

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

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ABSTRACT

A new mineral, siwaqaite, ideally $\text{Ca}_6\text{Al}_2(\text{CrO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$ [$P31c$, $Z = 2$, $a = 11.3640(2)$ Å, $c = 21.4485(2)$ Å, $V = 2398.78(9)$ Å³], 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 (10 $\bar{1}$ 0). Parting or twinning is not observed. The calculated density of siwaqaite is 1.819 g/cm³. Siwaqaite is optically uniaxial (–) with $\omega = 1.512(2)$, $\epsilon = 1.502(2)$ (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 $\text{Ca}_{6.01}(\text{Al}_{1.87}\text{Si}_{0.12})_{\Sigma 1.99}[(\text{CrO}_4)_{1.71}(\text{SO}_4)_{1.13}(\text{SeO}_4)_{0.40}]_{\Sigma 3.24}(\text{OH})_{11.63}\cdot 26\text{H}_2\text{O}$. X-ray diffraction (XRD), Raman, and infrared spectroscopy confirm the presence of OH[–] groups and H₂O molecules and absence of (CO₃)^{2–} groups. The crystal structure of this Cr⁶⁺-analog of ettringite was solved by direct methods using single-crystal synchrotron XRD data. The structure was refined to an agreement index $R_1 = 4.54\%$. The crystal structure of siwaqaite consists of $\{\text{Ca}_6[\text{Al}(\text{OH})_6]_2\cdot 24\text{H}_2\text{O}\}^{6+}$ columns with the inter-column space (channels) occupied by (CrO₄)^{2–}, (SO₄)^{2–}, (SeO₄)^{2–}, and (SO₃)^{2–} groups and H₂O 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, $\text{Ca}_6\text{Al}_2(\text{CrO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$ [$P31c$, $Z = 2$, $a = 11.3640(2)$ Å, $c = 21.4485(2)$ Å, $V = 2398.78(9)$ Å³], is a Cr⁶⁺-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, $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$, 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 within altered Ca-rich igneous, metamorphic, and mafic rocks (Möschner et al. 2009; Jiménez and Prieto 2015; Seryotkin et al. 2017). The ettringite group includes 13 mineral species and only one, bentorite, $\text{Ca}_6\text{Cr}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$,

found in pyrometamorphic rocks of the Hatrurim Complex in Israel, contains Cr³⁺ (Gross 1980; Seryotkin et al. 2019). There are two known minerals containing Cr⁶⁺ in rocks of the Hatrurim Complex: hashemite, BaCrO₄, which forms a solid solution with baryte, and chromatite, CaCrO₄ (Hauff et al. 1983; Sokol et al. 2011; Juroszek et al. 2018). The maximal content of Cr⁶⁺ as the chromate group (CrO₄)^{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–thaumasite–“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;

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Teraï et al. 2006; Jiménez and Prieto 2015). In cement and concrete, synthetic analogs of the ettringite group minerals largely control the solidification kinetics and play a significant role in the mechanical and corrosion strength (Brown and Hooton 2002; Scholtzová et al. 2015). Ettringite may immobilize and store various contaminants and toxic ions at both cationic and anionic sites due to substitution, sorption, and phase mixing. Many investigations have targeted these properties (Kumathasan et al. 1989; Pöllmann et al. 1993; Perkins and Palmer 2000; Zhang and Reardon 2003; Chrysochoou and Dermatas 2006; Teraï et al. 2006; Leisinger et al. 2010; Wu et al. 2012; Jiménez and Prieto 2015).

A synthetic chromate analog of ettringite is also known and has been investigated by many researchers. The growth rate and size of ettringite crystals formed after the reaction of tricalcium aluminate with various amounts of CaSO_4 and CaCrO_4 in Portland cement were examined by Teramoto and Koie (1976). Their observation suggests that Cr^{6+} -bearing ettringite has a higher solubility than its sulfate counterpart. Synthesis of ettringite with complete chromate and selenate substitutions and their X-ray diffraction (XRD) data were reported by Kumathasan et al. (1989). Pöllmann et al. (1993) carried out XRD, chemical, nephelometric, and colorimetric carminic acid analyses of the synthesized solid solutions of ettringite containing $(\text{SO}_4)^{2-}$, $(\text{CrO}_4)^{2-}$, and $\text{B}(\text{OH})_4$ groups. Perkins and Palmer (2000) synthesized a Cr^{6+} -rich ettringite and performed XRD, Fourier-transform infrared spectroscopy (FTIR), energy dispersive X-ray spectroscopy, and thermogravimetry analyses. They also measured the solubility of this phase in the temperature range 5–75 °C and at initial pH values between 10.5 and 12.5. Teraï et al. (2006) synthesized Cr^{6+} -bearing ettringite in portlandite suspensions and observed that the crystallization is more intense when the pH of the suspension solution is ≥ 10.9 . Leisinger et al. (2010) reported thermodynamic data of the chromate-sulfate ettringite solid solution.

Siwaqaite (IMA 2018-150) was approved by the Commission on New Minerals, Nomenclature and Classification, International Mineralogical Association (IMA). The type material with the catalog number 5277/1 was deposited in the mineralogical collection of the Fersman Mineralogical Museum, Moscow, Russia.

The name siwaqaite is derived from the name of area Siwaqa, where the mineral was found. This area with pyrometamorphic rocks is located 60 km south of Amman, Jordan.

Here we describe the new mineral, siwaqaite, from the type locality of North Siwaqa complex, Jordan, and compare its structural and spectroscopic data with those of other ettringite group members and synthetic counterparts.

EXPERIMENTAL METHODS

Scanning electron microscopy (SEM) and electron microprobe analysis (EMPA)

The preliminary chemical compositions and crystal morphology of siwaqaite and associated minerals were examined using an optical microscope and a Phenom XL SEM equipped with an energy-dispersive X-ray spectrometer (Faculty of Natural Sciences, University of Silesia, Poland). Quantitative chemical analyses of siwaqaite were carried out on a CAMECA SX100 electron microprobe (Institute of Geochemistry, Mineralogy and Petrology, University of Warsaw, Poland) at 15 kV and 10 nA using scanning mode of $\sim 5 \times 5 \mu\text{m}$, and the following lines and standards: $\text{CrK}\alpha = \text{Cr}_2\text{O}_3$; $\text{SK}\alpha = \text{baryte}$; $\text{SiK}\alpha$, $\text{CaK}\alpha = \text{diopside}$; $\text{AlK}\alpha = \text{orthoclase}$; $\text{SeL}\alpha = \text{Bi}_2\text{Se}_3$.

Confocal Raman spectroscopy (CRS)

The Raman spectrum of siwaqaite was recorded on a WITec α 300R Confocal Raman Microscope (Faculty of Natural Sciences, University of Silesia, Poland) equipped with an air-cooled solid laser 488 nm and a closed circuit display (CCD) camera operating at -61°C . The laser radiation was coupled to a microscope through a single-mode optical fiber with a diameter of $3.5 \mu\text{m}$. An air Zeiss (LD EC Epiplan-Neofluar DIC-100/0.75NA) objective was used. Raman scattered light was focused by an effective pinhole size of about $30 \mu\text{m}$ and a monochromator with a 600 mm^{-1} grating. The power of the laser at the sample position was 30 mW. Integration times of 10 s with an accumulation of 20 scans, and a resolution of 3 cm^{-1} were used. The monochromator was calibrated using the Raman scattering line of a silicon plate (520.7 cm^{-1}). Spectra processing, such as baseline correction and smoothing, were performed using the Spectralcalc software package GRAMS (Galactic Industries Corporation, New Hampshire, U.S.A.). The Raman bands were fitted using a Gauss-Lorentz cross-product function, with the minimum number of component bands used for the fitting process.

Infrared (IR) spectroscopy

Attenuated total Reflection-Fourier transform infrared (ATR-FTIR) spectrum of siwaqaite was obtained using Nicolet iS10 Mid FTIR Spectrometer (Thermo-Scientific) fitted with an ATR device with a diamond crystal plate (Faculty of Natural Sciences, University of Silesia, Poland). The sample was placed directly on the diamond crystal prior to data acquisition. Measurement conditions were as follows: spectral range $4000\text{--}400 \text{ cm}^{-1}$, spectral resolution 8 cm^{-1} , beam splitter Ge/KBr, detector DLaTGS with dynamic interferometer justification. The OMNIC 9 (Thermo-Fisher Scientific Inc.) analytical software was used.

Single-crystal X-ray diffraction (SC-XRD)

Single-crystal XRD experiments were carried out using synchrotron radiation (beamline X06DA, Swiss Light Source, Paul Scherrer Institute, Villigen, Switzerland). A semi-sphere of the reciprocal space was recorded in 1800 raw data frames (0.1° rotation and 0.2 s exposure per frame). The data collection was controlled by DA+ software (Wojdyla et al. 2018). Determination and refinement of the unit-cell parameters, as well as the data reduction, were performed using CrysAlisPro (Rigaku 2016). Data collection conditions and refinement parameters are listed in the CIF¹.

The atomic coordinates of ettringite (Berliner 1998) were used as a starting model for the structure refinement, which converged to a final agreement index of $R_1 = 4.54\%$ (SHELX-2014/7; Sheldrick 2015). All H-sites were located by difference Fourier analyses. Bond valence sum calculations were used to evaluate the valence of anions (Brown and Altermatt 1985; Rodríguez-Carvajal 2010). All atoms, except hydrogen, and the S6 site (low occupation) were modeled using anisotropic displacement parameters. Hydrogen positions were refined using a fixed value of $U_{\text{iso}} = 0.05 \text{ \AA}^2$. The OH distances were retained to $0.95(1) \text{ \AA}$.

