Magnesioneptunite, $\text{KNa}_2\text{Li(Mg,Fe)}_2\text{Ti}_2\text{Si}_8\text{O}_{24}$, a New Mineral Species of the Neptunite Group


A new mineral of the neptunite group, magnesioneptunite $\text{KNa}_2\text{Li(Mg,Fe)}_2\text{Ti}_2\text{Si}_8\text{O}_{24}$, a Mg-dominant analogue of neptunite and manganoneptunite, has been found in the Upper Chegem caldera near Mount Lakargi, Kabardino-Balkaria, the North Caucasus, Russia in a xenolith of altered sandstone located between skarnified carbonate xenoliths and ignimbrites. Magnesioneptunite occurs as nearly isometric grains and aggregates up to 0.1 mm in size in the cores of some grains of a Mg-rich variety of neptunite with Mg/(Fe + Mn) = 0.7–1.0. The chemical composition of magnesioneptunite with a maximum Mg content is as follows, wt%: 3.63 K$_2$O, 8.21 Na$_2$O, 1.73 Li$_2$O, 6.47 MgO, 0.04 MnO, 5.87 FeO, 0.07 Al$_2$O$_3$, 18.73 TiO$_2$, 56.88 SiO$_2$, 99.62 in total. The empirical formula is $(\text{K}_{0.67}\text{Na}_{0.32}\text{Ca}_{0.01})\Sigma_{1.00}\text{Fe}_{0.71}\text{Mg}_{1.39}\text{Ti}_{2.10}\text{Si}_{7.90}\text{Al}_{0.01}\text{O}_{24}\cdot$$(\text{Mg}_{1.39}\text{Fe}_{0.71}\text{Si}_{7.90}\text{Al}_{0.01})\Sigma_{2.10}\text{O}_{24}$. Grains of magnesioneptunite are dark brown to red-brown, translucent, with vitreous luster. $D_{\text{calc}} = 3.15$ g/cm$^3$, and the Mohs hardness is 5–6. Cleavage parallel to the (110) is perfect. The new mineral is optically biaxial, positive, $\alpha = 1.697(2)$, $\beta = 1.708(3)$, $\gamma = 1.725(3)$, $2V_\text{meas} = 45(15)^\circ$. The mineral is associated with quartz, alkali feldspar, rutile, aegirine, and neptunite. Magnesioneptunite and the Mg-rich variety of neptunite were formed as products of ilmenite alteration. Magnesioneptunite is monoclinic, $C2/c$; unit-cell parameters: $a = 16.327(7)$, $b = 12.4788(4)$, $c = 9.9666(4)$ Å, $\beta = 115.6519(5)^\circ$, $V = 1830.5(1)$ Å$^3$, $Z = 4$. The type specimen is deposited at the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow.

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INTRODUCTION

A new mineral magnesioneptunite was discovered at the interfluence of the Chegem and Kestanty rivers near Mount Lakargi in the Upper Chegem volcanic caldera located in the mountain part of Kabardino-Balkaria, the North Caucasus, Russia. The Upper Chegem caldera is about 110 km$^2$ in area with several volcanic centers of different ages. A sequence of rhyolites and rhyodacitic ignimbrites and tuffs 1.5 km thick intruded by granodiorite porphyry stock occupy the lower part of the volcanic edifice. The volcanic rocks are covered by moraine of Mindel glaciation, in turn, overlapped by lava flows of two-pyroxene andesite. The K/Ar age of ignimbrite is 2.8–3.0 Ma; the age of granodiorite porphyry is 2.5 ± 0.2 Ma (Borsuk, 1979) or 2.7 Ma (Ar–Ar method) (Lipman et al., 1993; Gazis et al., 1995).

Large xenoliths of marmorized and skarnified limestone, dolomite, mudstone, and siltstone were found on the eroded surface of the volcanic edifice close to the crest of a small ridge between the Lakargi and Vorlan peaks. The size of carbonate xenoliths ranges from a few meters to a few tens of meters; mudstone and siltstone xenoliths reach a few meters across (Gazeev et al., 2006). Carbonate xenoliths have been studied in more detail. Marble cores and skarn envelopes are distinguished. These xenoliths were repeatedly described in connection with new minerals found therein: calcioilivine $\gamma$-$\text{Ca}_2\text{SiO}_4$ (Zadov et al., 2008), lakargiite $\text{CaZrO}_3$ (Galuskin et al., 2008), chegemite $\text{Ca}_4(\text{SiO}_4)_3(\text{OH})_2$ (Galuskin et al., 2009), kumtyubeite $\text{Ca}_4(\text{SiO}_4)_3\text{F}_2$ (Galuskin et al., 2009), bitikleite-
(ZrFe), and bitikleite-(SnAl) (Galuskina et al., 2010). The location of the xenoliths and their numeration were published by Galuskin et al. (2009). In contrast to the aforementioned minerals, magnesioneptunite was found in the altered sandstone separating carbonate larnite–cupsidine skarn of xenolith no. 5 and host ignimbrite rather than in the skarn itself.

