# Pavlovskyite Ca<sub>8</sub>(SiO<sub>4</sub>)<sub>2</sub>(Si<sub>3</sub>O<sub>10</sub>): A new mineral of altered silicate-carbonate xenoliths from the two Russian type localities, Birkhin massif, Baikal Lake area and Upper Chegem caldera, North Caucasus

# EVGENY V. GALUSKIN,<sup>1,\*</sup> FRANK GFELLER,<sup>2</sup> VALENTINA B. SAVELYEVA,<sup>3</sup> THOMAS ARMBRUSTER,<sup>2</sup> BILJANA LAZIC,<sup>2</sup> IRINA O. GALUSKINA,<sup>1</sup> DANIEL M. TÖBBENS,<sup>4</sup> ALEKSANDR E. ZADOV,<sup>5</sup> PIOTR DZIERŻANOWSKI,<sup>6</sup> NIKOLAI N. PERTSEV,<sup>7</sup> AND VIKTOR M. GAZEEV<sup>7</sup>

<sup>1</sup>Department of Geochemistry, Mineralogy and Petrography, Faculty of Earth Sciences, University of Silesia, Bedzińska 60, 41-200 Sosnowiec, Poland

<sup>2</sup>Mineralogical Crystallography, Institute of Geological Sciences, University of Bern, Freiestrasse 3, CH-3012 Bern, Switzerland <sup>3</sup>Institute of the Earth Crust SB RAS, Lermontov Str. 128, 664033 Irkutsk, Russia

<sup>4</sup>Institute of Mineralogy und Petrography, University of Innsbruck, Innrain 52, A-6020 Innsbruck, Austria

<sup>5</sup>OOO Science Research Centre "NEOCHEM," Dmitrovskoye Highway 100/2, 127 238 Moscow, Russia

<sup>6</sup>Institute of Geochemistry, Mineralogy and Petrology, University of Warsaw, al. Żwirki i Wigury 93, 02-089 Warszawa, Poland

<sup>7</sup>Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry (IGEM) RAS, Staromonetry 35, Moscow, Russia

#### ABSTRACT

The new mineral pavlovskyite  $Ca_8(SiO_4)_2(Si_3O_{10})$  forms rims together with dellaite  $Ca_6(Si_2O_7)(SiO_4)$ (OH)<sub>2</sub> around galuskinite  $Ca_7(SiO_4)_3CO_3$  veins cutting calcio-olivine skarns in the Birkhin gabbro massif. In addition, skeletal pavlovskyite occurs in cuspidine zones of altered carbonate xenoliths in the ignimbrites of the Upper Chegem caldera (North Caucasus). The synthetic analog of pavlovskyite has been synthesized before and is known from cement-like materials. Isotypic to pavlovskyite, is the synthetic germanate analog  $Ca_8(GeO_4)_2(Ge_3O_{10})$ . The crystal structure of pavlovskyite, space group *Pbcn*, a = 5.0851(1), b = 11.4165(3), c = 28.6408(8) Å, V = 1662.71(7) Å<sup>3</sup>, Z = 4, has been refined from X-ray single-crystal data to R1 = 3.87%. The new colorless mineral has a Mohs hardness of 6-6.5, biaxial (-),  $\alpha = 1.656(2)$ ,  $\beta = 1.658(2)$ ,  $\gamma = 1.660(2)$  (589 nm), 2V (meas) =  $80(5)^\circ$ , 2V (calc) =  $89.9^\circ$ , medium dispersion: r > v, optical orientation: X = b, Y = c, Z = a.

For comparison with pavlovskyite, the crystal structure of kilchoanite  $Ca_6(SiO_4)(Si_3O_{10})$  from the Birkhin massif [space group *I2cm*, *a* = 11.4525(2), *b* = 5.0867(1), *c* = 21.996(3) Å, *V* = 1281.40(4) Å<sup>3</sup>, *Z* = 4] has been refined from single-crystal X-ray data to *R*1 = 2.00%.

Pavlovskyite represents a 1:1 member of a polysomatic series with calcio-olivine  $\gamma$ -Ca<sub>2</sub>SiO<sub>4</sub> and kilchoanite Ca<sub>6</sub>(SiO<sub>4</sub>)(Si<sub>3</sub>O<sub>10</sub>) as end-member modules. The structure is characterized by strongly folded trisilicate units (Si<sub>3</sub>O<sub>10</sub>) interwoven with a framework of CaO<sub>6</sub> and CaO<sub>8</sub> polyhedra. Olivine-like slices with orthosilicate groups are interstratified with the characteristic trisilicate module of Ca<sub>4</sub>(Si<sub>3</sub>O<sub>10</sub>) composition. Although the optical properties of pavlovskyite and kilchoanite are similar, both minerals can be distinguished by chemical analyses (different Ca/Si ratio), X-ray diffraction, and Raman spectroscopy. The new mineral is named after V.E. Pavlovsky (1901–1982), an outstanding geologist in the area of Eastern Siberia, in particular of the Baikal region.

Keywords: Pavlovskyite, kilchoanite, skarn, structure, Raman, Upper Chegem caldera, Birkhin massif, Russia

# INTRODUCTION

Funk (1957, 1958), among others, postulated the formation of a  $\gamma$ -Ca<sub>2</sub>SiO<sub>4</sub> phase (olivine structure type) with 0.3–0.5 H<sub>2</sub>O pfu mainly on the basis of weight loss and powder X-ray data of steam-treated (120–350 °C) Ca<sub>2</sub>SiO<sub>4</sub>. With the goal of clarifying the nature of this questionable " $\gamma$ -dicalcium silicate hydrate," Speakman et al. (1967) performed hydrothermal experiments between 150 and 600 °C at 15 to 350 bar. The synthesis products were identified by X-ray powder diffraction and three consecutive hydration reactions were identified (Speakman et al. 1967). (1) The reaction

9  $\gamma$ -Ca<sub>2</sub>SiO<sub>4</sub> + 2 H<sub>2</sub>O  $\rightarrow$  Ca<sub>8</sub>Si<sub>5</sub>O<sub>18</sub> + 2 Ca<sub>5</sub>(SiO<sub>4</sub>)<sub>2</sub>(OH)<sub>2</sub>

was complete after three days at 180 °C and 20 bars. Reaction products were the new phase  $Ca_8Si_5O_{18}$ , which is the synthetic analog of the new mineral pavlovskyite described in this paper, plus calcio-chondrodite known as the mineral reinhardbraunsite. In other words, the alleged " $\gamma$ -dicalcium silicate hydrate" turned out to be a mixture of two phases, both closely related to the olivine structure-type. (2) The hydration reaction of pavlovskyite:

$$4 Ca_8Si_5O_{18} + H_2O \rightarrow 4.5 Ca_6(SiO_4)(Si_3O_{10}) + Ca_5(SiO_4)_2(OH)_2$$

<sup>\*</sup> E-mail: evgeny.galuskin@us.edu.pl

was complete after seven days at 250 °C and 40 bars leading to kilchoanite and reinhardbraunsite. (3) The reaction

1.5  $Ca_6(SiO_4)(Si_3O_{10}) + 3 Ca_5(SiO_4)_2(OH)_2 \rightarrow$ 4  $Ca_6(Si_2O_7)(SiO_4)(OH)_2$ 

produced dellaite after three days at 600 °C and 200 bars.

