

The first occurrence of qandilite in Russia

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Abstract

Numerous small octahedra of a black, brittle, magnetic mineral were found in calciphyre and brucite marble, occurring in the northern part of the exocontact zone of the Kondyor ultramafic-alkalic massif (south-eastern part of the Aldan Shield, 250 km north west of sea port Ayan). Their composition corresponds to the group from titanium magnesioferrite (11.53% TiO₂) to titanium-rich magnesian spinel (27.34% TiO₂), similar to spinellide found in Greenland (Gittins *et al.*, 1982) and in Iraq (Al-Hermezi, 1985) and approved by the Commission on New Minerals as a new mineral named qandilite. Hardness, specific gravity, and reflectance of Kondyor qandilite are similar to those of the Iraq mineral. Peaks of IR-absorption spectra are equal to 580–590 cm⁻¹ (ν₁) and 431–438 cm⁻¹ (ν₂). There is a positive correlation between lattice parameters and the amount of Mg₂TiO₄: from 8.368 Å at 26.6% to 8.429 Å at 60.4%. Kondyor qandilite crystallized together with geikielite, oxidized alumina spinel (8.55% Fe₂O₃, f_{total} = 16.5%), periclase, and forsterite.

KEYWORDS: qandilite, Ti-spinellide, Kondyor, Russia.

Introduction

ALTHOUGH the end-members of (Mg,Fe)-Ti spinellide group were synthesized long ago, they have not been reported as occurring in nature as pure minerals. Whereas the absence of ulvöspinel (Fe₂²⁺TiO₄) is easily explained by its rapid oxidation to ilmenite, rare occurrences of Mg₂TiO₄ seem to be due to specific geochemical conditions of their genesis. Spinellides containing up to 32 mole% of Mg₂TiO₄ are known from carbonates but compositions close to the end-member (60 to 83 mole%) are known only from two skarns formed by contact metamorphism of dolomitic limestone. Qandilite is associated with forsterite, spinel, geikielite, perovskite, and periclase (Gittins *et al.*, 1982; Al-Hermezi, 1985). The Commission on New Minerals approved the name qandilite for spinel from Iraq (Al-Hermezi, 1985) as a new end-member of the (Mg,Fe)-Ti group, though it contains Mg₂TiO₄ 59.3, MgAl₂O₄ 9, MgFe₂O₄ 5, and FeFe₂O₄ 25 mole%. Thus, a problem arises, whether to use this name for the Mg₂TiO₄ end-member only or for any spinellide rich in this component. We use the second version.

Geological setting

We discovered qandilite in the contact aureole of the ring alkalic ultramafic Kondyor massif in

the south-eastern margin of the Aldan Shield (Fig. 1). The core of this massif consists of dunite surrounded by olivine and apatite-bearing clinopyroxenite which grades in some places into gabbro-monzonite (Andreev, 1987). As in the dunite core, there are also cross-cutting bodies of fine-grained and pegmatoid nepheline-syenite.

Similar to the previously described occurrences, qandilite occurs in dolomitic calciphyre and brucite marble at the northern contact of the massif, where they make up a series of stratiform bodies up to 40 m thick in biotite-cordierite and biotite-garnet schistose hornfels, replacing siltstone, which was reliably identified by its relics in hornfels. Marble and calciphyre bodies occur at a distance of up to 100 m from the Kondyor endocontact pyroxenites. Immediately at the contact with ultramafic rocks within the zone of maximum temperatures, fine- to medium-grained marble and calciphyre grade into coarse-grained monticellite skarns with perovskite and pleonaste and into medium-grained monticellite-melilite and grossular-fassaite skarns. Our studies have shown that oxygen isotopic composition of carbonates substantially decreases with the increase of temperature: from 17–20‰ ¹⁸O in marble to 10‰ ¹⁸O in monticellite skarn containing perovskite (analysed by V. I. Kiselev).

The studied calciphyre samples are composed of predominant calcite and larger tabular dolo-



Fig. 1. The location of qandilite occurrences.

mite grains (up to 15%). Abundant forsterite (up to 20%) and brownish-yellow spinel (up to 10%) form separate rounded grains and intimate intergrowths. Isometric and rarely tabular grains of monoclinic pyrrhotite (up to 2.5%) 0.2 to 0.9 mm in size are homogeneously distributed throughout the rock. Brucite marble differs from calciphyre in containing up to 40% of rounded brucite pseudomorphs after periclase and lower amounts of spinel and forsterite.

