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Mariakrite, $[Ca_4Al_2(OH)_{12}(H_2O)_4][Fe_2S_4]$: A new mineral and the first layered double hydroxide intercalated with dithioferrate (iron disulfide) chains

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Abstract

Mariakrite is a new mineral in the hydrotalcite supergroup, and a member of a novel family of layered double hydroxides, or LDH. It is the first reported LDH with dithioferrate, $[Fe^{3+}S_2]^-$ as an interlayer anion, the first cementitious layered Ca-aluminate (AFm phase) intercalated with sulfide, and the first sulfide-intercalated LDH with a completely solved crystal structure. Mariakrite was discovered in late hydrothermal assemblages confined to pyrometamorphic lithologies of the Hatrurim Formation, in the Negev Desert on the Israeli side of the Dead Sea. The mineral forms saber-like crystals up to 2 mm long, 0.1 mm wide, and 0.5 to 2 μm thick, residing in millimeter-sized cavities within larnite-jasmundite-brown-millerite rock. Associated minerals are katoite, portlandite, kuzelite, and hydrocalumite. Mariakrite has a purple-brown color with semimetallic luster; in transmitted light, it is transparent green-gray. The crystals are flexible and elastic. Mohs hardness is 3–3.5. Calculated density is 2.005 g cm^{-3}. In reflected light, the mineral exhibits extreme pleochroism, from gray to red-purple. Anisotropy is very strong. Reflectance values for four wavelengths recommended by the IMA Commission on ore mineralogy [in air, R_1/R_2, % (λ, nm)] are: 5.0/5.2 (470), 6.3/2.3 (546), 6.7/1.8 (589), 6.6/17.6 (659). Mariakrite is triclinic (pseudo-monoclinic and pseudo-trigonal), space group $P\bar{1}$, $a = 5.7107(2)$, $b = 9.9952(4)$, $c = 10.9095(4)$ Å, $\alpha = 98.678(3)$, $\beta = 90.100(3)$, $\gamma = 90.019(3)$ °, $V = 615.58(4)$ $Å^3$, $Z = 1$. The 7 strongest lines of X-ray powder diffraction pattern are [d in Å (I)(hkl)]: 10.83 (100)(001), 9.90 (39)(010), 5.42 (75)(002), 3.96 (22)($0\bar{2}2$),3.523 (19)($\bar{1}12$), 2.856 (37)(130), 2.400 (23)(132). The crystal structure, solved and refined to $R_1 = 0.045$ for 2379 independent observed reflections, consists of hydrocalumite-type LDH layers $[Ca_2Al(OH)_6(H_2O)_2]^+$ intercalated with the iron disulfide chains. The latter are composed of edge-sharing tetrahedra [FeS_4] forming dithioferrate (III) anion, $[Fe^{3+}S_2]^-$. The hydrocalumite-like layers and sulfide chains are linked via the system of O-H···S hydrogen bonds. Chemical composition (electron microprobe, wt%, H_2O based on the structural data) is: CaO 27.75, K_2O 1.85, Al_2O_3 13.93, Fe 14.23, S 16.94, H_2O 23.88, Total 98.58. The empirical formula calculated on the basis of Σ(Ca,K,Al,Fe,S) = 12 apfu is $(Ca_{3.73}K_{0.30})_{\Sigma 4.03}Al_{2.06}(OH)_{12.18}Fe_{1.92}S_{3.99}\cdot 3.91H_2O$, corresponding to the ideal formula $[Ca_4Al_2(OH)_{12}(H_2O)_4][Fe_2S_4]$. Mariakrite is the first example of dithioferrate in which disulfide chains have no contacts with cations or anions, being suspended between hydroxide layers via the system of hydrogen bonds. Therefore, the mineral might represent the near-ideal model for the study of physical and chemical properties of isolated quasi-one-dimensional dithioferrate chains.

Keywords: Hydrotalcite supergroup, hydrocalumite group, layered double hydroxide, LDH, AFm cementitious phase, intercalation, iron disulfide, dithioferrate