



Research Paper

Rotemite, $\text{Ca}_4\text{Cr}_2(\text{OH})_{12}\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ – the trigonal chromium analog of hydrocalumite and Friedel's salt – a new mineral from the Hatrurim Complex, Israel

Katarzyna Skrzyńska^{a,b,*}, Harald Müller^b, Rafał Juroszek^a, Biljana Krüger^c, Georgia Cametti^d, Anna Pakhomova^b, Irina Galuskina^a, Yevgeny Vapnik^e, Krzysztof Woźniak^f, Evgeny Galuskin^a

^a Faculty of Natural Sciences, University of Silesia in Katowice, Będzińska 60, Sosnowiec, Poland

^b European Synchrotron Radiation Facility, 71, avenue des Martyrs, CS 40220, 38043 Grenoble Cedex 9, France

^c Institute of Mineralogy and Petrography, University of Innsbruck, Innrain 52, A-6020 Innsbruck, Austria

^d Institute of Geological Sciences, University of Bern, Bern 3012, Switzerland

^e Department of Geological and Environmental Sciences, Ben-Gurion University of the Negev, POB 653, Beer-Sheva, Israel

^f Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland

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ABSTRACT

Rotemite, $\text{Ca}_4\text{Cr}_2(\text{OH})_{12}\text{Cl}_2 \cdot 4\text{H}_2\text{O}$, is a newly discovered mineral and the first Cr-bearing member of the hydrocalumite group within the hydrotalcite supergroup. The new mineral is a trigonal chromium analog of both hydrocalumite and its synthetic counterpart, Friedel's salt, representing a large family of novel compounds of lamellar/layered double hydroxides (LDH). This work presents the first comprehensive study of a Ca, Cr-bearing compound within the LDH family. Rotemite was discovered in pyrometamorphic rocks of the Hatrurim Complex, Israel. It forms tiny hexagonal platelet-shaped crystals that appear pale bluish-violet (daylight) to pinkish-violet (artificial light), depending on the type of illumination. The streak is pale light-purple. Optically, rotemite is negatively uniaxial with $\omega = 1.565(2)$, $e = 1.544(2)$ ($\lambda = 589\text{ nm}$). It has a hardness of 2.5–3 on the Mohs scale. The crystals exhibit perfect cleavage on {0001}. The electron microprobe analyses indicated the empirical formula of $(\text{Ca}_{3.94}\text{Sr}_{0.01})_{\Sigma 3.95}(\text{Cr}_{1.47}\text{Al}_{0.52}\text{Fe}_{0.05}^{3+})_{\Sigma 2.04}(\text{OH})_{12}[\text{Cl}_{1.68}(\text{OH})_{0.32}(\text{SO}_4)_{0.01}]_{\Sigma 2.01} \cdot 4\text{H}_2\text{O}$.

The calculated density, based on the empirical formula and unit cell parameters obtained from single-crystal X-ray diffraction data, is 2.18 g/cm^3 . Single-crystal X-ray diffraction measurements have revealed that rotemite represents a 6-layered polytype with trigonal symmetry ($R\bar{3}c$) and unit cell parameters: $a = 5.7944(2)\text{ Å}$, $c = 46.69(4)\text{ Å}$, $V = 1357.7(10)\text{ Å}^3$. The final structural model converged to $R_1 = 0.0866$. The structure consists of hydrocalumite-type layers $[\text{Ca}_4(\text{Cr},\text{Al})_2(\text{OH})_{12}(\text{H}_2\text{O})_4]^{2+}$ with intercalated Cl^- ions. Raman spectra of rotemite are characterized by a prominent band at $\sim 525\text{ cm}^{-1}$, typical of LDH compounds. Polarized Raman spectroscopy revealed that signals from O–H stretching vibrations at $3441\text{--}3442\text{ cm}^{-1}$ and $3609\text{--}3612\text{ cm}^{-1}$ strongly depend on the orientation of the crystal relative to the polarization of the incident laser beam. This indicates both an ordered arrangement of water molecules and a perpendicular arrangement of O–H bonds within the hydrocalumite layers, respectively. The origin of rotemite and other Cr^{3+} -bearing minerals is discussed, along with the possible role of the $[\text{Cr}(\text{OH})_6]^{3-}$ anion in their formation.

1. Introduction

The hydrotalcite supergroup of minerals includes a wide variety of complex layered structures and polytypes with variable compositions

(Bookin and Drits, 1993; Bookin et al., 1993; Mills et al., 2012). One of the most well-known minerals of this supergroup is hydrocalumite $\text{Ca}_4\text{Al}_2(\text{OH})_{12}(\text{Cl},\text{CO}_3,\text{OH})_2 \cdot 4\text{H}_2\text{O}$ (Friedel, 1897; Fischer et al., 1980), the parent compound of the hydrocalumite group. Rotemite,

* Corresponding author at: Faculty of Natural Sciences, University of Silesia in Katowice, Będzińska 60, Sosnowiec, Poland.

E-mail addresses: katarzyna.skrzynska@us.edu.pl (K. Skrzyńska), mueller@esrf.fr (H. Müller), rafal.juroszek@us.edu.pl (R. Juroszek), biljana.krueger@uibk.ac.at (B. Krüger), georgia.cametti@unibe.ch (G. Cametti), anna.pakhomova@esrf.fr (A. Pakhomova), irina.galuskina@us.edu.pl (I. Galuskina), vapnik@bgu.ac.il (Y. Vapnik), kwozniak@chem.uw.edu.pl (K. Woźniak), evgeny.galuskin@us.edu.pl (E. Galuskin).

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$\text{Ca}_4\text{Cr}_2(\text{OH})_{12}\text{Cl}_2 \cdot 4\text{H}_2\text{O}$, is a newly discovered mineral of this group, found in the pyrometamorphic rocks of the Hatrurim Complex, Israel. It is the first member of the hydrocalumite group in which another trivalent ion replaces the aluminum cation. Like all minerals of the hydro-talcite supergroup, rotemite belongs to a larger family of novel lamellar/layered double hydroxide (LDH) compounds.

The main structural motif of all LDH is based on a brucite-like layer. In the hydrocalumite-type of compounds, one-third of the divalent cations in this layer are substituted by trivalent cations, generating a positive charge according to the scheme $[(\text{M}_{1-x}^{2+}\text{M}_x^{3+})(\text{OH})_2]^{x+}$ (where $\text{M}^{2+} = \text{Mg}^{2+}$ or Ca^{2+} ; $\text{M}^{3+} = \text{Al}^{3+}$; $x \leq 0.33$ for hydrocalumite-type of compounds; Mills et al., 2012; Zhitova et al., 2023b). In order to balance the positive charge, anions such as chloride are intercalated between the layers, increasing the interlayer spacing. Notably, the negatively charged interlayer species in LDH compounds are exchangeable, and intercalation of neutral molecules, such as water, between the layers is also possible. Recently, the ion-exchange capability of LDH compounds, particularly of hydrocalumite and its synthetic counterpart, Friedel's salt (Friedel, 1897; Fischer et al., 1980), has attracted considerable attention due to their potential application in the immobilization of potentially toxic elements (PTEs), such as Cr(VI) (Bhattacharya et al., 2020; Paul and Chang, 2020; Ceballos et al., 2023). On the other hand, the catalytic properties of LDH compounds, including Cr^{3+} -LDH, have been extensively studied (Kuwahara and Yamashita, 2013; Sánchez-Cantú et al., 2015; Szabó et al., 2025). Therefore, the incorporation of both Cr(III) and Cr(VI) into the structure of hydrocalumite and its synthetic counterpart, Friedel's salt, remains an area of significant interest (Prasanna et al., 2007; Dai et al., 2009; Radha and Kamath, 2013). However, a detailed examination of Cr-bearing LDH compounds is challenging, as these phases typically occur as poorly crystallized, multi-phase mixtures, which hampers accurate structural and spectroscopic characterization as well as phase identification. Very recently, synthetic Ca_2Cr -layered double hydroxides were reported as catalysts for the retention and photochemical elimination of drugs in wastewater (Szabó et al., 2025). However, details on the stoichiometries, spectroscopic, and crystallographic characteristics of these phases were not reported.

