powder XRD pattern of colinowensite was determined using a Philips X'Pert diffractometer equipped with CuKα radiation and a graphite monochromator. Data, collected at 40 kV and 40 mA in the range 7–90°2θ, with 0.01° s⁻¹ scanning speed are given in Table 4. Unit-cell parameters refined from the powder data are *a* = 9.9762(4), *c* = 22.3200(9) Å, *V* = 2221.4(2) Å³. The *c*:*a* ratio calculated from the unit-cell parameters is 2.237. A Rietveld refinement yielded no major differences as compared to the results of the single-crystal structure refinement for colinowensite.

Discussion

Colinowensite

Colinowensite is a cyclosilicate with unbranched, isolated [Si₄O₁₂]⁸⁻ 4-membered single rings of twofold rotation symmetry (Fig. 3*a*). The copper atoms show almost square planar coordination (Fig. 4) linking the [Si₄O₁₂]⁸⁻ rings together along (001). The Cu–Cu distance of two neighbouring squares amounts to 2.73 Å. The large barium atoms are 10-coordinate (Fig. 5) to five different pairs of oxygen ligands with

TABLE 2. Atom coordinates and displacement parameters (\AA^2) for colinowensite $\text{BaCuSi}_2\text{O}_6$ and wesselsite $\text{Sr}_{0.9}\text{Ba}_{0.1}\text{CuSi}_4\text{O}_{10}$. Site symmetries (with Wyckoff positions in parentheses) are 2 (16e) for Ba, 2 (16d) for Cu, and 1 (32g) for Si, O1–O3 in colinowensite (space group No. 142, origin choice 2) and 4(4b) for Sr, 4 (4c) for Cu, 2 (8f) for O1, and 1 (16g) for Si, O2, O3 in wesselsite (space group No. 130, origin choice 2).

	x/a	y/b	z/c	$U_{\text{iso/eq}}$	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Colinowensite $\text{BaCuSi}_2\text{O}_6$										
Ba	0.25	0.98851(2)	0.5	0.00996(4)	0.01018(6)	0.01017(6)	0.00951(7)	0	−0.00200(3)	0
Cu	0	0.25	0.06372(2)	0.00724(6)	0.00650(12)	0.00677(12)	0.00845(12)	0	0	0.00020(7)
Si	0.27585(5)	0.75112(4)	0.87529(3)	0.00664(8)	0.00461(15)	0.00568(17)	0.00964(19)	−0.00074(12)	0.00002(18)	−0.00012(12)
O1	0.19127(12)	0.72096(14)	0.81559(6)	0.0123(2)	0.0071(4)	0.0167(5)	0.0130(6)	−0.0048(5)	−0.0024(4)	0.0006(5)
O2	0.37233(14)	0.87863(14)	0.85921(7)	0.0161(2)	0.0134(5)	0.0128(5)	0.0223(6)	0.0040(5)	−0.0043(5)	−0.0076(4)
O3	0.30795(12)	0.78098(14)	0.06477(6)	0.0118(2)	0.0077(4)	0.0159(5)	0.0118(6)	0.0042(5)	0.0011(4)	0.0008(5)
Wesselsite $\text{Sr}_{0.9}\text{Ba}_{0.1}\text{CuSi}_4\text{O}_{10}$										
Sr*	0.25	0.75	0	0.01133(13)	0.01139(16)	0.01139(16)	0.0112(2)	0	0	0
Cu	0.25	0.25	0.08879(5)	0.00932(15)	0.00656(19)	0.00656(19)	0.0148(3)	0	0	0
Si	0.51005(12)	0.93197(12)	0.15105(6)	0.00884(17)	0.0063(3)	0.0071(3)	0.0131(3)	−0.0007(3)	0.0014(3)	−0.0005(3)
O1	0.4674(4)	0.9674(4)	0.25	0.0287(10)	0.0336(15)	0.0336(15)	0.0191(16)	−0.0094(13)	0.0094(13)	−0.0058(19)
O2	0.7149(3)	1.0005(4)	0.13134(15)	0.0157(5)	0.0050(10)	0.0194(12)	0.0226(11)	0.0043(10)	−0.0004(8)	−0.0023(8)
O3	0.3685(3)	0.0176(3)	0.08686(17)	0.0154(5)	0.0114(10)	0.0068(10)	0.0281(12)	−0.0007(9)	−0.0061(9)	0.0022(8)

*Refined site occupancy: Sr 0.905(3) Ba 0.095(3).

