Synthesis and characterization of $K_2Ca_5(SO_4)_6 \cdot H_2O$, the equivalent of görgeyite, a rare evaporite mineral

J. Theo Kloprogge,[1,*] Liesel Hickey,[1] Loc V. Duong,[2] Wayde N. Martens,[1] and Ray L. Frost[1]

[1]Inorganic Materials Research Program, School of Physical and Chemical Sciences, Queensland University of Technology, 2 George Street, G.P.O. Box 2434, Brisbane, Qld 4001, Australia
[2]Analytical Electron Microscopy Facility, Faculty of Science, Queensland University of Technology, 2 George Street, GPO Box 2434, Brisbane, Qld 4001, Australia

Abstract

Görgeyite, $K_2Ca_5(SO_4)_6 \cdot H_2O$, is a very rare monoclinic double salt found in evaporites related to the slightly more common mineral syngenite. At 1 atmosphere with increasing external temperature from 25 to 150 °C, the following succession of minerals was formed: first gypsum and K_2O, followed at 100 °C by görgeyite. Changes in concentration at 150 °C due to evaporation resulted in the formation of syngenite and finally arcanite. Under hydrothermal conditions, the succession is syngenite at 50 °C, followed by görgeyite at 100 and 150 °C. Increasing the synthesis time at 100 °C and 1 atmosphere showed that initially gypsum was formed, later being replaced by görgeyite. Finally görgeyite was replaced by syngenite, indicating that görgeyite is a metastable phase under these conditions. Under hydrothermal conditions, syngenite plus a small amount of gypsum was formed, after two days being replaced by görgeyite. No further changes were observed with increasing time. Pure görgeyite showed elongated crystals approximately 500 to 1000 μm in length. The infrared and Raman spectra are mainly showing the vibrational modes of the sulfate groups and the crystal water (structural water). Water is characterized by OH-stretching modes at 3526 and 3577 cm⁻¹, OH-bending modes at 1615 and 1647 cm⁻¹, and an OH-libration mode at 876 cm⁻¹. The sulfate ν_1 mode is weak in the infrared but showed strong bands at 1005 and 1013 cm⁻¹ in the Raman spectrum. The ν_2 mode also showed strong bands in the Raman spectrum at 433, 440, 457, and 480 cm⁻¹. The ν_3 mode is characterized by a complex set of bands in both infrared and Raman spectra around 1150 cm⁻¹, whereas ν_4 is found at 650 cm⁻¹.

Introduction

Görgeyite is a very rare sulfate double salt closely related to syngenite, $K_2Ca(SO_4)_2 \cdot H_2O$. Although a large number of sulfate salt minerals have been found over the years associated with especially evaporite deposits, görgeyite has so far only been found in a small number of locations. It was first described by Mayrhofer (1953) from the Ischler salt deposit (Leopold-Horizon), Salzburg, Austria. In the same year, a similar mineral, mikheevite, was discovered at Lake Inder, Kazakstan, by Nefedov and reported by Mokievsky (1953). Fleischer (1955) later indicated that both minerals were probably identical. Further data reported by Nefedov (1955) were used by Meixner (1955) to confirm that the minerals were indeed identical. Smith and coworkers reported a third occurrence of görgeyite at Astakós in Western Greece in a Triassic evaporite sequence (Smith and Walls 1980; Smith et al. 1964). Seyfarth (1966) reported görgeyite as microscopic crystals in Zechstein salt deposits at Staßfurt, southern Harz, Germany. A year later, Hahne (1967) added another three locations in the same area, followed by another three in 1988 by Mötzing (1988). The only occurrence outside Europe was reported by Cai et al. (1985), who described görgeyite from the lower-middle Triassic polyhalite rocks in Nongle, Sichuan Province, China.
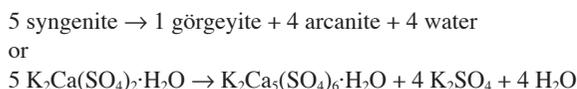
Cavaretta et al. (1982, 1983) were the first to report syngenite and görgeyite from a geothermal field at Cesano, north of Rome, Italy, characterized by brines enriched in Ca, Na, K, Sr, Rb, and Li as cations, and SO_4 and Cl as anions. They observed the görgeyite in a vein consisting of cesanite in association with pyrite. The crystals were weakly zoned with Sr content increasing from core to rim. They also indicated that a small amount of Na substituted in the crystal lattice for the divalent cations to reach stoichiometric balance.

As the chemical component potassiumpentacalcium sulfate, pentacalcium sulfate, or simply pentasalt, görgeyite has been known for a much longer period of time. Already in the early nineteen hundreds, van 't Hoff and Geiger synthesized görgeyite in the system K_2SO_4-$CaSO_4$-H_2O at temperatures above 32 °C in experiments aimed at understanding the formation conditions of marine evaporites (van 't Hoff 1912; van 't Hoff and Geiger 1904; van 't Hoff et al. 1905). More specific details were later reported by Krüll and Vetter (1933) and by Hill (1934). Precipitation and crystallization has been shown to take place mainly from saturated solutions.