Here is presented the new clay-like mineral rotemite $\text{Ca}_4\text{Cr}_2(\text{OH})_{12}\text{Cl}_2 \cdot 4\text{H}_2\text{O}$, a trigonal chromium analog of hydrocalumite and Friedel's salt. The structural and spectroscopic properties of rotemite, along with its geological origin, are discussed in detail. This work is the first comprehensive study of a Ca, Cr-bearing compound within the LDH family.

The Commission on New Minerals, Nomenclature, and Classification of the International Mineralogical Association has approved rotemite as a mineral (and its symbol Rot) under the number (IMA 2024-58) (Skrzyńska et al., 2024). The name rotemite is derived from the rotem plant (also known as retama), which commonly grows in the wadis of the Negev Desert. Rotem is a genus of blooming shrub characterized by dense clusters of small white to light purple flowers that densely overgrow the branches. Similarly, rotemite forms tiny purple crystals that cover the surface of the holotype specimen. The holotype specimen of rotemite has been deposited in the mineralogical collection of the Earth and Man National Museum, Sofia, Bulgaria, catalogue number 40450.

2. Methodology

2.1. Chemical composition analyses

The morphology and composition of rotemite and associated minerals were studied using a Phenom XL and a Quanta 250 scanning electron microscopes (SEM, Institute of Earth Sciences, Faculty of Natural Sciences, University of Silesia, Poland), and a Cameca SX100 electron microprobe analyzer (Faculty of Geology, University of Warsaw, Poland). Chemical analyses were performed using wavelength dispersive X-ray spectroscopy (WDS) mode (settings 15 kV, 8 nA and beam diameter 10 μm) using synthetic and natural standards: $\text{ClK}\alpha$ –

sodalite; $\text{CaK}\alpha$ – diopside; $\text{SK}\alpha$ – baryte; $\text{AlK}\alpha$ – orthoclase; $\text{SrL}\alpha$ – celestine; $\text{CrK}\alpha$ – Cr_2O_3 ; $\text{FeK}\alpha$ – Fe_2O_3 . Since rotemite dehydrates under microprobe conditions, its quantitative composition was also investigated using an energy dispersive spectroscopy (EDS) UltraDry X-ray microanalyzer coupled to a Quanta 250 SEM under conditions of accelerating voltage = 15 kV; beam current = 1 nA, using the following standards: $\text{NaK}\alpha$, $\text{AlK}\alpha$ – albite, $\text{ClK}\alpha$ – tugtupite; $\text{CaK}\alpha$, $\text{MgK}\alpha$ – diopside; $\text{SK}\alpha$ – celestine; $\text{KK}\alpha$ – orthoclase; $\text{CrK}\alpha$ – Cr_2O_3 ; $\text{FeK}\alpha$ – olivine. The contents of elements not specified above with atomic numbers higher than that of carbon were below detection limits.

2.2. Raman spectroscopy

Polarized Raman spectra of rotemite were collected using a WITec alpha 300R confocal Raman microscope (Institute of Earth Sciences, Faculty of Natural Sciences, University of Silesia, Poland) equipped with an air-cooled 488 nm laser and a CCD camera operating at -61°C . The Raman signal was recorded using a 600 g mm^{-1} grating monochromator calibrated to the Raman scattering line of a silicon plate (520.7 cm^{-1}). Data acquisition was carried out on a plate-like crystal with the (001) plane oriented both perpendicular and parallel to the laser beam polarization with an integration time of 3 s, with an accumulation of 40 scans and a resolution of 3 cm^{-1} . The power of the laser at the sample position was 40 mW. The spectra were deconvoluted using the GRAMS package software (Thermo Scientific™) with the Gauss-Lorentz function and a minimum number of band components, yielding R^2 values of 0.9997, 0.9996, 0.9992, and 0.9996 for the spectra presented in the paper.

2.3. Single Crystal X-ray Diffraction (SC-XRD)

Several dozen crystals were investigated using various diffractometers to obtain SC-XRD data (Institute of Geological Sciences; University of Bern; Department of Chemistry, University of Warsaw). Nevertheless, most attempts were unsuccessful due to difficulties in determining the unit cell parameter c . Eventually, SC-XRD data were successfully collected on the most promising crystal using an STOE IPDS-II imaging plate diffractometer with graphite monochromatized $\text{MoK}\alpha$ radiation (Institute of Mineralogy and Petrography, University of Innsbruck, Austria). A hemisphere of reciprocal space was acquired using ω -scans with a step size of 1° and an exposure time of 30 min per frame. Data reduction was carried out in X-Area software. However, the data quality was unsatisfactory ($R_{\text{int}} = 0.1319$) due to the poor I/σ ratio resulting from the low scattering power of the crystal (Table S1).

Therefore, synchrotron radiation was used for further investigation. Single crystals were placed on a diamond culet of a diamond anvil cell (without pressure medium) to perform the SC-XRD experiment at ambient conditions. The measurement was carried out at the European Synchrotron Radiation Facility on beamline ID27, which provides a highly focused beam ($\sim 1 \times 1\text{ }\mu\text{m}^2$) and is equipped with a detector CdTe Eiger2 9 M (Mezouar et al., 2024). The wavelength was $0.3738\text{ }\text{\AA}$. The rotation angle was $\pm 32^\circ$ with an exposure time of 0.5 s per frame. Before data reduction, various unit cell parameters were examined using CrysAlisPRO software in order to confirm the rare 6R polytype with unit cell parameters: $a = 5.7944(2)\text{ }\text{\AA}$ and $c = 46.69(4)\text{ }\text{\AA}$. Details of the tested unit cell parameters as well as reconstructed reciprocal space are given in Supplementary Materials (Text S1, Fig. S1). The synchrotron dataset shows well-defined structure factors (Table S1), albeit only 34.9 % completeness up to a d -spacing resolution of $0.8\text{ }\text{\AA}$. Therefore, both datasets, from the in-house diffractometer and the synchrotron, were merged in Sortav (Blessing, 1997), in order to improve the overall quality of the crystal structure of rotemite. Details of the merging procedure are provided in Supplementary Materials (Text S2). The comparison of SC-XRD experiments and merged datasets is presented in Table S1. The structure was solved and refined in the $R\bar{3}c$ space group