TABLE 3. Selected interatomic bond distances [Å] and angles (°) for colinowensite, BaCuSi₂O₆ and wesselsite, Sr_{0.9}Ba_{0.1}CuSi₄O₁₀.

BaCuSi ₂ O ₆		Sr _{0.9} Ba _{0.1} CuSi ₄ O ₁₀	
Ba–O1	2× 2.685(1)	Sr–O3	4× 2.550(3)
Ba–O3	2× 2.774(1)	Sr–O2	4× 2.769(3)
Ba–O2	2× 2.934(1)	<Sr–O>	2.660
Ba–O3	2× 3.103(1)		
Ba–O1	2× 3.219(1)		
<Ba–O>	2.943		
Cu–O1	2× 1.929(1)	Cu–O3	4× 1.924(3)
Cu–O2	2× 1.939(1)		
<Cu–O>	1.934		
Si–O3	1× 1.603(1)	Si–O3	1× 1.580(3)
Si–O1	1× 1.604(1)	Si–O1	1× 1.600(1)
Si–O2	1× 1.633(1)	Si–O2	1× 1.623(2)
Si–O2	1× 1.635(1)	Si–O2	1× 1.632(2)
<Si–O>	1.619	<Si–O>	1.619
O1–Si–O2	1× 105.85(8)	O1–Si–O2	1× 108.43(18)
O1–Si–O2	1× 109.52(8)	O1–Si–O2	1× 109.46(16)
O1–Si–O3	1× 116.90(7)	O1–Si–O3	1× 114.78(12)
O2–Si–O2	1× 108.32(11)	O2–Si–O2	1× 108.28(21)
O2–Si–O3	1× 110.18(8)	O2–Si–O3	1× 111.72(14)
O2–Si–O3	1× 105.84(8)	O2–Si–O3	1× 103.93(14)
<O–Si–O>	109.43	<O–Si–O>	109.43

distances in the range 2.68–3.22 Å. For a comparison with the high-temperature structure of BaCuSi₂O₆ see Sparta and Roth (2004). Colinowensite represents a unique structure type. Several other minerals with this type of unbranched 4-membered silicate rings are known, e.g. papagoite, verplanckite, baotite and representatives of the taramellite-, joaquinite- and the nenadkevichite-komarovite groups (subdivision 9.CE of the Strunz Mineralogical Tables; Strunz and Nickel, 2001). As examples, Fig. 6a illustrates a structure detail of taramellite, emphasizing the arrangement of the [Si₄O₁₂]⁸⁻ rings linked to MO₆ (M=Fe³⁺, Ti⁴⁺) octahedra. The M–M distance of two neighbouring M cations is 3.17 Å. In Fig. 6b a part of the structure of byelorusite-(Ce), a representative of the joaquinite group, is shown. Unbranched single 4-membered rings [Si₄O₁₂]⁸⁻ are also found in some synthetic compounds, e.g. in K₄Sc₂[Si₄O₁₂](OH)₂ (Pyatenko *et al.*, 1979) and Na₂BaNd₂[Si₄O₁₂][CO₃] (Malinovskii, 1983).

Wesselsite

The crystal structure of wesselsite, SrCuSi₄O₁₀, is characterized by 4-membered rings of SiO₄

tetrahedra, [Si₄O₁₀]⁴⁻, which are further connected into infinite sheets (Fig. 3b) parallel to (001). Copper atoms in nearly planar square coordination are attached on both sides of the sheets. Adjacent layers are linked together by the strontium atoms in distorted square-antiprismatic coordination. For a detailed description of the topology of gillespite-type structures the reader is referred to Miletich *et al.* (1997) and Knight *et al.* (2010). The latter authors explicitly discuss structure variations within the wesselsite–effenbergerite (Sr_{1-x}Ba_xCuSi₄O₁₀) solid solution series in terms of lattice parameters, unit-cell volume, bond lengths and angles, and rotation of building units. Based both on microprobe data and refined site occupancy, the composition of wesselsite in the present study is close to Sr_{0.9}Ba_{0.1}CuSi₄O₁₀. Respective structure details fit perfectly to these observations, Fig. 7 shows as an example the compositional dependence of the unit-cell volume.