For a detailed assignment of the elements to different sites, the program OccQp was used (Wright et al. 2000).

GEOLOGICAL SETTINGS

The high-temperature low-pressure pyrometamorphic rocks are distributed on both sides of the Dead Sea Transform Fault in Israel, West Bank, and Jordan (Fig. 1). They belong to the large unit known as the Hatrurim Complex or the Mottled Zone (Bentor et al. 1963; Gross 1977; Burg et al. 1991; Techer et al. 2006; Sokol et al. 2011; Geller et al. 2012; Novikov et al. 2013), and consist of high-temperature mineral assemblages, which form clinker-like rocks, represented mainly by spurrite marbles, lanite pseudoconglomerates, gehlenite hornfelses (Gross 1977; Novikov et al. 2013; Galuskin et al. 2014; Galuskin et al. 2015, 2016) and different paralavas (Sokol et al. 2007; Vapnik et al. 2007; Grapes 2010). These pyrometamorphic rocks are often altered, cracked, and cut by numerous veins filled by late-hydrothermal minerals, which are a product of rehydration and recarbonation of the high-temperature phases (Burg et al. 1991; Fleurance et al. 2013; Kolodny et al. 2014). Detailed geological settings and the main hypotheses on origin of the Hatrurim Complex were described by Kolodny and Gross (1974), Mat-

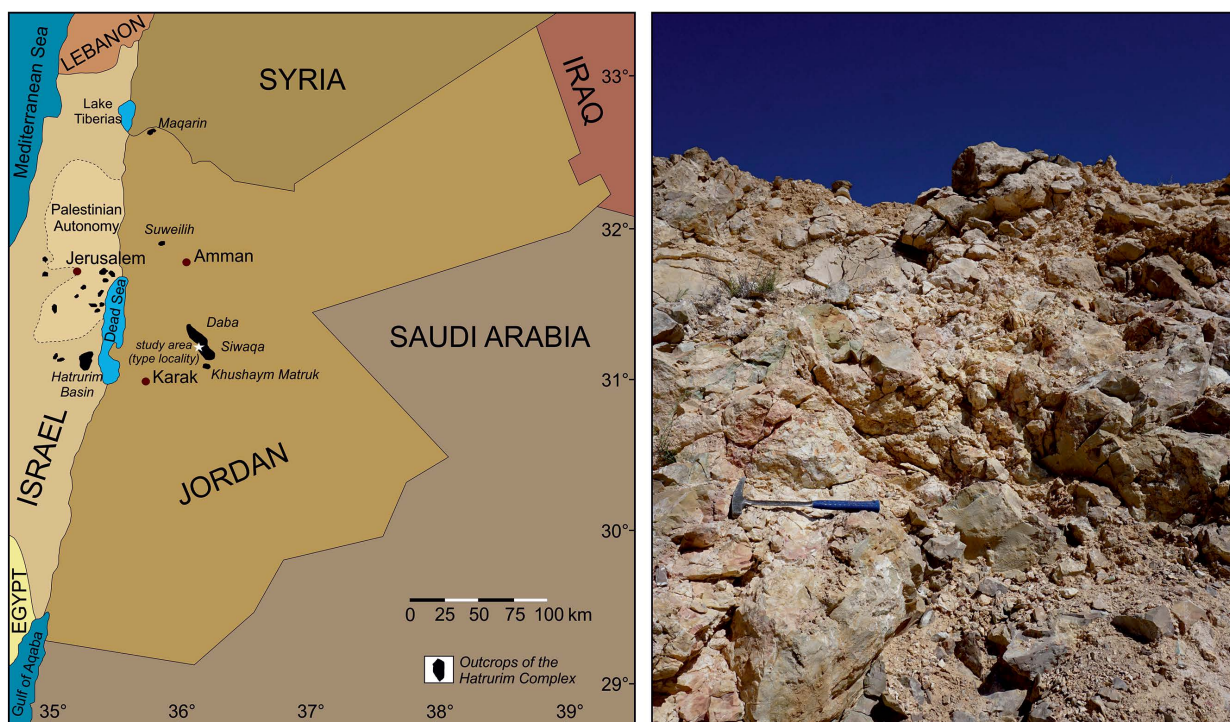


FIGURE 1. Geological scheme of the Middle East with localization of the pyrometamorphic Mottled Zone complexes along the Israel-West Bank-Jordan borders (left, modified after Techer et al. 2006) and siwaqaite type locality in North Siwaqa complex (right)—a pit wall of spurrite-apatite rocks with veins filled by low-temperature mineralization. (Color online.)

thews and Gross (1980), Sokol et al. (2010), Geller et al. (2012), Novikov et al. (2013), and Galuskina et al. (2014).

The North Siwaqa complex, Lisdan-Siwaqa Fault, Hashem region, Jordan (31°24.15'N; 36°14.34'E) is the type locality of the new mineral, siwaqaite, which was found herein in small cavities and thin veins within the spurrite marble (Figs. 1 and 2). The Daba-Siwaqa area, as well as the Suweilih, Maqarin, and Khushaym Matruk complexes in Jordan are composed of combustion metamorphic rocks, which are a lithological and stratigraphical equivalent to the Hatrurim Complex in Israel (Techer et al. 2006; Powell and Moh'd 2011; Geller et al. 2012; Fleurance et al. 2013; Khoury et al. 2014, 2016c). The Daba-Siwaqa complex located ca. 60 km south of Amman is the largest area of pyrometamorphic rocks, represented mostly by spurrite-fluorapatite marbles (Novikov et al. 2013; Khoury et al. 2014, 2015). This region is the type locality of hashemite, BaCrO_4 (Hauß et al. 1983), transjordanite, Ni_2P (Britvin et al. 2014), tululite, $\text{Ca}_{14}(\text{Fe}^{3+}, \text{Al})(\text{Al}, \text{Zn}, \text{Fe}^{3+}, \text{Si}, \text{P}, \text{Mn}, \text{Mg})_{15}\text{O}_{36}$ (Khoury et al. 2016c), qatranaite, $\text{CaZn}_2(\text{OH})_6(\text{H}_2\text{O})_2$ (Vapnik et al. 2019), nickolayite, FeMoP (Murashko et al. 2019), and khurayyimit, $\text{Ca}_7\text{Zn}_4(\text{Si}_2\text{O}_7)_2(\text{OH})_{10} \cdot 4\text{H}_2\text{O}$ (Galuskina et al. 2019).

The study area is located within a lithostratigraphical Maasrichtian to Paleocene unit known as the Muwaqqar Chalk-Marl Formation that is a part of the organic-rich calcareous Belqa Group sediments in Jordan, featured by high enrichment in trace, mostly redox-sensitive elements such as Cd, Zn, Cr, Mo, Ni, V, Se, and U (Abed et al. 2005; Techer et al. 2006; Powell and Moh'd 2011; Fleurance et al. 2013; Khoury 2015; Khoury et al. 2015, 2016b, 2016c, 2016a; Sokol et al. 2017; Vapnik et

al. 2019). The Muwaqqar Chalk-Marl Formation composed of marl, chalky marls, limestone, and chert concretions was deposited in a deep to moderate marine pelagic environment (Abed et al. 2005; Fleurance et al. 2013; Khoury et al. 2014, 2015, 2016c; Alqudah et al. 2015; Hakimi et al. 2016; Sokol et al. 2017; Vapnik et al. 2019). The bituminous marl, locally known as “oil shale horizon,” forms the lower part of the Muwaqqar Formation (Abed et al. 2005; Fleurance et al. 2013; Khoury et al. 2014; Hakimi et al. 2016). This geological unit, abundant in organic matter, contains up to 25–30% organic carbon and thus may be economically important (Sokol et al. 2017). The upper part of the Muwaqqar Chalk-Marl unit is represented mostly by varicolored marbles that form, as commonly suggested, as a result of spontaneous combustion metamorphism of bituminous marls in sub-surface conditions (Techer et al. 2006; Fleurance et al. 2013; Khoury et al. 2014, 2015, 2016b, 2016c; Abzalov et al. 2015; Sokol et al. 2017). In these marbles, two groups of mineral assemblages were identified: a prograde (high-temperature) group and a retrograde (low-temperature) group. They are similar to that of cement clinker and products of its hydration, respectively. The prograde group includes spurrite, wollastonite, gehlenite-akermanite, garnet, diopside, perovskite, monticellite, magnesioferrite, fluorapatite, etc. The retrograde group contains some calcium silicate hydrates: afwillite, jennite, tobermorite, apophyllite; sulfates: gypsum, minerals of ettringite-thaumasite and baryte-hashemite series; oxides and hydroxides: goethite, hydrocalumite, portlandite; and carbonates: calcite, aragonite, and vaterite (Techer et al. 2006; Khoury et al. 2014). More detailed geological, mineral-