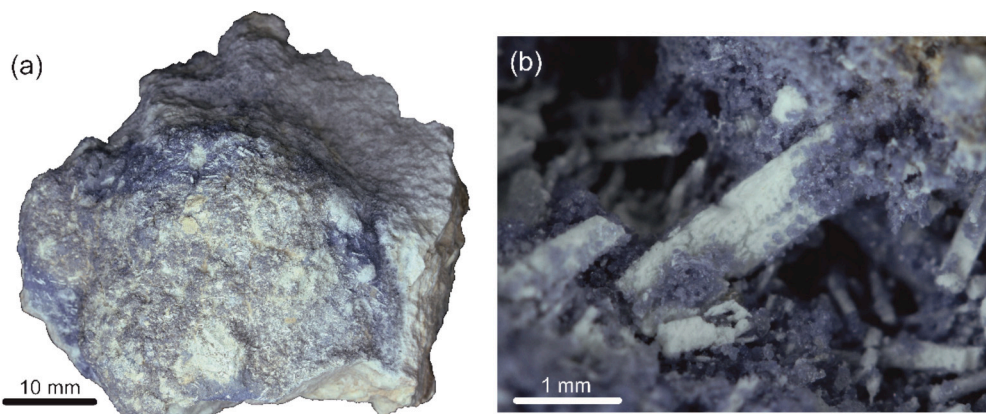


Fig. 1. (a) Rock sample covered by rotomite crystal aggregates, (b) crystals of rotomite (purple) on altered ettringite (white). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

using SHELXT and SHELXL programs in the Olex2 package (Sheldrick, 2008, 2014; Dolomanov et al., 2009). The model converged to $R_1 = 0.0866$. During the first refinement cycle, the sites of Ca and Cr (Ca1 and Cr1, respectively), as well as the oxygen sites (O1 and O2), were located. The Cl site was then added to the model. As expected from the chemical analyses, the Cr1 site showed a lower average electron number of $19.74 e^-$, indicating partial substitution of Cr with Al. Therefore, the site was refined using a Cr vs. Al mixed scattering curve, which converged to 0.63 (3) and 0.37(3), respectively (Table S2). All non-H sites were refined using anisotropic displacement parameters (Table S3). Finally, two peaks of $0.38 e^-/\text{\AA}$ of residual density at distances of 0.955 Å and 1.038 Å from oxygen O2 and $0.57 e^-/\text{\AA}$ at a distance of 1.207 Å from oxygen O1 were found in the residual electron density maps. Despite their low intensities, these peaks were inserted into the model as hydrogens with a constrained O—H bond distance of 0.98 Å. The final structure solution and refinement were carried out on the merged single-crystal dataset (CIF available in the online materials, Table S1). The powder diffractogram obtained by collapsing the single-crystal reflections (Fig. S2a) is in good agreement with the P-XRD pattern calculated from the CIF (Fig. S2b, Table S4).

2.4. Geological settings and mineral associations

The Hatrurim Complex is a world-famous locality abundant with new and rare minerals. The Complex is composed of pyrometamorphic rocks developed along the Dead Sea Rift on the territories of Israel, Jordan, and the Palestinian Autonomy. Despite discrepancies regarding the origin of the metamorphism (Sokol et al., 2010; Kolodny et al., 2013; Novikov et al., 2013), it is widely accepted that fine-grained high-temperature rocks, primarily composed of anhydrous Ca-Al-Fe-oxides and

Ca-silicates, were formed as a result of pyrometamorphic alteration of marly limestones. These metamorphic products subsequently underwent rehydration, leading to the formation of low-temperature rocks, commonly referred to as “low-grade” Hatrurim (Burg et al., 2000; Hirsch et al., 2008; Sokol et al., 2019).

High-temperature rocks of Hatrurim Complex include mainly marbles, spurrite and larnite rocks, as well as hornfels, and paralavas (Galuskina et al., 2014; Novikov et al., 2013; Vapnik et al., 2007). They formed at temperatures ranging from 750 to 1250 °C, locally reaching up to 1400 °C, while the total pressure did not exceed 25 bars (Vapnik et al., 2007; Sokol et al., 2010, 2011; Galuskin et al., 2023b). Over the past decade, mineralogists have intensively investigated high-temperature rocks, leading to the discovery of more than 70 new minerals, whereas the low-temperature rocks have been poorly studied. Therefore, recent studies have concentrated on low-temperature mineralization, resulting in the characterization of new and rare minerals from the zeolite family (Skrzyńska et al., 2022, 2023) and the hydrotalcite supergroup as reported by other researchers (Britvin et al., 2022, 2024; Murashko et al., 2025). “Low-grade” Hatrurim rocks mainly consist of hydrated calcium silicates.

They are porous and contain a large number of fractures filled with tiny crystals of afwillite, ettringite, and hydrocalumite, as well as calcite, baryte, and/or gypsum. Zeolite-rich rocks are less common. Most likely, these rocks were formed through the low-temperature alteration of Portland cement clinker assemblages (Sokol et al., 2011; Kolodny et al., 2014; Vapnik et al., 2018; Kruszewski et al., 2021). Their transformation can be attributed either to late hydrothermal fluid circulation (Sokol et al., 2011; Juroszek et al., 2020b) or to weathering processes involving circulation of meteoric water (Kolodny et al., 2014).

Most likely, the “low-grade” Hatrurim rocks formed from

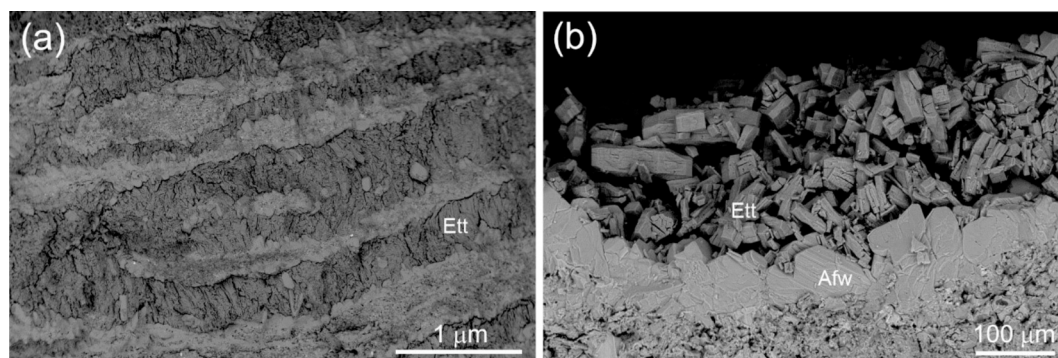


Fig. 2. Fragments of low-temperature rock, on the surface of which rotomite was found: (a) two types of interlayers composing of sample; (b) Interface between afwillite and ettringite layers. Ett = ettringite, Afw = afwillite.

