

Phosphoinnelite, $\text{Ba}_4\text{Na}_3\text{Ti}_3\text{Si}_4\text{O}_{14}(\text{PO}_4, \text{SO}_4)_2(\text{O}, \text{F})_3$, a New Mineral Species from Peralkaline Pegmatite of the Kovdor Pluton, Kola Peninsula¹

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Abstract—Phosphoinnelite, an analogue of innelite with $\text{P} > \text{S}$, has been found in a peralkaline pegmatite vein crosscutting calcite carbonatite at the phlogopite deposit, Kovdor pluton, Kola Peninsula. Cancrinite (partly replaced with thomsonite-Ca), orthoclase, aegirine-augite, pectolite, magnesioarfvedsonite, golvshchite, and fluorapatite are associated minerals. Phosphoinnelite occurs as lath-shaped crystals up to $0.2 \times 1 \times 6$ mm in size, which are combined typically in bunch-, sheaf-, and rosettelike segregations. The color is yellow–brown, with vitreous luster on crystal faces and greasy luster on broken surfaces. The mineral is transparent. The streak is pale yellowish. Phosphoinnelite is brittle, with perfect cleavage parallel to the $\{010\}$ and good cleavage parallel to the $\{100\}$; the fracture is stepped. The Mohs hardness is 4.5 to 5. Density is 3.82 g/cm^3 (meas.) and 3.92 g/cm^3 (calc.). Phosphoinnelite is biaxial (+), $\alpha = 1.730$, $\beta = 1.745$, and $\gamma = 1.764$, $2V$ (meas.) is close to 90° . Optical orientation is $Z^{\wedge}c \sim 5^\circ$. Chemical composition determined by electron microprobe is as follows (wt %): 6.06 Na_2O , 0.04 K_2O , 0.15 CaO , 0.99 SrO , 41.60 BaO , 0.64 MgO , 1.07 MnO , 1.55 Fe_2O_3 , 0.27 Al_2O_3 , 17.83 SiO_2 , 16.88 TiO_2 , 0.74 Nb_2O_5 , 5.93 P_2O_5 , 5.29 SO_3 , 0.14 F, $-\text{O}=\text{F}_2 = -0.06$, total is 99.12. The empirical formula calculated on the basis of $(\text{Si}, \text{Al})_4\text{O}_{14}$ is $(\text{Ba}_{3.59}\text{Sr}_{0.13}\text{K}_{0.01})_{\Sigma 3.73}(\text{Na}_{2.59}\text{Mg}_{0.21}\text{Ca}_{0.04})_{\Sigma 3.04}(\text{Ti}_{2.80}\text{Fe}_{0.26}^{3+}\text{Nb}_{0.07})_{\Sigma 3.13}[(\text{Si}_{3.93}\text{Al}_{0.07})_{\Sigma 4}\text{O}_{14}(\text{P}_{1.11}\text{S}_{0.87})_{\Sigma 1.98}\text{O}_{7.96}](\text{O}_{2.975}\text{F}_{0.10})_{\Sigma 3.075}$. The simplified formula is $\text{Ba}_4\text{Na}_3\text{Ti}_3\text{Si}_4\text{O}_{14}(\text{PO}_4, \text{SO}_4)_2(\text{O}, \text{F})_3$. The mineral is triclinic, space group $P\bar{1}$ or $P1$. The unit cell dimensions are $a = 5.38$, $b = 7.10$, $c = 14.76 \text{ \AA}$; $\alpha = 99.00^\circ$, $\beta = 94.94^\circ$, $\gamma = 90.14^\circ$; and $V = 555 \text{ \AA}^3$, $Z = 1$. The strongest lines of the X-ray powder pattern [d , Å in $(I)(hkl)$] are: 14.5(100)(001), 3.455(40)(103), 3.382(35)(022), 2.921(35)(005), 2.810(40)(114), 2.683(90)(200, $\bar{2}01$), 2.133(80)($\bar{2}22$), 2.059(40)(204, $\bar{1}33$, 221), 1.772(30)(041, $\bar{1}27$, $\bar{2}32$, $\bar{2}33$). The infrared spectrum is demonstrated. An admixture of P substituting S has been detected in the innelite samples from the Inagli pluton (South Yakutia, Russia). An innelite–phosphoinnelite series with a variable S/P ratio has been discovered. The type material of phosphoinnelite has been deposited at the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow.

