ПЕРВЫЙ ПРИРОДНЫЙ ГЕКСАФЕРРИТ СО СМЕШАННОЙ СТРУКТУРОЙβ'''-ФЕРРИТА (β-АЛЮМИНА) И МАГНЕТОПЛЮМБИТА

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FIRST NATURAL HEXAFERRITE WITH MIXED β'''-FERRITE (β-ALUMINA) AND MAGNETOPLUMBITE STRUCTURE

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A thin vein (~1-2 mm) filled with various ferrites was discovered in gehlenite-flamite hornfels at Harmun Mt. in the Judean Desert in the Palestinian Autonomy belonging to rocks of the pyrometamorphic Hatrurim Complex. The main minerals in the veins are magnesioferrite $(Mg_{0.48}Fe^{2+}_{0.23}Zn_{0.17}Ni_{0.06}Cu_{0.03}Ca_{0.03})_{\Sigma 1}(Fe^{3+}_{1.88}Al_{0.12})_{\Sigma 2}O_4$ and khesinite $Ca_4(Ca_{1.03}Mg_{0.74}Zn_{0.05}Fe^{3+}_{0.18})_{\Sigma 2}(Fe^{3+}_{9.64}Cr^{3+}_{0.19}Ti_{0.17})_{\Sigma 10}(Fe^{3+}_{7.23}Al_{3.09}Si_{1.68})_{\Sigma 12}O_{40}$. Less frequent are two potentially new minerals of less than 50 μm in maximum dimension: K-ferrite, $(K_{0.829}Ba_{0.163}Na_{0.013})_{\Sigma 1.005}(Fe^{3+}_{13.894}Mg_{1.261}Al_{0.813}Zn_{0.535}Ti_{0.034}Ca_{0.167}Ni_{0.139}Cu_{0.093}Cr^{3+}_{0.023}Mn_{0.023}Si_{0.017})_{\Sigma 16.999}O_{25}$ – the magnesium analogue of the synthetic phase $KFe^{2+}_2Fe_{15}O_{25}$ (β''-ferrite, Matsui et al., 1985) and Ba-ferrite, $(Ba_{0.818}Ca_{0.113}Na_{0.047}K_{0.022})_{\Sigma 1}(Fe^{3+}_{15.258}Mg_{1.085}Al_{0.690}Zn_{0.411}Ti_{0.110}Ca_{0.094}Ni_{0.160}Cu_{0.087}Mn_{0.032}Si_{0.012})_{\Sigma 17.939}O_{27}$, for which the synthetic analogue $BaMg_2Fe_{16}O_{27}$ is known (*W*-ferrite, Collomb et al., 1986; Pullar, 2012). Both synthetic analogues possess modular structures composed of 5-layered spinel blocks intercalated by *R*-blocks. The *R*-block in K-ferrite (β''-ferrite) is related to the one of β-alumina (Matsui et al., 1985), and in Ba-ferrite (*W*-ferrite) it resembles the one of magnetoplumbite (Collomb et al., 1986).

At first K-ferrite crystallized in the empty voids between magnesioferrite and khesinite crystals. Subsequently K-ferrite was replaced and overgrown by Ba-ferrite. Usually, Ba-ferrite formed reaction rims on K-ferrite. Less frequent, relatively homogenous zones with intermediate compositions were analysed on replaced aggregates of the K-phase. Thin zones of barioferrite, $(Ba_{0.817}Ca_{0.148}Na_{0.021}K_{0.014})_{\Sigma 1}(Fe^{3+}_{11.087}Al_{0.453}Ti_{0.244}Mg_{0.105}Zn_{0.073}Ca_{0.041})_{\Sigma 12.003}O_{19,}$ grew on primary Ba-ferrite. The crystal structure of barioferrite of ideal formula $BaFe_{12}O_{19}$, consists of only 3-layered spinel modules intercalated by *R*-modules of the magnetoplumbite type (*M*-ferrite; Townes et al., 1967; Pullar, 2012). For structural study, we managed to select a ferrite grain 0.05 × 0.05 × 0.01 mm in size with