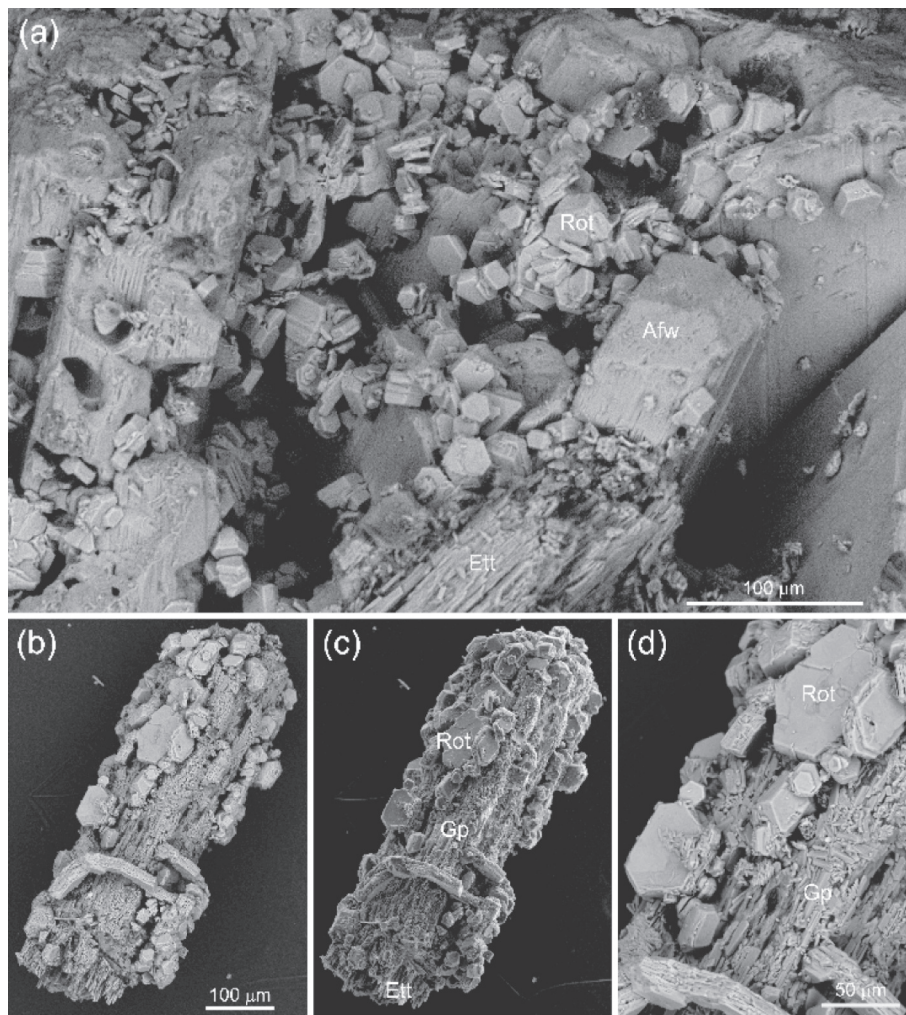


Fig. 3. (a) Rotemite crystals on afwillite crystals with traces of dissolution, partially dissolved crystal of ettringite is visible at the bottom of the image; (b, c) BSE and SE images of rotomite crystals on the surface of ettringite crystal partially replaced by gypsum; (d) BSE image of enlarged fragment of the crystal shown in Fig. 3b, c. Afw = afwillite, Ett = ettringite, Gp = gypsum, Rot = rotomite.

interactions between extremely alkaline solutions and high-temperature rocks, resulting in their rehydration and re-carbonation (Khouri et al., 1992; Milodowski et al., 2011; Vapnik et al., 2019). Thus, the altered pyrometamorphic rocks are generally considered as analogs of hydrated Portland cement, while the sulfur-rich rocks are interpreted as equivalents of hydrated calcium sulfoaluminate-type cements (Sokol et al., 2014).

Rotemite was found as a crust of aggregates on samples of rocks

altered at low temperatures (Fig. 1a, b). The holotype sample is composed of two distinct layers, consisting mainly of afwillite and ettringite, respectively (Fig. 2). In addition, the afwillite-rich layers contain an unidentified calcium hydrosilicate with high contents of phosphorus and aluminum, along with gypsum, baryte, minerals of the magnesioferrite-magnetite-chromite series and crystals of fluorapatite. The latter two are relicts of minerals from the primary high-temperature rock. Rotemite occurs on the surface of afwillite crystals that show traces

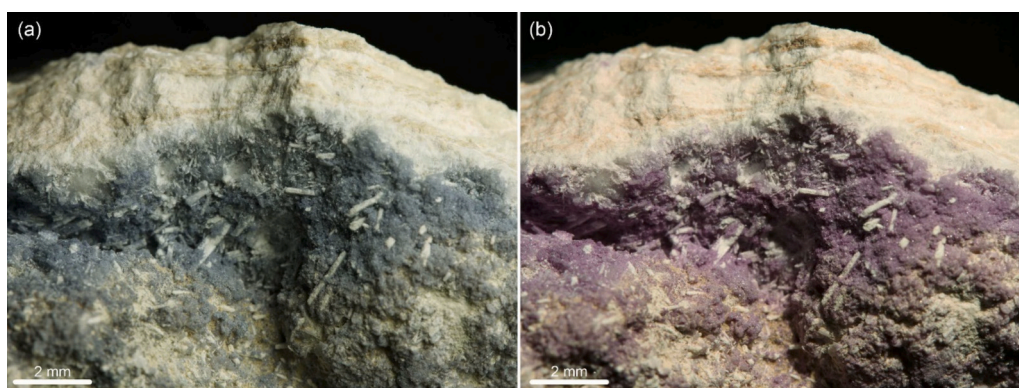


Fig. 4. Fragment of rock sample with rotomite crystals (a) in daylight, (b) in artificial light.

Table 1

Chemical composition of rotemite (wt%): 1 – WDS data, 2 – EDS data.

wt%	1				2		
	n = 21	s.d.	range	norm.100 %	n = 27	s.d.	range
SO ₃	0.10	0.06	0.14–0.24	0.09	0.12	0.12	0.00–0.33
Al ₂ O ₃	4.95	0.71	5.33–6.29	4.49	4.74	0.89	3.11–6.60
Cr ₂ O ₃	20.80	1.12	19.15–23.32	18.86	17.33	1.54	13.58–20.13
Fe ₂ O ₃	0.73	0.73	0.65–1.91	0.66	0.84	0.53	0.00–2.44
MgO	n.d.				0.06	0.09	0–0.32
CaO	40.97	0.48	40.97–42.17	37.15	35.46	0.93	31.94–36.98
SrO	0.21	0.07	0.22–0.36	0.19	n.d.		
K ₂ O	n.d.				0.03	0.05	0–0.16
Na ₂ O	n.d.				0.04	0.06	0–0.23
Cl	11.03	0.52	10.94–12.46	10.01	11.31	0.67	9.42–15.52
H ₂ O _{calc.}	23.70*/33.99*			30.80♦	29.17*		
-O=Cl	2.49			2.26	2.55		
Total	100*/110.29*			100♦	96.41		

(12 pfu OH) + 0.54 wt% H₂O^{Cl} site (0.32 pfu OH) + 13.38 wt% H₂O^H site (4 pfu H₂O)* H₂O calculated as difference to 100 %: 20.07 wt% H₂O^(OH) site (12 pfu OH) + 0.54 wt% H₂O^{Cl} site (0.32 pfu OH) + 3.09 wt% H₂O^H site (0.93 pfu H₂O).♦ H₂O calculated on the formula M₄²⁺M₂³⁺(OH)₁₂[Cl_{2-x}(OH)_x](H₂O)₄; 20.07 wt% H₂O^(OH) site.♦ H₂O calculated on the formula M₄²⁺M₂³⁺(OH)₁₂[Cl_{2-x}(OH)_x](H₂O)₄, normalized to 100 %: 18.20 wt% H₂O^(OH) site (12 pfu OH) + 0.48 wt% H₂O^{Cl} site (0.32 pfu OH) + 12.12 wt% H₂O^H site (4 pfu H₂O).♦ H₂O calculated on charge balance +4H₂O: 17.53 wt% H₂O^(OH) site (12.05 pfu OH) + 11.64 wt% H₂O^H site (4 pfu H₂O).

of dissolution (Fig. 3a) and large white “ettringite crystals” on the surface of the sample, that have been almost completely replaced by gypsum (Fig. 3 b-d).