The stability field of görgeyite is very small and is located close to the K_2O corner in the Jänecke-triangle, which represents

* E-mail: t.kloprogge@qut.edu.au

the stability field of various minerals with the oxides like K_2O on the corners, surrounded by the fields of syngenite, polyhalite, and anhydrite. With increasing temperature, the görgeyite stability field shows a small increase (GHACA 1942). Mötzing (1988) identified from thin sections that the görgeyite, from Volkenrode-Poethen (South Harz, Germany) is formed due to metasomatic alteration by descending fluids of extreme compositions. Sylvite and glaserite were found to be altered to görgeyite, which then could react to syngenite. In contrast to this reaction series, Triolo et al. (1988) reported the recrystallization of syngenite to görgeyite and arcanite at 225 °C according to the following reaction:

5 syngenite → 1 görgeyite + 4 arcanite + 4 water
or
$5\ K_2Ca(SO_4)_2 \cdot H_2O \rightarrow K_2Ca_5(SO_4)_6 \cdot H_2O + 4\ K_2SO_4 + 4\ H_2O$

In this paper, the synthesis of görgeyite will be described as a function of both temperature and pressure, as well as of time at constant temperature and pressure, followed by a detailed characterization using a variety of techniques including X-ray diffraction (XRD), infrared and Raman spectroscopy, scanning electron microscopy, and electron microprobe analysis. Up till now, characterization was basically based on XRD, chemical analysis, and optical microscopy (Cai et al. 1985; Cavarretta et al. 1983; Mayrhofer 1953; Mötzing 1988). The vibrational spectroscopy has been hardly described. Only two papers have reported an infrared spectrum, but the description and assignment of the bands is only very limited (Cai et al. 1985; Cavarretta et al. 1983).

CRYSTAL STRUCTURE OF GÖRGEYITE

The crystal structure has been described in a number of papers (Braitsch 1965; Cavarretta et al. 1983; Mukhtarova et al. 1980, 1981; Smith and Walls 1980). Görgeyite is monoclinic and contains four formula units in a cell of dimensions $a = 17.51$ Å, $b = 6.82$ Å, $c = 18.21$ Å, and $\beta = 113.3°$ (Smith and Walls 1980). These dimensions are very close to the original dimensions reported by Braitsch (1965), Mukhtarova et al. (1980, 1981) (although they reported a monoclinic cell in which the b- and c-axes have been inverted), and Cavaretta et al. (1983). The space group has been reported as $C2/c$ (no. 15). In the structure, three different Ca atoms can be recognized. Two of them are in ninefold coordination by O atoms with average Ca-O distances of 2.52 Å. The third Ca atom is in eightfold coordination with an average Ca-O distance of 2.46 Å. The K atom is also in eightfold coordination. The three sulfate anions are approximately regular with mean S-O distances of 1.472, 1.477, and 1.470 Å respectively, but their behavior in providing O atom coordination is different for each. The water molecules are situated in voids around the twofold axes. Although the positions of the hydrogen atoms have not been determined, it is highly likely that hydrogen bonds are present in the structure of görgeyite.

EXPERIMENTAL METHODS

Synthesis

Two stock solutions were prepared containing the proper amounts of K_2SO_4 and $CaSO_4$ to obtain the stoichiometric ratio necessary for the synthesis of görgeyite. In series 1a, the K_2SO_4 solution was added to the $CaSO_4$ solution, whereas in series

1b, the opposite was the case. After precipitation the samples were split in half and either aged in the original solution for three days or hydrothermally treated in an autoclave under autogeneous water vapor pressure, which is the equilibrium water vapor pressure corresponding to that temperature (samples denoted with extension –HT). In series 2, the influence of temperature was investigated either at 1 atm (~100 kPa) in an oil bath or under hydrothermal conditions (at autogeneous water vapor pressure: 50 °C 12.34 kPa, 100 °C 101.32 kPa, and 150 °C 475.72 kPa) in an autoclave. Series 3 focused on the kinetics of the formation of syngenite at 100 °C either at 1 atm (~100 kPa) or under hydrothermal conditions (at autogeneous water vapor pressure, 101.32 kPa) with increasing from 1 day to 7 days. An overview is given in Table 1. After the treatments, each sample was separated from the solution by vacuum filtration, followed by intensive washing with deionized water, and dried at 60 °C for 1 hour.

X-ray diffraction

The crystalline materials were characterized by powder X-ray diffraction (XRD), at Queensland University of Technology. The XRD analyses were carried out on a Philips wide-angle PW 1050/25 vertical goniometer (Bragg Brentano geometry) applying Co$K\alpha$ radiation ($\lambda = 1.7902$ Å, 40 kV, 40 mA). The samples were measured at 50% relative humidity in step-scan mode with steps of 0.02 °2θ and a scan speed of 1.00° per min from 2 to 75 °2θ.

Scanning electron microscopy

Scanning electron microscope (SEM) photos were obtained on an FEI QUAN-TA 200 Environmental Scanning Electron Microscope operating in this case at high vacuum and 15 kV, at Queensland University of Technology. This system is equipped with an energy dispersive X-ray spectrometer with a thin window capable of analyzing all elements of the periodic table down to carbon. A counting time of 100 seconds was applied for the analyses. Due to the presence of a carbon coating, necessary for the removal of the electrons from the electron beam from the sample surface to prevent charging on the görgeyite, no quantitative analyses could be obtained of the impurities on the surface of the görgeyite crystals.