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INTRODUCTION

Peralkaline pegmatites of very uncommon mineralogy and geochemistry at the phlogopite deposit of the Kovdor ultramafic alkaline pluton, Kola Peninsula, Russia, have been known for a long time but are poorly documented. Only fragmentary data on these pegmatites can be found in the literature (Kukharensko et al., 1965; Rimskaya-Korsakova and Krasnova, 2002;

Ivanyuk et al., 2002). In recent years, we have studied in detail the mineralogy, geochemistry, and genetic features of these attractive rocks, which satisfy well the term *crossing pegmatite* proposed by A.E. Fersman for open granitic pegmatite systems and implying a contamination of fluid-saturated pegmatitic melt with host rocks of different chemical composition. In Kovdor, we have observed peralkaline crossing pegmatites (Chukanov et al., 2003), which form veins crosscutting calcite carbonatite, diopside–melilite and phlogopite–diopside–forsterite rocks. According to some researchers, these bodies are derivatives of the Lesser Kovdor pluton located nearby (Rimskaya-Korsakova and Krasnova, 2002). Our investigation demonstrates an abun-

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dance of pegmatitic veins at the Kovdor phlogopite deposit. The major geochemical feature of these pegmatites is the highly accentuated calcic specialization expressed already at the early, ultraperalkaline stage; as well, the Ca concentration increases with time with decreasing total alkalinity. Many minerals from these pegmatites are enriched in Ca. Cancrinite is a rock-forming feldspathoid instead of nepheline; Ca analogues occur instead of eudialyte; thomsonite-Ca, scolecite, and mesolite are the dominant zeolites (Pekov et al., 2004); pectolite and calcite are abundant. Owing to the effect of country carbonatite, CO_3 anion is contained in many pegmatitic minerals as a major (calcite) or auxiliary (cancrinite, golyshevite, mogovidite, and apatite) component. At the same time, similar pegmatites hosted in ijolite of the Kovdor pluton are distinguished by the absence of calcite and contain nepheline, "common" eudialyte and natrolite instead of cancrinite, Ca-rich eudialyte-like minerals, and calcic zeolites, respectively.

The geochemical singularity of the Kovdor crossing peralkaline pegmatites is because of their unusual mineralogy, which has been emphasized by the discovery of five new mineral species: three Ca-rich members of the eudialyte group, including feklchevite (Pekov et al., 2001), golyshevite, and mogovidite (Chukanov et al., 2005), and two layered Na,Ba-titanosilicates, nabalamprophyllite (Chukanov et al., 2004) and phosphoinnelite (this study). Phosphoinnelite is an analogue of innelite $\text{Ba}_4(\text{Na}, \text{Ca})_3\text{Ti}_3\text{Si}_4\text{O}_{14}(\text{SO}_4)_2(\text{O}, \text{OH}, \text{F})_4$ with (PO_4) prevailing over (SO_4) . The name phosphoinnelite was given to stress this specific chemical feature. The type specimen of phosphoinnelite has been deposited at the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow, registration number 3288/1.

MODE OF OCCURRENCE AND MORPHOLOGY

The new mineral species was found at the northeastern wall of the phlogopite open pit in a 10–15-cm thick vein of hydrothermally altered pegmatite that crosscuts calcite carbonatite with diopside, phlogopite, and apatite. Cancrinite (dominant), orthoclase, alkali pyroxene (aegirine-diopside), and pectolite are the major primary minerals, which have been retained in relatively unaltered segments of the pegmatite vein. Ca-bearing magnesioarfvedsonite, golyshevite (Ca-rich member of the eudialyte group with additional CO_3 anion), titanite, fluorapatite, and pyrrhotite are minor minerals. A 3–5-cm thick zone composed of coarse-grained calcite is impregnated with euhedral crystals of cancrinite, pectolite, golyshevite, pyroxene; CO_3 -bearing fluorapatite occurs at the contact of pegmatite vein with carbonatite. The hydrothermal alteration resulted in replacement of cancrinite, phlogopite, and pectolite with thomsonite-Ca, vermiculite, and smectite, respectively, and in crystallization of late-stage calcite.