In addition, Speakman et al. (1967) concluded that Ca<sub>8</sub>Si<sub>5</sub>O<sub>18</sub> is not an equilibrium product at any condition, and that Ca<sub>8</sub>Si<sub>5</sub>O<sub>18</sub> has an interstratified structure composed of alternate layers of kilchoanite and  $\gamma$ -Ca<sub>2</sub>SiO<sub>4</sub> (calcio-olivine). Most astonishing, the structure of kilchoanite was not known in detail at this time but was only solved five years later by Taylor (1971). The structural predictions for Ca<sub>8</sub>Si<sub>5</sub>O<sub>18</sub> by Bennett et al. (1966) and Speakman et al. (1967) are based on similarities of the X-ray powder patterns and periodicities of selected-area electron diffraction patterns resembling both  $\gamma$ -Ca<sub>2</sub>SiO<sub>4</sub> and kilchoanite. With the solved structure of kilchoanite, Taylor (1971) produced also a sketch of the Ca<sub>8</sub>Si<sub>5</sub>O<sub>18</sub> structure. The formula may be rewritten to  $Ca_8(SiO_4)_2(Si_3O_{10})$  indicating the different SiO<sub>4</sub> entities. Ca<sub>8</sub>Si<sub>5</sub>O<sub>18</sub> has occasionally been described in cement materials (e.g., Mitsuda et al. 1985; Garbev et al. 2002; Yanagisawa et al. 2006; Meller et al. 2009), but its structure could not be refined because of the microcrystalline appearance of this compound. The structure of  $Ca_{7.96}Cu_{0.04}Ge_5O_{18}$  (Redhammer et al. 2006) is isotypic with the Ca<sub>8</sub>Si<sub>5</sub>O<sub>18</sub> model presented by Taylor (1971).

Kilchoanite and calcio-olivine ( $\gamma$ -Ca<sub>2</sub>SiO<sub>4</sub>) are structural modules building pavlovskyite (Bennett et al. 1966; Taylor 1971), thus these minerals and their synthetic analogs deserve a short review.

The synthetic analog of kilchoanite began as phase Z synthesized by Roy (1958a, 1958b) and was initially believed to be of hydrous composition: 9CaO·6SiO<sub>2</sub>·H<sub>2</sub>O. However, subsequent hydrothermal synthesis at 715 °C and 1.1 kbar produced an essentially anhydrous phase Z, which upon heating to 1090 °C transformed to rankinite, Ca<sub>3</sub>Si<sub>2</sub>O<sub>7</sub> (Roy et al. 1960). It was further assumed that at high-temperature synthesis-conditions phase Z actually represents a metastable product because long duration runs produced phase Y [dellaite, Ca<sub>6</sub>(Si<sub>2</sub>O<sub>7</sub>)(SiO<sub>4</sub>)(OH)<sub>2</sub>] and wollastonite or foshagite (Roy et al. 1960). Metastable formation of phase Z may be favored due to its strong structural similarity to  $\gamma$ -Ca<sub>2</sub>SiO<sub>4</sub>, allowing heterogeneous nucleation.

Agrell and Gay (1961) reported the first natural occurrence of phase Z in limestones thermally metamorphosed by gabbro and named it kilchoanite after the close-by village in Ardnamurchan, Scotland. At this locality, kilchoanite occurs as a retrograde replacement product of rankinite. Kilchoanite is also described from skarns in the Lake Baikal area, Eastern Siberia, Russia (Savelyeva et al. 1992).

Records of an orthorhombic phase of Ca<sub>2</sub>SiO<sub>4</sub> composition are first mentioned by Day et al. (1906). The name calcio-olivine for a synthetic compound was chosen when O'Daniel and Tscheischwili (1942) emphasized the structural relation of  $\gamma$ -Ca<sub>2</sub>SiO<sub>4</sub> to the olivine group. Natural  $\gamma$ -Ca<sub>2</sub>SiO<sub>4</sub> has been described before (e.g., Bridge 1966) but without detailed investigation allowing definition of a mineral species (Zadov et al. 2008). The mineral name calcio-olivine was approved in 2007 for a  $\gamma$ -Ca<sub>2</sub>SiO<sub>4</sub> sample from the high-temperature skarns at Lakargi Mountain, Northern Caucasus, Kabardino-Balkaria, Russian Federation (Zadov et al. 2008).  $\gamma$ -Ca<sub>2</sub>SiO<sub>4</sub> is the low-temperature polymorph of Ca<sub>2</sub>SiO<sub>4</sub> but has a strong tendency of metastable formation at high temperature (Smith et al. 1965).

We present in this paper, besides the description of the new mineral pavlovskyite, a comparison of the kilchoanite and pavlovskyite structures from Birkhin skarns. New mineral status and mineral name pavlovskyite were approved by CNMNC IMA in January 2011. The mineral is named in memory of the well-known Russian geologist Pavlovsky Evgeny Vladimirovich (1901–1982). E.V. Pavlovsky is known for his geological work in Eastern Siberia (Belichenko et al. 2001, 2011). In 1941, he defended his habilitation with the topic "geological structure and geological history of the Baikal mountain region." He was one of the first scientists engaged in the geology of the Birkhin magmatic massif where we discovered pavlovskyite. In addition, E.V. Pavlovsky was one of the founders of the Irkutsk Scientific Centre of the Siberian branch of the Russian Academy of Science.

Pavlovskyite, an ortho-trisilicate  $Ca_8(SiO_4)_2(Si_3O_{10})$ , was almost simultaneously discovered at two Russian localities, at the Birkhin massif, Olkhon area, Baikal Lake (holotype material), and in the Upper Chegem caldera, Northern Caucasus, Kabardino-Balkaria (co-type material). In both cases, pavlovskyite occurs in altered silicate-carbonate xenoliths (skarns) included in igneous rocks.

The holotype sample of pavlovskyite (Birkhin) and a co-type specimen (Lakargi) are deposited in the collections of the Fersman Mineralogical Museum of the Russian Academy of Science, catalog numbers 4023/1 and 4024/1, respectively.

## **O**CCURRENCE

Pavlovskyite was detected in small (a few meters in diameter), altered silicate-carbonate xenoliths within the Birkhin gabbro massif (52.7°N 106.5°E). The Birkhin gabbroid massif (~500 Ma) is situated in the territory of Eastern Siberia within the Olkhon region, which includes the west coast of the Baikal Lake and Olkhon Island. The region is interpreted to be a portion of a collision system that was active in the Early Paleozoic. During this activity, several terranes accreted along the margins of the Siberian Craton (Donskaya et al. 2000). The structure of the Olkhon region is considered to be a stack of shear slabs composed of metamorphic and magmatic rocks (Fedorovsky et al. 2010; Fedorovsky and Sklyarov 2010).