In the type locality of magnesioneptunite, fragments of sand, hornfels after sandstone, and unaltered arkosic sandstone were found as a residual material. The contact of carbonate xenolith with rhyodacitic ignimbrite is stripped there. Fragments of sandstone up to 10–15 cm in size are traced along the contact between ignimbrite and sand, and relics of reaction zones with both contacting rocks are observed in some fragments. The fine-grained, substantially quartz sandstone, occasionally with small quartz pebbles, is composed of angular and rounded quartz grains, minor potassic feldspar, and sodic plagioclase. Sandstone is enriched in Cs (up to 0.5 ppm), which concentrates in the micrograins of pollucite and Cs-bearing analcime. The texture of sandstone is inequigranular psammitic with basal and less frequent reaction zones with both contacting rocks are observed in some fragments. The fine-grained magnesianeptunite, visually indistinguishable Mg–rich variety of neptunite (Table 1) were identified in altered sandstone (hornfels) containing SiO₂, CaO, and a little Na₂O and K₂O. The minerals of neptunite–magnestonite (glass) containing SiO₂, CaO, and α-quartz grains up to 1–2 mm in size, newly formed in altered sandstone (hornfels) containing quartz, Mg-rich variety of neptunite (Table 1) were identified in the Dara-i-Pioz alkaline pluton, Alai Ridge, Tajikistan (Dusmatov and Kabanova, 1967). This finding was unique, because a background content of MgO in the Dara-i-Pioz neptunite is <1 wt % (personal communication of L.A. Pautov and our data). Natural Mg-dominant neptunite was repeatedly predicted (Semenov, 1972; Mineraly ..., 2003). The described new mineral was named after its chemical composition and its belonging to the neptunite group. The idealized formula of the end member is KNa₂LiMg₂Ti₂Si₈O₂₄, but taking into account real chemical compositions of the Lakargi samples, the simplified formula of the new mineral, KNa₂Li(Mg,Fe₂)₂Ti₂Si₈O₂₄, is more correct.

The Mg/(Fe + Mg) value of the neptunite-group minerals from Lakargi ranges from 0.68 (neptunite) to 1.39 (magnesioneptunite). These minerals are characterized by deficiency in K (K₀.₆₋₀.₇) and a small excess of Na (Na₀.₁₋₀.₃) relative to the idealized formula KNa₂Li(Mg,Fe₂)₂Ti₂Si₈O₂₄. Characteristic admixtures reach, wt %: 0.4 MnO, 0.3 Al₂O₃, 0.4 CaO, 0.3 V₂O₅, 0.2 ZrO₂ and 0.2 Cr₂O₃. The representative compositions of magnesioneptunite, accompanying neptunite and other members of the group are given in Table 1.

The physical properties of all minerals of the neptunite group are similar (Table 3). The cleavage of magnesioneptunite is perfect parallel to the (110), and the color ranges from dark brown to red-brown.

The new mineral is biaxial, positive, nₑ = 1.697(2), nₑ = 1.708(3), nₑ = 1.725(3), 2V(calc) = 78° 2V(meas) = 78°. The absorption of magnesioneptunite is similar to that of other titanium members of the group (Nm > Np > Ng), but pleochroic colors are lighter: Ng, from light greenish brown to very light brown; Nm, light brown; and Np, brown. The refractive indices (Table 3) and pleochroism of magnesioneptunite are almost identical to those of Mg–rich neptunite from Dara-i-Pioz (nₑ = 1.723, nₑ = 1.698) reported by Dusmanov and Kabanova (1967), undoubtedly owing to close chemical compositions of the minerals from both localities.

X-RAY CRYSTALLOGRAPHY

The X-ray powder diffraction pattern (Table 4) of magnesioneptunite (camera RKD 57.3, FeKα radiation, Mn filter) is little different from the X-ray powder diffraction patterns of the other titanium members of the group.

The crystal structure of magnesioneptunite was studied on a single crystal 0.04 × 0.16 × 0.08 mm in size with an XCaliburS equipped with a CCD detector (λMoKα = 0.7107 Å, graphite monochromator). Magnesioneptunite is monoclinic, space group C2/c; the unit cell dimensions are a = 16.327(7), b = 12.4788(4), c = 9.9666(4) Å, β = 115.651(5)°, V = 1830.5(1) Å³, Z = 4; R = 2.5%.

A detailed description of the crystal structure of magnesioneptunite will be published in a separate paper. Here, only major attributes of the crystal struc-