Infrared spectroscopy

The samples (1 mg) were finely mixed with oven-dried spectroscopic grade KBr (250 mg) and pressed into a disc under vacuum. The infrared absorption (IR) spectrum of each sample was recorded in triplicate by accumulating 64 scans at 4 cm^{-1} resolution between 400 cm^{-1} and 4000 cm^{-1} using the Perkin-Elmer 1600 series Fourier transform infrared spectrometer equipped with a LITA detector at Queensland University of Technology.

Raman microscopy

The samples were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10×, 20×, and 50× objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a two-dimensional CCD detector (1024 × 1024 pixels). The Raman spectra were excited by a Spectra-Physics model 127 He-Ne laser producing highly polarized light at 633 nm and collected at a resolution of 2 cm^{-1} and a precision of ±1 cm^{-1} in the range between 200 and 4000 cm^{-1}. Repeated measurements were made on the crystals using the highest magnification (50×) to improve the signal to noise ratio in the spectra. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer.

Spectral manipulations

Baseline adjustment, smoothing, and normalization were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, U.S.A.). Band component analysis was carried out using the "Peakfit" software package by Jandel Scientific. Lorentz-Gauss cross-product functions were used throughout and peakfitting was carried out until values of $r^2 > 0.995$ were obtained.

RESULTS AND DISCUSSION

Effect of temperature, pressure and time on the synthesis of görgeyite

Figure 1a shows the effect of increasing the external temperature up to 150 °C at 1 atm. Figure 1b shows the same experiment

TABLE 1. Experimental results of the synthesis of görgeyite as function of pressure and temperature

Sample	Starting solutions	Treatment	Time	Crystalline products	Figure
1a	$K_2SO_4 + CaSO_4$	Water 25 °C	3 days	Gp + K_2O	Not shown
1b	$CaSO_4 + K_2SO_4$	Water 25 °C	3 days	Gp + K_2O	Not shown
1a-HT	$K_2SO_4 + CaSO_4$	Hydrothermal	3 days	Anh + K_2O	Not shown
1b-HT	$CaSO_4 + K_2SO_4$	Hydrothermal	3 days	Anh + K_2O	Not shown
2a	$K_2SO_4 + CaSO_4$	Oil bath 50 °C	7 days	Gp + Cc	1a
2b	$K_2SO_4 + CaSO_4$	Oil bath 100 °C	7 days	Syn	1a
2c	$K_2SO_4 + CaSO_4$	Oil bath 150 °C	1 day	Gör	1a
2d	$K_2SO_4 + CaSO_4$	Oil bath 150 °C	7 days	Syn + Gör + trace Gp	1a
2a-HT	$K_2SO_4 + CaSO_4$	Hydrothermal 50 °C	7 days	Syn + Gp	1b
2b-HT	$K_2SO_4 + CaSO_4$	Hydrothermal 100 °C	7 days	Gör	1b,c
2c-HT	$K_2SO_4 + CaSO_4$	Hydrothermal 150 °C	7 days	Anh + trace Gör	1b
3a	$K_2SO_4 + CaSO_4$	Oil bath 100 °C	1 day	Gp + trace Gör	Not shown
3b	$K_2SO_4 + CaSO_4$	Oil bath 100 °C	2 days	Gp + Görg	Not shown
3c	$K_2SO_4 + CaSO_4$	Oil bath 100 °C	3 days	Gör + trace Gp	Not shown
3d	$K_2SO_4 + CaSO_4$	Oil bath 100 °C	4 days	Syn + trace Gör	Not shown
3f	$K_2SO_4 + CaSO_4$	Oil bath 100 °C	6 days	Gör + Syn + Arc	Not shown
3a-HT	$K_2SO_4 + CaSO_4$	Hydrothermal 100 °C	1 day	Syn + trace Gp	1b,c
3b-HT	$K_2SO_4 + CaSO_4$	Hydrothermal 100 °C	2 days	Gör + trace Syn	1c
3c-HT	$K_2SO_4 + CaSO_4$	Hydrothermal 100 °C	3 days	Gör + trace Syn	1c
3d-HT	$K_2SO_4 + CaSO_4$	Hydrothermal 100 °C	4 days	Gör + trace Syn	1c
3e-HT	$K_2SO_4 + CaSO_4$	Hydrothermal 100 °C	5 days	Gör + trace Syn	Not shown
3f-HT	$K_2SO_4 + CaSO_4$	Hydrothermal 100 °C	6 days	Gör	1c

Notes: Gp = gypsum, Anh = anhydrite, Cc = calcite, Syn = syngenite, Gör = görgeyite.

but at autogeneous water vapor pressure. All results, also the ones not shown in the figures, are summarized in Table 1. At 1 atm and 25 °C (samples 1a and 1b), gypsum ($CaSO_4 \cdot 2H_2O$), and potash (K_2O) are formed as crystalline products. When the temperature is increased to 100 °C (sample 2b) syngenite is formed (Fig. 1a). Further increases in temperature results in the replacement of syngenite ($K_2Ca(SO_4)_2 \cdot H_2O$), by görgeyite (sample 2c). After increasing the synthesis time, syngenite appears again as a reaction product next to görgeyite (sample 2d).