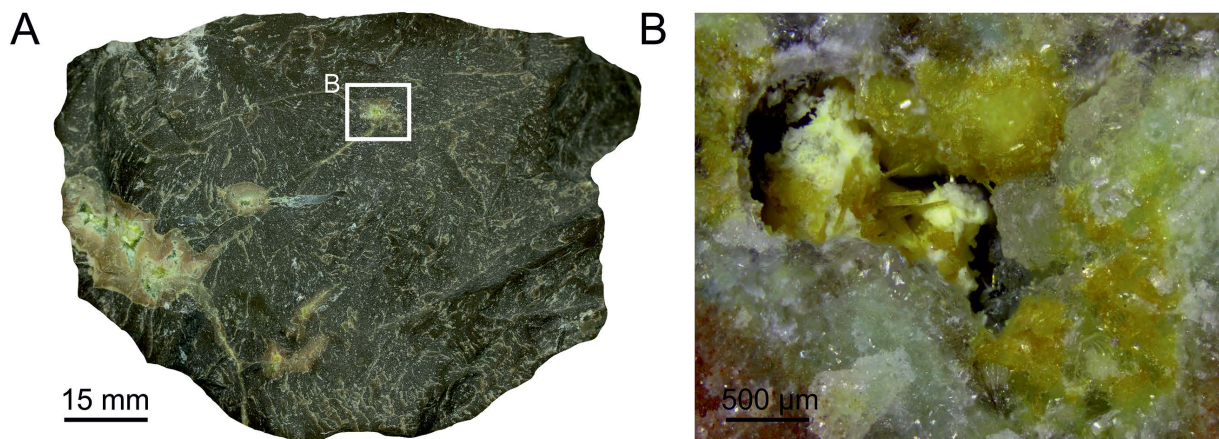


FIGURE 2. Spurrite marble specimen with thin veins and cavities filled by siwaqaite (a). Cavity containing hexagonal, prismatic siwaqaite crystals, and siwaqaite-calcite aggregates along the edge of the cavity (b). (Color online.)

ogical, and stratigraphical information concerning this locality can be found in Powell and Moh'd (2011), Fleurance et al. (2013), and Khoury et al. (2015).

PHYSICAL AND OPTICAL PROPERTIES OF SIWAQAITE

Siwaqaite was found in 2–3 mm thick creamy yellow veins and in small cavities within unaltered dark brown spurrite marble in which calcite, fluorapatite, and brownmillerite occur as main rock-forming minerals (Fig. 2a). Cuspidine, fluormayenite, gehlenite, perovskite, and lakargiite were noted as accessory phases. Siwaqaite is associated with calcite, minerals of the baryte-hashemite series, and highly hydrated undiagnosed Ca-silicate with Al and Cr impurities. In the holotype specimen, ettringite with a low Cr content was also noted.

Euhedral siwaqaite crystals are very rare; they occur as single elongated hexagonal prisms up to 250 μm in size, terminated by a hexagonal pyramid or a pinacoid. They only occur in small cavities within spurrite marble (Fig. 2b). Most common are anhedral aggregates of siwaqaite (~50 μm in size), which fill veins and occur with calcite along the edges of cavities (Fig. 2b).

Siwaqaite crystals exhibit a canary yellow color and a yellowish-gray streak. The mineral is transparent and has a vitreous luster. It shows perfect cleavages on (10 $\bar{1}$ 0). Parting or twinning is not observed. The tenacity is brittle and the fracture is uneven or irregular. It is soluble in 10% HCl and loses color in ethanol at room temperature.

The density could not be measured due to the high tendency to fracture and the rarity of siwaqaite crystals. The calculated density obtained on the basis of the empirical formula and unit-cell volume is 1.819 g/cm³. We were not able to measure its micro-hardness because of high brittleness and fractures of siwaqaite crystals. Based on the scratch test, its hardness is about 2 on the Mohs scale.

Siwaqaite is optically uniaxial (–), with $\omega = 1.512(2)$, $\epsilon = 1.502(2)$ (589 nm). It is non-pleochroic and the optical orientation is $\epsilon = C$. For the ideal formula, the Gladstone-Dale compatibility index (Mandarino 1981) is $1 - (K_p/K_c) = 0.010$ (superior).

RESULTS

Chemical composition

Preliminary chemical analyses were carried out on siwaqaite single crystals, which were mounted on a carbon tape, using SEM/EDS. The results reveal the presence of Ca, Al, Cr, S, Se, Si, and O (Fig. 3).

Afterward, some crystals were picked from the rock specimen, embedded in epoxy and polished for subsequent EMPA using wavelength-dispersive X-ray spectroscopy (WDS). As noted previously, minerals belonging to the ettringite group are unstable under electron beam and tend to dehydrate (Pushcharovsky et al. 2004; Chukanov et al. 2012, 2016; Pekov et al. 2012; Thiéry et al. 2017; Gatta et al. 2019). Consequently, we utilized defocused beams with a large scanning area of $5 \times 5 \mu\text{m}$. In addition to the above elements, EMPA revealed small amounts of Fe, Mg, Mn, and Na. Other elements with atomic numbers higher than 8 were below the detection limit. The H₂O and CO₂ contents were not determined directly because of the small size and rarity of siwaqaite crystals. The absence of CO₂ groups and the presence of water molecules and OH groups in siwaqaite were confirmed by Raman, FTIR, and XRD. The average chemical composition (in wt%) of the new mineral is given in Table 1. The empirical formula of the holotype siwaqaite calculated on the basis of 8 framework cations (Ca+Al+Si) and 26 water molecules is $\text{Ca}_{6.01}(\text{Al}_{1.87}\text{Si}_{0.12})_{\Sigma 1.99}[(\text{CrO}_4)_{1.71}(\text{SO}_4)_{1.13}(\text{SeO}_4)_{0.40}]_{\Sigma 3.24}(\text{OH})_{11.63} \cdot 26\text{H}_2\text{O}$, which may be simplified to $\text{Ca}_6(\text{Al},\text{Si})_2[(\text{Cr},\text{S},\text{Se})\text{O}_4]_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$. The end-member formula is $\text{Ca}_6\text{Al}_2(\text{CrO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$, which corresponds to CaO 25.59, Al₂O₃ 7.75, CrO₃ 22.81, and H₂O 43.85 (wt%).

Raman and IR spectroscopic data

The main bands in the Raman spectrum of siwaqaite (Fig. 4) are related to the symmetric stretching vibrations of anionic (CrO₄)^{2–}, (SO₄)^{2–}, and (SeO₄)^{2–} groups, which are observed at 856, 987, and 842 cm^{–1}, respectively (Alia et al. 1999; Frost 2004; Renaudin et al. 2007; Guo et al. 2017). Bands at 893 and 908 cm^{–1} are assigned to the asymmetric stretching vibra-

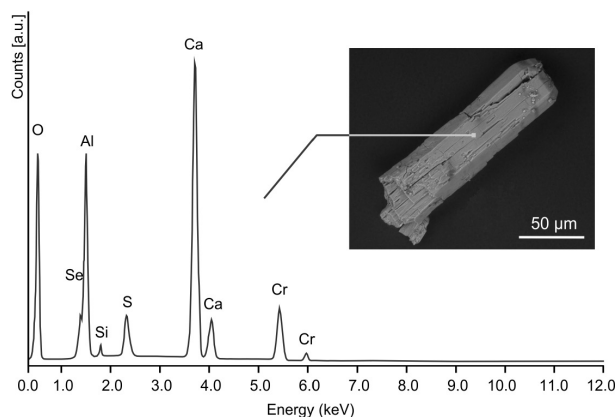


FIGURE 3. EDS spectrum and backscattered electron (BSE) image of siwaqaite.

TABLE 1. Chemical composition (wt%) of holotype siwaqaite from Siwaqa, Jordan

Constituent	Mean	S.D.	Range
n = 12			
CrO ₃	12.80	0.20	12.47–13.19
SO ₃	6.78	0.35	5.99–7.21
SeO ₃	3.80	0.27	3.26–4.11
SiO ₂	0.55	0.12	0.39–0.79
Al ₂ O ₃	7.14	0.26	6.61–7.45
CaO	25.20	0.25	24.87–25.66
H ₂ O	42.89		
Total	99.16		

Calculated on the basis of 8 cations

Cr ⁶⁺	1.71
S ⁶⁺	1.13
Se ⁶⁺	0.40
Sum T	3.24
Si ⁴⁺	0.12
Al ³⁺	1.87
Sum M	1.99
Ca ²⁺	6.01

Note: Water was calculated on the basis of stoichiometry; S.D. = 1σ = standard deviation; n = number of analyses.

tions of selenate and chromate groups. The spectral region between 350 and 410 cm⁻¹ corresponds to the Cr-O bending vibrations of the (CrO₄)²⁻. The band at 332 cm⁻¹ is attributed to the selenate symmetric bending mode. The band at 546 cm⁻¹ is ascribed to Al-OH vibrations of Al(OH)₆. Bands in the range 1688–1714 cm⁻¹ may be interpreted as the bending vibration of H₂O molecules or overtones. The OH region in the Raman spectrum of siwaqaite is characterized by four wide (3275, 3383, 3455, 3536 cm⁻¹), and one sharp (3641 cm⁻¹) bands, which are related to the H₂O and OH stretching vibrations, respectively (Renaudin et al. 2007).