Geological characterization, including a geological sketch of the area, is summarized by Lazic et al. (2011). They also introduce the new mineral galuskinite  $Ca_7(SiO_4)_3CO_3$ , which is associated with pavlovskyite. Skarns of the Birkhin gabbroid massif are famous for very large kilchoanite aggregates (Savelyeva et al. 1992).

Pavlovskyite forms in symmetric veins cutting calcio-olivine (larnite) skarn (Fig. 1a). The central part of these veins is composed of galuskinite and its low-temperature alteration products. Selvages consist of sub-parallel aggregates of fibrous pavlov-skyite crystals (up to 0.3–0.4 mm in length, 10–30 µm thick) nucleating at the vein walls and dellaite, filling space between pavlovskyite crystals and separating it from calcio-olivine (Figs. 1a–1c). Occasionally, galuskinite veins are partially replaced by spurite (or vice versa), and have a margin composed of



FIGURE 1. Birkhin massif: (a) Backscattered electron (BSE) image of a galuskinite vein cutting calcio-olivine skarn with symmetric selvages composed of aggregates of pavlovskyite and dellaite. (b and c) Microscopic image [(b) plane-polarized light, (c) crossed polarizers] of sub-parallel aggregates of elongate pavlovskyite crystals between galuskinite and calcio-olivine (after larnite). Dellaite occurs between pavlovskyite crystals and on boundary with calcio-olivine. (d) BSE image of pavlovskyite spherolites; the central part of the galuskinite vein is replaced by spurrite. (e) BSE image of a xenomorphic grain of pavlovskyite in calcio-olivine skarn. (f) BSE image of pavlovskyite, ca-ol = calico-olivine, Del = dellaite, Gal = galuskinite, Bgh = baghdadite, Prv = perovskite, Spu = spurrite, Ves = vesuvianite, Cln = clintonite, Klch = kilchoanite, Mnt = monticellite.

pavlovskyite spherolites growing into calcio-olivine (Fig. 1d). Rare amoeba-like, highly-fractured grains of pavlovskyite up to 1–2 mm in size occur in calcio-olivine (Fig. 1e). The following minerals are noted in Birkhin skarns: calcio-olivine, galuskinite, larnite, bredigite, merwinite, monticellite, spurrite, kilchoanite, dellaite, cuspidine, hydroxylellestadite, spinel, magnetite, members of the gehlenite-åkermanite series, garnet of the grossular-andradite-schorlomite-kerimasite series, baghdadite, chlorbartonite, pyrrhotite, clintonite, fluor- and hydroxylapatite, hillebrandite, perovskite, wollastonite, and vesuvianite.

The development of retrograde monticellite-dellaite symplectites is characteristic of mervinite-gehlenite high-temperature skarns at Birkhin (Armbruster et al. 2011). In retrograde kilchoanite skarns containing mervinite and gehlenite, pavlovskyite



**FIGURE 2.** Upper Chegem caldera: (**a** and **b**) BSE images of aggregates of pavlovskyite in cuspidine skarn. (**c**) BSE image of pavlovskyitehillebrandite aggregate (after rankinite) in a rusinovite zone of skarn. (**d**–**f**) Quartz grain on the boundary between ignimbrite and skarn, the grain is partially replaced by pavlovskyite, rankinite, wollastonite, and hillebrandite aggregates. (**d**) BSE, (**e**) plane-polarized light, (**f**) crossed polarizers. Pav = pavlovskyite, Rus = rusinovite, Ran = rankinite, Wol = wollastonite, Cus = cuspidine, Wad = wadalite, Hil = hillebrandite, Q = quartz, Ap = fluorapatite, Hgr = hydrogrossular.

and monticellite symplectites formed (Fig. 1f). Subsequently, pavlovskyite was replaced by dellaite.

Pavlovskyite was also discovered in the altered carbonate xenolith number 3 [numbering after Gazeev et al. (2006) and Galuskin et al. (2009)], which is confined to the Upper Chegem caldera situated at the junction of the Chegem and Kenstanty (right branch of the Baksan River) Rivers, Kabardino-Balkaria, North Caucasus, Russia (Gazeev et al. 2006; Galuskin et al. 2008). The high-temperature rocks in which pavlovskyite was found are skarned carbonate xenoliths located close to the divide on a small ridge between the Lakargi and Vorlan mountain peaks (coordinates 43°17'N 43°6'E). This is the type locality of lakargiite CaZrO<sub>3</sub>, megawite CaSnO<sub>3</sub>, chegemite Ca<sub>7</sub>(SiO<sub>4</sub>)<sub>3</sub>(OH)<sub>2</sub>, kumtyubeite  $Ca_5(SiO_4)_2(OH)_2$ , calcio-olivine  $\gamma$ -Ca<sub>2</sub>SiO<sub>4</sub>, vorlanite CaUO<sub>4</sub>, toturite Ca<sub>3</sub>Sn<sub>2</sub>SiFe<sub>2</sub>O<sub>12</sub>, irinarassite Ca<sub>3</sub>Sn<sub>2</sub>SiAl<sub>2</sub>O<sub>12</sub>, bitikleite-(ZrFe) Ca<sub>3</sub>ZrSbFe<sub>3</sub>O<sub>12</sub>, bitikleite-(SnAl) Ca<sub>3</sub>SnSbAl<sub>3</sub>O<sub>12</sub>, bitikleite-(SnFe) Ca<sub>3</sub>SnSbFe<sub>3</sub>O<sub>12</sub>, elbrusite-(Zr) Ca<sub>3</sub>UZrFe<sub>3</sub>O<sub>12</sub>, magnesioneptunite KNa<sub>2</sub>LiMg<sub>2</sub>Ti<sub>2</sub>Si<sub>8</sub>O<sub>24</sub>, and rusinovite Ca10(Si2O7)3Cl2.

Pavlovskyite was detected as irregular grains in their characteristic skeletal form within cuspidine zones of the skarn with larnite relics (Figs. 2a–2b). Larnite zones, replaced by cuspidine, toward the contact with slightly altered ignimbrite are transformed to rankinite-wollastonite zones. In these zones pavlovskyite develops on rankinite (+wollastonite) pseudomorphs after quartz phenocrysts of the ignimbrite. This is especially evident for grains of partially replaced quartz on the boundary "skarn-ignimbrite" (Figs. 2d–2f). Here, pavlovskyite is associated with the recently described new mineral rusinovite  $Ca_{10}(Si_2O_7)_3Cl_2$  (Figs. 2c–2d), which also develops after rankinite (Galuskin et al. 2011).

Early high-temperature minerals such as larnite, rankinite, wollastonite, wadalite, rondorfite, kerimasite, tazheranite, baddeleyite, lakargiite, perovskite, apatite, and magnesioferrite are preserved in association with pavlovskyite in Caucasian skarns. Secondary minerals include trabzonite, killalaite, hydrogarnet, hillebrandite, afwillite, tobermorite-like minerals, jennite, taumasite-ettringite, hydrocalumite, and other undetermined Ca-hydrosilicates.