Under hydrothermal conditions (increased water vapor pressure), the reaction series is significantly different (Fig. 1b). At 50 °C, syngenite is already formed (sample 2a-HT). Increasing the temperature results in the formation of görgeyite at 100 °C (sample 2b-HT), whereas at higher temperatures and autogeneous water vapor pressures, anhydrite ($CaSO_4$), is formed as the only crystalline component (sample 2c-HT). These results are more in agreement with the recrystallization reaction reported by Triolo et al. (1988), although at temperatures much lower than the 225 °C used in their experiments.

The second series of experiments involved time studies at 100 °C in order to evaluate the kinetics involved and the stability of the minerals formed (Fig. 1c). At 1 atm, increasing the duration of the experiment from 1 to 3 days resulted in a decrease in the amount of gypsum, while syngenite was being replaced by görgeyite (samples 3a to 3c). Further increasing the time resulted in the formation of syngenite replacing görgeyite (samples 3d and 3f). This result indicates that, under these temperature conditions at 1 atm, syngenite rather than görgeyite is the thermodynamically stable phase. Thus, görgeyite is formed metastably.

As with the temperature experiments, the results under autogenous water vapor pressures is significantly different. After 1 day, syngenite is formed together with a small amount of gypsum. Here the increase in time results in the disappearance of the syngenite and replacement by görgeyite after 2 days (samples 3a-Ht and 3b-HT). Further increasing the time results in diminishing amounts of syngenite (up to 6 days), while after 7 days only görgeyite is formed (samples 3b-HT to 3f-HT), indicating

that under these increased pressure conditions, görgeyite seems to be the stable phase instead of syngenite.

Characterization of görgeyite

Figure 2 shows the XRD pattern of the purest görgeyite sample obtained (2b-HT, hydrothermally treated at 100 °C for 7 days), which was also used for the SEM and spectroscopic investigation. The pattern is in good agreement with data on PDF 18-997 (ICDD-PDF) except for the absence of the $\overline{2}02$ reflection in our pattern. The reflections are sharp and intense indicating that the crystals are well developed and with a reasonable size.

SEM confirms the XRD observations showing mostly elongated, almost needle-like crystals approximately 500 to 1000 μm in length. Although the crystals are not developed completely, regularly some of the crystal faces can be recognized (Fig. 3a). EDS analysis confirms the composition of görgeyite (Fig. 3b). On the surface of most crystals, small secondary equidimensional particles and very small needles are visible (Figs. 3c and 3d). All the XRD patterns showed a very minor calcite impurity, possibly formed from dissolved CO_2 from the atmosphere reacting with Ca cations in solution. Upon further enlargement of the small equidimensional particles, the characteristic crystal morphology of calcite becomes evident. EDS analysis confirmed that these particles are indeed calcite, while the needles have the composition of gypsum. The amount of gypsum, however, is so small that it could not be identified in the XRD patterns (Figs. 3e and 3f).