The IR spectrum of siwaqaite (Fig. 5) shows absorption bands at 3318 and 3620 cm⁻¹ related to the OH stretching vibrations of H₂O molecules and OH groups, respectively. Bands observed at 1629 and 1650 cm⁻¹ correspond to the bending vibration of H₂O molecules (Chukanov et al. 2012; Scholtzová et al. 2015). Asymmetric stretching and bending vibrations attributed to the (SO₄)²⁻ groups exhibit bands at 1108 and 540 cm⁻¹, respectively (Myneni et al. 1997; Scholtzová et al. 2015). The band at 540 cm⁻¹ coincides with a band ascribed to the Al-OH bending vibrations of Al(OH)₆ octahedra (Myneni et al. 1997). The most intense and

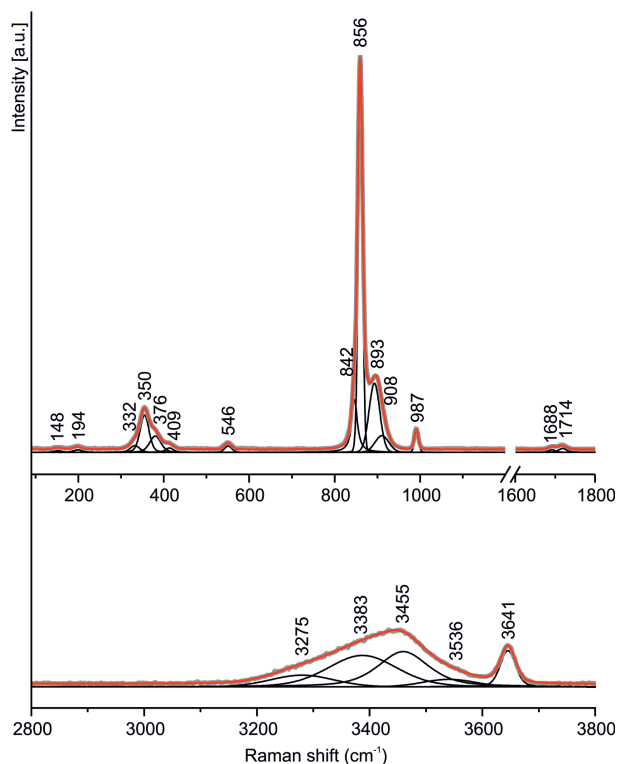


FIGURE 4. Raman spectrum of siwaqaite. (Color online.)

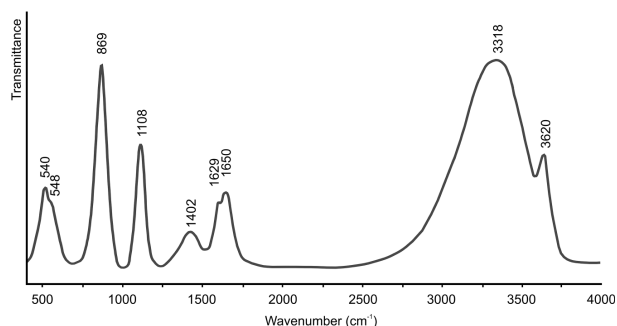


FIGURE 5. FTIR spectrum of siwaqaite.

sharp band observed at 869 cm⁻¹ is assigned to the asymmetric stretching vibrations of (CrO₄)²⁻ groups (Povarennykh 1978; Perkins and Palmer 2000; You et al. 2007) and may overlap with the band corresponding to (SeO₄)²⁻ modes (Hassett et al. 1990). The IR spectrum confirms the presence of very low content of (CO₃)²⁻ groups (broadband at 1402 cm⁻¹). The presence of this band can be related to calcite impurities in siwaqaite.

Crystal structure of siwaqaite

The structure of siwaqaite is composed of {Ca₆[Al(OH)₆]₂·24H₂O}⁶⁺ columns with the inter-column space (channels) occupied by (CrO₄)²⁻, (SO₄)²⁻, (SeO₄)²⁻, and (SO₃)²⁻ groups or H₂O molecules (Fig. 6). As in the ettringite structure (Moore and Taylor 1970), the fully occupied Ca-sites in siwaqaite are coordinated by four hydroxyl groups (belonging to the coor-

dination of two neighboring M sites) and four water molecules. The structure contains two octahedral (M) sites, which exhibit almost equal bond distances and similar scattering values ($M1 = 13.6 e^-$; $M2 = 13 e^-$). Due to structural similarity with ettringite, Cr^{3+} -bearing ettringite, and thaumasite, these sites are expected to be occupied by Al, Si, and Cr. The M1 site shows a higher scattering density due to the occurrence of Cr and likely Si. The

(Al,Si):Cr ratio at the M1-site was refined, and the amount of Si was calculated from EMPA.

The channels in the siwaqaite structure are occupied by different anion groups. After considering the (M)-sites, 1.7 Cr apfu, 1.125 S apfu, and 0.4 Se apfu are not accounted for. These remaining cations are distributed over four “tetrahedral” (T) sites (Fig. 7).

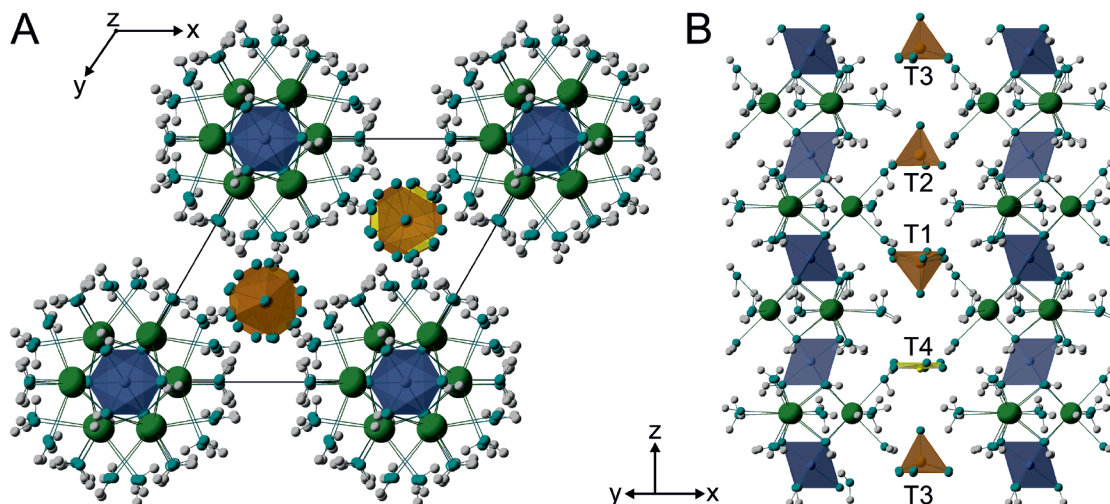


FIGURE 6. Crystal structure of siwaqaite: projection along [001] (a) and [110] (b). Ca atoms are green, $Al(OH)_6$ octahedra are depicted in blue, $(CrO_4)^{2-}$ tetrahedra in brown, and $(SO_3)^{2-}$ triangle in yellow. Oxygen and hydrogen atoms are shown as marine and gray spheres, respectively. (Color online.)

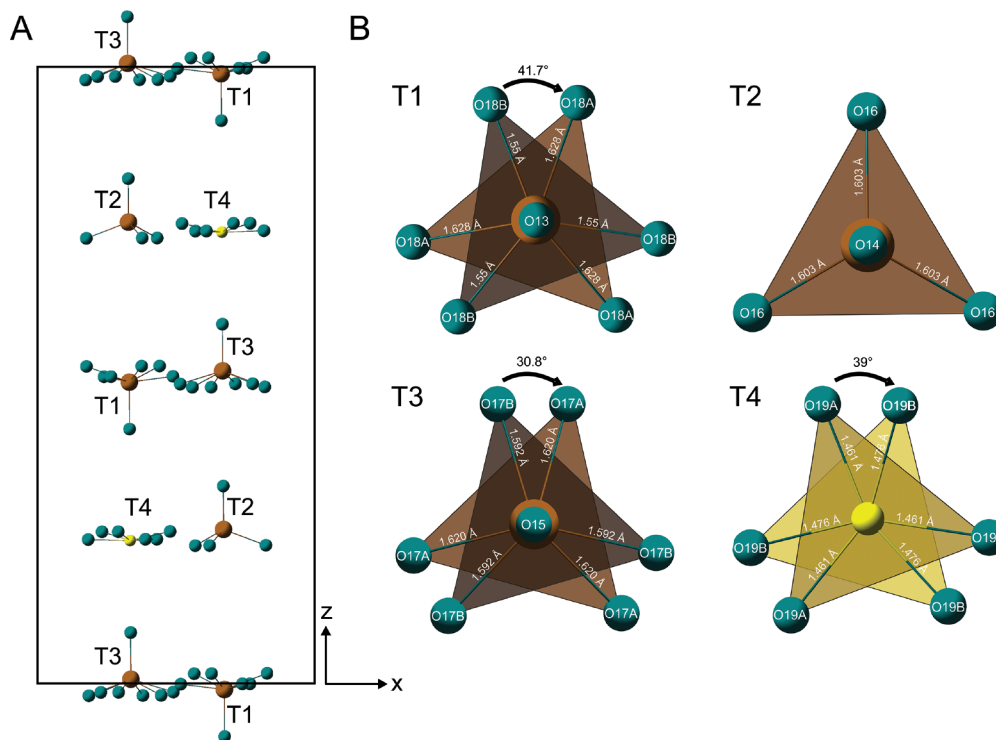


FIGURE 7. (a) The configuration of $(CrO_4)^{2-}$, $(SO_4)^{2-}$, $(SeO_4)^{2-}$, and $(SO_3)^{2-}$ anion groups in the channels of the siwaqaite structure along [001]. (b) Projection of three tetrahedra T1, T2, T3, and $(SO_3)^{2-}$ group on “T4” sites normal to [001], with positional disorder defined by splitting of O atoms. T1 = $(CrO_4)^{2-}/(SeO_4)^{2-}/(SO_4)^{2-}$; T2 = $(CrO_4)^{2-}/(SO_4)^{2-}$; T3 = $(CrO_4)^{2-}/(SO_4)^{2-}/(SeO_4)^{2-}$; T4 = $(SO_3)^{2-}$. (Color online.)

