Rusinovite, Ca₁₀(Si₂O₇)₃Cl₂: a new skarn mineral from the Upper Chegem caldera, Kabardino-Balkaria, Northern Caucasus, Russia

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Abstract: Rusinovite, $Ca_{10}(Si_2O_7)_3Cl_2$, was discovered in an altered carbonate-silicate xenolith enclosed in ignimbrites of the Upper Chegem volcanic caldera. The mineral is named after Vladimir Leonidovich Rusinov (1935–2007), a Russian petrologist and expert in the field of thermodynamics of non-equilibrium mineral systems. A synthetic analogue of rusinovite is also known. The new mineral has an OD structure of which only the average structure could be determined based on strong and sharp reflections recorded by single-crystal X-ray diffraction: space group *Cmcm*, a = 3.7617(2), b = 16.9385(8), c = 17.3196(9) Å, V = 1103.56(10) Å³, Z = 2. The average structure ($R_1 = 3.18$ %) is characterized by columns of face-sharing disilicate units extending parallel to **a**. However, in the true structure only each second (Si₂O₇) unit is occupied. Although rusinovite has a stoichiometry similar to the apatite-group mineral nasonite, Pb₆Ca₄ (Si₂O₇)₃Cl₂, the two structures are considerably different. Rusinovite has following optical properties: $\alpha = 1.645(2)$, $\beta = 1.664(2)$, $\gamma = 1.675(3)$; $\Delta = 0.030$, $2V_{meas} = -75(10)$ °; $2V_{calc} = -74.6$ °; the Mohs hardness is 4–5, the density is 2.91 g/cm³. The mineral forms fibrous crystals often intergrown into spherolites and displays good cleavage parallel to (010). The Raman spectrum of rusinovite strongly resembles that of another skarn calcium-disilicate: rankinite, Ca₃Si₂O₇.

Key-words: rusinovite, disilicate, new mineral, chlorine, crystal structure, Raman, Caucasus, Russia.

1. Introduction

High-temperature skarns forming under sanidinite-facies conditions are genetically connected with intrusions of volcanic or subvolcanic rocks. The skarns are characterized by the presence of minerals with high chlorine content, such as rondorfite MgCa₈(SiO₄)₄Cl₂, rustumite Ca₁₀(SiO₄)(Si₂O₇)₂Cl₂(OH)₂, wadalite Ca₁₂Al₁₀Si₄O₃₂Cl₆, "chlormayenite" Ca₁₂Al₁₄ O₃₂Cl₂, "chlordellaite" Ca₆(SiO₄)(Si₂O₇)Cl(OH) and others (Agrell, 1965; Tsukimura *et al.*, 1993; Kanazawa *et al.*, 1997; Michailovich *et al.*, 2004; Grapes, 2006; Galuskin *et al.*, 2009; Galuskina *et al.*, 2009; Armbruster *et al.*, 2011). These skarns are promising for finding new chlorine-containing mineral species.

The new mineral rusinovite, Ca₁₀(Si₂O₇)₃Cl₂, approved by CNMNC IMA in January 2011, was discovered in an altered carbonate-silicate xenolith about 10 m in size enclosed in ignimbrites of the Upper Chegem volcanic caldera (Lakargi Mt., Kabardino-Balkaria, Russia). The mineral is named in memory of the well-known Russian petrologist Professor Vladimir Leonidovich Rusinov (1935–2007), a specialist in the field of metasomatism and secondary wall-rock alteration, who worked for half a century at the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences (IGEM RAS). Professor V.L. Rusinov belonged to the D.S. Korzhinskii scientific school of physico-chemical petrology and pioneered studying the thermodynamics of non-equilibrium mineral systems following the theoretical approach of self-organizing mineral-forming systems. The holotype sample of rusinovite is deposited at the Fersman Mineralogical Museum, Russian Academy of Sciences, under registration number 4022/1.

The artificial analogue of rusinovite, $Ca_{10}(Si_2O_7)_3Cl_2$, was synthesized as needle-like single crystals from $CaCl_2$ flux (Hermoneit *et al.*, 1981). According to oscillation and Weissenberg X-ray photographs the strong and sharp reflections of this compound could be indexed with an orthorhombic unit cell: a = 3.763(1) Å, b = 34.70(1) Å, c = 16.946(5) Å, V = 2213 Å³. The diffraction pattern showed additional diffuse reflections and thus the structure was interpreted as an OD structure and the determined cell dimensions are characteristic of a superposition structure.