intermediate composition $(K_{0.566}Ba_{0.384}Na_{0.050})_{\Sigma 1}(Fe^{3+}_{14.081}Mg_{1.423}Zn_{0.586}Al_{0.800}Ti_{0.024}Ca_{0.143}Ni_{0.157}Cu_{0.093}Mn_{0.031}Si_{0.022})_{\Sigma 17.36}O_{25.54}$. The other ferrites in the sample disintegrated to superfine plates. The crystal structure of this intermediate ferrite was studied using a Bruker SMART APEX II CCD (University of Bern, Switzerland) single-crystal diffractometer and gave unexpected results. The studied K-Ba-ferrite has hexagonal symmetry ($a = 5.9137(2)$, $c = 33.1450(15)$ Å) of space $P\text{-}6m2$ (Z = 2) and was refined to R1 = 0.06. The structural model of K-Ba-ferrite can be interpreted as sequence of ordered layers ("supermodules", each spanning a half unit cell parallel to **c**) of β''-ferrite $KMg_2Fe_{15}O_{25}$ with R-blocks of the β-alumina type and W-ferrite $BaMg_2Fe_{16}O_{27}$ with R-blocks of the magnetoplumbite type (Fig. 1).
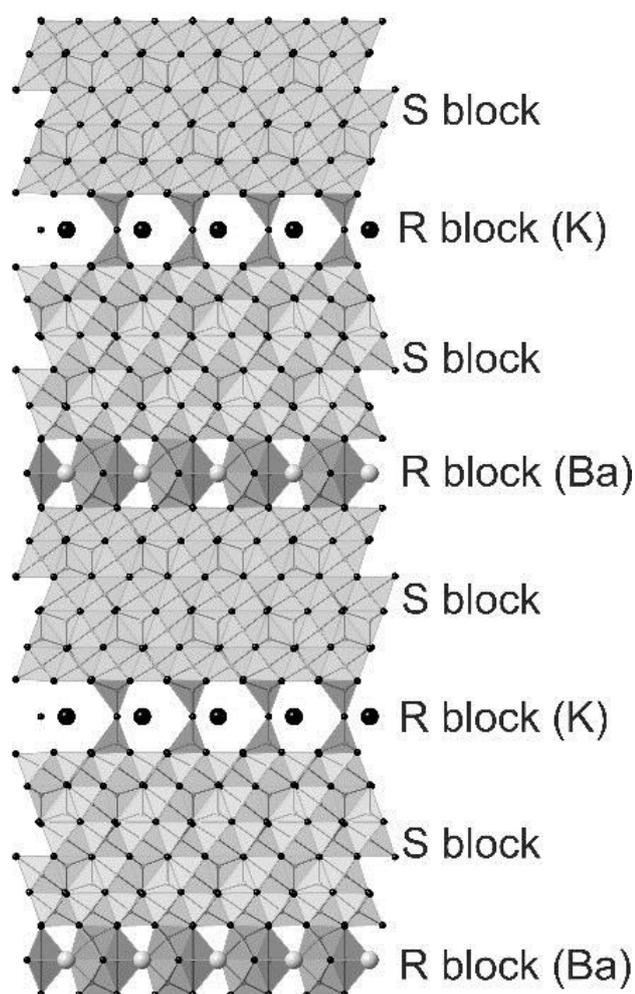

Fig. 1. Structure of K-Ba-hexaferrite with ordered intercalation along the **c** axis of magnetoplumbite blocks (R block of Ba) and β-alumina (R block of K), joint by spinel modules (S blocks). Projection on (010).

The refined K/Ba ratio of 0.59/0.41 for the natural K-Ba-ferrite may be derived from the reference structures $0.59 \times KMe^{2+}_2Me^{3+}_{15}O_{25} + 0.41 \times BaMe^{2+}_2Me^{3+}_{16}O_{27} = K_{0.59}Ba_{0.41}Me^{2+}_2Me^{3+}_{15.41}O_{25.82}$. The refined composition, without distinction between Me^{3+} and Me^{2+}, is $K_{0.59}Ba_{0.41}Me_{17.38}O_{25.56}$. For charge balance the formula may be rewritten to $K_{0.59}Ba_{0.41}Me^{2+}_{2.43}Me^{3+}_{14.95}O_{25.56}$, which is close to the formula obtained

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from EPMA data. K-Ba-ferrite from Harmun Mt. in Palestine is a potentially new mineral and the first natural ferrite with ordered *R*-blocks of magnetoplumbite and *β*-alumina type. Currently, two synthetic phases $Nd_{0.9}Na_{1.3}Al_{23}O_{36.5}$ (*P*-6*m*2; *a* = 5.57, *c* = 22.25 Å; Kahn, Thery, 1986) and $Sr_2MgAl_{22}O_{36}$ (*P*-6*m*2; *a* = 5 5.583, *c* = 5 22.225 Å; Iyi, Göbbels, 1996) with mixed structures, formed by intercalation of magnetoplumbite and *β*-alumina *R*-blocks, are known.

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