The T1 and T3 sites are clearly occupied by more than one species, as can be seen from split oxygen positions in their coordination (Fig. 7). Therefore, the coordination of T1 can be split into two tetrahedra, (1) O13 (1.639 Å) and 3 × O18a (1.628 Å), and (2) O13 (1.639 Å) and 3 × O18b (1.55 Å). The resulting mean bond distance $d_{\text{T-O}}$ is 1.631 Å for (1) and 1.572 Å for (2) (Table 2). Furthermore, the two T1-tetrahedra are rotated by 41.7° (O18a-T1-O18b; Fig. 7b).

The coordination of T3 may be split into (1) O15 (1.620 Å) and 3 × O17a (1.620 Å), and (2) O15 (1.620 Å) and 3 × O17b (1.592 Å) (Table 2). Splitting of the central T1 and T3 sites cannot be observed, as it probably is masked by thermal displacement. Two complement tetrahedra T1O4a and T1O4b occur in a ratio 76 to 24%. For T3, this ratio is similar 77/23, although the difference in the tetrahedral size is smaller ($d_{\text{T-O}} = 1.620$ Å for (1) and 1.599 Å for (2)). In addition, tetrahedra (1) and (2) are rotated by 30.8° (O17a-T3-O17b; Fig. 7b).

The T2 site is occupied by two different species. The distances between the central atom and four surrounding oxygen atoms range from 1.516 to 1.603 Å (Table 2). These distances are larger than expected for SO_4 but too short for other types of TO_4 tetrahedra. Moreover, the solid solutions show total or partial substitution of $(\text{SO}_4)^{2-}$ and $(\text{CrO}_4)^{2-}$, with bonds lengths between 1.48 Å for “pure” SO_4 and 1.65 Å for “pure” CrO_4 -tetrahedra (Quareni and de Pieri 1965; Hill 1977). Therefore, we modeled this tetrahedrally coordinated site with Cr and S. The cation distribution of Cr, Se, and S over the T1 and T3 sites was optimized by the method of Wright et al. (2000). OccQp simultaneously minimizes the differences between observed and calculated values for chemical composition, site scattering, bond valence sums, and bond lengths.

The T4 site exhibits a low site scattering of 3.5 e. Oxygen atoms O19a and O19b create two sets of planar threefold coordination $(\text{SO}_3)^{2-}$ groups with $d_{\text{T-O}}$ values of 1.461 and 1.476 Å, respectively (Table 2) and a rotation angle (O19a-T4-O19b) of 39.0° (Fig. 7b).

Our modeling of T4 with S resulted in a refined occupancy of 0.228. The obtained occupancies of O19a and O19b are 0.25 and 0.40, respectively. The excess oxygen atoms may belong to water molecules, although it is possible that they are artifacts of structure refinement with multiple twinned crystals.

Attempts to collect powder XRD data of siwaqaite were not successful, because we could not separate enough material. Consequently, powder XRD data were calculated from the structure model using PowderCell 2.4 (Kraus and Nolze 1996). Diffraction lines ($I > 2\%$) are listed in Supplemental¹ Table S1.

DISCUSSION

Relationship to other members of the ettringite group and synthetic analogs

The general formula of the ettringite group minerals is $\text{Ca}_6\text{M}_2(\text{OH})_{12}\text{T}_{3-4}\cdot n\text{H}_2\text{O}$, where $\text{M} = \text{Al}^{3+}$, Cr^{3+} , Fe^{3+} , Si^{4+} , Mn^{4+} , or Ge^{4+} , and $\text{T} = (\text{SO}_4)^{2-}$, $(\text{CrO}_4)^{2-}$, $(\text{SeO}_4)^{2-}$, $(\text{CO}_3)^{2-}$, $(\text{SO}_3)^{2-}$, $(\text{PO}_3\text{OH})^{2-}$, or $\text{B}(\text{OH})_4^-$, and $n = 22\text{--}26$ (Moore and Taylor 1970; Chukanov et al. 2012, 2016; Pekov et al. 2012). Currently, 13 mineral species have been identified in this group. The members of the ettringite group belong to three related structure types and crystallize in two hexagonal ($P6_3/m$ and

TABLE 2. Selected interatomic distances (Å) and bond-valence calculations (BVS) for siwaqaite

Ca1		Ca2	
Ca1-O1	2.411(6)	Ca2-O2 _{ii}	2.431(6)
Ca1-O1 _i	2.431(5)	Ca2-O2 _i	2.411(6)
Ca1-O3	2.385(5)	Ca2-O4 _{iii}	2.401(6)
Ca1-O3 _i	2.466(6)	Ca2-O4 _{iv}	2.417(6)
Ca1-O6	2.468(10)	Ca2-O5	2.410(9)
Ca1-O8	2.447(8)	Ca2-O7	2.442(9)
Ca1-O10	2.627(10)	Ca2-O9	2.638(7)
Ca1-O12	2.621(10)	Ca2-O11	2.672(9)
Average	2.482	average	2.478
BVS	2.04	BVS	2.08
M1 = 0.83Al1+0.12Si1+0.05Cr1		M2 = Al2	
M1-O1 _v	1.881(7)	M2-O3	1.882(7)
M1-O1 _{vi}	1.881(7)	M2-O3 _i	1.882(7)
M1-O1 _{vii}	1.881(7)	M2-O3 _i	1.882(5)
M1-O2 _v	1.924(6)	M2-O4	1.924(7)
M1-O2 _{vi}	1.924(6)	M2-O4 _i	1.924(7)
M1-O2 _{vii}	1.924(6)	M2-O4 _i	1.924(7)
Average	1.902	average	1.903
BVS	2.88	BVS	2.80
T1 = 0.5Cr3+0.3Se3+0.2S3			
T1-O13	1.639(15)	T1-O13	1.639(15)
T1-O18a	1.628(10)	T1-O18b	1.55(3)
T1-O18a	1.628(10)	T1-O18b	1.55(3)
T1-O18a	1.628(10)	T1-O18b	1.55(3)
Average	1.631	average	1.572
BVS	5.72	BVS	6.06
T2 = 0.65Cr4+0.35S4			
T2-O14		1.516(11)	
T2-O16		1.603(6)	
T2-O16		1.603(6)	
T2-O16		1.603(6)	
Average		1.581	
BVS		6.23	
T3 = 0.55Cr5+0.35S5+0.1Se5			
T3-O15	1.620(8)	T3-O15	1.620(8)
T3-O17a	1.620(7)	T3-O17b	1.592(17)
T3-O17a	1.620(7)	T3-O17b	1.592(17)
T3-O17a	1.620(7)	T3-O17b	1.592(17)
Average	1.620	average	1.599
BVS	5.56	BVS	5.85
T4 = S6			
T4-O19a	1.461(15)	T4-O19b	1.476(13)
T4-O19a	1.461(15)	T4-O19b	1.476(13)
T4-O19a	1.461(15)	T4-O19b	1.476(13)
Average	1.461	average	1.476
BVS	4.93	BVS	4.8

$P6_3$) and one trigonal ($P31c$) space groups. The first hexagonal structure type of $P6_3/m$, includes carraraite, $\text{Ca}_3\text{Ge}(\text{SO}_4)(\text{CO}_3)(\text{OH})_6\cdot 12\text{H}_2\text{O}$ (Merlino and Orlandi 2001) and kottenheimite, $\text{Ca}_3\text{Si}(\text{SO}_4)_2(\text{OH})_6\cdot 12\text{H}_2\text{O}$ (Chukanov et al. 2012), which have centrosymmetric structures. The second type of $P6_3$ contains phases with non-centrosymmetric structures: jouravskite, $\text{Ca}_3\text{Mn}^{4+}(\text{SO}_4)(\text{CO}_3)(\text{OH})_6\cdot 12\text{H}_2\text{O}$ (Granger and Protas 1969), thaumasite, $\text{Ca}_3\text{Si}(\text{OH})_6(\text{CO}_3)(\text{SO}_4)\cdot 12\text{H}_2\text{O}$ (Effenberger et al. 1983; Gatta et al. 2012), micheelsenite, $(\text{Ca}, \text{Y})_3\text{Al}(\text{PO}_3\text{OH})(\text{CO}_3)(\text{OH})_6\cdot 12\text{H}_2\text{O}$ (McDonald et al. 2001), hielscherite, $\text{Ca}_6\text{Si}_2(\text{SO}_4)_2(\text{SO}_3)_2(\text{OH})_{12}\cdot 22\text{H}_2\text{O}$ (Pekov et al. 2012), imayoshiite, $\text{Ca}_3\text{Al}(\text{CO}_3)[\text{B}(\text{OH})_4](\text{OH})_6\cdot 12\text{H}_2\text{O}$ (Nishio-Hamane et al. 2015), and tatarinovite, $\text{Ca}_3\text{Al}(\text{SO}_4)[\text{B}(\text{OH})_4](\text{OH})_6\cdot 12\text{H}_2\text{O}$ (Chukanov et al. 2016). All these minerals contain four anion groups, which indicate that their T-site occupancy is complete. Moreover, the ratio between Ca atoms and T-anions is equal to 3:2 in both structure types. Mineral phases of the trigonal type are also char-