Subsequent investigations on synthetic $Ca_{10}(Si_2O_7)_3Cl_2$ were motivated by the composition of combustion ashes formed after incineration of waste. These ashes contain Ca-silicates with high Cl content (Stemmermann & Pollmann, 1992). These authors indexed an X-ray powder pattern of Ca₁₀(Si₂O₇)₃Cl₂ in monoclinic setting: a =18.665(1) Å, b = 14.107(1) Å, c = 18.139(1) Å, $\beta =$ $111.65(1)^{\circ}$. Both Hermoneit *et al.* (1981) and Stemmermann & Pollmann (1992) reported corresponding d-values for $Ca_{10}(Si_2O_7)_3Cl_2$. Investigation of the CaO-SiO₂-CaCl₂ system showed that in this ternary system only Ca₁₀(Si₂O₇)₃Cl₂ possesses high stability in aqueous media and can be deposited without danger of chloride mobilization (Stemmermann & Pollmann, 1992). Synthetic Ca₁₀(Si₂O₇)₃Cl₂ is also used as a matrix for luminescence materials (Ding et al., 2007) by partial replacement of Ca by Eu^{2+} .

"Chesofiite", $Ca_{10}(Si_2O_7)_3Cl_2$, a non-approved species with cell dimensions refined in monoclinic setting: a =18.656(1), b = 14.112(1), c = 18.1396(5) Å, $\beta =$ 111.65(1)°, is an anthropogenic phase (Chesnokov *et al.*, 1994) related to rusinovite. The samples were collected on burnt waste of the coal mine no. 42 (near town Kopeisk of Chelyabinsk Region, Russia).

The mineral nasonite $Pb_6Ca_4(Si_2O_7)_3Cl_2$ displays a stoichiometry similar to rusinovite but nasonite is a member of the polysomatic apatite group (Baikie *et al.*, 2010), crystallizing in the hexagonal system (Frondel & Bauer, 1955; Giuseppetti *et al.*, 1971).

2. Analytical methods

The morphology and composition of rusinovite 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 μ m beam diameter, Institute of Geochemistry, Mineralogy and Petrology, University of Warsaw). The following lines and standards were used for rusinovite analyses: CaK α , SiK α – wollastonite; ClK α – tugtupite.

Raman spectra of crystals of rusinovite and associated rankinite were recorded using a Dilor XY spectrometer equipped with a 1800 line mm⁻¹ grating monochromator, a charge-coupled device (CCD), Peltier-cooled detector (1024 × 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 100x objective lens varied from 30 to 50 mW. Raman spectra were recorded in backscatter geometry in the range $100-4000 \text{ cm}^{-1}$ with resolution of 2 cm⁻¹. Collection times of 20 s and accumulation of 5 scans were chosen. The monochromator was calibrated using the Raman scattering line of a silicon plate (520.7 cm⁻¹).

Single-crystal X-ray study of rusinovite was carried out using a Bruker APEX II SMART diffractometer (Mo $K\alpha$, $\lambda = 0.71073$ Å). Diffraction data were collected with ω scans at different φ settings (φ - ω scan) (Bruker, 1999). Data were processed using SAINT (Bruker, 1999). An empirical absorption correction using SADABS (Sheldrick, 1996) was applied. The structure was solved by direct methods with subsequent analyses of difference-Fourier maps. The rusinovite structure was refined using neutral atom scattering factors with the program SHELX97 (Sheldrick, 2008) to $R_1 = 3.18 \%$.

X-ray powder diffraction data were collected using a X'Pert PRO 3040/60 diffractometer (Co $K\alpha$, $\lambda = 1.78901$ Å, Bragg-Brentano geometry).

