Siwaqaite, Ca$_6$Al$_2$(CrO$_4$)$_3$(OH)$_{12}$·26H$_2$O, a new mineral of the ettringite group from the pyrometamorphic Daba-Siwaqa complex, Jordan

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ABSTRACT

A new mineral, siwaqaite, ideally Ca$_6$Al$_2$(CrO$_4$)$_3$(OH)$_{12}$·26H$_2$O [$P3_1c$, $Z = 2$, $a = 11.3640(2)$ Å, $c = 21.4485(2)$ Å, $V = 2398.78(9)$ Å$^3$], a member of the ettringite group, was discovered in thin veins and small cavities within the spurrite marble at the North Siwaqa complex, Lisdan-Siwaqa Fault, Hashem region, Jordan. This complex belongs to the widespread pyrometamorphic rock of the Hatrurim Complex. The spurrite marble is mainly composed of calcite, fluorapatite, and brownmillerite. Siwaqaite occurs with calcite and minerals of the baryte-hashemite series. It forms hexagonal prismatic crystals up to 250 μm in size, but most common are grain aggregates. Siwaqaite exhibits a canary yellow color and a yellowish-gray streak. The mineral is transparent and has a vitreous luster. It shows perfect cleavage on (10T0). Parting or twinning is not observed. The calculated density of siwaqaite is 1.819 g/cm$^3$.

Siwaqaite is optically uniaxial (−) with $\omega = 1.512(2)$, $\varepsilon = 1.502(2)$ (589 nm), and non-pleochroic. The empirical formula of the holotype siwaqaite calculated on the basis of 8 framework cations and 26 water molecules is Ca$_{6.01}$(Al$_{1.87}$Cr$_{0.13}$)(SO$_4$)$_{1.13}$(SeO$_4$)$_{0.40}$26H$_2$O. X-ray diffraction (XRD), Raman, and infrared spectroscopy confirm the presence of OH$^-$ groups and H$_2$O molecules and absence of (CO$_3$)$_2$-$ groups. The crystal structure of this Cr$^{6+}$-analog of ettringite was solved by direct methods using single-crystal synchrotron XRD data. The structure was refined to an agreement index $R$ = 4.54%. The crystal structure of siwaqaite consists of [Ca$_6$[Al(OH)$_6$],·24H$_2$O]$^+$ columns with the inter-column space (channels) occupied by (CrO$_4$)$_2$~, (SO$_4$)$_2$~, (SeO$_4$)$_2$~, and (SO$_4$)$_2$$^-$ groups and H$_2$O molecules. The tetrahedrally coordinated site occupied by different anion groups is subjected to disordering and rotation of these tetrahedra within the structure. The temperature of siwaqaite formation is not higher than ~70–80 °C, as is evident from the mineral association and as inferred from the formation conditions of the natural and synthetic members of the ettringite group minerals, which are stable at conditions of $T < 120$ °C and pH = 9.5–13. The name siwaqaite is derived from the name of the holotype locality—Siwaqa area, where the mineral was found.

Keywords: Siwaqaite, new mineral, ettringite group, crystal structure, Raman, FTIR, Daba-Siwaqa, Jordan

INTRODUCTION

Siwaqaite, Ca$_6$Al$_2$(CrO$_4$)$_3$(OH)$_{12}$·26H$_2$O [$P3_1c$, $Z = 2$, $a = 11.3640(2)$ Å, $c = 21.4485(2)$ Å, $V = 2398.78(9)$ Å$^3$], is a Cr$^{6+}$-analog of ettringite and a new member of the ettringite group. It was found in small cavities and thin veins cutting spurrite marbles at the North Siwaqa complex, Lisdan-Siwaqa Fault, Hashem region, Jordan (31°24.15′N; 36°14.34′E). Ettringite, Ca$_6$Al$_2$(SO$_4$)$_3$(OH)$_{12}$·26H$_2$O, is a rare mineral with high water content, which occurs in natural alkaline environments. It is a typical phase of low-temperature hydrothermal mineral association with altered Ca-rich igneous, metamorphic, and mafic rocks (Moschner et al. 2009; Jiménez and Prieto 2015; Seryotkin et al. 2017). The ettringite group includes 13 mineral species and only one, bentoite, Ca$_6$Cr$_3$(SO$_4$)$_3$(OH)$_{12}$·26H$_2$O, found in pyrometamorphic rocks of the Hatrurim Complex in Israel, contains Cr$^{3+}$ (Gross 1980; Seryotkin et al. 2019). There are two known minerals containing Cr$^{6+}$ in rocks of the Hatrurim Complex: hashemite, BaCrO$_4$, which forms a solid solution with baryte, and chromatite, CaCrO$_4$ (Hauff et al. 1983; Sokol et al. 2011; Juroszek et al. 2018). The maximal content of Cr$^{6+}$ as the chromate group (CrO$_4$)$_2$~ in minerals of the ettringite group from pyrometamorphic rocks of Nabi Musa, West Bank, reaches 0.36 atom per formula unit (apfu), and these minerals are considered as the members of the ettringite–thauasite–“chromate-ettringite” triple solid-solution series (Drebushchak et al. 2013).

Ettringite is an important phase in common materials such as cement, fly ashes, cement pastes, mortars, and concrete (Perkins and Palmer 1999, 2000; Gatta et al. 2019). Ettringite is formed in the early stage of Portland cement hydration as a hydration product of tri-calcium aluminate (hatrurite) with sulfate ions and water (Gougar et al. 1996; Hall et al. 1996;...