Conclusions

The present paper describes colinowensite, BaCuSi₂O₆, a new barium copper silicate from the Wessels mine, Kalahari Manganese Field, South

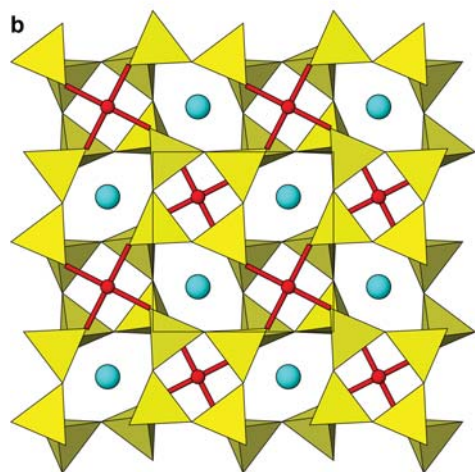
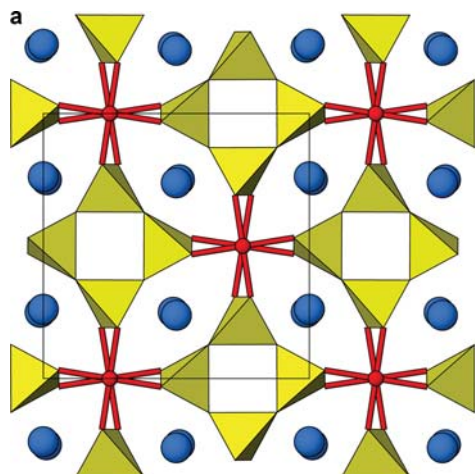


FIG. 3. Single sheets of colinowensite (a) and wesselsite (b) projected along [001]. Silicate rings are shown in yellow, CuO_4 squares in red and Ba/Sr atoms indicated as dark/light blue spheres. All crystal structure drawings were done with *ATOMS* (Dowty, 2011).

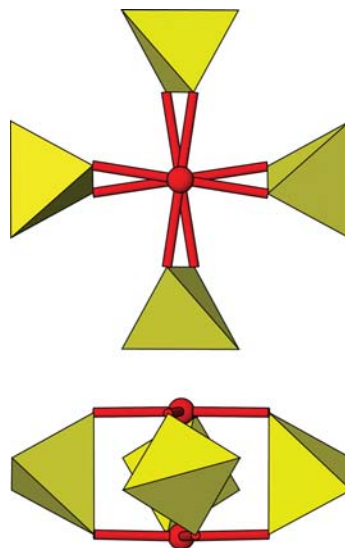


FIG. 4. Arrangement of CuO_4 squares in colinowensite projected along [001] (upper) and [100] (lower). SiO_4 tetrahedra are shown in yellow and CuO_4 squares in red.

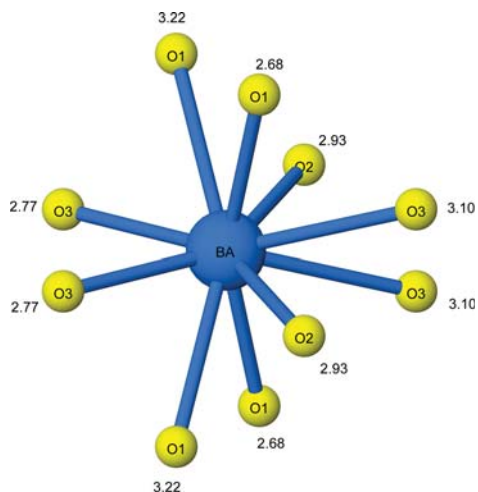


FIG. 5. Irregular 10-coordination of the Ba atom in colinowensite projected along [001] with Ba–O distances [Å]. The site symmetry for Ba (with Wyckoff position in parentheses) is $2 (16e)$.

TABLE 4. Powder XRD data for colinowensite, BaCuSi₂O₆.