3. Occurrence and description

Rusinovite was found in altered carbonate-silicate xenolith no. 3 within ignimbrites of the Upper Chegem volcanic caldera, Lakargi Mt. type locality (Kabardino-Balkaria Republic, Northern Caucasus, Russia). A geological scheme with location of xenoliths and description of the studied area was reported by Gazeev et al. (2006) and Galuskin et al. (2009). The xenolith no. 3 is the type locality of toturite Ca₃Sn₂Fe₂SiO₁₂ (Galuskina et al., 2010) and pavlovskyite $Ca_8(SiO_4)_2(Si_3O_{10})$ (Galuskin et al., 2011). Rusinovite was detected within a thin endocontact zone of skarn which replaced ignimbrite. Rusinovite forms fibres intergrown to monomineralic spherulites displaying in thin section bright interference colours (Fig. 1). Detailed investigation of skarn zonation revealed a rusinovite zone, composed of fine-needles and fibrous aggregates of rusinovite, often with inclusions of numerous wadalite grains (Fig. 1e). Relics of earlier (hightemperature characteristic) skarn minerals, such as larnite β -Ca₂SiO₄, rondorfite $MgCa_8(SiO_4)_4Cl_2$, rankinite Ca₃Si₂O₇, pavlovskyite Ca₈(SiO₄)₂(Si₃O₁₀), cuspidine $Ca_4(Si_2O_7)F_2$, tazheranite ZrO_2 (cub.), baddeleyite ZrO_2 (mon.), garnet group minerals of the kerimasite-kimzeyitetoturite series $Ca_3(Zr,Sn)_2(Fe,Al)_2SiO_{12}$, lakargiite CaZrO₃, perovskite CaTiO₃ and magnesioferrite MgFe₂O₄, are preserved (Fig. 2). Low-temperature alteration is evidenced by the minerals hillebrandite, afwillite, tobermorite, hydrogarnet, hydrocalumite and ettringitegroup minerals. Trabzonite and jennite crystallized after rusinovite, herein wadalite is replaced by hydrogarnet of the hibschite-katoite series (Fig. 1d, e). In several cases, fibrous pseudomorphs of wollastonite after quartz, in which solitary crystals or sheaf-like aggregates of rusinovite replace wollastonite, are noted (Fig. 2d).

In thin-section, rusinovite is colourless, transparent, non pleochroic. The mineral shows high interference colours if



Fig. 1. Rusinovite spherulite in endoskarn: A, B – transmitted light, parallel nicols (a) and crossed nicols (b). (c) – BSE image, the frames indicate magnified fragments shown in Fig. 1d and e. (d) – replacement of rusinovite by trabzonite. Trabzonite has wadalite inclusions, which are altered to hydrogrossular. (e) –Rusinovite and wadalite aggregates on the border to a rusinovite spherulite, which was not altered by hydration. Rus – rusinovite, Wad – wadalite, Hgr – hydrogrossular (hibschite-katoite series), Trb – trabzonite, Jen – jennite.

inspected with crossed nicols (Fig. 1b). In hand specimens the mineral is white with white streak, luster is vitreous, silky. It shows good cleavage on (010), the fracture is conchoidal. Microhardness VHN₂₀ = 320 kg/mm² (3 measurements) corresponds to hardness 4–5 on Mohs scale. Refractive indices are: $\alpha = 1.645(2)$, $\beta = 1.664(2)$, $\gamma = 1.675(3)$; $\Delta = 0.030$, $2V_{\text{meas}} = -75(10)^{\circ}$; $2V_{\text{calc}} = -74.6^{\circ}$. Density obtained by the sink and float method in heavy liquids is 2.93(1) g cm⁻³, the calculated density is 2.931 g cm⁻³. Optical orientation of rusinovite crystals is as follows: X = a(?), Y = c, Z = b(?). Synthetic needle-like crystals of Ca₁₀(Si₂O₇)₃Cl₂ have X parallel to the needle axis, corresponding to **a** (Hermoneit *et al.*, 1981). The compatibility index is superior (*CI*_{meas} = -0.013 and *CI*_{calc} = -0.0002).

Rusinovite is characterized by rather invariable composition, very close to stoichiometric $Ca_{10}(Si_2O_7)_3Cl_2$ (Table 1). A small deficiency of chlorine is conspicuous, it can be due to both a partial hydration of rusinovite and methodological problems of chlorine measurements using the microprobe analyzer (choice of standards, mineral behaviour under electron beam *etc.*). It must be emphasized that occasionally a weak and very blurred band near 3580–3600 cm⁻¹ is observed in Raman spectra of rusinovite. This absorption is probably related to impurity phases (trabzonite?) as this band is absent in Raman spectra of relatively large rusinovite crystals.