Physical and chemical properties

Qandilite in Kondyor calciphyre and marble occurs in layers 1 to 1.5 cm thick, rich in forsterite and spinel (sometimes pyrrhotite); where it constitutes up to 2.5% and was previously mistaken for magnetite (Andreev, 1987). It forms separate isometric grains and octahedra 0.03 to 0.35 mm in size, homogeneously dispersed in the rock. It contains inclusions of calcite, brownish-

yellow spinel, and forsterite; sometimes it is embedded in spinel and forsterite. Qandilite is black and has a black streak; it is brittle, opaque, and strongly magnetic. VHN_{70} is 750 to 800 kg/mm^2 (Sample 182) and 750 kg/mm^2 (Sample 184). The lower VHN, compared with that of the Iraq analogue ($VHN_{100} = 960-1045 kg/mm^2$) (Al-Hermezi, 1985), is presumably due to either a significant amount of MnO in one Kondyor qandilite sample (2.69%, Sample 182), or a lower Ti content in another sample (Sample 184), transitional to magnesio-ferrite characterized by lower VHN. The specific gravity determined on these two qandilite samples is 4.03 and 4.08 g/cm^3 , respectively. In reflected light, Kondyor qandilite is grey and isotropic. Reflectance in air (%), measured from 700 μm at an interval of 60 μm , is 15.1-14.6, 14.4-13.9, 14.8-13.5, 13.3-13.0 and 13.2-12.9 for Samples 182 and 184, respectively.

The reflectance spectrum of Sample 182 is close to that of Iraq qandilite (Al-Hermezi, 1985); reflectance increases with a decrease of TiO_2 content.

IR-absorption spectra of Kondyor qandilite (Fig. 2) (analysed by G. A. Narnov) have two peaks (ν_1 and ν_2), showing atomic variations in tetrahedra and octahedra of spinellides (Waldron, 1955). In Samples 179, 184, 182, 186, and 188, their values are (cm^{-1}): ν_1 —580, 580, 585, 595, and 595; ν_2 —431, 431, 433, 435, and 433, respectively; i.e. we observe the shift of absorption peaks into the short wavelength area accompanied by an increase in the titanium content, which is in the octahedral position; isomorphous substitutions in that position have the main influence upon the position of absorption spectral

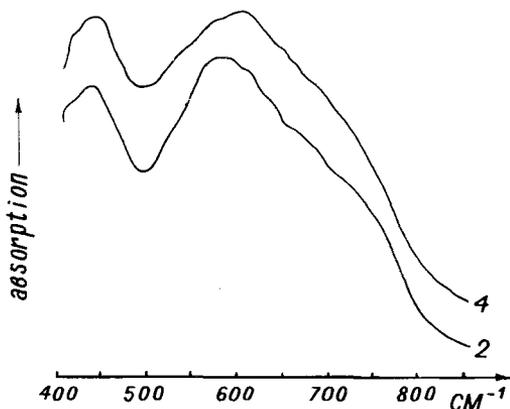


Fig. 2. IR-spectra of qandilite. For numbers of the samples see Table 1.

lines (Khudolozhkin *et al.*, 1986). All points of studied spinellides fall on the Mg_2TiO_4 - $MgFe_2O_4$ line.

Chemical analyses of studied spinellides yield a group from qandilite (Nos. 1-3, Table 1, Fig. 3), containing 21.07 to 27.34% TiO_2 , to titanium magnesioferrite (11.5 to 12.9% TiO_2) (N 1, 2), containing more Al_2O_3 , somewhat less MgO , and variable MnO . The calculations of iron valence are based on the assumption that all titanium was incorporated in the spinellide structure as an Mg_2TiO_4 component. Perfect agreement between the calculated iron valence and that obtained for Iraq qandilite by chemical analysis and the alignment of points of every studied spinellide along the Mg_2TiO_4 - $MgFe_2^{3+}O_4$ line (Fig. 3) are evidence for the validity of that assumption. As testified by precision measurements of lattice parameters, this is valid only for spinellides with low and moderate Ti contents (Table 1, Fig. 4). For the spinellides containing 0.0 to 0.5 formula unit Ti, there is a good agreement between

measured and calculated a_0 values, and for minerals with higher Ti contents, the difference between them becomes substantial. The majority of points in the diagram (Fig. 4) fall below the Mg_2TiO_4 - $MgFe_2^{3+}O_4$ line, caused by addition of $MgAl_2O_4$ component with low a_0 parameter (8.08 Å). With increase of Ti content, some titanium could be incorporated in the structure as Fe_2TiO_4 ($a_0 = 8.52$ Å), compensating for the effect of $MgAl_2O_4$; thus, the calculations of iron valence for that area could be erroneous. The calculation using the difference between calculated and measured a_0 shows that approximately 20% Ti should be in the form of Fe_2TiO_4 for that spinellide area.