Pavlovskyite from both localities has the same composition and physical properties. The mineral is colorless in thin section. In hand specimens it is white with white streak. The mineral is transparent with vitreous luster. It does not show fluorescence in UV light (250–350 nm); hardness (Mohs) = 6–6.5; VHN load 20 g, mean (3) = 520 kg/mm<sup>2</sup>. Pavlovskyite is brittle with uneven cleavage on (001), irregular fracture. The mineral is biaxial (–),  $\alpha = 1.656(2)$ ,  $\beta = 1.658(2)$ ,  $\gamma = 1.660(2)$  (589 nm), 2V (meas) = 80(5)°, 2V (calc) = 89.9°, medium dispersion: r > v, optical orientation: X = b, Y = c, Z = a (a, b, c according to *Pbcn* setting). Density (meas) = 2.97(2) g/cm<sup>3</sup> was determined by the sink and float method in heavy liquids, density (calc) = 2.998 g/cm<sup>3</sup> (Birkhin; Table 1, analysis 1); 2.996 g/cm<sup>3</sup> (Birkhin, Table 1,

TABLE 2. Crystal data for pavlovskyite and kilochoanite

Crystal data	Pavlovskyite	Kilchoanite
Unit-cell dimensions (Å)	a = 5.08510(10)	a = 11.4525(2)
	b = 11.4165(3)	b = 5.08670(10)
	c = 28.6408(8)	c = 21.9963(3)
Space group	<i>Pbcn</i> (no. 60)	/2cm (no. 46)
Volume (ų)	1662.71(7)	1281.40(4)
Z	4	4
Chemical formula	$Ca_8(SiO_4)_2(Si_3O_{10})$	$Ca_6(SiO_4)(Si_3O_{10})$
μ (mm-1)	2.996	2.945
Intensity	measurement	
Crystal shape	prism	prism
Crystal size (mm)	$0.05 \times 0.04 \times 0.02$	$0.15 \times 0.05 \times 0.05$
Diffractometer	APEX II SMART	APEX II SMART
X-ray radiation	ΜοΚα	ΜοΚα
X-ray power	50 kV, 30 mA	50 kV, 30 mA
Monochromator	Graphite	Graphite
Iemperature	293 K	293 K
Detector to sample distance	5.95 cm	5.95 cm
Measurement method	$\phi$ and $\omega$ scans	$\phi$ and $\omega$ scans
Radiation width	0.5°	0.5°
Total number of frames	2056	2589
Time per frame	30 s	30 s
Max. θ-range for data collection	30.5°	40.24°
Index ranges	$-6 \le h \le 7$	$-20 \le h \le 20$
	$-16 \le k \le 16$	$-9 \le k \le 9$
	-34 ≤ / ≤ 40	-39 ≤ / ≤ 37
No. of measured reflections	14962	18573
No. of unique reflections	2543	4083
No. of observed reflections $[l > 2\sigma (l)]$	)] 1685	3757
Refinemen	t of the structure	
NO. OF parameters	140	110
used in refinement	143	Πδ 0.0221
K <sub>int</sub>	0.0098	0.0331
	0.0741	0.0259
KI, I > 20(I)	0.0387	0.0200
$\pi$ I dil udid	0.0099	0.0233
	0.1012	0.047
$\Delta_{0} \min(\alpha \Lambda^{-3})$	1.021	1.USZ
$\Delta \rho \min(-e A^{-})$	-0.02 Close to O5	-0.394 Close (0 U2
Δp max (e·A -)	0.57 Close to 03	0.455 close to U5

**TABLE 1.** Chemical composition of pavlovskyite and kilchoanite from Russia

	1			2			3			4
	wt%	s.d.	range	wt%	s.d.	range	wt%	s.d.	range	
SiO <sub>2</sub>	39.62	0.17	39.34–39.99	39.97	0.20	39.69-40.37	40.02	0.19	39.67-40.02	41.80
TiO <sub>2</sub>	n.d.			n.d.			0.04	0.04	0-0.13	n.d.
MgŌ	0.05	0.02	0.03-0.09	0.05	0.03	0.02-0.09	0.01	0.01	0-0.04	n.d.
CaO	59.22	0.65	58.13-60.03	59.31	0.35	58.70-60.00	60.26	0.18	60.03-60.53	57.93
MnO	0.08	0.06	0-0.18	0.04	0.04	0-0.12	0.02	0.03	0-0.08	n.d.
FeO	0.18	0.06	0.06-0.27	0.36	0.09	0.18-0.50	0.07	0.07	0-0.20	n.d.
Total	99.15			99.73			100.42			99.73
Ca	7.988			7.949			8.029			5.976
Mn <sup>2+</sup>	0.009			0.004			0.002			
Mg	0.009			0.009			0.002			
Fe <sup>2+</sup>	0.019			0.038			0.007			
Si	4.988			5.000			4.976			4.024
Ti⁴+							0.004			

Notes: 1 = Pavlovskyite from symmetrical veins with galuskinite and dellaite in calico-olivine skarn, Birkhin (mean of 23, Figs. 1a–1c); 2 = irregular pavlovskyite grains in calico-olivine, Birkhin (mean of 16, Fig. 1); 3 = pavlovskyite from Lakargi skarns (mean of 19, Figs. 2a–2b); 4 = kilchoanite from Birkhin (mean of 5).

analysis 2); 2.997 g/cm<sup>3</sup> (Lakargi, Table 1, analysis 3). Admixtures of calcio-olivine, dellaite, and kilchoanite have only minor bearing on the experimental density determination, because the latter minerals have densities (2.97–2.99 g/cm<sup>3</sup>) very similar to pavlovskyite. The following Gladstone-Dale relationships were calculated  $[1 - (K_p/K_c)] = -0.049$  (good, Birkhin; Table 1, analysis 1), -0.050 (good, Birkhin; Table 1, analysis 2), -0.049 (good, Lakargi; Table 1, analysis 3).

#### **ANALYTICAL METHODS**

The morphology and composition of pavlovskyite and associated minerals were investigated using a Philips/FEI ESEM XL30/EDAX scanning electron microscope (Faculty of Earth Sciences, University of Silesia) and a CAMECA SX100 (WDS mode, 15 kV, 10–20 nA, 1–3 µm beam diameter, Institute of Geochemistry, Mineralogy and Petrology, University of Warsaw). The following lines and standards were used for pavlovskyite analyses: CaK $\alpha$ , SiK $\alpha$  = wollastonite; MgK $\alpha$  = diopside; MnK $\alpha$  = rhodonite; TiK $\alpha$  = rutile; and FeK $\alpha$  = hematite. Results are presented in Table 1.

