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Discovery and Investigation of a Natural Analog of Calcio-Olivine (γ-Ca_2SiO_4)

A. E. Zadov[a], V. M. Gazeev[b], N. N. Pertsev[b], A. G. Gurbanov[b],
N. A. Yamnova[c], E. R. Gobechiya[c], and N. V. Chukanov[d]

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A natural mineral analogous to γ-Ca_2SiO_4 calcio-olivine well-known in the cement industry was discovered in carbonate xenolithes in the Middle–Later Pliocene acid ignimbrites of the Verkhnechegemsk caldera (Kabardino-Balkaria, Russian Federation). The mineral was first discovered in the form of crystals sufficient for chemical, optical, and crystal chemical investigation. As was established by the Rietveld method, the mineral structure is analogous to synthetic γ-Ca_2SiO_4: $a = 5.07389(7)$ Å, $b = 11.21128(14)$ Å, $c = 6.75340(9)$ Å, $V = 384.170(5)$ Å^3, Space group *Pbnm*, $Z = 4$. Glassy luster, $n_p = 1.642(2)$; $n_m = 1.653(2)$; $n_g = 1.657(2)$; $2V_{\text{meas}} = -69$–$81°$. Hardness = 4.5 (Mohs' scale). Empirical formula (electrone microprobe): $Ca_{1.98}Na_{0.02}Mg_{0.01}Al_{0.01}Si_{1.00}O_4$. Larnite ($\beta$-$Ca_2SiO_4$) is also present in the rock, but not in direct contact with calcio-olivine. Calcio-olivine occurs in paragenesis with spurrite or surrounded by secondary minerals. Hillebrandite is the main product of calcio-olivine secondary alteration. Afwillite, ettringite, thaumasite, rondorfite, wadalite, and hematite are also identified in the rock. The name "calcio-olivine" as a mineral specie was affirmed by the International Commission on New Minerals, Nomenclature, and Classification (CNMNC) of the International Mineralogical Association September 6, 2007, no. 07–B.

Ca_2SiO_4 polymorphism was first investigated in a Portland cement clinker in 1882 by Le Chatelier. Five most distributed polymorphic modifications of Ca_2SiO_4 are known today [1]. The first data on the rhombic polymorph (γ-Ca_2SiO_4) was published in 1906 [2]. The closeness of structures between γ-Ca_2SiO_4, Na_2BeF_4, and olivine was shown in 1942, and γ-Ca_2SiO_4 was named calcio-olivine [3]. Beginning from that moment, term calcio-olivine was used everywhere in chemistry, silicate technology, and metallurgy for representing γ-Ca_2SiO_4. A similar name "Kalk-Olivin" (German) was used in 1877 by K. Oëbbeke [4] for natural olivine with the following composition (in %): SiO_2—42.581, MgO—35.682, CaO—14.088, MnO—6.488, Total—98.784. Probably, a mixture of forsterite and monticellite was analyzed. N. Bowen [5] used term "lime-olivine" for monticellite and the subsequently discredited calcium orthosilikate "shannonite." In Russian translation [6] "Kalk-Olivin" and "lime-olivine" were called calcio-olivine, and in such form were preserved when retranslated into English ("calcio-olivine"). Even now, this name is periodically used by mistake for olivines enriched in CaO. The authors use the term calcio-olivine only for the rhombic polymorph γ-Ca_2SiO_4.

γ-Ca_2SiO_4 was first described in geological objects (without use of the term calcio-olivine and chemical composition determination) for the skarns of Marble Canyon (United States) only in 1966 [7]. More recently, calcio-olivine was discovered in skarnated xenoliths among alkaline volcanites near the Eifel region (Germany), but it was not investigated in detail [8]. We separately note γ-Ca_2SiO_4 occurrence in the burnt coal waste piles of the Kopeysk town region (Chelyabinsk oblast) [9]. Calcio-olivine is mentioned in some mineralogical reference books. It was proposed to change the nomenclature of Ca_2SiO_4 polymorphs and because of this, synthetic calcio-olivine was mentioned as α-Ca_2SiO_4 in the reference book of H. Struntz [10]. This nomenclature was also preserved in later

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[a] *Regenerator Open Joint-Stock Company NPO, Ltd., Moscow, Russia*

[b] *Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences, Staromonetny per. 35, Moscow,119017 Russia*

[c] *Moscow State University, Moscow, 119991 Russia*

[d] *Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, pr. Akademika Semenova 1, Moscow oblast, 142432 Russia*