Discussion

Table 1 shows that the content of the magnesioferrite component decreases from 47.9 to 4.8% in the titanium magnesioferrite to the qandilite

Table 1.

Chemical composition and lattice parameter of the qandilite and coexisting minerals

Component	1	2	3	4	5	6	7	8	9	10	11	12
TiO_2	11.53	12.93	21.07	24.32	27.34	26.41	38.58	18.26	6.96	0.51	1.19	61.51
Al_2O_3	7.76	6.13	4.85	4.92	3.33	4.83	2.75	3.56	2.74	69.97	62.11	3.59
Cr_2O_3	0.07	0.06	-	0.07	0.13	0.00	-	-	-	-	-	-
Fe_2O_3	51.16	48.21	39.28	33.05	27.01	28.27	11.82	38.50	53.66	0.00	8.55	0.00
FeO	2.60	9.76	1.44	7.42	14.62	10.32	6.26	16.92	10.84	3.78	1.59	3.78
MnO	1.90	0.48	2.69	0.97	1.89	0.76	0.41	0.81	0.26	0.13	0.00	0.27
MgO	25.09	21.90	30.75	30.13	26.47	29.62	39.09	20.48	16.58	25.93	26.16	31.09
Total	100.11	99.41	100.21	100.89	100.79	100.21	99.21	99.30	97.41	100.51	99.60	100.24
Mg_2TiO_4	26.6	30.9	47.2	54.3	60.4	59.3	82.9	44.4	17.9	0.9	2.2	0.00
$MgAl_2O_4$	14.0	11.1	6.6	8.6	0.0	8.6	0.7	6.8	5.5	91.2	90.8	0.0
$MnFe_2O_4$	5.0	1.3	6.6	2.5	5.0	2.0	1.0	2.1	0.8	0.0	0.0	0.0
$MgFe_2O_4$	47.9	30.3	34.1	16.4	0.0	4.8	0.0	3.3	43.1	0.0	1.5	0.0
$FeFe_2O_4$	6.5	25.9	3.4	18.2	26.2	25.3	11.4	42.8	32.7	0.0	5.4	0.0
f_o	94.7	81.6	96.1	80.1	62.5	71.1	63.0	67.2	74.1	0.0	82.9	0.0
a_o (Å) m	8.368	8.378	8.390	8.409	8.429	8.403	-	-	-	-	-	-
a_o (Å) c	8.363	8.372	8.393	8.395	8.416	8.399	8.422	8.398	8.382	8.087	0.105	-

Note on Table 1. Kondyor titanium magnesioferrite - 1,2 and qandilite - 3-5, Samples 179, 184, 182, 186, and 188, respectively; Iraq qandilite - 6 (Al-Hermezi, 1985); East Greenland qandilite - 7,8 and titanium magnesioferrite - 9 (Gittings *et al.*, 1982); Kondyor spinel - 10, 11 and geikielite - 12, associated with qandilite, Samples 182, 188, and 186, respectively.

Analysed by V.I.Sapin and V.I.Taskaev (JXXI-5A microprobe) and T.B.Afanasyeva (a_o). Calculated end members: $MnAl_2O_4$ (0.3%) for 10; $Fe_2Al_2O_4$ (6.0 and 3.9%) for 5 and 7 respectively; Fe_2TiO_4 (2.4%) for 5; FeV_2O_4 (0.5%) for 8; $FeTiO_3$ (7.2%) and $MnTiO_3$ (0.4%) for 12. a_o - measured (m) and calculated (c) lattice parameter; $f_o = Fe^{3+} / \sum Fe$ (at %).

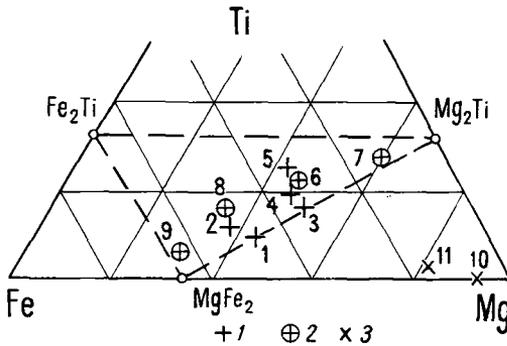


FIG. 3. The compositions of titanium magnesioferrite, qandilite (1—Kondor; 2—Iraq and East Greenland), and alumina spinel (3) associated with qandilite (at. %). Figures correspond to Table 1.