acterized by a non-centrosymmetric structure. In contrast to the hexagonal members, they show a doubling of the c parameter. The trigonal members are: ettringite, $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$ (Moore and Taylor 1970), bentorite, $\text{Ca}_6\text{Cr}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$ (Gross 1980; Juroszek et al. 2017; Seryotkin et al. 2019) and sturmanite, $\text{Ca}_6\text{Fe}_2^{3+}(\text{SO}_4)_2.5[\text{B}(\text{OH})_4](\text{OH})_{12} \cdot 25\text{H}_2\text{O}$ (Peacor et al. 1983; Pushcharovsky et al. 2004). Powder XRD investigation of two other ettringite group minerals, charlesite, $\text{Ca}_6\text{Al}_2(\text{SO}_4)_2\text{B}(\text{OH})_4(\text{OH},\text{O})_{12} \cdot 26\text{H}_2\text{O}$ (Dunn et al. 1983) and buryatite, $\text{Ca}_3(\text{Si},\text{Fe}^{3+},\text{Al})(\text{SO}_4)\text{B}(\text{OH})_4(\text{OH},\text{O})_6 \cdot 12\text{H}_2\text{O}$ (Malinko et al. 2001), was performed. In both cases, because of the poor crystallinity of samples, the space group was assumed to be $P31c$ by the analogy to ettringite. Mostly, these trigonal phases have a Ca:T ratio of 2:1, but in buryatite, the ratio is 3:2, as in hexagonal members of the ettringite group.

Siwaqaite, $\text{Ca}_6\text{Al}_2(\text{CrO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$, is a chromate analog of ettringite (Moore and Taylor 1970) and an Al-dominant, chromate analog of bentorite (Gross 1980; Juroszek et al. 2017; Seryotkin et al. 2019). Otherwise, siwaqaite is assumed to be isostructural with three other B-containing members of this group: charlesite (Dunn et al. 1983), sturmanite (Peacor et al. 1983; Pushcharovsky et al. 2004), and buryatite (Malinko et al. 2001) (Supplemental¹ Table S2). The differences among these six members are reflected by their crystal morphology. The phases containing B usually occur as tabular, euhedral or subhedral crystals with a hexagonal dipyramidal form, whereas B-free members such as ettringite, bentorite, and siwaqaite, exhibit elongate, prismatic, hexagonal crystal shapes (Gross 1980; Dunn et al. 1983; Peacor et al. 1983). A more detailed comparison based on crystallographic data, optical properties, and XRD patterns is shown in Supplemental¹ Table S2.

As reported previously, the symmetry of ettringite group minerals is controlled by the occupancy of the four crystallographically distinct T sites in channels within the structure (Moore and Taylor 1970; Seryotkin et al. 2017, 2019). In case of minerals with the space group $P31c$, the T-sites are occupied by $(\text{SO}_4)^{2-}$, $(\text{CrO}_4)^{2-}$, $\text{B}(\text{OH})_4$, $(\text{SeO}_4)^{2-}$, $(\text{CO}_3)^{2-}$, $(\text{SO}_3)^{2-}$ groups and H_2O molecules. Each T-site is located on the threefold axes and can be ordered or disordered, depending on the anionic groups occupying the specific site.

In ettringite (Fig. 8), where the three standard T-sites are occupied by $(\text{SO}_4)^{2-}$ groups and the fourth site by water molecules, the arrangement of all anion groups is ordered (Moore and Taylor 1970). Seryotkin et al. (2019) determined the crystal structure of bentorite from powder XRD data. This structure, similar to ettringite, differs only in the atom type at the M site (Al^{3+} in ettringite and Cr^{3+} in bentorite), and thus the anionic groups' arrangement at the T-sites is also ordered. Seryotkin et al. (2017, 2019) suggested that the disorder of anionic groups may be related to the occupancies at the M sites and commonly takes place in intermediate members of the ettringite-bentorite solid-solution series. Juroszek et al. (2017) presented new data on a re-investigation of the bentorite structure. Their results show that the M site is partially occupied by Al and Cr, and the three T-sites are occupied by $(\text{SO}_4)^{2-}$ groups, as occurred in ettringite. The fourth T-site is occupied by $(\text{CO}_3)^{2-}$ groups and H_2O molecules. In this structure, the disordering of anionic groups result from two orientations of carbon groups at the T4 site (Fig. 8) and may

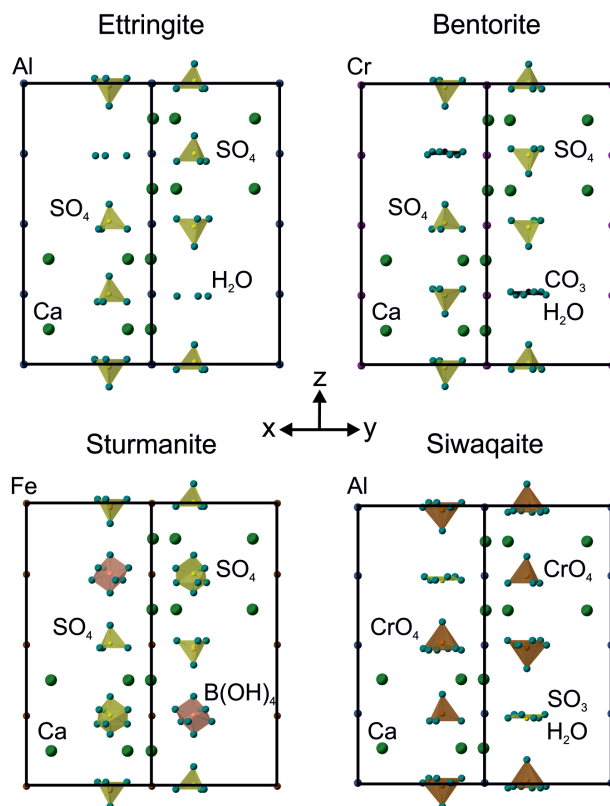


FIGURE 8. A comparison of the component and arrangement of T anions in $P31c$ structures of the ettringite group members. The structures for ettringite, bentorite, and sturmanite are based on Moore and Taylor (1970), Juroszek et al. (2017), and Pushcharovsky et al. (2004), respectively. (Color online.)

be associated with nonhomogeneous occupancy at the M site. Anionic groups in channels of the sturmanite structure exhibit distinct disorder. Like in ettringite and bentorite, the three sites (T1-T3) are formed by SO_4 tetrahedra, but the water molecules at T4 are replaced by $\text{B}(\text{OH})_4$ tetrahedra (Fig. 8; Pushcharovsky et al. 2004). The T1-site occupied by SO_4 group is partially replaced by $\text{B}(\text{OH})_3$. The $\text{B}(\text{OH})_4$ and SO_4 tetrahedra, located at T4 and T2 sites, respectively, are in two opposite orientations, which is associated with oxygen site splitting. Similar disorder of anionic groups is observed in siwaqaite. At each of the three standard sites (T1-T3), the $(\text{CrO}_4)^{2-}$ groups prevail (Fig. 8). The rest of the positions are filled by $(\text{SO}_4)^{2-}/(\text{SeO}_4)^{2-}$ or $(\text{SO}_4)^{2-}$ groups over T1/T3 and T2-sites, respectively. The T4 site (occupied by H_2O molecules in ettringite) is partially replaced by SO_3 triangles. In addition, T1O₄ and T3O₄ tetrahedra, as well as $(\text{SO}_3)^{2-}$ groups in T4 exhibit rotational disorder with two possible orientations within the structure. In the ettringite group, only hielscherite, $\text{Ca}_6\text{Si}_2(\text{SO}_4)_2(\text{SO}_3)_2(\text{OH})_{12} \cdot 22\text{H}_2\text{O}$ (Pekov et al. 2012) contains sulfate and sulfite groups, which form tetrahedra and trigonal pyramids, respectively. The presence of a planar TO_3 geometry is not consistent with the strongly pyramidal arrangement expected for sulfite $(\text{SO}_3)^{2-}$ in the siwaqaite structure. In this case, the crystal has multiple twinning including inversion, and the “planar SO_3 ” could be (1) the average position of two different orienta-

tions of “pyramidal” SO_3 or two different orientations (point-up/point-down) of SO_4 groups or/and (2) due to the “overlap” of SO_4 and CO_3 , if the CO_3 group is present, in small amounts, like in thaumasite and hielscherite.

The structure of ettringite, refined using single-crystal neutron diffraction (Gatta et al. 2019), shows a presence of 27 H_2O molecules pfu: $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 27\text{H}_2\text{O}$, instead of 26 H_2O in the accepted formula of ettringite (Moore and Taylor 1970). In the ettringite structure, 24 independent H_2O molecules pfu are in the $\{\text{Ca}_6[\text{Al}(\text{OH})_6]_2 \cdot 24\text{H}_2\text{O}\}^{6+}$ columns. According to the difference Fourier nuclear density maps, the inter-column “free” H_2O molecules are distributed disorderedly over the two half-occupied sites (OW19 and OW20) and give the remaining 3 H_2O pfu (Gatta et al. 2019). In siwaqaite there are 26 H_2O molecules pfu. In our refinement, we did not identify additional protons associated with O19a and O19b in the channels. The sum of the O19a and O19b occupancy is equal to 0.65. Thus, the total number of H_2O molecules is close to 26 in siwaqaite: $0.65 \times 3 + 24 = 25.95$. The number of H_2O in siwaqaite may be slightly lower, as some of the O19a and O19b atoms may be coordinated to additional T4 site (Figs. 6 and 7).