3. Results and discussion

3.1. Physical and optical properties of rotemite

Rotemite is characterized by a pale bluish-violet (daylight) to pinkish-violet (artificial light) colour, depending on the type of illumination (Fig. 4). The streak is pale light-purple. The new mineral forms tiny hexagonal plates and tabular crystals, which occur as crust-like polycrystalline aggregates of several dozen μm in size and a maximum crust thickness of 1 mm on the host rock (Fig. 3). The dimensions of individual single crystals typically range from a few μm up to rarely exceeding 60 μm in-plane, with a maximum thickness of 20 μm. The luster of transparent crystals is vitreous. Optically, crystals are negatively uniaxial with $\omega = 1.565(2)$, $\varepsilon = 1.544(2)$ for a wavelength $\lambda = 589$ nm. No pleochroism was observed. Micro-indentation hardness tests were unsuccessful due to high brittleness. On the Mohs scale, the hardness is 2.5–3 based on the scratch test. Crystals exhibit perfect cleavage on {0001}. The calculated density is 2.18 g/cm³ based on the empirical formula and single crystal X-ray diffraction unit-cell parameters.

3.2. Chemical composition of rotemite

Measurement of rotemite composition by electron microprobe (WDS mode) revealed substantial water loss, likely due to beam- and vacuum-induced dehydration. Therefore, we studied rotemite both on the microprobe (WDS mode) and on the SEM using EDS mode. The comparison of results of different approaches to water content calculations is presented in Table 1. All data were evaluated based on 6 cations in order to determine empirical crystal chemical formulas, which clearly show dominance of Cr³⁺ over Al³⁺. The cation ratios obtained by both methods are in good agreement. However, the evaluation of water content revealed discrepancies. Calculating water content from the microprobe analyses as a sum to 100 % yields 12 (OH)⁻ per formula unit (pfu) and only 0.93 H₂O pfu (* in Table 1), which is significantly lower compared to the stoichiometry refined from the crystal structure (4 H₂O and 12 (OH)⁻ pfu). On the other hand, calculating the stoichiometric water content as obtained from structural analysis gives a sum of 110.29 % (♦ in Table 1). Therefore, the final empirical formula was calculated

using the stoichiometric water content from structural analysis and normalized to 100 % (♦ in Table 1), resulting in (Ca_{3.94}Sr_{0.01})_{Σ3.95}(Cr_{1.47}Al_{0.52}Fe_{0.05})_{Σ2.04}(OH)₁₂[Cl_{1.68}(OH)_{0.32}(SO₄)_{0.01}]_{Σ2.01}·4H₂O. Also, EDS data were evaluated using stoichiometric water content, yielding the following empirical formula (Ca_{3.92}Mg_{0.01}Na_{0.01})_{Σ3.94}(Cr_{1.41}Al_{0.58}Fe_{0.07})_{Σ2.06}(OH)_{12.05}[Cl_{1.98}(SO₄)_{0.01}]_{Σ1.99}·4H₂O.

The simplified formula of rotemite is Ca₄(Cr,Al)₂(OH)₁₂[Cl, (OH)]₂·4H₂O, leading to the end-member formula of Ca₄Cr₂(OH)₁₂Cl₂·4H₂O, which requires 37.73 wt% of CaO, 25.57 wt% of Cr₂O₃, 18.18 wt% of OH and 12.12 wt% of H₂O, and 6.39 wt% of Cl, in total 100 wt%.

3.3. Raman spectroscopy of rotemite

Fig. 5 presents spectra of the platelet-shaped crystal of rotemite with various orientations relative to the polarization of the laser beam. No significant changes in wavenumber or band intensity were observed in the spectra from the crystal with the (001) plane aligned perpendicularly to the laser beam (Fig. 5a, b). In contrast, Fig. 5c and d display spectra from a crystal with the (001) plane oriented parallel to the laser beam, where a comparison reveals notable variations in band intensities. The most significant change is observed for the band at 3443 cm⁻¹, which completely vanishes in one of the vertical orientations (Fig. 5c, d) while remains prominent in all other spectra. Furthermore, the band at 3612 cm⁻¹ in Fig. 5c exhibits an approximately threefold increase in intensity compared to Fig. 5a and b. Also, its intensity is about 70 % higher than that of the 3609 cm⁻¹ band in Fig. 5d. Apart from O–H stretching vibrations, the most prominent feature in all four spectra is the band at 525/526 cm⁻¹, with intensity differences not exceeding 54 %. Slight changes are observed as well in the intensities of the 781/777 cm⁻¹ and 852/849 cm⁻¹ bands in Fig. 5c and d. In general, the spectrum shown in Fig. 5d is comparable to those in Fig. 5a and b, whereas the spectrum in Fig. 5c is notably distinct. It is worth mentioning that all Raman spectra obtained on rotemite do not exhibit any bands of 1050–1080 cm⁻¹. Signals in this spectral region are typical for carbonate anion (CO₃)²⁻, the presence of which can be excluded in rotemite.

Raman spectroscopy has been increasingly used to investigate LDH over the last decade (Frost and Erickson, 2004; Frost et al., 2011, 2014b; Mora et al., 2014; Yue et al., 2018; Zhitova et al., 2020, 2023a; Yang et al., 2021). As the intensities of the measured Raman signals strongly depend on the crystal orientation with respect to the incident laser beam polarization, and the peak intensities may vary to an important degree (Zhitova et al., 2023a). Therefore, the interpretation of spectra still