Thus far, two papers have published infrared spectra of natural görgeyite. The spectrum of evaporitic görgeyite from China reported by Cai et al. (1985) closely resembles the spectrum obtained from the synthetic görgeyite in this study. In contrast, the spectrum of the geothermal görgeyite reported by Cavaretta et al. (1983) shows major differences. Even though they reported a low-resolution spectrum, it is clear that the crystal water OH-stretching modes are shifted by more than 50 cm^{-1} toward lower wavenumbers. The same is true for the corresponding water OH-bending mode around 1600 cm^{-1}, although to a lesser degree.
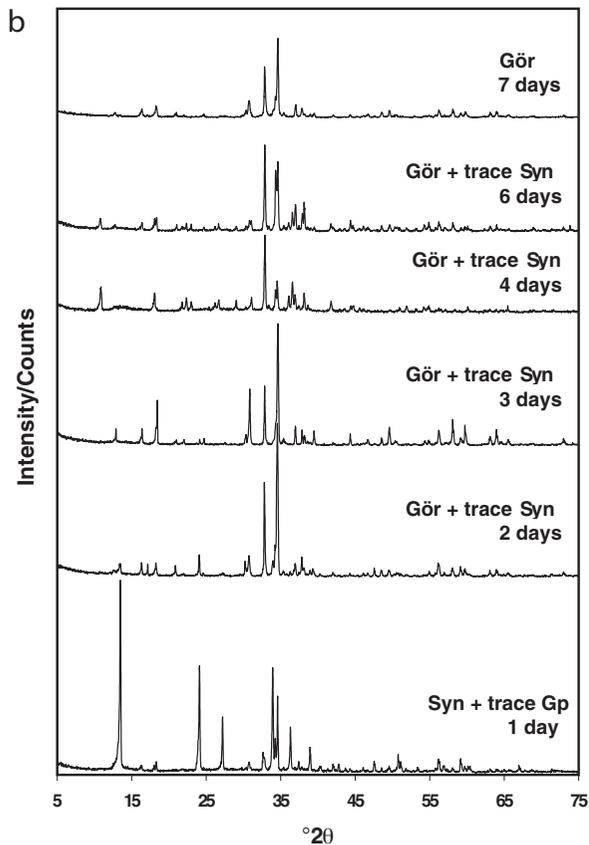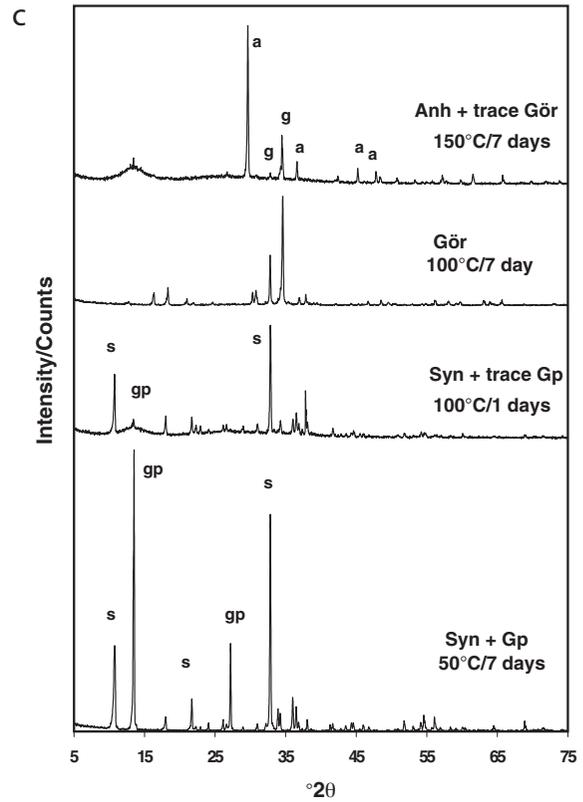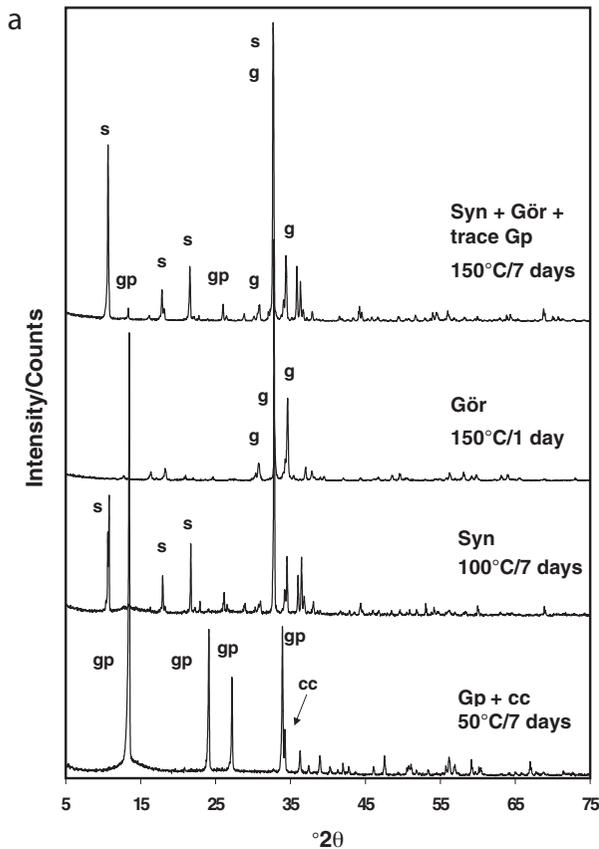
FIGURE 1. Powder XRD patterns of the products formed: (**a**) 7 days at 1 atm with increasing temperature, (**b**) 7 days under hydrothermal conditions with increasing temperature, and (**c**) with increasing time at a constant temperature of 100 °C at 1 atmosphere. Abbreviations used in the figure are listed in Table 1.
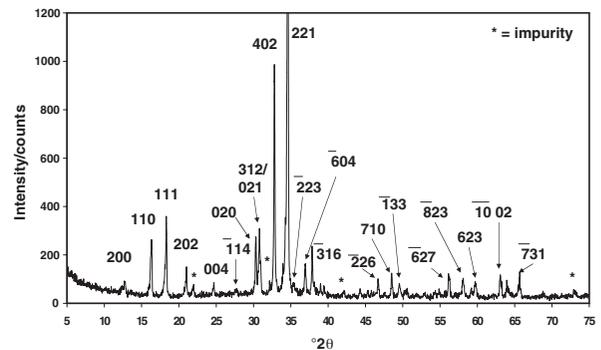

FIGURE 2. Powder XRD pattern of görgeyite containing a minor amount of calcite impurity.