Phosphoinnelite was found in small amounts within the inner portion of the vein. This mineral is hosted in

segregations of white or greenish thomsonite-Ca that replaces cancrinite. Relationships to other minerals indicate that phosphoinnelite belongs to the pegmatitic assemblage of pectolite, golyshevite, etc. This mineral has not been altered by the late hydrothermal fluids. The new mineral forms lath-shaped, split, and distorted crystals up to $0.2 \times 1 \times 6$ mm in size with skewed heads (Fig 1). The major form is probably the $\{010\}$ face (inferred from coincidence with the plane of the most perfect cleavage). Striation parallel to elongation is characteristic of these faces. Crystals of phosphoinnelite are combined typically in bunch-, sheaf-, and rosettelike segregations.

P-rich innelite with an S/P atomic ratio of 1.03 (Table 1, analysis 2) was observed in a small monomineralic apatite pocket within the same pegmatite. Innelite forms yellow–brown lath-shaped crystals up to 1 mm long, visually indistinguishable from phosphoinnelite.

PHYSICAL AND OPTICAL PROPERTIES

Phosphoinnelite is a transparent mineral with strong vitreous luster on crystal faces and a greasy luster on broken surfaces. The color of the mineral is yellow–brown, honey, and occasionally brown. The yellowish streak is very pale. Phosphoinnelite does not show fluorescence in either ultraviolet or cathode radiation. The mineral is brittle, with perfect cleavage parallel to the (010) and good cleavage parallel to the $\{100\}$; the fracture is stepped. The Mohs hardness is 4.5 to 5. The density measured by flotation in heavy liquids is $3.82(5)$ g/cm³; the calculated density is 3.92 g/cm³. Phosphoinnelite is biaxial positive with $\alpha = 1.730$, $\beta = 1.745$, and $\gamma = 1.764$; $2V$ (meas.) is close to 90° ; $2V$ (calc.) = 84° . Optical orientation: $Z \wedge c \sim 5^\circ$. Dispersion of optical axes is not observed. Microscopically, the mineral is colorless or pale yellowish and is not pleochroic.

INFRARED SPECTROSCOPY

The infrared-absorption spectrum of phosphoinnelite in water-free KBr disk with inserted mineral powder was measured with a Specord 75 IR spectrophotometer. Frequencies are measured with accuracy to ± 1 cm⁻¹; standards are polystyrene and gaseous ammonia. Absorption bands (cm⁻¹; frequencies of the strongest bands are underlined; sh is shoulder) are as follows: 1184, 1132, 1105sh, 1055sh, 1015, 946, 921, 866, 692, 665, 638, 614, 591, 553, 503, 453, and 392. The bands corresponding to the H_2O and OH vibrations are absent in the spectrum of the new mineral. The infrared spectrum of phosphoinnelite is very similar to that of innelite from the Inagli ultramafic alkaline pluton in southern Yakutia (Fig. 2). However, three bands corresponding to the S–O-stretching modes (1184, 1132, and 1105 sh cm⁻¹) are much weaker in the phosphoinnelite spectrum than similar bands in the innelite

Table 1. Chemical composition (wt %) of phosphoinnelite, innelite, and yoshimuraite