group and completely disappears in Sample 188 which has the highest TiO_2 content (27.3%). The name of a natural end-member of the magnesium-spinel group is most appropriate for the last composition lacking magnesioferrite molecule, despite a decreased content of MgO (26.47%) resulting in the presence of hercynite and ulvöspinel components. On the other hand, these samples have 'excess' TiO_2 relative to MgO (Table 1), which results in the shift of their points to the $\text{Mg}_2\text{TiO}_4\text{--Fe}_2\text{TiO}_4$ line. In these samples

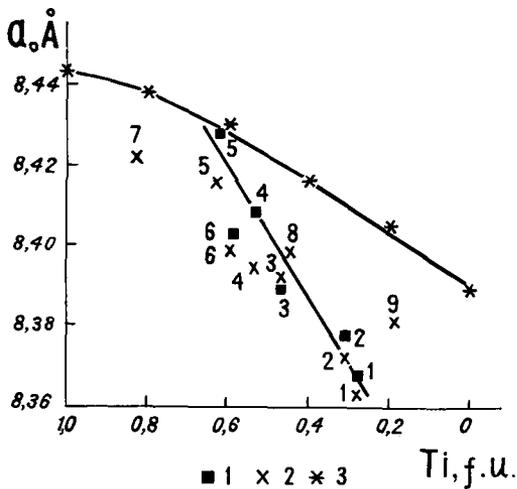


FIG. 4. Lattice parameter of qandilite and titanium magnesioferrite versus titanium content. 1—measured; 2—calculated; 3—parameter of synthetic species of $\text{Mg}_2\text{TiO}_4\text{--MgFe}_2\text{O}_4$ group, according to Urusov and Karabtsov (1983). For numbers of samples see Table 1. F.U. — formula units based on 4 oxygen atoms.

(186, 184), high-magnesian geikielite (Table 1, N 12) and oxidized pleonaste ($\text{Fe}^{3+}/\Sigma\text{Fe} = 82.9$ at.%, Table 1, N 11) are associated with the highest titanium qandilite, whereas alumina spinel (Table 1), N 10) is associated with lower titanium qandilite (Sample 182). Similar regularities were observed for Iraq and Greenland qandilite and titanium magnesioferrite (Table 1, N 6–9).

Thermodynamic conditions of qandilite crystallization have been inferred. High oxidation grade of both qandilite and alumina spinel undoubtedly suggests oxidizing conditions of crystallization; the synthesis of the whole $\text{Mg}_2\text{TiO}_4\text{--MgFe}_2^{3+}\text{O}_4$ group in air supports this view (Urusov and Karabtsov, 1983). The presence of both MgFe_2O_4 and FeFe_2O_4 components in qandilite is evidence for its crystallization at the boundary of the magnetite–hematite field, which corresponds to $f_{\text{O}_2} = 10^{-11}$ to 10^{-18} bar for the temperature range from 700 to 800 °C. The reaction of dolomite dissociation into calcite and periclase occurring at 830 °C (1 kbar) determines the temperature of qandilite crystallization. No qandilite was identified in higher temperature monticellite skarns containing perovskite and pleonaste. The thickness of overlying rocks (Andreev, 1987) suggests that the qandilite assemblages formed below 0.5 kbar. Thus, thermodynamic conditions of qandilite stability correspond to magnesium skarn facies, i.e. increased T and f_{O_2} and low P .

The geological setting of the qandilite occurrences shows that it formed in the carbonate rocks rich in titanium and magnesium and poor in iron. The appearance of titanium which prefers a clastic form in chemogenic or biogenic rocks is not clear. All qandilite occurrences are at the contact of dolomitic limestones and alkalic intrusions enriched in titanium, suggesting a fluid supply with titanium to the host rocks. But in the Kondyor calciphyre and marble, qandilite is found only in thin (1–1.5 cm) layers far from the contact with intrusive body. As in the previous qandilite occurrences, no signs of titanium metasomatism were observed in that zone even directly at the contact.

At the same time, thin layers enriched in titanium are rather common in carbonate sediments of every epoch. Such a layer 1.5 to 2 cm thick was drilled in the Pacific and studied in detail (Shcheka, 1981). There, an enrichment in the titanium of the neogene calcareous muds was caused by the presence of small grains of high-titanium varieties of glass, magnetite, pyroxene and amphibole. A source of the clasts is established to be alkali basalt explosives from adjacent islands. The presence of alkalic explosive breccias

in the host rocks of the Kondyor massive suggests that the source of titanium was the same.

Thus, in both Kondyor carbonate rocks and other cases, volcanic explosives are presumably the source of titanium in carbonate sediments altered together with carbonate material during later contact metamorphism. A relative rarity of such conditions (the combination of high titanium and magnesium contents) probably explains the rarity of qandilite occurrences in nature.

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