Single-crystal X-ray studies on pavlovskyite were carried out using a Bruker APEX II SMART diffractometer (MoK $\alpha$ ,  $\lambda = 0.71073$  Å) and gave the following data (orthorhombic, space group: *Pbcn*, *Z* = 4): Birkhin *a* = 5.0851(1), *b* = 11.4165(3), *c* = 28.6408(8) Å, *V* = 1662.71(7) Å<sup>3</sup> (holotype); Lakargi *a* = 5.0839(1), *b* = 11.4195(3), *c* = 28.6338(8) Å, *V* = 1662.35(7) Å<sup>3</sup> (co-type). Experimental details of the best crystal are summarized in Table 2. The best crystal of the holotype material (Birkhin) was only 0.05 mm in maximum dimension and showed

minor admixtures of calcio-olivine and dellaite. Thus, the diffraction pattern of the major fragment has been manually separated from the admixtures. All studied crystals of co-type material (Upper Chegem Caldera) represented an oriented intergrowth of pavlovskyite and kilchoanite with superposition along **a** and **b** and distinct only by the periodicity along **c**. Thus, only cell dimensions are reported for the co-type material.

The structure refinement of end-member  $Ca_6(SiO_4)(Si_3O_{10})$  kilchoanite (Taylor 1971) is of mediocre quality, including isotropic displacement parameters. As a result, we decided to re-collect a single-crystal X-ray data set of kilchoanite from the Birkhin deposit using the same experimental procedure as for pavlovskyite. For kilchoanite, atom labeling and space group *I2cm* (no. 46) setting was chosen according to Taylor (1971).

Diffraction data were collected with  $\omega$  scans at different  $\varphi$  settings ( $\varphi$ - $\omega$  scan) (Bruker 1999). Data were processed using SAINT (Bruker 1999). An empirical absorption correction using SADABS (Sheldrick 1996) was applied. For pavlovskyite, the systematic absences were consistent with the space group *Pbcn* (no. 60). The structure was solved by direct methods with subsequent analyses of difference-Fourier maps. The pavlovskyite and kilchoanite structures were refined to  $R_1 =$ 3.87 and 2.00%, respectively, using neutral atom scattering factors and the program SHELX97 (Sheldrick 2008). All sites were refined with anisotropic displacement parameters. As the space group *I2cm* of kilchoanite is non-centrosymmetric, we refined inversion twinning converging to twin contributions of 79(2) and 21(2)%. For direct comparison with synthetic Ca<sub>6</sub>(GeO<sub>4</sub>)(Ge<sub>3</sub>O<sub>10</sub>), the pavlovskyite structure was refined in space group *Pbcn* (no. 60) and all atom labels and sites are chosen according to Redhammer et al. (2006). Thus for better comparison of pavlovskyite with kilchoanite **a** and **b** must be interchanged, corresponding to the space-group setting *Pcan* (Table 3). Atomic coordinates and anisotropic displacement parameters of the parameters and anisotropic displacement parameters.

TABLE 3. Cell dimensions (Å) and refractive indices of olivine, pavlovskyite, and kilchoanite structure types in a setting with common orientation of the **a** and **b** axes

Structure type, setting	CaO-SiO <sub>2</sub>	CaO-GeO <sub>2</sub>				
calcio-olivine	$a = 11.21128(14) \parallel \alpha 1.633(3) - 1.642(2)$	a = 11.3919(7)				
Pnam	$b = 5.07389(7)    \gamma 1.645(3) - 1.657(3)$	b = 5.2424(3)				
	$c = 6.75340(9) \parallel \beta 1.640(3) - 1.653(2)$	<i>c</i> = 6.77800(4)				
	Cell dimensions and upper refractive indices (Zadov et al. 2008),	Redhammer et al. (2008)				
	lower refractive indices (Bridge 1966).					
Pavlovskyite	<i>a</i> = 11.4165(3)    α 1.656(2)	a = 11.6079(5)				
Pcan	$b = 5.0851(1) \parallel \gamma 1.660(2)$	b = 5.2436(2)				
	$c = 28.6408(8) \parallel \beta 1.658(2)$	<i>c</i> = 28.9238(11)				
	This study	Redhammer et al. (2006)				
Kilchoanite	<i>a</i> = 11.4525(2)    ? α 1.647(2)					
l2cm	$b = 5.0867(1)   ? \gamma 1.650(2)$					
	$c = 21.9963(3)   ? \beta 1.649(2)$					
	Cell dimensions (this study)					
	Refractive indices (Agrell and Gay 1961)					
	optical orientation (?) in analogy to pavlovskyite					
	synthetic Ca <sub>4.66</sub> Mn <sub>1.33</sub> (SiO <sub>4</sub> )(Si <sub>3</sub> O <sub>11</sub> ) (Kimata 1989)					
	<i>a</i> = 11.356(2)					
	b = 5.007(1)					
	c = 21.817(1)					

Note: Questionable optic orientations are indicated by "?".

**TABLE 4.** Atomic coordinates and isotropic equivalent displacement parameters (*U*<sub>en</sub>) for pavlovskyite, *Pbcn* setting

**TABLE 6.** Atomic coordinates and isotropic equivalent displacement parameters  $(U_{co})$  for kilchoanite

	parameters ( $U_{eq}$ ) for pavlovskylte, <i>Pbcn</i> setting				parameters ( $U_{eq}$ ) for kilchoanite				
Atom	х	у	Z	$U_{\rm eq}$	Atom	х	у	Z	$U_{\rm eq}$
Si1	0.57130(16)	0.40471(8)	0.44237(3)	0.01033(17)	Ca1	0.01150(3)	0	0	0.00918(5)
Si2	0.44100(16)	0.59487(8)	0.32685(3)	0.01072(18)	Ca2	0.31064(3)	0.99909(6)	0.25	0.00740(5)
Si3	0.5	0.76288(10)	0.25	0.0104(2)	Ca3	0.03527(2)	0.00353(4)	0.168222(10)	0.00937(4)
Ca1	0.49692(12)	0.71708(5)	0.44226(2)	0.01152(13)	Ca4	0.241867(19)	0.49751(4)	0.104083(10)	0.00734(4)
Ca2	0	0.5	0.5	0.01216(18)	Si1	0.12152(4)	0.42774(8)	0.25	0.00589(7)
Ca3	0.99397(13)	0.48889(6)	0.37768(2)	0.01380(14)	Si2	0.43213(3)	0.94159(6)	0.100328(14)	0.00624(5)
Ca4	0.50366(12)	0.28416(5)	0.33030(2)	0.01147(14)	Si3	0.26486(4)	0	0	0.00626(7)
Ca5	0	0.51645(8)	0.25	0.01329(18)	01	0.18816(8)	0.29836(15)	0.19132(4)	0.00859(13)
01	0.7049(4)	0.53615(19)	0.44034(8)	0.0129(4)	O2	0.99064(11)	0.2935(2)	0.25	0.00872(19)
02	0.7027(4)	0.3358(2)	0.39786(8)	0.0138(5)	O3	0.12178(13)	0.7475(2)	0.25	0.00947(19)
O3	0.7018(4)	0.34189(19)	0.48832(8)	0.0129(5)	O4	0.36993(8)	0.80255(16)	0.15865(4)	0.00880(13)
04	0.2523(4)	0.4051(2)	0.44082(8)	0.0124(4)	O5	0.05900(8)	0.69266(17)	0.09191(4)	0.00949(14)
O5	0.3015(4)	0.6569(2)	0.37139(8)	0.0141(5)	06	0.35498(8)	0.81255(16)	0.04103(4)	0.00821(12)
06	0.3092(4)	0.4676(2)	0.32021(9)	0.0142(5)	07	0.42751(9)	0.25721(16)	0.09613(4)	0.00901(13)
07	0.3118(4)	0.67239(19)	0.28132(8)	0.0123(5)	08	0.18431(8)	0.17820(17)	0.04188(4)	0.01153(14)
08	0.7570(4)	0.5992(2)	0.32323(8)	0.0129(5)					
09	0.6745(4)	0.8431(2)	0.28283(9)	0.0168(5)					