Component	Phosphoinnelite	Innelite			Yoshimuraite	
	1	2	3	4	5	6
Na ₂ O	6.06 (5.8–6.2)	5.83	5.76	5.63	0.16	bdl
K ₂ O	0.04 (0.0–0.2)	0.06	0.01	0.72	0.03	"
CaO	0.15 (0.1–0.2)	0.63	0.66	0.72		"
SrO	0.99 (0.5–1.4)	0.81	0.10		4.62	3.01
BaO	41.60 (40.3–43.0)	44.24	41.54	44.16	33.51	39.08
MgO	0.64 (0.2–0.9)	0.67	0.97	0.83	0.56	0.18
MnO	1.07 (0.6–1.5)	1.06	0.09	1.04	17.64	15.15
ZnO	bdl	bdl	bdl		0.50	bdl
FeO				0.57	1.47	
Fe ₂ O ₃	1.55 (1.3–2.1)	1.72	0.39	0.66	1.32	8.04
Al ₂ O ₃	0.27 (0.0–0.5)	0.10	0.09	0.23		bdl
SiO ₂	17.83 (17.6–18.3)	17.90	19.39	18.78	18.25	17.00
TiO ₂	16.88 (15.1–17.8)	15.64	16.98	18.50	10.00	8.12
Nb ₂ O ₅	0.74 (0.2–2.1)	0.78	0.16			bdl
P ₂ O ₅	5.93 (5.7–6.3)	5.11	4.51		3.98	4.21
SO ₃	5.29 (4.5–5.6)	5.96	6.93	7.19	5.40	3.92
H ₂ O ⁺				0.88	2.34	(1.23) calc.
F	0.14 (0.0–0.3)	0.56	0.16	0.40		
Cl	bdl	bdl	bdl		0.41	
–O=(F,Cl) ₂	–0.06	–0.24	–0.07	–0.17	–0.09	
Total	99.12	100.83	97.67	100.14	100.10	99.94

Notes: (1–2) Kovdor (original electron microprobe data): (1) average from 14 analyses; ranges of contents are given in parentheses; REE, V, and Ta contents are below detection limit (bdl); (2) single analysis; (3) Inagli (original electron microprobe data; REE, V, and Ta are below detection limit; (4) Inagli (chemical analysis, after Kravchenko et al., 1961); (5) Noda–Tamagawa Mine, Iwate Prefecture, Japan (chemical analysis, after Watanabe et al., 1961); (6) Taguchi Mine, Aichi Prefecture, Japan (electron microprobe data, after McDonald et al., 2000).

spectrum (1184, 1134, and 1092 cm^{–1}). In contrast to innelite, phosphoinnelite gives a band at 1055 cm^{–1} corresponding to the P–O-stretching vibrations. The strongest band corresponding to the Si–O-stretching modes (1015 cm^{–1}) in the infrared spectrum of phosphoinnelite is shifted to higher frequencies in comparison with innelite (1007 cm^{–1}). This may be caused by resonance between the Si–O- and P–O-stretching modes in phosphoinnelite. The similarity of infrared spectra of innelite from Inagli (absorption bands, cm^{–1}: 1184, 1134, 1092, 1007, 955, 913, 861, 638, 613, 590, 557, 505, 460, and 410) and phosphoinnelite from Kovdor indicates that the crystal structures of these mineral are identical; different intensities of bands corresponding to the Si–O- and P–O-stretching vibrations reflect a distinct S/P value.

CHEMICAL COMPOSITION

Chemical analyses of the new mineral were determined on a Camebax microbeam electron microprobe

operating at 20 kV and 20 nA, with a 3-μm beam diameter. The following standards were used: albite (Na), orthoclase (K, Al), CaSO₄ (Ca), SrSO₄ (Sr), BaSO₄ (Ba, S), Mg₂SiO₄ (Mg), MnTiO₃ (Mn, Ti), andradite (Fe, Si), LiNbO₃ (Nb), fluorapatite (P), MgF₂ (F). Water is not detected by direct methods due to lack of material.

The chemical composition of phosphoinnelite is given in Table 1. The empirical formula calculated on the basis of (Si,Al)₄O₁₄ by analogy with innelite (Chernov et al., 1971) and other members of the meroplesio-type bafertisite series (Ferraris et al., 2001) is (Ba_{3.59}Sr_{0.13}K_{0.01})_{Σ3.73}(Na_{2.59}Mg_{0.21}Mn_{0.20}Ca_{0.04})_{Σ3.04}(Ti_{2.80}Fe_{0.26}Nb_{0.07})_{Σ3.13}(Si_{3.93}Al_{0.07})_{Σ4}O₁₄[(P_{1.11}S_{0.87})_{Σ1.98}O_{7.96}](O_{2.975}F_{0.10})_{Σ3.075}. The simplified formula is Ba₄Na₃Ti₃Si₄O₁₄(PO₄,SO₄)₂(O,F)₃.