The crystal-chemical formula of rusinovite may also be written as $Ca_3Si_2O_7 \times 1/3CaCl_2$ (Rus) and thus strongly resembles rankinite $Ca_3Si_2O_7$ (Ran). For this reason it is also not surprising that both minerals have similar Raman spectra (Fig. 3). Bands of (Si_2O_7) group vibrations dominate both spectra (cm⁻¹): v₁ 900 (Rus) and 891 (Ran), v₃ 1036 (Rus) and 1007 (Ran), v₂ 365 (Rus) and 347 (Ran), v₄ 652, 635 (Rus) and 671 (Ran). A specific feature of the Raman spectrum of rusinovite is a split band assigned to symmetric bending vibrations of (Si_2O_7) group (bands 652 and 635 cm⁻¹), which are deemed sensitive to variation of



Fig. 2. (a) – fragment of rankinite partially replaced by rusinovite and trabzonite. (b) – fragment of pavlovskyite pseudomorph with cuspidine rims after an early rankinite pseudomorph (after wollastonite?) in a rusinovite zone. (c) – rondorfite relics in the rusinovite zone. (d) – solitary rusinovite crystals in pseudomorph of wollastonite after quartz (central fragment of oval pseudomorph). Rusinovite displays a clear zonal structure emphasized by dispersed inclusions of wollastonite in the grey central sectors). BSE images, Rus – rusinovite, Wol – wollastonite, Wad – wadalite, Cus – cuspidine, Hgr – hydrogrossular, Rnd – rondorfite, Pav- pavlovskyite, Trb – trabzonite, Ran – rankinite, Hil – hillebrandite, Hds – unidentified hydrosilicates.

Table 1. Chemical composition of rusinovite (mean 45).

	wt.%	s.d.	Range	Atom	pfu
SiO ₂	37.16	0.23	36.67-37.52	Si	6.007
CaÕ	57.66	0.19	57.25-57.99	Ca	9.987
Cl	6.78	0.12	5.56-6.98	Cl	1.857
H_2O^*	0.13			OH	0.143
-O=Cl	1.53				
Total	100.20				

Note: *Calculated on charge balance.

the Si-O-Si bond angle (Hermoneit *et al.*, 1981) (Fig. 3). This fact could indicate two types of (Si_2O_7) groups in rusinovite with slightly different Si-O-Si angles as confirmed by single-crystal structure refinement of the average structure (see below).

4. Structure

The rusinovite structure was refined on the basis of single-crystal X-ray data to $R_1 = 3.18$ % (Tables 2–5).

Single-crystal rotation photographs of synthetic Ca₁₀(Si₂O₇)₃Cl₂ by Hermoneit *et al.* (1981) and their interpretation clearly indicate that this phase has an OD structure, characterized by strong family reflections yielding an orthorhombic unit cell and additional weak and diffuse superstructure reflections. In general, our results on rusinovite confirm these findings although we cannot validate their doubled b axis of 34.70 Å (our corresponding c axis is halved). We cannot exclude the possibility that the crystals investigated by us were too small to detect doubling of the *b* axis or any diffuse contributions. Nevertheless, the structure solution was straightforward in space group *Cmcm.* The result of disordered, half occupied (Si_2O_7) units stacked along the a axis is characteristic of the average structure model indicating that MDO (maximum degree of order) polytypes must have at least doubled a. The average structure (Fig. 4) exhibits bow-tie like (Si₂O₇) units (Fig. 5), linked by sharing of tetrahedral faces parallel to (100). Only each second of these (Si_2O_7) units is actually occupied and thus face-sharing is an artifact of the family structure (Fig. 5). There are two types of symmetry-independent disilicate units (Si1 and Si2), which have connecting O atoms (O2 and O3, respectively) shifted by ¹/₂ along **a**. The Si2-O2-Si2 and Si1-O3-Si1 angles are 156.5(8)° and



Fig. 3. Raman spectra of rusinovite (1) and rankinite (2) from Lakargi skarns.

 $151.0(3)^{\circ}$, respectively. Cl has a distorted tetrahedral coordination surrounded by 2 × Ca1 and 2 × Ca2 ions. Ca3 is only coordinated by O atoms. The measured X-ray powder pattern of rusinovite is close to diffraction patterns of both orthorhombic (Hermoneit *et al.* 1981) and monoclinic (Stemmermann & Pöllmann, 1992) Ca₁₀(Si₂O₇)₃Cl₂

Table 2. Parameters for X-ray data collection and crystal structure refinement.