Table 1. Physical characteristics of calcio-olivine and γ-Ca_2SiO_4

Properties	Calcio-olivine (Mountain Lakargi)	γ-Ca_2SiO_4		
		Marble Canyon [7]	Synthetic [2]	From burnt coal waste piles [9]
2V° measured	−69(2)…−81(3)	−57(3)	−60	Negative
n_p	1.642(2)	1.633(3)	1.640	1.632
n_m	1.653(2)	1.640(3)	1.645***	1.640
n_g	1.657(2)	1.645(3)	1.654	1.644
Density D, g/cm^3:				
measured	2.91(2)*	–	–	2.77*
calculated	2.98**	–	2.96 [1]	2.986
Hardness (Mohs' scale)	4.5	–	–	5.5

* Measured by counterweighting in heavy liquid of fractured mineral grain; ** for average composition Ca_2SiO_4 (see Table 2); *** does not correspond to negative sign of 2V.

issues of this reference book. In the reference literature, data on the synthetic phase is presumably given.

Calcio-olivine was discovered by the authors in the Verkhnechegemsk caldera near the mountain Lakargi (Northern Caucasus, Kabardino–Balkaria, Russian Federation) in the skarnated xenoliths from acid ignimbrites [11]. Xenoliths are located near the neck canal of the volcanic apparatus of Middle–Late Pliocene age. Skarnated contacts of the xenoliths are greatly altered, and carbonate cores of the xenoliths are composed of brucite and lime marble. Primary skarn is composed of larnite and spurrite–calcite that corresponds to 800–1000°C of the skarn formation temperature. Calcio-olivine occurs in the paragenesis with spurrite and apparently with wadalite or surrounded by later minerals. Hillebrandite, afwillite, ettrigite, thaumasite, rondorfite, and hematite are common among the later minerals. Aggregates of larnite (β-Ca_2SiO_4) occur somewhat apart from calcio-olivine. These minerals are also characteristic of the mentioned skarns of the Eifel region [8].

Table 2. Chemical compositions of calcio-olivine and larnite β-Ca_2SiO_4 (Mountain Lakargi)

Contents of oxides, mas %	Calcio-olivine γ-Ca_2SiO_4		Larnite β-Ca_2SiO_4
	Contents of oxides, mas %		
	average of four analyses	smallest and largest values	average of eight analyses
Na_2O	0.38	0.3–0.47	0.06
MgO	0.10	0–0.25	0.02
Al_2O_3	0.11	0–0.3	0.16
SiO_2	34.72	33.99–35.15	34.63
CaO	64.29	63.66–64.24	64.55
P_2O_5	0.12	0–0.3	0.01
Total	99.72	99.05–100.19	99.42
Element	Formula coefficients		
O	4	4	4
Na	0.02	0.02–0.03	0.02
Mg	0.01	0–0.01	0.00
Al	0.01	0–0.01	0.01
Si	1.00	0.99–1.01	1.00
Ca	1.98	1.96–2.0	2.00
P	<0.01	0–0.01	0.00

Note: All investigations were performed with the help of scanning electron microscope JSM–5300 with spectrometer Link ISIS by analyst A.V. Mokhov.

Calcio-olivine forms rounded grains (up to 2–3 mm in size) irregularly colored in very light yellowish rose color with glassy luster. The rose color is caused by the presence of microinclusions of bernalite $Fe(OH)_3$ (calcio-olivine in the burnt coal waste piles [9] has a light rose and light green-gray color). In thin sections of the discovered and investigated calcio-olivine, one may sometimes distinguish the following coarse crystal forms: rectangular prism (main form) and pyramid. According to the measurements in thin section, the angle between the prism and the pyramid facies accounted for 125(5)°. Optical axe N_g is directed along the crystal elongation parallel to prism. Crystals of synthetic γ-Ca_2SiO_4 are prismatic [1], and natural crystals from Marble Canyon are fibrous [7].

Crystals from the Verkhnechegemsk calcio-olivine are divided by fractures into very fine irregular fragments less than 100 microns in size and displaced one from another by 2°–3°. Sometimes in the crystals an outer rim occurs. This rim has slightly bigger birefringence. According to complete information, the authors assume that the discovered calcio-olivine was formed during the progressive stage of skarn formation. The

Table 3. Atomic coordinates, parameters of atomic displacements B_{iso}, occupation density q, cation–anion distances of basis atoms in the structure of natural calcio-olivine

Atom	x	y	z	B_{iso}, Å^2	q
Ca(1)	0	0	0	3.9(2)	0.5
Ca(2)	0.9890(15)	0.2796(6)	0.25	3.8(2)	0.5
Si	0.4297(19)	0.0991(8)	0.25	3.4(3)	0.5
O(1)	0.741(3)	0.0902(17)	0.25	3.6(6)	0.5
O(2)	0.295(3)	0.9619(15)	0.25	1.7(5)	0.5
O(3)	0.300(2)	0.1604(10)	0.0596(17)	2.6(4)	1.0