eters for pavlovskyite and kilchoanite are given in Tables 4–7 (Tables 5 and 7<sup>1</sup> as supplementary data), respectively. Corresponding interatomic distances are listed in Tables 8 and 9 (supplementary data<sup>1</sup>). Due to the small size ( $0.05 \times 0.04 \times 0.02 \text{ mm}^3$ ) of the "best" pavlovskyite crystal (used for structure refinement), which was additionally contaminated by admixtures of calcio-olivine and dellaite, the idea of collecting powder X-ray diffraction data had to be discarded. Instead, the X-ray powder pattern (Table 10, for CuK $\alpha$  1.540598 Å, supplementary data<sup>1</sup>) was calculated from crystal-structure data using the program LAZY PULVERIX (Yvon et al. 1977). This calculated powder-diffraction pattern corresponds to the measured diffraction pattern of synthetic analog of pavlovskyite Ca<sub>8</sub>(SiO<sub>4</sub>)<sub>2</sub>(Si<sub>3</sub>O<sub>10</sub>) (JCPDS 29-0368) and is different from the one of kilchoanite [JCPDS 00-029-0370, strong lines 2.880(100) – 2.669(70) – 3.050(60) – 3.550(50) – 1.965(35)].

Raman spectra of crystals of pavlovskyite and kilchoanite were recorded using a Dilor XY spectrometer equipped with a 1800 line mm<sup>-1</sup> grating monochromator, a charge-coupled device (CCD), Peltier-cooled detector ( $1024 \times 256$ ), and an Olympus BX40 confocal microscope (Bayerisches Geoinstitute, University of Bayreuth, Germany). The incident laser excitation was provided by a water-cooled argon laser-source operating at 514.5 nm. The power at the exit of a  $100 \times$  objective lens varied from 30 to 50 mW. Raman spectra were recorded in backscatter geometry in the range 100-4000 cm<sup>-1</sup> with resolution of 2 cm<sup>-1</sup>. Collection times of 20 s and an accumulation of 5 scans were chosen. The monochromator was calibrated using the Raman scattering line of a silicon plate (520.7 cm<sup>-1</sup>).

Vibrational spectra of both phases were calculated in the harmonic approximation at the  $\Gamma$ -point (Pascale et al. 2004) from fully relaxed energy optimizations of the crystal structures presented herein, using 3D-periodic density functional theory with Gaussian basis sets and the software CRYSTAL 09 (Dovesi et al. 2009). Calculations followed previously tested procedures (Többens and Kahlenberg 2011), using for the Hamiltonian a variation of the PBE0 hybrid functional (Adamo and Baronea 1999) with 1/6 Hartree-Fock contribution, a Pack-Monkhorst k net with  $4 \times 4 \times 4$  points in the Brillouin zone, and the following atomic basis sets: for calcium a 86-511G(21) contraction based on the 86-511G(3) contraction given by Catti et al. (1991), for silicon a 86-311G(1) contraction (Pascale et al. 2005), for oxygen a 8-411G(1) contraction based on the 8-411G contraction given by Towler et al. (1994). For all basis sets the exponents of the two most diffuse sp shells and of the most diffuse d shell have been optimized to the following values: sp(Ca) = 0.463, 0.279; d(Ca) = 0.343; sp(Si) = 0.333, 0.13; d(Si) = 0.682, 0.22; sp(O) =0.460, 0.170; d(O) = 0.556. The lattice parameters of the fully relaxed structure were in very good agreement with the experimental values, with the calculated values  $0.6 \pm 0.1\%$  too large; for the unit-cell volume the deviation was 1.8%. The agreement of the calculated Raman frequencies with the observed ones was very good, with maximum deviations of ±12 cm<sup>-1</sup>. Tables of the observed and calculated frequencies and modes symmetries are given in the supporting information (Tables 11, 12, supplementary data1). Animations of all modes for the energy-optimized structures can be viewed using web-based software (Noel 2008; Canepa 2011) using the CRYSTAL output files, also provided as supplementary material.

#### STRUCTURE

In general, our investigations confirmed the correctness of the structure model proposed by Taylor (1971). Structures of pavlovskyite and kilchoanite differ by means of an additional module of  $Ca_2(SiO_4)$  composition intercalated into the pavlovskyite structure (Fig. 3). The structure of pavlovskyite is best described as 1:1 polysome with kilchoanite and calcio-olivine ( $\gamma$ -Ca<sub>2</sub>SiO<sub>4</sub>) as end-members of the series. The modular structure of pavlovskyite and kilchoanite may also be described by following units:  $2 \times Ca_2(SiO_4)$  and  $Ca_4(Si_3O_{10})$ ; and  $Ca_2(SiO_4)$  and  $Ca_4(Si_3O_{10})$ , respectively (Figs. 3 and 4).

The unit-cell dimensions of pavlovskyite in *Pcan* setting along **a** and **b** (Table 3) correspond to the related phases calcioolivine and kilchoanite. The structure is built by infinite bands



**FIGURE 3.** The structures of (**a**) pavlovskyite (*Pcan*), (**b**) kilchoanite (*I2cm*), and (**c**) calcio-olivine (*Pnam*) have two axes of the same dimension while the **c** axis varies. All of them show layer-like stacking along the 5 Å axis with a shift of ½ along the 11 Å axis. The view along the 5 Å axis shows that kilchoanite and pavlovskyite can be described as modules of Ca<sub>2</sub>SiO<sub>4</sub> (calcio-olivine) in yellow and Ca<sub>4</sub>Si<sub>3</sub>O<sub>10</sub> modules in brown. The modules are connected by the Ca3-octahedra, belonging to both modules. One unit cell of kilchoanite consists of  $2 \times Ca_2SiO_4$  and  $2 \times Ca_4Si_3O_{10}$  while the unit cell of pavlovskyite is formed by  $4 \times Ca_2SiO_4$  and  $2 \times Ca_4Si_3O_{10}$ .