<i>I</i> rel	<i>d</i> obs.	<i>d</i> calc.	<i>h</i>	<i>k</i>	<i>l</i>
31	5.577	5.573	0	0	4
30	4.997	4.983	0	2	0
31	4.560	4.549	0	2	2
2	3.831	3.822	1	2	3
7	3.722	3.715	0	2	4
70	3.533	3.524	2	2	0
5	3.158	3.152	1	2	5
100	2.985	2.978	2	2	4
9	2.983	2.979	0	2	6
4	2.789	2.787	0	0	8
1	2.751	2.743	2	3	1
57	2.499	2.492	0	4	0
3	2.410	2.403	1	4	1
1	2.354	2.349	2	3	5
1	2.305	2.2996	1	4	3
23	2.280	2.275	0	4	4
2	2.235	2.229	2	4	0
8	2.191	2.185	2	4	2
5	2.189	2.186	2	2	8
2	2.074	2.069	2	4	4
3	2.037	2.035	0	2	10
1	1.991	1.985	3	4	1
1	1.930	1.925	1	4	7
4	1.915	1.911	2	4	6
3	1.861	1.857	0	4	8
3	1.859	1.858	0	0	12
1	1.847	1.845	1	2	11
19	1.767	1.762	4	4	0
1	1.733	1.730	1	4	9
1	1.693	1.690	3	4	7
5	1.684	1.6798	4	4	4
1	1.647	1.643	0	6	2
13	1.645	1.643	2	2	12
13	1.580	1.576	2	6	0
2	1.579	1.576	2	4	10
1	1.542	1.538	1	6	5
16	1.520	1.516	2	6	4
1	1.520	1.516	0	6	6
1	1.518	1.517	0	2	14
3	1.492	1.489	4	4	8
5	1.492	1.489	0	4	12
1	1.461	1.457	3	6	3
1	1.413	1.410	3	6	5
4	1.394	1.393	0	0	16
1	1.375	1.372	4	6	2
1	1.375	1.372	2	6	8
1	1.343	1.342	0	2	16
1	1.335	1.332	0	6	10
1	1.299	1.295	4	6	6
1	1.297	1.296	2	4	14
4	1.297	1.296	2	2	16

TABLE 4. (contd.)

<i>I</i> rel	<i>d</i> obs.	<i>d</i> calc.	<i>h</i>	<i>k</i>	<i>l</i>
2	1.281	1.278	4	4	12
3	1.249	1.246	0	8	0
1	1.238	1.234	1	8	1
1	1.219	1.216	0	8	4
7	1.218	1.216	0	4	16
1	1.205	1.202	2	8	2
6	1.204	1.202	2	6	12
2	1.178	1.175	6	6	0
1	1.177	1.175	4	6	10
2	1.152	1.149	6	6	4
1	1.140	1.137	0	8	8
3	1.117	1.114	4	8	0
2	1.096	1.093	4	8	4
4	1.095	1.093	4	4	16

The strongest lines are shown in bold.

(continued)

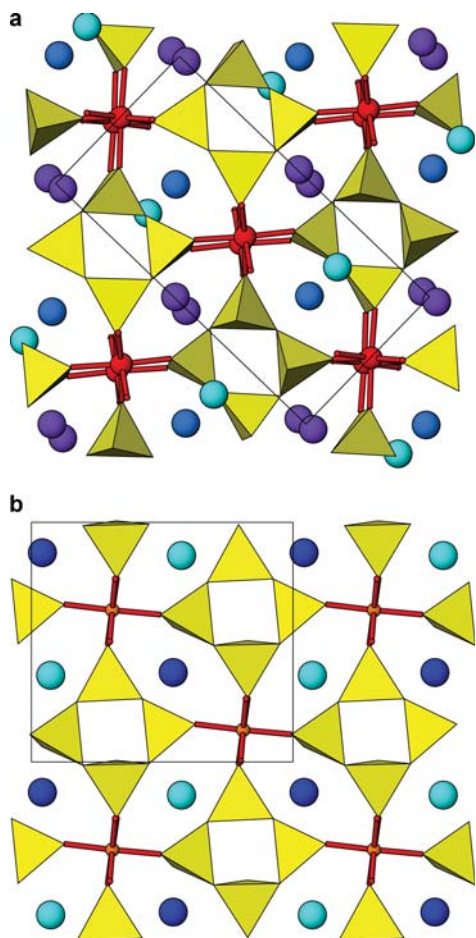


FIG. 6. Structure detail of (a) taramellite (Mazzi and Rossi, 1980) projected along [100] and of (b) byelorussite-(Ce) (Zubkova *et al.*, 2004). Silicate rings are shown in yellow, M–O₆ bonds in red and Ba atoms are indicated as spheres with different shades of blue-purple.