Unit-cell dimensions (Å)	a = 3.7617(2)
	b = 16.9385(8)
	c = 17.3196(9)
	$lpha=eta=\gamma=90^\circ$
Volume (Å ³)	1103.56(10)
Space group	<i>Cmcm</i> (No. 63)
Z	2
Chemical formula	$Ca_{10}(Si_2O_7)_3Cl_2$
$\mu (mm^{-1})$	3.044
Crystal shape	prism
Crystal size (mm)	0.08 imes 0.05 imes 0.05
Temperature	293 K
Rotation width	0.5 °
Total number of frames	2664
Frame size	512×512 pixels
Time per frame	30 s
Max. $\hat{\theta}$ range for data collection	29.30°
Index ranges	$-5 \le h \le 5$
	$-22 \le k \le 22$
	$-23 \le l \le 23$
Completeness	100 %
No. measured reflections	9452
No. unique reflections	889
No. observed reflections $I > 2\sigma(I)$	707
No. of parameters	85
R _{int}	0.0910
$R1, I > 2\sigma(I)$	0.0318
R1, all data	0.0454
wR2 (on F^2)	0.0742
GoF	1.056
$\Delta \rho_{\min} (e \dot{A}^{-3})$	-0.45 close to Ca3
$\Delta \rho_{\rm max} (e A^{-3})$	0.713 close to O1

(Table 6). Unit-cell parameters refined from the powder data are as follows: *Cmcm*, a = 3.763(2), b = 16.930(3), c = 17.333(3) Å, V = 1104.3(1) Å³, Z = 2.

5. Discussion

A zone enriched in rusinovite (Ca/Si ratio = 1.66/1) occurs between a larnite zone (Ca/Si ratio = 2/1) and a rankinite (Ca/Si ratio = 1.5) (+wollastonite) zone. The reaction of

Table 3. Atom coordinates, $U_{eq.}$ (Å²) and site occupancies for the average structure of rusinovite.

Atom	x	у	Z	$U_{ m eq}$	Occ.
Cal	0	0.43099(6)	0.75	0.0136(2)	1
Ca2	0.5	0.21839(4)	0.60865(5)	0.01749(19)	1
Ca3	0	0.03277(4)	0.59699(5)	0.0211(2)	1
Si1	0.4328(3)	-0.11805(7)	0.55041(7)	0.0105(5)	0.50
Si2	0.9300(5)	0.11164(11)	0.75	0.0139(7)	0.50
01	0.451(3)	-0.05630(18)	0.61745(18)	0.014(2)	0.50
O2	0.5	0.1194(6)	0.7321(7)	0.027(4)	0.25
O3	0	0.0957(3)	0.4601(3)	0.0129(10)	0.50
O4	0.4268(10)	0.09543(19)	0.53484(19)	0.0165(12)	0.50
05	0	0.29067(14)	0.56891(16)	0.0179(6)	1
O6	0.948(4)	0.1480(2)	0.6698(2)	0.023(3)	0.50
O7	0	0.0166(2)	0.75	0.0188(8)	1
Cl1	0.5	0.31227(7)	0.75	0.0188(3)	1

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cal	0.0141(5)	0.0141(5)	0.0126(5)	0	0	0
Ca2	0.0147(4)	0.0144(4)	0.0234(4)	-0.0005(3)	0	0
Ca3	0.0163(4)	0.0119(3)	0.0351(5)	0.0031(3)	0	0
Si1	0.0098(14)	0.0099(5)	0.0117(5)	0.0005(4)	-0.0005(4)	-0.0001(5)
Si2	0.016(2)	0.0117(8)	0.0137(8)	0	0	0.0000(7)
01	0.013(7)	0.0131(13)	0.0155(14)	0.0005(11)	-0.0007(17)	0.0033(16)
O2	0.009(4)	0.035(6)	0.037(13)	0.005(5)	0	0
03	0.010(2)	0.010(2)	0.019(3)	-0.001(2)	0	0
O4	0.015(4)	0.0203(15)	0.0142(16)	0.0039(12)	0.0054(13)	0.0015(13)
05	0.0183(14)	0.0091(11)	0.0264(15)	0.0031(11)	0	0
06	0.026(8)	0.0187(14)	0.0241(17)	0.0078(13)	-0.010(2)	0.0019(18)
O7	0.0191(19)	0.0088(16)	0.029(2)	0	0	0
C11	0.0185(7)	0.0133(6)	0.0247(7)	0	0	0

Table 4. Anisotropic displacement parameters (Å²) for rusinovite.