The IR band positions of siwaqaite are comparable with those reported before and compiled in Table 3. The most significant bands related to the asymmetric stretching vibrations of chromate and sulfate groups in siwaqaite and ettringite are observed at 869 and 1113 cm^{-1} , respectively (Scholtzová et al. 2015; this study). A band assigned to ν_3 of $(\text{SO}_4)^{2-}$ group occurs at 1108 cm^{-1} in the siwaqaite spectrum. In synthetic phases, this band is located in the range 1100–1200 cm^{-1} for Cr^{6+} -bearing ettringite and at 1138 cm^{-1} in ettringite (Myneni et al. 1997; You et al. 2007). Symmetric stretching (ν_1) and asymmetric bending vibrations (ν_4) assigned to $(\text{SO}_4)^{2-}$ group, presented in the ettringite spectra at 989 cm^{-1} and in the range 610–639 cm^{-1} (Myneni et al. 1997; Scholtzová et al. 2015), are not in siwaqaite and its synthetic analogs. The band around 540 cm^{-1} corresponds to the Al-OH bending vibration of $\text{Al}(\text{OH})_6$ unit in columns within the structures of siwaqaite and ettringite (Myneni et al. 1997; Scholtzová et al. 2015; this study). Scholtzová et al. (2015) assigned this band to the asymmetric bending vibrations of sulfate groups. Using FTIR spectroscopy, Perkins analyzed solid solutions between $(\text{SO}_4)^{2-}$ - and $(\text{CrO}_4)^{2-}$ -bearing ettringite and observed that the bands at ~1140 and ~880 cm^{-1} , which are attributed to the sulfate and chromate groups, exhibit varying intensities, depending on the dominant element quantity (Perkins 2000). Moreover, the type and number of elements occupying a specified site in the structure may affect the band shift. We assume that the lower

wavenumber of $(\text{CrO}_4)^{2-}$ asymmetric stretching vibrations in siwaqaite in comparison to the synthetic counterpart (Perkins and Palmer 2000; You et al. 2007) is associated with the tetrahedrally coordinated sites occupied by Cr, S, and Se. Povarennykh (1978) determined the IR band limits of characteristic polyhedral vibrations. The ranges of asymmetric stretching vibrations for chromate and selenate groups partially overlap and occur in the intervals 800–930 and 800–870 cm^{-1} , respectively. Therefore, in the IR spectrum of siwaqaite, the band related to $(\text{CrO}_4)^{2-}$ may overlap with the band of $(\text{SeO}_4)^{2-}$. In synthetic sulfate-selenate ettringite, this band is at 879 cm^{-1} (Hassett et al. 1990).

The broad infrared band at ~1400 cm^{-1} assigned to asymmetric stretching C-O vibrations (ν_3) of the $(\text{CO}_3)^{2-}$ group is detected in siwaqaite, synthetic Cr^{6+} ettringite, and Cr-free ettringite (Table 3). Its presence in siwaqaite may be related to calcite, which occurs in the mineral association. In the case of the synthesized phases, it could be related to the reagents used during the synthesis process, or it came from the atmosphere during IR measurements. For all phases listed in Table 3, OH bending vibrations of water molecules are in the range 1620–1700 cm^{-1} . For siwaqaite, these bands occur at 1629 and 1650 cm^{-1} . In the high wavenumber region, two characteristic bands appear: a broad band in the range 2800–3500 cm^{-1} , which is centered at 3318 cm^{-1} , and a band at 3620 cm^{-1} . The broad band is related to the OH stretching vibrations of water molecules, and the second band is attributed to OH stretching vibrations of OH unit (Myneni et al. 1997; Perkins and Palmer 2000; You et al. 2007; Scholtzová et al. 2015). Similar bands were observed in synthetic chromate, selenate, and sulfate ettringites (Table 3).

Table 4 lists the characteristic types of vibrational modes associated with the dominant anionic groups in tetrahedrally coordinated sites in hashemite, ettringite, Se-ettringite, and siwaqaite. The Raman band positions of chromate, sulfate, and selenate groups, which occupy tetrahedrally coordinated sites in the siwaqaite structure, are comparable with those reported previously. The positions of asymmetric stretching (ν_3) and symmetric/asymmetric bending vibration (ν_2/ν_4) of $(\text{CrO}_4)^{2-}$ group in siwaqaite are within the ranges of the modes in the Raman spectrum of hashemite, BaCrO_4 (Juroszek et al. 2018). The minor band shift of symmetric stretching $(\text{CrO}_4)^{2-}$ vibration (ν_1), shown as the most intense peak at 856 cm^{-1} in the siwaqaite spectrum, may be related to the presence of a heavier element over the same site. Vibrational modes of a sulfate group, which are dominant in the Raman spectrum of ettringite (Renaudin et al. 2010), are represented by the low intensity symmetric stretching vibration observed at 987 cm^{-1} in siwaqaite. In the siwaqaite spectrum, the

TABLE 3. Types of the vibrational modes and corresponding wavenumbers (cm^{-1}) of siwaqaite in comparison to similar phases

Phase number/Band assignment	Band position (cm^{-1})					
	1	2	3	4	5	6
Al-OH bending vibration	540	523			542	547
ν_4 $(\text{SO}_4)^{2-}$				610	616	610–639
ν_3 $(\text{CrO}_4)^{2-}/(\text{SeO}_4)^{2-}$	869	883	886/867–902	879		
ν_1 $(\text{SO}_4)^{2-}$					989	989
ν_3 $(\text{SO}_4)^{2-}$	1108	–	1100–1200	1113	1113	1138
ν_3 $(\text{CO}_3)^{2-}$	1402	1387	~1400	1420		1430–1489
(OH) ⁻ bending vibration of H_2O	1629–1650	1620	1600–1700	1635	1631–1678	1647
(OH) ⁻ stretching vibration of H_2O	3318	3380	3400–3500	3100–3600	3432	3235–3400
(OH) ⁻ stretching vibration of OH unit	3620	3607	3600–3700	3635	3637	3560

Note: 1 = siwaqaite (this study); 2 = synthesized $\text{Ca}_6\text{Al}_2(\text{CrO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$ (Perkins and Palmer 2000); 3 = synthesized Cr^{6+} ettringite (You et al. 2007); 4 = synthesized sulfate-selenate ettringite (Hassett et al. 1990); 5 = ettringite $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$ (Scholtzová et al. 2015); 6 = synthesized ettringite (Myneni et al. 1997).

TABLE 4. Comparison of vibrational mode types and wavenumbers for phases containing $(\text{CrO}_4)^{2-}$, $(\text{SO}_4)^{2-}$, and $(\text{SeO}_4)^{2-}$ groups

Phase	Dominant anionic group	Wavenumber cm^{-1}			
		ν_1	ν_2	ν_3	ν_4
Hashemite ^a	$(\text{CrO}_4)^{2-}$	864	346–360	871–909	400–422
Ettringite ^b	$(\text{SO}_4)^{2-}$	988	452, 492	1120	610
Se-ettringite ^c	$(\text{SeO}_4)^{2-}$	842	345	884	415
Siwaqaite ^d	$(\text{CrO}_4)^{2-}$	856	350, 376	908	409
	$(\text{SO}_4)^{2-}$	987			
	$(\text{SeO}_4)^{2-}$	842	332	893	

^a Juroszek et al. (2018).^b Renaudin et al. (2010).^c Guo et al. (2017).^d This study.

bands attributed to the selenate group occur at 842 (ν_1), 332 (ν_2), and 893 cm^{-1} (ν_3). They have similar positions as in Se-bearing ettringite (Guo et al. 2017). The insignificant differences exist for symmetric bending (ν_2) and asymmetric stretching (ν_3) vibrations, which may result from the overlapping of chromate and selenate bands in these spectral ranges. Therefore, we cannot exclude that Raman band at 893 cm^{-1} can be also assigned to the asymmetric stretching vibration of $(\text{CrO}_4)^{2-}$ group. A common feature of siwaqaite, ettringite, and Se ettringite is the presence of $\text{Al}(\text{OH})_6$ unit at octahedral coordination in their structures. In the Raman spectra of these phases, the vibrations related to this unit are at 546 cm^{-1} , 549 cm^{-1} , and in the range 530–550 cm^{-1} (Renaudin et al. 2010; Guo et al. 2017).

Genetic aspect and origin of trace elements

Siwaqaite, after ettringite, bentorite, and thaumasite, is the next member of the ettringite group, which was recognized and described from pyrometamorphic rocks of the Hatrurim Complex. Moreover, only within these unique rocks, bentorite, and siwaqaite have been found so far (Gross 1980). All ettringite group minerals are components of secondary, low-temperature mineral assemblages. They usually crystallize in cavities, cracks, fissures, and fill veins that cut altered pyrometamorphic rocks (Kolodny et al. 2014). It is assumed that these minerals form during retrograde metamorphism or as a result of low-temperature alteration (Matthews and Gross 1980; Sokol et al. 2011; Kolodny et al. 2014).