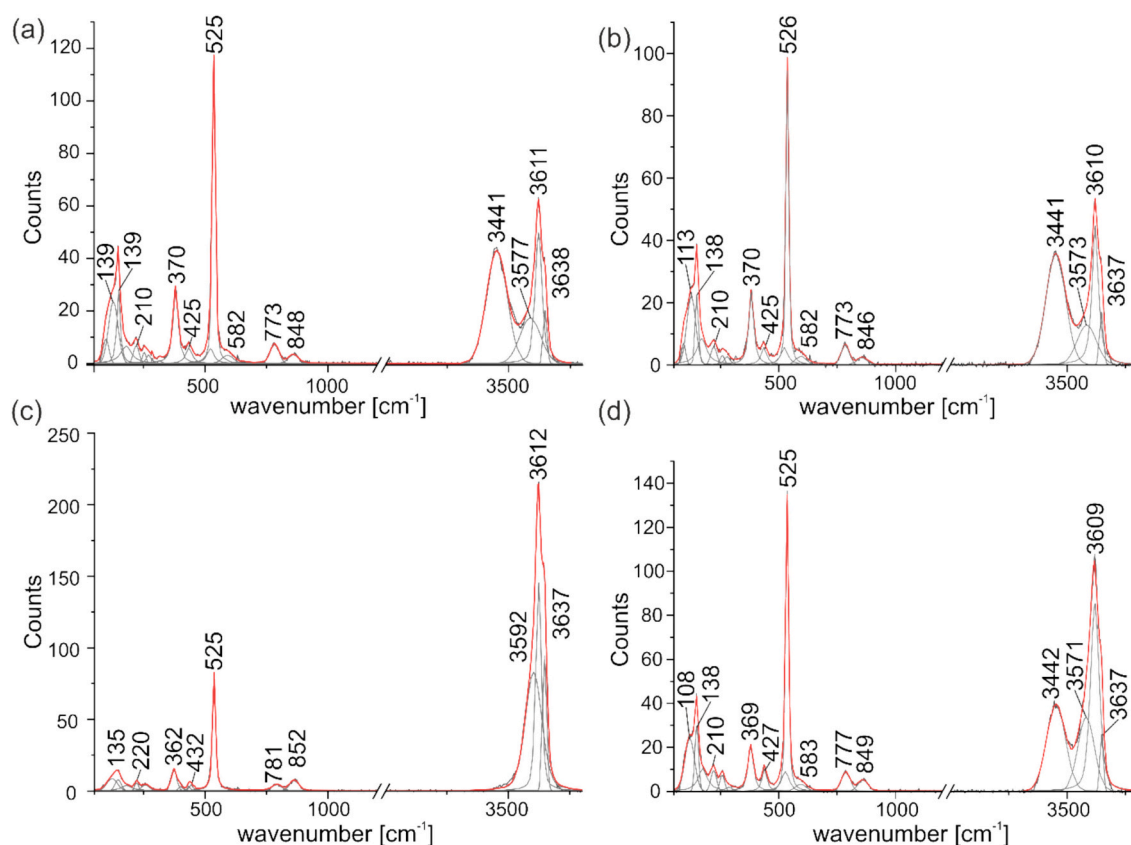


Fig. 5. Raman spectra of rotemite collected on different crystal orientations with respect to the laser beam polarization: **(a, b)** crystal plate with the (001) plane oriented perpendicularly to the laser beam; **(c, d)** crystal with the (001) plane oriented parallel to the laser beam.

poses difficulties, and band assignments are often only tentative. This may lead to considerable discrepancies in assignments, as shown in Tables S7 and S8, where the Raman bands of rotemite and other natural and synthetic LDH phases are compared. Bands below 400 cm^{-1} are assigned to lattice vibrations, whereas the most intense band between 130 and 150 cm^{-1} is attributed to O–M–O bending vibrations (Mora et al., 2014; Yang et al., 2021). The most prominent signal in the range of 400 – 300 cm^{-1} corresponds to Ca–O stretching vibrations (Frost et al., 2011, 2014b; Yue et al., 2018; Zhitova et al., 2020), but has also been interpreted as O–M–O bending modes (Frost et al., 2014a). The weak band at around 420 cm^{-1} is commonly ascribed to M–O stretching vibrations (Frost et al., 2014a; Zhitova et al., 2019, 2021; Yang et al., 2021). Alternative interpretations associate this signal with lattice modes involving M^{2+} and M^{3+} (Mills et al., 2011), symmetric stretching bands of hydrogen bonds between carbonate ions and water molecules (Mora et al., 2014), or ν_2 bending modes of sulfate SO_4^{2-} (Frost et al., 2014b), respectively. The latter two interpretations appear most unlikely in the case of rotemite, considering the negligible sulfate content and the absence of carbonate groups. The intensities of bands in the low wavenumber range are slightly affected by the relative orientation to the laser beam polarization (Fig. 5). The assignment of an intense signal at 525 cm^{-1} , is highly controversial. Several authors have associated this band with ν_2 or ν_4 vibrations of the carbonate group (Frost and Erickson, 2004; Mills et al., 2011; Yang et al., 2021), while others proposed symmetric stretching vibrations between carbonate and water as origin (Mora et al., 2014). Interestingly, a band near 530 cm^{-1} is unique for all LDH compounds (Frost et al., 2011), irrespective of whether they contain carbonate or sulfate groups. Therefore, M–O stretching vibrations (Frost et al., 2011; Yue et al., 2018; Zhitova et al., 2019, 2021) or M–O–M bends are presumably the origin of this signal (Theiss et al., 2015; Zhitova et al., 2020, 2023a, 2023b). However, no significant shift in the band wavenumber was detected for rotemite, regardless of

whether Cr or Al occupied the M^{3+} site. This might be attributed to the inactive Raman modes of the $6b$ Wyckoff position, which is occupied by trivalent cations in this structure (Table S2, S9). Consequently, the band at $\sim 530\text{ cm}^{-1}$ plausibly originates from the movement of oxygen atoms. Bands located around 770 and 850 cm^{-1} also have a wide range of interpretations. Some researchers assign these to vibrations of the carbonate group (ν_4) (Frost and Erickson, 2004; Frost et al., 2011; Theiss et al., 2015), while others attribute these to M–OH bending or deformation vibrations (Frost and Erickson, 2004; Mills et al., 2011; Frost et al., 2014b; Yue et al., 2018; Zhitova et al., 2019, 2023a). Given the absence of a carbonate group in rotemite, the second interpretation seems more plausible. In the high wavenumber region, two bands around 3442 and 3610 cm^{-1} arise undoubtedly from O–H stretching vibrations. The first signal corresponds to O–H stretching vibrations of water molecules forming hydrogen bonds with chloride anions (Zhitova et al., 2019, 2023a, 2023b). The band around 3610 cm^{-1} was deconvoluted into three bands at 3575 , 3611 , and 3637 cm^{-1} , and is assigned to O–H stretching vibrations of the hydroxyl groups in the brucite layer. The difference in the wavenumber of O–H stretching vibrations of the hydroxyl group might result from the mixed (Cr, Al) occupancy of the octahedral site. The high sensitivity of the band at 3442 cm^{-1} suggests an ordered arrangement of the water molecules within the structure, as has been shown in the recent work of Śródek and Dulski (2025). Moreover, a significant increase (about 3 times) in the intensity of the bands around 3612 cm^{-1} in the given orientation indicates a perpendicular arrangement of O–H bonds relative to the layers.