Table 5. Selected interatomic distances (Å) for rusinovite.

Atom1	Atom2	Bond			
Two positions for O1, only one is occupied					
Cal	01	$2.313(3) \times 2$			
Ca1	07	$2.375(2) \times 2$			
Ca1	Cl1	$2.7534(12) \times 2$			
Ca2	Cl1	2.9192(10)			
Ca2	O5	$2.3474(15) \times 2$			
Ca2	O4	2.459(3) two options			
Ca2	O6	$2.619(11) \times 2^{-1}$			
Ca2	02	2.718(12)			
Ca2	O5	$2.3474(15) \times 2$			
Ca2	O4	2.459(3) two options			
Ca2	O6	$2.320(11) \times 2^{-1}$			
Ca3 coord	ination, with two O3 atoms	s			
Ca3	O4	$2.633(4) \times 2$			
Ca3	O1	$2.583(9) \times 2$			
Ca3	O7	2.6642(10)			
Ca3	O6	2.332(4) two options			
Ca3	O3	2.389(5)			
Ca3	O3	2.600(5)			
Ca3 coord	ination, with one O3 atom				
Ca3	07	2.6642(10)			
Ca3	O6	2.332(4) two options			
Ca3	O3	2.600(5)			
Ca3	O1	$2.296(9) \times 2$			
Ca3	O4	$2.633(4) \times 2$			
Ca3 coord	ination, with another O3 at	tom			
Ca3	07	2.6642(10)			
Ca3	O6	2.332(4) two options			
Ca3	O4	$2.205(3) \times 2$			
Ca3	O1	$2.583(9) \times 2$			
Ca3	O3	2.389(5)			
Si1	O5	1.599(3)			
Si1	O4	1.614(3)			
Si1	O1	1.623(4)			
Si1	O3	1.6817(18)			
Si2	O6	$1.587(5) \times 2$			
Si2	07	1.631(4)			
Si2	O2	1.652(3)			
Cl1	Cal	$2.7534(12) \times 2$			
Cl1	Ca2	$2.9193(10) \times 2$			

Note: two different coordinations of Ca2, depending on whether O2 is locally occupied or not.



Fig. 4. Crystal structure of rusinovite projected along **a**; two types of Si_2O_7 disilicate units are distinguished; Si1 and Si2 tetrahedra are red and yellow, respectively. Oxygen sites are represented as small light blue spheres, Ca sites are dark blue, Cl is green; unit cell is shown by solid black outlines.

rusinovite formation is $3Ca_3Si_2O_7$ (rankinite) + $CaCl_2$ (in fluid) $\rightarrow Ca_{10}(Si_2O_7)_3Cl_2$ (rusinovite). Rusinovite is a high-temperature mineral replacing rankinite (Fig. 2a). Rankinite is stable above 745 °C (the transition temperature between rankinite and its low-temperature dimorph kilchoanite, Pertsev, 1977). As shown before (Gazeev *et al.*, 2006; Galuskin *et al.*, 2008, 2009), the high-temperature and low-pressure skarns at the Lakargi Mt. locality formed under the sanidinite metamorphic facies and Korzhinskii's larnite-merwinite depth facies (Korzhinskii, 1993; Pertsev, 1977; Zharikov *et al.*, 1998; Callegari & Pertsev, 2007). The formation temperature of these skarns can significantly exceed 900 °C (P_{CO2} < 300 bar) as confirmed by experimental data on rankinite stability (Zharikov & Shmulovich, 1969).



Fig. 5. "Face-sharing" disilicate units extending parallel to \mathbf{a} are characteristic of the refined average structure. In the true structure only each second disilicate group is occupied.