Natural and synthetic ettringite-type phases are usually stable at restricted conditions ($T < 120^\circ\text{C}$, $\text{pH} = 9.5\text{--}13$) (Wieczorek-Ciurowa et al. 2001; Jallad et al. 2003; Zhou et al. 2004; Jiménez and Prieto 2015; Matschei and Glasser 2015). In addition, the formation of synthetic $\text{Ca}_6\text{Al}_2(\text{CrO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$ becomes more intensive, when the pH of the suspension solution is ≥ 10.9 (Terai et al. 2006). Based on the synthesis data of different ettringite related minerals, as well as the mineral association of the holotype specimen, we assume that siwaqaite, the natural chromate analog of ettringite, forms in the temperature not higher than $\sim 70\text{--}80^\circ\text{C}$.

The redox-sensitive elements Cr and Se in siwaqaite arise from the Belqa Group sediments (Late Cretaceous to Early Tertiary) composed mainly of carbonate-rich lithologies. All strata were deposited after the Oceanic Anoxic Event (on the Cenomanian and Turonian boundary) on the southern epicontinental shelf of Neo-Tethys (Abed et al. 2005; Fleurance et al. 2013; Sokol et al. 2017). It is assumed that high Cd, Cr, Fe, Mo, Ni, Se, Sr, U, V, and Zn enrichment in these sediments is mostly

due to direct precipitation from seawater enriched with exogenic metal flux that corresponds to the leaching of ophiolites from Troodos (Cyprus) and Baer Bassit (Syria NW) (Fleurance et al. 2013; Khoury et al. 2014, 2015). A further enrichment by redox-sensitive elements took place during spontaneous combustion of the Belqa Group organic-rich levels, composed of bituminous marls and limestone. As a result of these processes, the varicolored marbles formed, and the significant rock volume loss was caused by decarbonation and burning of the organic matter (Fleurance et al. 2013; Khoury et al. 2014). In the altered metamorphic marbles, characterized by fracture zones and numerous veins, the trace elements such as Cr, Zn, Se, U, and V, were concentrated in these areas and formed unique mineralization (Khoury et al. 2015; Vapnik et al. 2019).

ENVIRONMENTAL IMPLICATIONS

Chromium is a redox-sensitive transition element that plays a significant role in industry, environmental protection, and the biology of organisms (Liu et al. 2017). Most frequently, compounds containing chromium in the trivalent and hexavalent states are stable. Cr^{3+} is a component of ores, while Cr^{6+} occurs naturally in rare minerals such as crocoite, PbCrO_4 . Hexavalent chromium has anthropogenic sources as a result of, for example, chromite ore processing, metallurgy, electric energy, and chemical industry (Irwin et al. 1971; Motzer and Enginners 2004). Due to the high solubility and oxidizing potential, hexavalent Cr is a toxic, teratogenic, carcinogenic, and mutagenic element in the biological system, which can damage kidney and tissue structures (Irwin et al. 1971; Singh et al. 2015).

In the pyrometamorphic rocks of the Hatrurim Complex, Cr^{6+} is present, mainly, as $(\text{CrO}_4)^{2-}$, in low-temperature hydrothermal minerals, represented by Cr^{6+} -bearing ettringite, siwaqaite, chromate, and minerals of the baryte-hashemite solid solution. It was included in their structures as a result of the Cr^{3+} oxidation, which in turn was removed from other minerals, such as ferrites, via hyper-alkaline solutions during hydrothermal alteration of metamorphic rocks (Sokol et al. 2011; Juroszek et al. 2018).

Ettringite is an interesting mineral because of its capability of extensive ion exchanges. Slight changes of the chemical composition do not modify the structure, so in literature, such terms as “remarkable host phase” or “anion-exchanger” can be found (Jiménez and Prieto 2015; Guo et al. 2017). Ca^{2+} , Al^{3+} , $(\text{SO}_4)^{2-}$, and $(\text{OH})^-$ can be substituted in the ettringite structure (Kumarathasan et al. 1989; Gougar et al. 1996; You et al. 2007; Guo et al. 2017). Ca^{2+} may be substituted by other divalent cations including Ba^{2+} , Cd^{2+} , Co^{2+} , Mn^{2+} , Ni^{2+} , Pb^{2+} , Sr^{2+} , and Zn^{2+} (Kumarathasan et al. 1989; Gougar et al. 1996; You et al. 2007; Wu et al. 2012; Jiménez and Prieto 2015; Guo et al. 2017). This type of replacement was reported only in cement hydrated phases and some synthetic analogs (Gougar et al. 1996). An unusual substitution was noted in micheelsenite, $(\text{Ca}, \text{Y})_3\text{Al}(\text{PO}_3\text{OH})(\text{CO}_3)(\text{OH})_6\cdot 12\text{H}_2\text{O}$ (McDonald et al. 2001), where Ca is partially replaced by trivalent Y. The octahedral M site occupied by Al^{3+} in the ettringite structure can be replaced by Cr^{3+} , Fe^{3+} , Ge^{3+} , Mn^{4+} , Si^{4+} , Co^{3+} , Ga^{3+} , Ni^{3+} , and Ti^{3+} (Gougar et al. 1996; Cody et al. 2004; Guo et al. 2017). In the ettringite group, several members, including jouravskite, bentorite, sturmanite, thaumasite, and cararaite with a total or partial of Al replacement were described

(Granger and Protas 1969; Gross 1980; Effenberger et al. 1983; Peacor et al. 1983; Merlino and Orlandi 2001). The only notable substitution of OH groups by oxygen was reported in thaumasite and charlesite (Dunn et al. 1983; Effenberger et al. 1983). The tetrahedral T site is characterized by the wide variety of oxyanion substitutions. This site, occupied normally by $(\text{SO}_4)^{2-}$, can be substituted by $\text{B}(\text{OH})_4^-$, $(\text{CrO}_4)^{2-}$, $(\text{SO}_3)^{2-}$, $(\text{CO}_3)^{2-}$, and $(\text{HPO}_4)^{2-}$ (McDonald et al. 2001; Chukanov et al. 2012, 2016; Pekov et al. 2012; Nishio-Hamane et al. 2015). Moreover, $(\text{SeO}_4)^{2-}$, $(\text{MoO}_4)^{2-}$, $(\text{AsO}_4)^{3-}$, and $(\text{VO}_4)^{3-}$ substitutions were also described by Kumrathasan et al. (1989), Gougar et al. (1996), Zhang and Reardon (2003), You et al. (2007), and Guo et al. (2017).

Such variety in the ettringite structure for ionic substitutions suggests that this phase can be an effective host for toxic cations and oxyanions. The wide usage of Cr in industry, such as the production of stainless steel, metal finishing, wood preservatives, and refractory products, causes a release of high concentrations of chromates to surface water (Irwin et al. 1971). Therefore, ettringite could be used for product removal by absorbing toxic ions into its structure. Nevertheless, the unsuccessful testing of chromium removal from liquid industrial wastes as a result of ettringite formation was described by Kowalski et al. (2010). It was found that during the synthesis of Cr^{6+} -ettringite in the presence of sulfate ions, the latter is incorporated into the structure of the synthesized phase, whereas $(\text{CrO}_4)^{2-}$ ions remain in solution. Removing Cr waste by precipitation as ettringite in wastewater is impossible because the solubility equilibrium value of calcium chromate is higher than that of calcium sulfate.

Hexavalent chromium is present as chromate in concrete and forms as a result of Cr^{3+} oxidation during Portland cement clinker production (Bae et al. 2018). The present study suggests that the ground granulated blast-furnace slag (GGBS), often included in concrete, even with minor Portland cement-based material replacement, may be a suitable host for Cr^{6+} reduction and immobilization.

The observed $(\text{CrO}_4)^{2-}$ - $(\text{SO}_4)^{2-}$ substitution in siwaqaite is not uncommon in minerals. There are several mineral solid solutions, where total or partial substitution of these ions is observed (Abdul-Samad et al. 1982; Kampf et al. 2012; Yang et al. 2017). The baryte-hashemite solid solution is a well-known example (Jurosze et al. 2018). Similar coordinations, identical charges, and comparable radii of the chromate and sulfate anions result in mutual substitution and formation of the siwaqaite-ettringite solid solution.

ACKNOWLEDGMENTS

H.K. acknowledges help from V. Kahlenberg, T. Gstir, and A. Pauluhn during the synchrotron experiments. The authors thank F. Bosi and anonymous reviewers for their careful revisions that improved an early version of the manuscript.

FUNDING

This work was supported by the National Sciences Centre (NCN) of Poland, grant no. 2016/23/N/ST10/00142 (R.J.) and OeAD, CEEPUS CIII-RO-0038, ICM-2018-12254 (R.J.). The research has also received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No. 730872, project CALIPSOplus.

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MANUSCRIPT RECEIVED JULY 15, 2019

MANUSCRIPT ACCEPTED OCTOBER 20, 2019

MANUSCRIPT HANDLED BY G. DIEGO GATTA

Endnote:

¹Deposit item AM-20-37208, Supplemental Tables. Deposit items are free to all readers and found on the MSA website, via the specific issue's Table of Contents (go to http://www.minsocam.org/MSA/AmMin/TOC/2020/Mar2020_data/Mar2020_data.html).