3.4. Crystal structure of rotemite

Rotemite crystallizes in the trigonal crystal system ($R\bar{3}c$, space group #167) with a six-layered cell ($6R$ polytype) and following unit cell parameters $a = 5.7944(2)\text{ Å}$, $c = 46.69(4)\text{ Å}$, $V = 1357.7(10)\text{ Å}^3$. It is

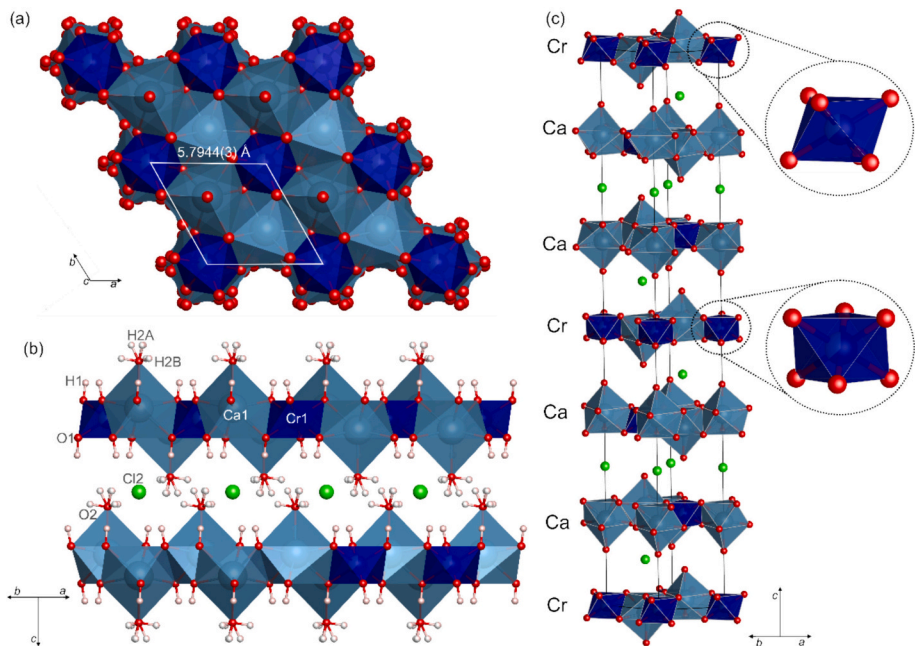


Fig. 6. (a) Brucite layer in the crystal structure of rotomite, view along the *c* axis. The indicated $M^{3+} - M^{3+}$ distance corresponds to unit cell parameter *a*; (b) Interlayer space in the rotomite structure, view on (110); (c) Stacking of layers in the unit cell of rotomite with labelled vertical polyhedral alignment in consecutive layers along the *c*-axis. Highlighted are differently oriented Cr, Al – octahedra, which induce the 6-layered polytype structure. The solid line indicates the unit-cell, dark blue octahedra represent the coordination sphere of Cr1, and pale blue polyhedra represent the coordination sphere of Ca1, respectively. Chlorine (Cl2), oxygen (O1, O2), and hydrogen (H1, H2a, H2b) atoms are shown as green, red, and pale pink spheres, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

characterized by a hydrocalumite-type structure and belongs to the lamellar double hydroxide (LDH) family (Fig. 6). In rotomite, the M^{2+} site (Ca1) exhibits the characteristic sevenfold coordination typical of hydrocalumite-type structures, involving six OH^- groups (O1) and one H_2O molecule (O2) with disordered hydrogen atoms (H2a, H2b). In contrast, the trivalent cations (Cr1, Al1) are coordinated octahedrally with six OH^- groups each (O1) (Table 3). Chloride anions (Cl1) are intercalated between the layers composed of M^{2+} and M^{3+} polyhedra, where chloride forms hydrogen bonds with the hydroxyl groups of the $[M^{3+}(OH)_6]^{3-}$ octahedra and the water molecules attached to the Ca-polyhedra (Fig. 6, Table 3).

In hydrocalumite-type structures, such as represented by rotomite, M^{3+} cations (as Al^{3+} or Cr^{3+}) and M^{2+} cations, such as Ca^{2+} , are strictly ordered into a honeycomb pattern with an M^{2+}/M^{3+} ratio equal to 2:1. Consequently, the unit cell parameter *a* is approximately 5.7 Å, which corresponds to the distance between M^{3+} octahedral sites within the layer (Fig. 6a, Mills et al., 2012). Moreover, a long-range order along [0001] arises from the strictly ordered interlayer species together with the systematic shift of successive brucite-like layers. As a result, the Cr, Al – octahedra are not vertically aligned in the adjacent layers along the *c*-axis, but are separated by two Ca-polyhedra (Fig. 6c). Such a stacking sequence would typically produce a three-layered polytype with vertical

Table 3
Distances for atomic bonds in the brucite layer and hydrogen bonds between charge balancing anion and the layer.

Atom 1	Atom 2	Bond distance [Å]
Ca1	O1 × 3	2.350(8)
	O1 × 3	2.450(7)
	O2 × 2	2.495(15)
	mean	2.414
Cr1/Al1	O1 × 6	1.955(7)
hydrogen bonds		
Cl•••H2A – O2		2.82666(10)
Cl•••H2B – O2		2.51231(18)
Cl•••H1 – O1		2.63(7)

polyhedral order of Cr – Ca – Ca in consecutive layers and a unit cell parameter *c* of 23.337(5) Å (Fig. 6c, Text S1, Fig. S1). In rotomite, however, applying 23.337(5) Å reveals extra reflections along the *c*-axis (Text S1, Fig. S1b), indicating the doubling of the unit cell parameter *c*. It implies that two adjacent sets of three layers that are not identically oriented, as highlighted on Cr, Al-octahedra in Fig. 6c. In the result, rotomite is a 6-layered polytype with exceptionally large unit cell parameter *c* of 46.69(4) Å. Although 6-layered polytypes are rare, almost identical unit cell parameters and symmetry to those of rotomite

Table 2
Structural comparison of rotomite, trigonal hydrocalumite (Fischer et al., 1980), Friedel’s salt (Renaudin et al., 1999), and recently discovered mineral of the hydrocalumite group – carbocalumite (Britvin et al., 2022).

	this work	(Renaudin et al., 1999)	(Fischer et al., 1980)	(Britvin et al., 2022)
	merged dataset			
ideal formula	$Ca_4Cr_2(OH)_{12}Cl_2 \cdot 4H_2O$	$Ca_4Al_2(OH)_{12}Cl_2 \cdot 4H_2O$	$Ca_4Al_2(OH)_{12} \cdot Cl_2 \cdot 4H_2O$	$Ca_4Al_2(OH)_{12}(CO_3) \cdot 6H_2O$
crystal system	trigonal	trigonal	trigonal	trigonal
space group	$R\bar{3}c$	$R\bar{3}c$	$R\bar{3}c$ or $R3c$	$R\bar{3}c$
unit cell	<i>a</i>	5.724(2)	5.765(1)	5.7646(1)
	<i>c</i>	46.689(5)	46.978(5)	49.409(1)
	<i>V</i>	1357.7(10)	1352.3	1421.92

have been reported for hydrocalumite from the Bellerberg volcano, Germany (Fischer et al., 1980), carbocalumite from the Hatrurim Complex, Israel (Britvin et al., 2022), and the high-temperature polymorph of Friedel's salt, $\text{Ca}_2\text{Al}(\text{OH})_6\text{Cl}_2 \cdot \text{H}_2\text{O}$, (Friedel, 1897; Renaudin et al., 1999, 2004; Rapin et al., 2002) (Table 2). A possible rhombohedral lattice with the unit cell parameters of $a = 5.2745(7) \text{ \AA}$ and $c = 45.36(1) \text{ \AA}$ has been discussed for the mineral quintinite to explain diffuse scattering along the c^* axis (Krivovichev et al., 2010). In conclusion, rotemite can be considered as the trigonal Cr^{3+} -analog of carbonate-free hydrocalumite as well as the Cr^{3+} -analog of trigonal Friedel's salt.