Cation–anion distances, Å

Ca(1)–octahedron		Ca(2)–octahedron		Si–tetrahedron	
Ca(1)–O(1) × 2	2.367(7)	Ca(2)–O(1)	2.470(10)	Si–O(1)	1.580(11)
O(2) × 2	2.295(6)	O(2)	2.321(10)	O(2)	1.686(11)
O(3) × 2	2.390(7)	O(3) × 2	2.436(7)	O(3) × 2	1.600(7)
	⟨2.351⟩	O(3)* × 2	2.395(7)		⟨1.617⟩
			⟨2.409⟩		

Note: In brackets standard deviations are noticed; *—1/2 + x, 1/2 – y.

main product of calcio-olivine hydrothermal alteration is hillebrandite $Ca_2SiO_3(OH)_2$.

Calcio-olivine is colorless and transparent in thin section; cleavage (or jointing) is indistinct across the elongation. The same mineral from the Kopeysk burnt coal waste piles showed cleavage or jointing in two directions and was also greatly fractured [9]. Optical and other features of the mineral are presented in Table 1.

The chemical composition of the Verkhnechegemsk calcio-olivine corresponds to Ca_2SiO_4, but there are always slight amounts of trace elements in analyses (Table 2). Sometimes certain differences between the chemical composition of the crystal core and edges occur. Analyses of larnite associated with calcio-olivine contain significantly lesser amounts of trace elements (Table 2). Larnite is colorless and contains admixtures of Na, Al, P, and Mg in a form of solid solution in β-Ca_2SiO_4 and due to this fact has a somewhat enlarged unit cell with the following parameters: a = 5.5041 Å, b = 6.7622 Å, c = 9.3241 Å, β = 94.172°, space group $P21/n$ (analog of the ICSD no.63–5747).

The IR-spectrum of calcio-olivine containing strong lines 943, 931, 915, 855 (strongest line), 817, 810 (shoulder), 705, 559, 512, 500, 452, and 440 cm^{-1} differs from the IR-spectrum of larnite.

The Verkhnechegemsk calcio-olivine structure was investigated by the Rietveld method. The X-ray diffraction spectrum of the mineral was obtained with the help of the STOE STUDY MP diffractometer with a curved primary Ge (111) monochromator (λCu$K_{\alpha1}$). The atomic coordinates of synthetic γ-Ca_2SiO_4 from [12] are used as the base mineral model (a = 5.0821 Å, b = 11.2237 Å, c = 6.7638 Å, Z = 4, space group $Pbnm$, ICSD no. 81095). While processing the X-ray diagram and unit cell parameters refinement, "extra" reflexes corresponding to hillebrandite $Ca_2SiO_3(OH)_2$ (a = 3.6389 Å, b = 16.3110 Å, c = 11.829 Å, space group $Cmc2_1$, Z = 6, ICSD no. 80127) and wadalite $Ca_6Al_5Si_2O_{16}Cl_3$ (a = 12.001 Å, space group $I/43d$, Z = 4, ICSD no. 72504) were discovered. The contents of the mentioned mineral phases in the investigated mineral sample are as follows (in %): γ-Ca_2SiO_4, 83; hillebrandite, 13; and wadalite, 4. After addition of hillebrandite and wadalite structural models from [13, 14], the convergence of experimental and theoretical X-ray diagrams becomes improved and the reliability factor R_{wp} was significantly decreased. The increased value (8.52%) of the final R_{wp} is due to the presence of nonidentified admixture phases in the sample. Admixture phases are not identified because of their insignificant amounts and low reflex intensities. The main crystallographic data of natural calcio-olivine are as follows: a = 5.07389(7) Å, b = 11.21128(14) Å, c = 6.75340(9) Å, V = 384.170(5) Å^3, space group $Pbnm$, Z = 4.

The identified final coordinates of base atoms and corresponding cation–anion distances (Table 3) proved that calcio-olivine is isostructural with the synthetic γ-Ca_2SiO_4. The structure basis of calcio-olivine is composed of olivine-like "dentate" strips formed along the unit cell axe c by elongated zigzag columns of Ca(1)–octahedrons connected by mutual ribs, and incrusted by Ca(2)–octahedrons also combined with them by mutual ribs. Strips of Ca(2)–octahedrons located at two levels along the axe a and displaced by 0.5T along the axe b form the three-dimensional framework. Vacancies of the framework are filled with isolated SiO_4 tetrahedrons. Every tetrahedron is rigidly connected with Ca–octahedrons by three mutual ribs.

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