Africa, as well as providing additional data for wesselsite, SrCuSi₄O₁₀. These minerals occur in an assemblage closely associated with effenbergerite, BaCuSi₄O₁₀ and scottyite, BaCu₂Si₂O₇. It is worth noting that complete solid solution has been observed for the synthetic compounds and also to some extent for natural samples between wesselsite and effenbergerite. Contrary to this, in colinowensite and scottyite no significant substitution of barium by strontium was found and no isotopic strontium copper silicates are known. Yang *et al.* (2013) have pointed out that replacement of larger Ba²⁺ by smaller Sr²⁺ ions in scottyite potentially would worsen the bonding

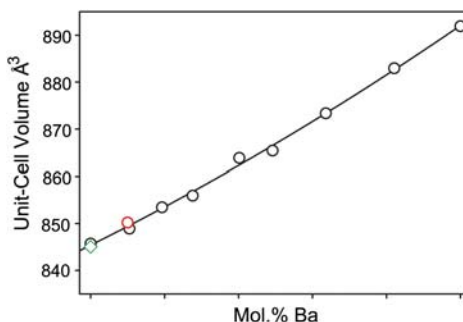


FIG. 7. Unit-cell volumes in the wesselsite-effenbergerite solid solution series [modified after Knight *et al.*, 2010] in addition to values taken from the original description (Giester and Rieck, 1996: green rhomb) and the present study (red circle).

energetics for these sites (by narrowing of the Si–O–Si angles in the Si₂O₇ groups) and thus might destabilize the entire structure.

References

- Berke, H. (2007) The invention of blue and purple pigments in ancient times. *Chemical Society Reviews*, **36**, 15–30.
- Cairncross, B. and Beukes, N.J. (2013) *The Kalahari Manganese Field: the Adventure Continues*. Random House Struik, Capetown.
- Chakoumakos, B.C., Fernandez-Baca, J.A. and Boatner, L.A. (1993) Refinement of the structures of the layer silicates M₂CuSi₄O₁₀ (M = Ca, Sr, Ba) by Rietveld analysis of neutron powder diffraction data. *Journal of Solid State Chemistry*, **103**, 105–113.
- Chen, Y., Zhang, Y. and Feng, S. (2014) Hydrothermal synthesis and properties of pigments Chinese purple BaCuSi₂O₆ and dark blue BaCu₂Si₂O₇. *Dyes and Pigments*, **105**, 167–173.
- Dowty, E. (2011) *ATOMS for Windows V6.4.0*. Shape Software, Kingsport, Tennessee, USA.
- Finger, L.W., Hazen, R.M. and Hemley, R.J. (1989) BaCuSi₂O₆: a new cyclosilicate with four-membered tetrahedral rings. *American Mineralogist*, **74**, 952–955.
- Giester, G. and Rieck, B. (1994) Effenbergerite, BaCuSi₄O₁₀, a new mineral from the Kalahari Manganese Field, South Africa: description and crystal structure. *Mineralogical Magazine*, **58**, 663–670.
- Giester, G. and Rieck, B. (1996) Wesselsite, SrCuSi₄O₁₀, a further new gillespite-group mineral from the Kalahari Manganese Field, South Africa. *Mineralogical Magazine*, **60**, 795–798.
- Giester, G., Lengauer, C.L., Pristacz, H., Rieck, B., Topa, D. and von Bezings, K.L. (2016) Cairncrossite, a new