CRYSTALLOGRAPHY

Single-crystal X-ray study was impossible due to the low quality of phosphoinnelite crystals. X-ray powder pattern of the new mineral is practically identical to



Fig. 1. Lath-shaped crystals of phosphoinnelite in white thomsonitized cancrinite; the large crystal is 6 mm long. The Kovdor phlogopite deposit. Photo by N.A. Pekova.

that of innelite² (Table 2). By analogy with innelite (Table 3), phosphoinnelite was suggested to be triclinic, the space group is $P\bar{1}$ or $P1$, and the unit cell parameters are as follows: $a = 5.38(2)$, $b = 7.10(2)$, $c = 14.76(5)$ Å; $\alpha = 99.00(7)^\circ$, $\beta = 94.94(6)^\circ$, $\gamma = 90.14(8)^\circ$; $V = 555(1)$ Å³, $Z = 1$, $a : b : c = 0.7577 : 1 : 2.0789$.

DISCUSSION

Innelite is a layered titanosilicate, a member of the meroplesiotype bafertisite series (Ferraris et al., 2001). The crystal structure contains the *HOH* stack [formed by the octahedral (*O*) Ti–Na layers, which are sandwiched between two heteropolyhedral (*H*) layers consisting of $[\text{Si}_2\text{O}_7]$ pyrogroups and tetragonal pyramids centered by Ti] and interstack filling of Ba atoms and isolated (SO_4) tetrahedrons (Chernov et al., 1971). The structural identity of innelite and phosphoinnelite is confirmed by their close stoichiometry, unit cell parameters, X-ray powder patterns, infrared spectra, and physical properties, including optical parameters (Tables 1–3). The difference between these minerals lies in the P/S value.

Innelite was described from the Inagli pegmatites as a P-free mineral with the site within isolated tetrahedrons (XO_4) occupied only by S atoms (Kravchenko et al., 1961; Efimov et al., 1963; Chernov et al., 1971); see analysis 4 in Table 1. We have additionally studied several samples of the Inagli innelite, which are distinguished in morphology and color. This study showed that the samples contain an admixture of phosphorus that is occasionally significant, but $\text{S} > \text{P}$ in all samples.

² X-ray powder pattern of catapleiite was given falsely in the first description of innelite (Kravchenko et al., 1961) and reproduced in the JCPDS–ICDD catalogue, card No. 15-71 (innelite). The true X-ray powder patterns of innelite are listed in the subsequent publications (Efimov et al., 1963; Raade and Berg, 2000; JCPDS–ICDD catalogue, card No. 73-755).

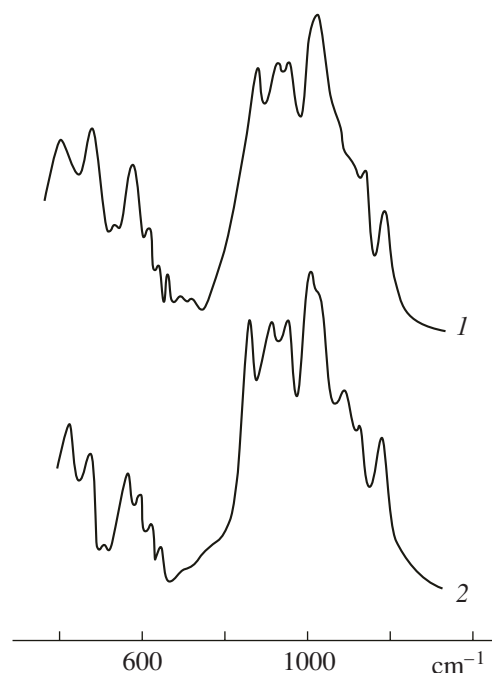


Fig. 2. Infrared spectra of phosphoinnelite from Kovdor (1) and innelite from Inagli (2).

