

Hanswilkeite, KFeS_2 , a new peralkaline sulfide mineral

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ABSTRACT

Hanswilkeite, $\text{KFe}^{3+}\text{S}_2$, is a new potassium-rich natural sulfide discovered in the pyrometamorphic suite of the Hatrum Formation, southern Negev Desert, Dead Sea basin, Israel. The mineral occurs in sulfide-calcite assemblages confined to black-colored calcite-spurrite marbles. It forms single-crystal grains up to 1 mm in size, isometric to lath-like, and often intergrown with a less-common rasvumite, KFe_2S_3 . Associated minerals include srebrodolskite, tilleyite, fluormayenite, cuspidine, fluorapatite, oldhamite, pyrite, and andradite. Macroscopically, hanswilkeite has a deep-purple color, dull metallic luster, and brown-black streak. The Mohs hardness is 2. Moderate cleavage was observed along the *c*-axis. The calculated density is 2.654 $\text{g}\cdot\text{cm}^{-3}$. The Raman spectrum contains the following bands: 379, 357, 289, 236, 167, 131, and 124 cm^{-1} . In reflected light, the mineral has very strong pleochroism from yellow-pink to dark-gray. Anisotropy is very strong, $\Delta R_{589} = 69\%$. Reflectance values for COM required wavelengths measured in air, $R_{\text{max}}/R_{\text{min}}$ (λ , nm) (%): 16.0/9.2 (470); 19.6/9.3 (546); 18.5/9.0 (589); 32.0/9.3 (650). Chemical composition (electron microprobe, average of 6 points, wt%): K 23.78, Ca 0.44, Fe 34.75, Mn 0.60, Zn 0.47, S 39.46, Total 99.5, which corresponds to empirical formula $(\text{K}_{0.98}\text{Ca}_{0.02})_{1.00}(\text{Fe}_{1.00}\text{Mn}_{0.02}\text{Zn}_{0.01})_{1.03}\text{S}_{1.98}$ ($\Sigma = 4$ apfu) or ideally $\text{KFe}^{3+}\text{S}_2$. Single-crystal X-ray diffraction shows that the mineral is monoclinic, space group $C2/c$ (#15), with unit-cell parameters $a = 7.0914(5)$, $b = 11.3154(5)$, $c = 5.3992(3)$ Å, $\beta = 113.244(7)^\circ$, $V = 398.08(4)$ Å³, and $Z = 4$. Strongest lines of X-ray powder diffraction pattern [d in Å(hkl)]: 5.68(100)(020,110); 3.270(31)(130); 3.227(29)(111); 2.921(45)($\bar{2}21$); 2.510(12)(131); 2.198(12)($\bar{1}32$); 1.880(10)(330). The crystal structure has been solved and refined to $R_1 = 0.038$ for 454 unique observed reflections [$I \geq 2\sigma(I)$]. The structure consists of infinite chains of edge-sharing tetrahedra $[\text{FeS}_4]^-$ centered with Fe^{3+} ; the sulfide chains are linked by K^+ ions. Hanswilkeite is the third discovered dithioferrate mineral: a sulfosalt that contains $[\text{FeS}_2]^-$ anion with iron in Fe^{3+} state. Other known natural dithioferrates are erdite, $\text{NaFeS}_2 \cdot 2\text{H}_2\text{O}$, and raguinite, TlFeS_2 . Hanswilkeite has a synthetic counterpart and a group of related synthetic sulfides and selenides, which were well studied due to specific electrical and magnetic properties owed to their quasi-one-dimensional structures. The mineral can be considered as an indicator of an extreme potassium-rich environment superimposed onto anhydrous and oxidizing formation conditions. The association with oldhamite is herein discussed in view of super-reduced conditions previously supposed for oldhamite geosynthesis.

Keywords: Hanswilkeite, KFeS_2 , rasvumite, oldhamite, peralkaline, potassium, marble, Hatrum Formation