Furthermore, the bands between 1980 and 2380 cm^{-1} were assigned to OH in the görgeyite structure. This assignment seems very unlikely and the bands are probably due to hydrocarbon impurities in their system. No details are visible in the v_1 and v_3 region between 1000 and 1200 cm^{-1}. Cavaretta et al. (1983) gives no indication about sample preparation, but the fact that a transmission spectrum is shown suggest that a powdered sample was

a

b

c

d

e

f
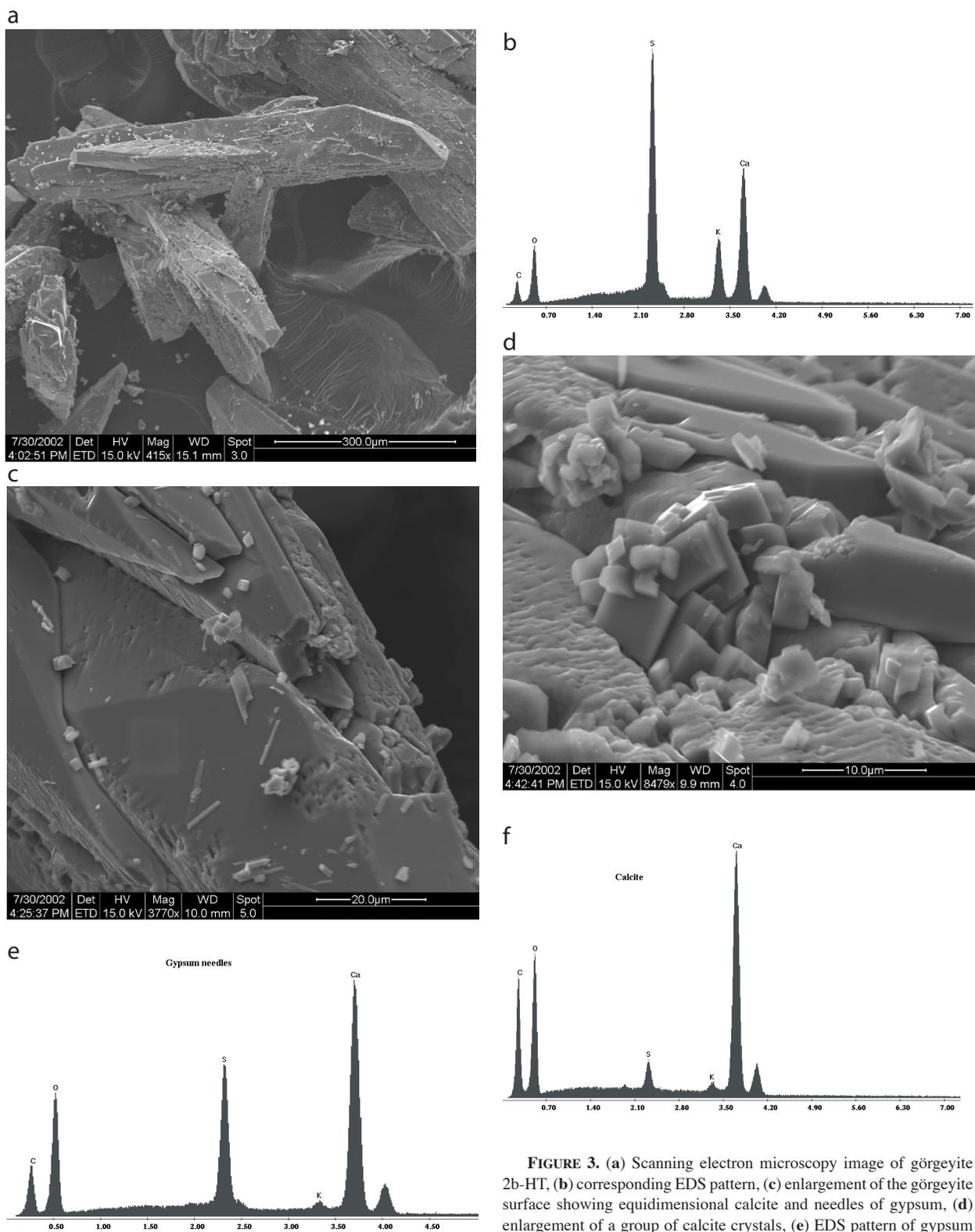
FIGURE 3. (**a**) Scanning electron microscopy image of görgeyite 2b-HT, (**b**) corresponding EDS pattern, (**c**) enlargement of the görgeyite surface showing equidimensional calcite and needles of gypsum, (**d**) enlargement of a group of calcite crystals, (**e**) EDS pattern of gypsum and (**f**) EDS pattern of calcite. Both the EDS patterns of gypsum and calcite show a background signal of the görgeyite.

used. Due to the fact that the görgeyite was retrieved from core samples where it is associated with cesanite [$Na_3Ca_2(SO_4)_3(OH)$] and pyrite leaves open the possibility that the sample used for the infrared analysis was not completely pure. The presence of cesanite and/or hydrocarbons would explain the shift in OH-modes and the loss of details in the sulfate modes.