As was mentioned above, P-rich innelite was found in Kovdor in apatite pockets hosted in phosphoinnelite-bearing pegmatite. The partitioning of P and S between simultaneously crystallizing phosphate (apatite) and phosphate–sulfate–silicate (innelite) probably took place. Typical compositions of the P-rich innelite from Inagli and Kovdor are shown in Table 1 (analyses 2 and 3). The negative correlation between P and S in innelite and phosphoinnelite at a constant Si content indicates that phosphorus is localized solely in isolated tetrahedrons (XO_4) replacing sulfur. General crystallochemical reasoning testifies in favor of this assumption. In light of the second Pauling rule, incorporation of P^{5+} and, all the more so, S^{6+} into the $[\text{Si}_2\text{O}_7]$ pyrogroup instead of Si^{4+} is unlikely due to the appearance of excess positive charge at the oxygen bridge.

Thus, a continuous innelite–phosphoinnelite isomorphous series with a variable P/S ratio is established, and innelite from Kovdor with $\text{S/P} = 1.03$ (Table 1, analysis 2) is close in composition to the midpoint of this series.

A similar isomorphic substitution of (SO_4) with (PO_4) in interlayer isolated tetrahedrons (XO_4) was established by McDonald et al. (2000) in yoshimuraite $\text{Ba}_4\text{Mn}_4\text{Ti}_2\text{Si}_4\text{O}_{14}(\text{PO}_4, \text{SO}_4)_2(\text{O}, \text{OH})_4$, which is closely related to innelite in stoichiometry, unit cell dimensions (Table 3), and crystal structure. These minerals differ only in the composition of the octahedral layer (*O*). Yoshimuraite contains $(\text{Mn}, \text{Fe})_4$ instead of $\text{Ti}(\text{Na}, \text{Ca})_3$ in innelite. The structural formula of the studied yoshimuraite sample is

Table 2. X-ray powder-diffraction data on phosphoinnelite and innelite

1			2		3		4		<i>hkl</i>
<i>I</i> _{meas}	<i>d</i> _{meas} , Å	<i>d</i> _{calc} , Å	<i>I</i> _{meas}	<i>d</i> _{meas} , Å	<i>I</i> _{meas}	<i>d</i> _{meas} , Å	<i>I</i> _{calc}	<i>d</i> _{meas} , Å	
100	14.5	14.52	100	14.7	95	14.327	100	14.52	001
					26	7.214	0.2	7.261	002
					51	4.831	8	4.841	003
					6	4.259	4	4.261	$\bar{1}\bar{1}1$
20	4.18	4.145	40	4.20	15	4.150	17	4.147	$\bar{1}\bar{1}1$
20	3.95	3.943	30	3.95	21	3.923	28	3.954	$\bar{1}\bar{1}2$
20	3.735	3.738	40	3.71	15	3.738	14	3.738	$\bar{1}\bar{1}2$
					6	3.645	21	3.657	$\bar{1}\bar{1}2$
					7	3.542	10	3.557	0 $\bar{2}1$
					10	3.523	0.3	3.526	020
40	3.455	3.417	40	3.48	21	3.455	4	3.444	103
					14	3.433	31	3.424	112
35	3.382	3.371	80	3.37	19	3.350	23	3.388	0 $\bar{2}2$
					21	3.330	4	3.309	021
					44	3.247	3	3.253	$\bar{1}\bar{1}3$
					7	3.177	27	3.174	$\bar{1}\bar{1}3$
10	3.125	3.136	30	3.10	29	3.127	6	3.137	$\bar{1}04$
					9	3.078	21	3.090	023
5	3.008	3.008			14	2.9824	12	3.012	$\bar{1}\bar{1}4$
35	2.921	2.904			100	2.9049	18	2.904	005
					16	2.8626	5	2.858	$\bar{1}2\bar{1}$
					18	2.8132	10	2.828	$\bar{1}22$
40	2.810	2.808	70	2.810	28	2.8003	16	2.807	$\bar{1}\bar{1}4$
					20	2.7778	18	2.775	121
90	2.683	2.680, 2.677	100	2.709	79	2.6857	17, 22	2.680, 2.678	200, $\bar{2}01$
10	2.600	2.601	10	2.593	7	2.5876	9	2.603	$\bar{1}\bar{1}5$
					7	2.4868	4	2.508	124
10	2.387	2.393, 2.387, 2.344	20	2.362			2, 2, 3	2.396, 2.379, 2.351	$\bar{1}24$, $\bar{1}\bar{1}5$, 024
20	2.262	2.252	30	2.274	16	2.2501	8	2.253	$\bar{2}04$
10	2.209	2.184			9	2.1882	5	2.186	016
80	2.133	2.131, 2.131, 2.124	90	2.140	42	2.1277	7	2.131	$\bar{2}22$
					16	2.0683	7	2.074	$\bar{2}22$
40	2.059	2.071, 2.054, 2.043	30	2.072	22	2.0592	6, 4, 5	2.070, 2.061, 2.050	204, $\bar{1}33$, 221
25	1.994	1.999, 1.986	20	2.010			5, 3	2.008, 1.995	$\bar{1}34$, 033
5	1.909	1.909					2	1.911	017
10	1.832	1.838, 1.831					3, 2	1.845, 1.836	034, 0 $\bar{3}6$
30	1.772	1.774, 1.770, 1.750, 1.744	40	1.790			8, 2, 2	1.784, 1.770,	0 $\bar{4}1$, $\bar{1}27$, $\bar{2}32$,
							2	1.753, 1.751	$\bar{2}33$
15	1.532	1.532					3	1.534	$\bar{1}29$
10	1.478	1.478, 1.477, 1.475					3,2,2	1.482, 1.482, 1.478	$\bar{2}40$, 234, $\bar{2}35$
5	1.451	1.452					3	1.452	0.0.10
5	1.350	1.359, 1.349					1, 1	1.361, 1.349	$\bar{3}27$, $\bar{1}2.10$