3.5. Origin of rotemite and Cr-bearing minerals in the Hatrurim Complex

The high concentration of chromium in the pyrometamorphic rocks of the Hatrurim Complex is associated with a marine sedimentary protolith rich in organic matter, including oil shales and phosphorites, which are widespread on both sides of the Dead Sea Transform Fault (Sokol et al., 2011; Fleurance et al., 2013; Khoury et al., 2014). The high Cr^{3+} concentrations in high-temperature metamorphic rocks are mainly related to opaque, usually rock-forming and accessory phases, such as minerals of the spinel group, perovskite, brownmillerite, but also oxides and accessory phosphides and sulfides (Sharygin et al., 2008; Sokol et al., 2010; Juroszek et al., 2018; Galuskina et al., 2021; Galuskin et al., 2023a). During late hydrothermal alteration, Cr^{3+} was removed from these minerals by hyper-alkaline solutions (Sokol et al., 2011; Juroszek et al., 2018, 2020b, 2020a) and accumulated in the structure of low-temperature minerals, such as bentorite, $\text{Ca}_6\text{Cr}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$, and volkonskoite, $\text{Ca}_{0.3}(\text{Cr,Mg})_2(\text{Si,Al})_4\text{O}_{10}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, (Gross, 1980; Kolodny et al., 2014; Seryotkin et al., 2019). Subsequent oxidation of trivalent Cr(III) to hexavalent Cr(VI) results in the formation of unusual CrO_4^{2-} -bearing minerals, such as Cr^{6+} -bearing ettringite, chromatite, CaCrO_4 , siwaqaite, $\text{Ca}_6\text{Al}_2(\text{CrO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$, and minerals of the baryte-hashemite solid solution, $\text{BaSO}_4 - \text{BaCrO}_4$, (Hauff et al., 1983; Sokol et al., 2011; Drebuschak et al., 2013; Juroszek et al., 2018, 2020a).

The formation of the new Cr-mineral rotemite, found in the Halamish quarry, is undoubtedly related to a low-temperature alteration. Two low-temperature parageneses, afwillite-ettringite, and rotemite-gypsum, can be distinguished in the holotype specimen (Fig. 2). Afwillite $\text{Ca}_3[\text{SiO}_4][\text{SiO}_2(\text{OH}_2)] \cdot 2\text{H}_2\text{O}$ is stable only in Ca-rich environments at temperatures below 200°C (Heller and Taylor, 1952; Kusachi et al., 1989). Similarly, the existence of ettringite group minerals and their synthetic counterparts is restricted to low-temperature and alkaline conditions ($T < 120^\circ\text{C}$, $\text{pH} = 9.5\text{--}13$) (Wieczorek-Ciurowa et al., 2001; Jallad et al., 2003; Jiménez and Prieto, 2015; Matschei and Glasser, 2015; Juroszek et al., 2020a, 2020b). The infiltration of rainwater and hydration of clinker-like rocks from the Hatrurim Complex, which retained residual heat from pyrometamorphic processes (Khoury et al., 1992; Techer et al., 2006; Skrzyńska et al., 2022), might have provided the most favorable conditions ($\text{pH} \sim 11\text{--}12$, $T \leq 70^\circ\text{C}$) for the crystallization of ettringite and afwillite.

Subsequently, a change of the pH value presumably occurred in the environment, leading to the replacement of ettringite by gypsum and the partial dissolution of afwillite (Fig. 3), hence enabling eventually the formation of rotemite crystals. The Cr^{3+} ions might have been released either from minerals of the ettringite-bentorite series or directly from minerals of the magnesioferrite-magnetite-chromite series. However, no bentorite crystals were found in the holotype specimen, although this mineral is a common mineral in the quarry. Furthermore, it should be noticed that bentorite is highly responsive to changes in temperature and humidity (Gross, 1980; Drebuschak et al., 2013; Seryotkin et al., 2019) and begins to decompose at about 45°C , as shown by an SC-XRD experiment (Juroszek et al., 2020a). Hence, the formation of rotemite might occur above 45°C , precluding the crystallization of bentorite. In this context, it is tempting to speculate on the possible role of the $[\text{Cr}(\text{OH})_6]^{3-}$, which forms crystalline salts, such as $\text{Ca}_3[\text{Cr}(\text{OH})_6]_2$, from highly alkaline, aqueous solutions at moderate pressures and temperatures (Scholder and Pättsch, 1934; Hinz, 2000; Albrecht et al., 2019, 2020). The reaction conditions employed for the synthesis of these salts closely resemble the characteristics of highly alkaline fluids circulating in pyrometamorphic rocks ($T \geq 45^\circ\text{C}$; $p \leq 25 \text{ bar}$), which are presumed to be the origin of the chromium-bearing secondary minerals of the Hatrurim Complex. Therefore, $[\text{Cr}(\text{OH})_6]^{3-}$ may be interpreted as another, stable monomeric hydrolysis product of Cr(III) and could be considered as a vehicle for the transport of Cr^{3+} in these fluids. Moreover, as $[\text{Cr}(\text{OH})_6]^{3-}$ readily oxidizes to CrO_4^{2-} (Albrecht et al., 2020). Hence, this anion could serve as a potential source of both Cr(III) and Cr(VI) in this highly alkaline geological environment.

4. Conclusions

Comprehensive structural and spectroscopic studies of LDH compounds are highly challenging due to their tendency to crystallize in a multiphase powder form, implying difficulties in the determination of phase purity, crystal structure, and, eventually, chemical composition. Samples of the mineral rotemite, a Ca, Cr-LDH compound studied herein, allowed us to overcome these challenges and enabled, for the first time, an unambiguous determination of the physical and optical properties of this phase. The multimethodological approach used in this work provided valuable insights into the crystal structure and chemical composition of Cr-LDH. In contrast to most LDH compounds (Garand et al., 2010; Sasai et al., 2019), no evidence for the presence of carbonate anions in the crystal structure of rotemite has been found. SC-XRD revealed that the investigated crystals represent an unusual 6R polytype of LDH compounds with a large unit cell parameter c , resulting from a strictly ordered structure. Polarized Raman spectroscopy showed a strong dependence of the O—H stretching mode intensity on the polarization of the incident laser beam, indicating an ordered arrangement of water molecules and a perpendicular orientation of the O—H bonds within the hydrocalumite layer. Conversely, SC-XRD revealed a slight distortion of O—H bonds towards Cl^- due to hydrogen bonding. The proposed origin and formation conditions of the new mineral have been presented, including a possible role of the $[\text{Cr}(\text{OH})_6]^{3-}$ anion, might offer interesting perspectives for future synthetic work of Ca, Cr-LDH compounds.

CRedit authorship contribution statement

Katarzyna Skrzyńska: Writing – original draft, Project administration, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization. Harald Müller: Writing – review & editing, Validation, Formal analysis, Conceptualization. Rafał Juroszek: Writing – review & editing, Writing – original draft, Formal analysis. Biljana Krüger: Writing – review & editing, Investigation. Georgia Cametti: Writing – review & editing, Supervision. Anna Pakhomova: Writing – review & editing, Investigation. Irina Galuskina: Writing – review & editing, Supervision. Yevgeny Vapnik: Writing – review & editing, Formal analysis. Krzysztof Woźniak: Writing – review & editing. Evgeny Galuskin: Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Katarzyna Skrzyńska reports financial support was provided by National Science Centre Poland. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.clay.2025.108002>.

Data availability

The crystallographic data are shared in the submitted files. Other data will be shared upon request.

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