Figure 4 shows the infrared absorption and the Raman spectra of görgeyite 2b-HT (bottom and middle spectra). For comparative purposes, the infrared spectrum of syngenite is also included in the figure (top spectrum). The spectra consist of vibrational modes associated with crystal water, sulfate groups, or the lattice modes. The crystal structure of görgeyite indicates the presence of one type of water present at a C_1 point-group site, whereas three different sulfate groups are present in the structure; all of them are also present at C_1 point-group sites. The observation in the OH-stretching region between 2900 and 4000 cm^{-1} confirms the C_1 point-group site for water, with two distinct bands visible in the infrared spectrum at 3526 and 3577 cm^{-1} together with, compared to the infrared spectrum, two weak bands at slightly different wavenumbers at 3525 and 3579 cm^{-1} in the Raman spectrum. The spectrum is clearly different from that of syngenite, which is characterized by a very broad band consisting of various overlapping OH-stretching modes at 3248,

3377, and 3510 cm^{-1} (Kloprogge et al. 2002). The corresponding OH-bending modes are observed at 1615 and 1647 cm^{-1} in the infrared spectrum. The corresponding libration mode is present in the infrared spectrum at 876 cm^{-1}.

Theoretically (Ross 1974), when the sulfate retains its full symmetry (T_d), four modes of vibration will be observed: $v_1(A_1)$ at 983 cm^{-1}, $v_2(E)$ at 450 cm^{-1}, v_3 at 1105 cm^{-1}, and $v_4(F_2)$ at 611 cm^{-1}. The A_1 (symmetric stretching) and E (bending) modes are Raman active only, whereas the F_2 stretching and bending modes are both Raman and infrared active. Ross (1974) reported a site symmetry of C_s or C_1 for the sulfate group in syngenite. In görgeyite, the sulfate group is also present at C_1 sites. This site symmetry C_1 will lead to either $6 A' + 3 A''$ or $9 A$, therefore nine Raman and nine infrared active modes for each sulfate group. As a result, the Raman and infrared spectra of görgeyite are very complex in the region below 1400 cm^{-1}. Table 2 gives an overview of all the peak positions.

The v_1 sulfate mode is weak in the infrared but very strong and sharp in the Raman spectrum with two strong bands at 1005 and 1013 cm^{-1}. Similarly, the v_2 mode is very weak in the infrared spectrum but strong in the Raman spectrum, with four clearly visible bands around 433, 440, 457, and 480 cm^{-1}. The v_3 is characterized by a complex set of bands around 1150 cm^{-1} in both the infrared and Raman spectra. Here, the bands are distinctly stronger in the infrared than in the Raman spectrum. The same holds true for the v_4 mode around 650 cm^{-1}.
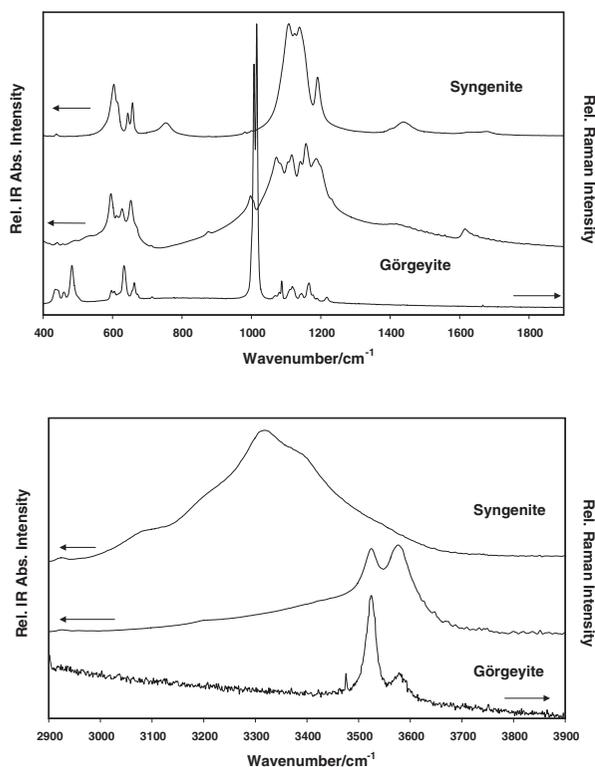

FIGURE 4. Infrared and Raman spectra of görgeyite 2b-HT in comparison to the infrared spectrum of syngenite in the range between (**a**) 400 and 1900 cm^{-1} and (**b**) 2900 and 3900 cm^{-1}.

TABLE 2. Infrared and Raman band positions for görgeyite in comparison to syngenite (Kloprogge et al. 2002)

IR görgeyite (cm^{-1})	Raman görgeyite (cm^{-1})	IR syngenite (cm^{-1})	Assignment
	281		lattice
418	433		$v_2 SO_4$
440	440	439	
457	457		
474	480		
491			
595	595	596	$v_4 SO_4$
612	602	604	
628	631	617	
653	654	657	
670	661		
712	711		
876		754	Water OH-libration
		980	$v_1 SO_4$
997		999	
1006	1005		
	1013		
1072	1067		
	1078		
1084	1085		
1105	1108	1110	$v_3 SO_4$
1117	1115	1125	
1141	1137	1136	
1158	1161	1148	
	1164		
	1175		
1188	1187	1193	
1232	1215		
1615			Water OH-bending
1647		1631	
		3248	Water OH-stretching
		3377	
3526	3525	3510	
3579	3579		

REFERENCES CITED

Braitsch, O. (1965) Zur Gittermetrik des Gorgeyit $K_2Ca_5(SO_4)_6 \cdot H_2O$. Neues Jahrbuch fuer Mineralogie, Monatshefte, 4, 126–8.