Notes: (1) phosphoinnelite, Kovdor (RKU-114.6 camera, FeK $_{\alpha}$ radiation, Mn filter); (2) P-bearing innelite, Inagli (RKG-86 camera, FeK $_{\alpha}$ radiation, Mn filter, original data); (3) innelite, Inagli (Siemens D5005 diffractometer, CuK $_{\alpha_1}$ radiation, after Raade and Berg, 2000); (4) theoretical XRD pattern calculated from structural data of innelite (Chernov et al., 1971) using a LAZY PULVERIX program (Yvon et al., 1977).

Table 3. Comparative characteristics of phosphoinnelite, innelite, and yoshimuraite

Property	Phosphoinnelite	Innelite	Yoshimuraite
Simplified formula	$\text{Ba}_4\text{Na}_3\text{Ti}_3\text{Si}_4\text{O}_{14}(\text{PO}_4, \text{SO}_4)_2(\text{O}, \text{F})_3$	$\text{Ba}_4(\text{Na}, \text{Ca})_3\text{Ti}_3\text{Si}_4\text{O}_{14}(\text{SO}_4)_2(\text{O}, \text{OH}, \text{F})_4$	$\text{Ba}_4\text{Mn}_4\text{Ti}_2\text{Si}_4\text{O}_{14}(\text{PO}_4, \text{SO}_4)_2(\text{O}, \text{OH})_4$
Symmetry	triclinic	triclinic	triclinic
Space group	$P1$ or $P\bar{1}$	$P1$	$P\bar{1}$
Unit cell parameters			
a , Å	5.38	5.38	5.386
b , Å	7.10	7.14	6.999
c , Å	14.76	14.76	14.748
α , °	99.00	99	90.0
β , °	94.94	95	93.6
γ , °	90.14	90	95.5
Z	1	1	1
Optical parameters			
N_p	1.730	1.726	1.763–1.768
N_m	1.745	1.737	1.777
N_g	1.764	1.766	1.785–1.794
$2V$	+84° (calc.)	+82°	+(80–90°)
Source	This study	Kravchenko et al. (1961); Chernov et al. (1971)	Watanabe et al., 1961; Hirowatari, Isono, 1966; McDonald et al., 2000

$(\text{Ba}_{3.90}\text{Sr}_{0.56})\{(\text{Mn}_{3.28}\text{Fe}_{0.98}\text{Mg}_{0.06})[(\text{Ti}_{1.56}\text{Fe}_{0.44})\text{O}_2\text{Si}_4\text{O}_{14}(\text{OH})_2](\text{P}_{0.46}\text{S}_{0.34}\text{Si}_{0.17})\text{O}_4)_2$ (McDonald et al., 2000). Analyses of yoshimuraite both with $P > S$ and $S > P$ are known (Table 3, analyses 5 and 6; Watanabe et al., 1961; Hirowatari and Isono, 1966; McDonald et al., 2000). Like the innelite–phosphoinnelite series, a continuous innelite–yoshimuraite solid solution series with a variable S/P ratio probably exists.