- Ca-Sr(-Na) phyllosilicate from the Wessels Mine, Kalahari Manganese Field, South Africa. *European Journal of Mineralogy*, DOI: 10.1127/ejm/2016/0028-2519
- Janczak, J. and Kubiak, R. (1992) Structure of the cyclic barium copper silicate $\text{Ba}_2\text{Cu}_2[\text{Si}_4\text{O}_{12}]$ at 300 K. *Acta Crystallographica*, **C48**, 8–10.
- Knight, K.S. and Henderson, C.M.B. (2007) Structural basis for the anomalous low-temperature thermal expansion behaviour of the gillespite-structured phase $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{CuSi}_4\text{O}_{10}$. *European Journal of Mineralogy*, **19**, 189–200.
- Knight, K.S., Henderson, C.M.B. and Clark, S.M. (2010) Structural variations in the wesselsite–effenbergerite ($\text{Sr}_{1-x}\text{Ba}_x\text{CuSi}_4\text{O}_{10}$) solid solution. *European Journal of Mineralogy*, **22**, 411–423.
- Liu, Z., Mehta, A., Tamura, N., Pickard, D., Rong, B., Zhou, T. and Pianetta, P. (2007) Influence of Taoism on the invention of the purple pigment used on the Qin terracotta warriors. *Journal of Archaeological Science*, **34**, 1878–1883.
- Malinovskii, Y.A. (1983) The crystal structure of $\text{Na}_2\text{BaNd}_2(\text{OH})_2(\text{Si}_4\text{O}_{12})(\text{CO}_3)$. *Doklady Akademii Nauk SSSR*, **272**, 1375–1378.
- Mandarino, J.A. (1981) The Gladstone–Dale relationship: Part IV. The compatibility concept and its application. *The Canadian Mineralogist*, **70**, 441–450.
- Mazzi, F. and Rossi, G. (1980) The crystal structure of taramellite. *American Mineralogist*, **65**, 123–128.
- Miletich, R., Allan, D.R. and Angel, R.J. (1997) The synthetic Cr^{2+} silicates $\text{BaCrSi}_4\text{O}_{10}$ and $\text{SrCrSi}_4\text{O}_{10}$: the missing links in the gillespite-type $\text{ABSi}_4\text{O}_{10}$ series. *American Mineralogist*, **82**, 697–707.
- Pabst, A. (1943) Crystal structure of gillespite, $\text{BaFeSi}_4\text{O}_{10}$. *American Mineralogist*, **28**, 372–390.
- Pabst, A. (1959) Structures of some tetragonal sheet silicates. *Acta Crystallographica*, **12**, 733–739.
- Pyatenko, Y.A., Zhdanova, T.A. and Voronkov, A.A. (1979) About the structure of $\text{K}_4\text{Sc}_2(\text{OH})_2(\text{Si}_4\text{O}_{12})$. *Doklady Akademii Nauk SSSR*, **248**, 868–871.
- Rieck, B. (2013) Colinowensite, IMA 2012–060. CNMNC Newsletter No. 15, February 2013, page 6; *Mineralogical Magazine*, **77**, 1–12.
- Rumsey, M.S., Welch, M.D., Kampf, A.R. and Spratt, J. (2013) Diegogattaite, $\text{Na}_2\text{CaCu}_2\text{Si}_3\text{O}_{20}\cdot\text{H}_2\text{O}$: a new nanoporous copper sheet silicate from Wessels Mine, Kalahari Manganese Fields, Republic of South Africa. *Mineralogical Magazine*, **77**, 3155–3162.
- Sheldrick, G.M. (2008) A short history of SHELX. *Acta Crystallographica*, **A64**, 112–122.
- Sparta, K.M. and Roth, G. (2004) Reinvestigation of the structure of $\text{BaCuSi}_2\text{O}_6$ – evidence for a phase transition at high temperature. *Acta Crystallographica*, **B60**, 491–494.
- Strunz, H. and Nickel, E.H. (2001) *Strunz Mineralogical Tables. Chemical-Structural Mineral Classification System. 9. Edition.* E. Schweitzerbart'sche Verlagsbuchhandlung (Nägele und Obermiller), Stuttgart, Germany.
- Xia, Y., Ma, Q.L., Zhang, Z.G., Liu, Z.D., Feng, J., Shao, A.D., Wang, W.F. and Fu, Q.L. (2014) Development of Chinese barium copper silicate pigments during the Qin Empire based on Raman and polarized light microscopy studies. *Journal of Archaeological Science*, **49**, 500–509.
- Yang, H., Downs, R.T., Evans, S.H. and Pinch, W.W. (2013) Scottyite, the natural analog of synthetic $\text{BaCu}_2\text{Si}_2\text{O}_7$, a new mineral from the Wessels mine, Kalahari Manganese Fields, South Africa. *American Mineralogist*, **98**, 478–484.
- Yang, H., Downs, R.T., Evans, S.H. and Pinch, W.W. (2014) Lavinskyite, $\text{K}(\text{LiCu})\text{Cu}_6(\text{Si}_4\text{O}_{11})_2(\text{OH})_4$, isotopic with planch ete, a new mineral from the Wessels mine, Kalahari Manganese Fields, South Africa. *American Mineralogist*, **99**, 525–530.
- Zubkova, N.V., Pushcharovskii, D.Y., Giester, G., Tillmanns, E., Pekov, I.V. and Krotova O.D. (2004) Crystal Structure of byelorussite-(Ce) $\text{NaMnBa}_2\text{Ce}_2(\text{TiO})_2[\text{Si}_4\text{O}_{12}]_2(\text{F},\text{OH})\cdot\text{H}_2\text{O}$. *Crystallography Reports*, **49**, 964–968.