Table 6. Powder X-ray diffraction data for rusinovite.

h	k	l	$d_{\rm obs}$	I _{obs}	$d_{\rm cal}$	$I_{\rm cal}$
0	0	2	8.671	7	8.667	7
0	2	0	8.471	39	8.465	39
0	2	1	7.615	10	7.615	15
0	2	3	4.770	1	4.770	1
0	4	0	4.238	1	4.233	1
0	4	1	4.113	4	4.113	4
0	2	4	3.859	6	3.857	6
1	1	2	3.376	5	3.376	7
0	2	5	3.209	33	3.209	43
1	3	0	3.134	25	3.134	27
1	3	1	3.082	100	3.081	100
0	4	4	3.030	79	3.028	79
1	3	2	2.946	43	2.946	43
0	0	6	2.889	74	2.889	74
0	6	0	2.822	6	2.826	6
1	3	3	2.753	2	2.754	2
0	6	2	2.683	21	2.684	21
0	6	3	2.537	74	2.537	51
1	5	1	2.491	3	2.492	3
0	4	6	2.386	8	2.387	8
1	5	4	2.178	6	2.178	5
0	0	8	2.167	6	2.166	6
1	3	6	2.124	3	2.124	1
0	8	2	2.056	3	2.056	3
1	1	5	2.037	13	2.036	13
1	3	7	1.942	17	1.943	17
1	7	3	1.919	6	1.920	6
2	0	0	1.882	9	1.881	9
0	8	5	1.808	1	1.808	1
1	5	7	1.765	6	1.766	6
0	10	1	1.687	6	1.686	6

Synthetic Ca₁₀(Si₂O₇)₃Cl₂ formed in a CaO-SiO₂-CaCl₂ flux system at temperatures above 850 °C (Stemmermann & Pöllmann, 1992). Above 1065°C, Ca₁₀(Si₂O₇)₃Cl₂ decomposes according to the scheme: Ca₁₀(Si₂O₇)₃Cl₂ \rightarrow 3Ca₃Si₂O₇ + CaCl₂ (melt) (Hermoneit *et al.*, 1981). Due to the similarity of the chemical formulae of $Ca_{10}(Si_2O_7)_3Cl_2$ (rusinovite) and Pb_6Ca_4 (Si_2O_7)_3 Cl_2 (nasonite), it has been speculated (Stemmermann & Pöllmann, 1992) that not only nasonite but also $Ca_{10}(Si_2O_7)_3Cl_2$ (rusinovite) is a member of the polysomatic apatite group (Baikie *et al.*, 2010). In nasonite (Fig. 6), trigonal prisms of CaO_6 build face-sharing columns along the hexagonal **c** axis. Laterally, these columns are connected to a channel by Si_2O_7 groups, aligned parallel to the **c** axis. The centre of the channels is occupied by Cl surrounded by 3 Pb at two different height levels corresponding to the 6_3 axis through the Cl positions. Pb is five-fold coordinated by three O and two Cl. In contrast, if in rusinovite only the Ca positions (Ca3) that do not bond to Cl are drawn, the structure (Fig. 7) is characterized by undulating walls parallel to (010) with



Fig. 6. Hexagonal crystal structure of nasonite (Giuseppetti *et al.*, 1971) projected along the **c** axis. (001) Face-sharing trigonal prisms of CaO₆ are grey and connected to channels by red Si₂O₇ dimers extending also parallel to **c**. Pb sites are shown as white spheres, Cl is green.



Fig. 7. Average structure of rusinovite projected along **a** as in Fig. 4 but, in addition, $Ca3O_8$ cubes are shown to emphasize undulating layers parallel to (010). Si₂O₇ dimers extend parallel to **a**.

 Si_2O_7 groups attached on opposite sides of the walls. These undulating layers enclose Cl, Ca1, and Ca2. The dense nature of the polyhedral layer composed of distorted Ca3O₈ cubes is an artifact of the average structure. In the true structure Ca3 is 7-coordinated because O3 is only half occupied. Thus, in spite of the similar formula, the detailed structures of nasonite and rusinovite are considerably different although both have disilicate groups in common.

Acknowledgements: The authors thank Prof. Leonid Dubrovinsky, Bayerisches Geoinstitut, Universität Bayreuth, Germany for affording Raman spectroscopic investigations. The work was partly supported by the Ministry of Science and Higher Education of Poland, grants no. N307 100238 (E.V.) and no. N307 097038 (I.G.).

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Received 11 April 2011 Modified version received 24 July 2011 Accepted 2 August 2011

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