**FIGURE 4.** Structural drawing of pavlovskyite in space-group setting *Pcan* with SiO<sub>4</sub> tetrahedra in red and CaO<sub>6</sub> polyhedra in yellow, illustrating the ABAB... layer-stacking sequence along the **b** axis. The A-layer is drawn with solid polyhedra and is above the translucent, gray glide plane. The glide plane transforms the A-layer into the B-layer by the operation (x + 1/2, -y + 1/2, z). The B-layer, situated below the glide plane, is drawn with striped polyhedra.

of Ca polyhedra along **c** connected by isolated SiO<sub>4</sub> tetrahedra and units of Si<sub>3</sub>O<sub>10</sub>. The Ca- and Si- polyhedra build up layers parallel to (010). These layers of edge and corner shearing polyhedra are stacked along **b** in an ABAB... sequence (Fig. 4). The structure contains three symmetrically independent Si sites. The Sil tetrahedron belonging to the calcio-olivine module is the most regular one in terms of Si-O distances (Table 5). Oxygen atoms of all SilO<sub>4</sub> apices are four-coordinate by additional three Ca

<sup>&</sup>lt;sup>1</sup> Deposit item AM-12-016, CIFs, Tables 5, 7–12. Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at http://www.minsocam.org, go to the *American Mineralogist* Contents, find the table of contents for the specific volume/ issue wanted, and then click on the deposit link there.

sites. In projections along b (Pcan setting), the triangular base of the Si1 tetrahedron is built by O1, O2, and O3. This triangle fits in the cavity formed by the edge-sharing octahedra around Ca1, Ca2, and Ca3. The apex (O4) of the Si1 tetrahedron binds to the triple-point where three calcium octahedra meet. The Si1-O4 bond-length is the shortest, thus the O-Si1-O4 angles are slightly too wide compared to the ideal tetrahedral angle, whereas the angles at the triangular base are slightly too acute. Si2 and Si3 form the Si<sub>3</sub>O<sub>10</sub> entities with Si3 in the center and Si2 at both flanks. Si2 and Si2' share O7 and O7' with Si3. The Si2-O7-Si3 angle is 120.70(13)° and is thus identical to the corresponding Si2-O6-Si3 angle of 120.89(5)° in kilchoanite. Kilchoanite and pavlovskyite have also in common that the corresponding Si2-O6 (kilchoanite) and Si2-O7 (pavlovskyite) distances are long [1.7067(9) and 1.707(2) Å, respectively]. The reason is that the oxygen sites linking two tetrahedra bond additionally to two Ca sites thus the Si-O bonds are rather weak. The same argument also holds for the lengthened Si3-O6 (kilchoanite) and Si3-O7 (pavlovskyite) distances. The shortest Si-O distances (ca. 1.58 Å) in both structures are found for Si3-O8 (kilchoanite) and Si3-O9 (pavlovskyite) because corresponding oxygen sites are only three-coordinated and bond to two additional CaO<sub>6</sub> octahedra.

In pavlovskyite, the calcium sites Ca1–Ca4 are sixfold coordinated and form distorted octahedra with mean bond-lengths between 2.36 Å (Ca5) and 2.40 Å (Ca2). Ca5 is eightfold coordinated and shows a mean bond-length of ca. 2.5 Å. In kilchoanite, the corresponding eightfold-coordinated Ca site is labeled Ca1.

### **RAMAN SPECTROSCOPY STUDY**

Infrared spectra of kilchoanite and synthetic  $Ca_8(SiO_4)_2(Si_3O_{10})$  (pavlovskyite analog) are essentially identical (Speakman et al. 1967), whereas Raman spectra of pavlovskyite and kilchoanite are differentiated by the position of the main bands (Fig. 5). Interpretation of the observed bands was done based on ab initio calculations of the vibrational spectra.

Symmetry-representation analysis gives the species of the modes for kilchoanite as  $\Gamma = 37A_1 + 33 A_2 + 35 B_1 + 39 B_2$ . One mode  $A_1$ ,  $B_1$ ,  $B_2$  each is an acoustic mode, all 141 optical modes are Raman active, and only the  $A_2$  modes are IR inactive. The presence of double-active modes could give rise to LO-TO splitting in the Raman spectrum, which however was neither calculated nor observed. For pavlovskyite, the species of the modes are  $\Gamma = 44A_g + 47 A_u + 46 B_{1g} + 49 B_{1u} + 46 B_{2g} + 49 B_{2u} + 44 B_{3g} + 47 B_{3u}$ . One  $B_{1u}$ ,  $B_{2u}$ ,  $B_{1u}$  mode each is acoustic. All 180 g-modes are Raman active, all optical  $B_u$ -modes are IR-active, and the  $A_u$  modes are silent.

In both compounds the bands in the region  $0-450 \text{ cm}^{-1}$  are Ca-O modes, while all bands above  $450 \text{ cm}^{-1}$  are dominated by Si-O displacements. The density of theoretically possible modes is too high to allow for an unequivocal assignment. The most distinctive difference between the Raman spectra of the compounds is the three medium-strong bands kilchoanite has in the region above 950 cm<sup>-1</sup>. In contrast, pavlovskyite has only one strong band in this region (Fig. 5). In both minerals all modes in this region are *s*(Si-O) stretching modes of terminal oxygen atoms of the trimeric group. Whether they belong to the terminal or the central tetrahedron of the trimeric group is not clear. Both compounds are very similar in the strong bands (Fig. 5) at 858,



**FIGURE 5.** Raman spectra of pavlovskyite (1 = Birkhin, 2 = Lakargi) and kilchoanite (3 = Birkhin).

847, and 821 cm<sup>-1</sup> (pavlovskyite), respectively 871, 864, and 828 cm<sup>-1</sup> (kilchoanite). The modes contributing to these bands are *s*(Si-O) stretching modes of the isolated tetrahedra and/or terminal O atoms of the terminal tetrahedra of the trimers. The isolated band at  $670 \pm 1$  cm<sup>-1</sup> in both compounds is a *s*(Si-O-Si) mode (Fig. 5). The three silicon atoms in the trimeric group all move outward simultaneously, so that both Si-O bonds of the bridging oxygen are stretched. While there is some *b*(O-Si-O) bending, the stretching dominates the deformations. At 709 cm<sup>-1</sup> both structures have theoretical modes, properly described as *s*(Si-O) stretching and *b*(O-Si-O) and *b*(Si-O-Si) bending, with all movements involving the bridging oxygen. The stretching of the two Si-O bonds is in counter-tact, and the bending motions are dominant. These modes belong to very weak bands at the detection limit.