On the basis of cation composition and by analogy with innelite, the simplified formula of phosphoinnelite was suggested as $\text{Ba}_4\text{Na}_3\text{Ti}_3\text{Si}_4\text{O}_{14}(\text{PO}_4, \text{SO}_4)_2(\text{O}, \text{OH}, \text{F})_4$. However, an IR study showed the absence of OH-groups and H_2O molecules. Hence, compensation of charge disbalance arising due to the substitution of $(\text{PO}_4)^{3-}$ with $(\text{SO}_4)^{2-}$ by replacing of equivalent part of $\text{O}^{2-}(\text{OH})^-$ or $(\text{H}_2\text{O})^0$ is impossible. Thus, the charge-balanced simplified formula of phosphoinnelite appears as $\text{Ba}_4\text{Na}_3\text{Ti}_3\text{Si}_4\text{O}_{14}(\text{PO}_4, \text{SO}_4)_2(\text{O}, \text{F})_3$, which probably implies $\text{Ba}_4\text{Na}_3\text{Ti}_3\text{Si}_4\text{O}_{14}(\text{PO}_4, \text{SO}_4)_2(\text{O}, \square, \text{F})_4$.

The similarity of peralkaline pegmatites from Inagli (Efimov et al., 1963), where innelite has been discovered, and Kovdor (especially concerning accessory and late hydrothermal mineralization) is conspicuous. The rare minerals pertaining to the batisite–“K-batisite” and innelite–phosphoinnelite series, which are not characteristic of other alkaline plutons, were found both in Inagli and Kovdor. Nabalamprophyllite and aqualite were described so far only from these two localities.

Aqualite is a mineral of the eudialyte group strongly depleted in Na, Fe, and Mn and enriched in K, Ba, and (SO_4) (Johnsen et al., 2003; Pekov, 2005). Thomsonitization is the leading late process in pegmatites both in Kovdor and Inagli (Efimov et al., 1963; Pekov et al., 2004). Taking such a similarity into account, it is expedient to recognize a special mineralogical–geochemical type of peralkaline pegmatites genetically related to the ultramafic alkaline plutons in ancient crystalline shields.

Accessory mineralization in the studied Kovdor pegmatites is markedly enriched in barium. The enrichment of pegmatites in barium minerals relative to strontium species attracts special attention, because the rocks of the Kovdor pluton are distinguished by an elevated Sr content (Kukharensko et al., 1965). Most likely, this is caused by the important role of CO_2 , which promotes partition of barium, which concentrates in silicate form, and strontium, which largely accumulates in carbonates in the mineral-forming system of the crossing pegmatites (Pekov, 2005). Thomsonite from the Kovdor pegmatites is indeed strongly depleted in Sr in comparison with that from Inagli (Pekov et al., 2004), where carbonates are not abundant in both pegmatites and host rocks. The low-Sr apatite from the Kovdor pegmatites opposes the strontiumapatite abundant in Inagli. At the same time, calcite from the Kovdor carbonate that is crossed by pegmatites is characterized by an elevated Sr content (Chukanov et al., 2004). In the Kovdor pegmatites, barium concentrates in sili-

cates, including potassium batisite (19 wt % BaO), nabalamprophyllite (25 to 26 wt % BaO), and members of the innelite–phosphoinnelite series (41 to 44 wt % BaO). Kovdor aqualite contains 2 wt % BaO (Pekov, 2005), which is the highest concentration of this element in minerals of the eudialyte group. At the same time, the Sr content in the Ba-rich silicates from these pegmatites does not exceed 1 wt % SrO.

The occurrence of phosphoinnelite and P-rich innelite in Kovdor pegmatites emphasizes the geochemical specialization of this ultramafic alkaline pluton, where apatite–magnetite–forsterite rocks are abundant and the apatite deposit is being mined, while the Inagli pluton is relatively depleted in phosphorus.

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