Cai, K., Zhao, D., Liao, L., and Huang, X. (1985) The mineralogy of gorgeyite. Earth Science. Journal of China University of Geoscience, 10, 21–28.

Cavarretta, G., Mottana, A., and Tecce, F. (1982) Goergeyite e syngenite nei pozzi geotermici di Cesano (Lazio). In Atti del Congresso della Societa Italiana di Mineralogia e Petrologia, 38, p. 902. Pavia, Italy.

——— (1983) Görgeyite and syngenite in the Cesano geothermal field (Latium, Italy). Neues Jahrbuch fuer Mineralogie, Abhandlungen, 147, 304–314.

Fleischer, M. (1955) New mineral names. American Mineralogist, 40, 551.

GHACA (1942) Kalium. Gmelins Handbuch der anorganischen Chemie, Anhangband. Verlag Chemie GmbH, Weinheim/Bergstr. und Berlin.

Hahne, B. (1967) Sulfat mineralien im Bereich der Sudharzgruben Volkenroda und Pöthen (Kaliwerk Volkenroda). Universität Jena, Jena.

Hill, A.E. (1934) Ternary systems XIX, calcium sulfate, potassium sulfate and water. Journal of the American Chemical Society, 56, 1071–1078.

Kloprogge, J.T., Schuiling, R.D., Ding, Z., Hickey, L., Wharton, D., and Frost, R.L. (2002) Vibrational spectroscopic study of syngenite formed during the treatment of liquid manure with sulphuric acid. Vibrational Spectroscopy, 28, 209–221.

Krull, F. and Vetter, O. (1933) Die kristallographischen und kristallopischen Eigenschaften des Kaliumpentacalciumsulfats und seine Dichte. Zeitschrift fuer Kristallographie, 86, 389–394.

Mayrhofer, H. (1953) Gorgeyit, ein neues Mineral aus der Ischler Salzlagerstatte. Neues Jahrbuch fuer Mineralogie, Monatshefte, 35–44.

Meixner, H. (1955) Zur Identität von Mikheewit (Micheewit) mit Görgeyite. Geologie, Berlin, 6, 576–578.

Mokievsky, V.A. (1953) The scientific session of the Fedorov Institute together with the All-Union mineralogical Society. Zapiski Vses Mineral Obshchestva, 82, 311–317.

Mötzing, R. (1988) Goergyeit im Zechstein 2. Chemie der Erde, 48, 233–244.

Mukhtarova, N.N., Kalinin, V.R., Rastsvetaeva, R.K., Ilyukhin, V.V., and Belov, N.V. (1980) Crystal structure of gorgeyite $K_2Ca_5(SO_4)_6 \cdot H_2O$. Soviet Physics, Doklady, 25, 323–325.

Mukhtarova, N.N., Rastvetaeva, R.K., Ilyukhin, V.V., and Belov, N.V. (1981) Crystal chemistry of sulfates. Structural features of gorgeyite. Mineralogicheskii Zhurnal, 3, 24–35.

Nefedov, E.I. (1955) Neue Minerale. Geologie, 5, 526–528.

Ross, S.D. (1974) Sulphates and other oxy-anions of group VI. In V.C. Farmer, Ed., The Infrared Spectra of Minerals, p. 423–444. Mineralogical Society England.

Seyfarth, H.-H. (1966) Umbildungserscheinungen in Salzgesteinen der Stassfurtserie. Universität Jena, Jena.

Smith, G.W. and Walls, R. (1980) The crystal structure of görgeyite $K_2SO_{4.5}$ $CaSO_4 \cdot H_2O$. Zeitschrift fuer Kristallographie, 151, 49–60.

Smith, G.W., Walls, R., and Whyman, P.I. (1964) An occurrence of görgeyite in Greece. Nature, 203, 1061–1062.

Triolo, I., Mottana, A., and Giampaolo, C. (1988) Synthesis and thermal behaviour of syngenite. Terra Cognita, 8, 79.

van 't Hoff, J.H. (1912) Untersuchungen über die Bildungsverhältnisse der ozeanischen Salzablagerungen insbesondere des Stassfurter Salzlagers, p. 275–277. Akademische Verlagsgesellschaft, Leipzig.

van 't Hoff, J.H. and Geiger, A. (1904) Untersuchungen über die Bildungsverhätnisse der ozeanischen Salzablagerungen. XXXVII. Kaliumpentakalziumsulfat und eine dem Kaliborit verwandte Doppelverbindung, p. XXVIII, 935–937. Preussischen Akademie der Wissenschaften zu Berlin.

van 't Hoff, J.H., Voermann, G.L., and Blasdale, W.C. (1905) Untersuchungen über die Bildungsverhätnisse der ozeanischen Salzablagerungen. XLI. Die Bildungstemperatur des kaliumpentacalciumsulfats., p. XII, 305–310. Sitzungsberichte der Königlichen Preussischen Akademie der Wissenschaften zu Berlin.