It is interesting to compare this pattern with the corresponding bands in the Raman spectrum of  $\alpha$ -Y<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> (Kaindl et al. 2010), which also contains trimers and isolated SiO<sub>4</sub> tetrahedra. There, the strong band is at higher frequencies, at 728 cm<sup>-1</sup>, a *b*(Si-O-Si) bending mode, and the weak band at 685 cm<sup>-1</sup> is a *s*(Si-O) stretching mode. However, again the strong band results from vibrational modes in which the two Si-O bonds of the bridging oxygen stretch simultaneously, while in the modes of the weak band they are in counter-tact. It is thus the simultaneous stretching of the bridging Si-O bonds that gives rise to strong Raman bands. The position is defined by the geometry of the trimer. In the structures described here it is bent, and the movements of the atoms result in stretching modes and corresponding high frequencies. In  $\alpha$ -Y<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>, the trimers are stretched, giving the strong band a bending character with the corresponding lower frequencies.

### DISCUSSION

Pavlovskyite is a product of the interaction of hydrothermal fluids enriched in SiO<sub>2</sub> with calcio-olivine (or larnite) metasomatic rocks. As an example, in synthetic runs (Speakman et al. 1967) calcio-olivine reacted with SiO<sub>2</sub> (either quartz or amorphous silica) at 180 °C and 10 bars to form pavlovskyite. At 250 °C and 40 bars, additional SiO<sub>2</sub> reacts to replace pavlovskyite by kilchoanite (Speakman et al. 1967):  $3 \operatorname{Ca}_8(\operatorname{SiO}_4)_2(\operatorname{Si}_3O_{10}) + \operatorname{SiO}_2$  $\rightarrow$  4 Ca<sub>6</sub>(SiO<sub>4</sub>)(Si<sub>3</sub>O<sub>10</sub>). Kilchoanite (Agrell 1965; Speakman et al. 1967) is believed to be stable at pressures of few hundred bars over a narrow temperature range at 600 °C. According to Agrell (1965), between 500 and 550 °C, dellaite and wollastonite are possibly the stable solid phases. For saturated steam pressures and the addition of SiO<sub>2</sub>, kilchoanite may be stable at 180-350 °C. Both synthetic analogs of kilchoanite (Ca:Si = 1.5:1) and pavlovskyite (Ca:Si = 1.6:1) are formed as a result of a reaction of γ-Ca<sub>2</sub>SiO<sub>4</sub> with SiO<sub>2</sub>-bearing solutions (Bennett et al. 1966; Speakman et al. 1967).

Pavlovskyite (Ca:Si = 1.6:1) is easily distinguished by its composition from kilchoanite (Ca:Si = 1.5:1). Optical properties of pavlovskyite and kilchoanite are similar, but pavlovskyite has a larger 2V and does not show anomalous interference colors. In addition, X-ray diffraction methods and positions of main bands observed in Raman spectra (Fig. 5) enable distinction between pavlovskyite and kilchoanite.

# STRUCTURAL RELATIONS BETWEEN PAVLOVSKYITE, KILCHOANITE, AND CALCIO-OLIVINE

Taylor (1971) showed that there are olivine-like slices intercalated in the structure of kilchoanite  $Ca_6(SiO_4)(Si_3O_{10})$ and pavlovskyite  $Ca_8(SiO_4)_2(Si_3O_{10})$ . This raises the question of whether an independent  $M_4^{2+}(Si_3O_{10})$  structure exists, which has similarity with the corresponding module in kilchoanite. In the review of trisilicate structures (Wierzbicka-Wieczorek et al. 2010), there is only kinoite  $Cu_2Ca_2(Si_3O_{10}) \cdot (H_2O)_2$  with fivefold-coordinated  $Cu^{2+}$  (Laughorn 1971) and a germanate  $Ca_4(Ge_3O_{10}) \cdot H_2O$  (Nevskii et al. 1978), which may possibly qualify as representing the kilchoanite-like  $M_4^{2+}(Si_3O_{10})$  module. However, both hydrous structures are strongly different to the atomic arrangement in the  $M_4^{2+}(Si_3O_{10})$  module of kilchoanite. Thus, this module in kilchoanite and pavlovskyite appears to be stabilized by the olivine-like slices acting as pillars.

Interestingly, in the CaO-GeO<sub>2</sub> phase diagram (Shirvinskaya et al. 1966) there is no kilchoanite analog of Ca<sub>6</sub>(GeO<sub>4</sub>) (Ge<sub>3</sub>O<sub>10</sub>) composition, however a pavlovskyite-like analog Ca<sub>8</sub>(GeO<sub>4</sub>)<sub>2</sub>(Ge<sub>3</sub>O<sub>10</sub>), although Cu doped, has been synthesized (Redhammer et al. 2006). Thus in the related CaO-GeO<sub>2</sub> system, only the olivine-type structure of  $\gamma$ -Ca<sub>2</sub>(GeO<sub>4</sub>) and the 1:1 polysome Ca<sub>8</sub>(GeO<sub>4</sub>)<sub>2</sub>(Ge<sub>3</sub>O<sub>10</sub>) are known but not the second end-member Ca<sub>6</sub>(GeO<sub>4</sub>)(Ge<sub>3</sub>O<sub>10</sub>). As Ca<sub>8</sub>(GeO<sub>4</sub>)<sub>2</sub>(Ge<sub>3</sub>O<sub>10</sub>) has been produced (Redhammer et al. 2006) 40 years after the first "complete" phase diagram (Shirvinskaya et al. 1966), it may well be that proper crystallization techniques or specific doping will lead to the kilchoanite analog,  $Ca_6(GeO_4)(Ge_3O_{10})$ .

The difference of angles and distances among the calcioolivine-like modules in kilchoanite and pavlovskyite relative to the calcio-olivine structure are rather difficult to interpret due to the difference in symmetry. However, differences sum up in cell dimensions. The lengths of all *b* axes (ca. 5 Å, Table 3) of the listed calcium silicates are very similar. However, according to Table 3 the olivine-like modules in kilchoanite and pavlovskyite are parallel to **a** (11 Å axis), ca. 2% expanded relative to calcio-olivine. A corresponding behavior is observed for the isostructural phases in the system CaO-GeO<sub>2</sub>. If the *c* periodicity of pavlovskyite and kilchoanite are subtracted, the *c* translation of the olivine module is obtained. This value of 6.6341 Å is significantly shorter (1.8%) than the *c* axis of calcio-olivine (Table 3). Thus the olivine-module expansion in pavlovskyite parallel to **a** is balanced by a compression parallel to **c**.

A surprising find is the distribution of  $Mn^{2+}$  in synthetic Mn-bearing kilchoanite (Kimata 1989). In olivine-group glaucochroite CaMn(SiO<sub>4</sub>),  $Mn^{2+}$  prefers the more symmetric M1 site, whereas Ca occupies M2 (Lager and Meagher 1978). The corresponding site to M1 in olivine is Ca2 in kilchoanite, whereas M2 in olivine corresponds to Ca3 in kilchoanite. Within the kilchoanite structure the preference is opposite; Ca3 has the strongest  $Mn^{2+}$  selectivity and there is no  $Mn^{2+}$  at Ca2 (Kimata 1989). It seems that the different  $Mn^{2+}$  order in kilchoanite compared to glaucochroite is due to strain reduction in the more complex kilchoanite structure.

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