



## Article

# The crystal structure of Ni-rich gordaite–thérèsemagnanite from Cap Garonne, France

Stuart J. Mills<sup>1\*</sup>, Owen P. Missen<sup>1,2</sup> and Georges Favreau<sup>3</sup>

<sup>1</sup>Geosciences, Museums Victoria, GPO Box 666, Melbourne 3001, Victoria, Australia; <sup>2</sup>School of Earth, Atmosphere and Environment, Monash University, Clayton 3800, Victoria, Australia; and <sup>3</sup>421 Avenue Jean Monnet, Aix-en-Provence, 13090, France

### Abstract

The crystal structure of Ni-rich gordaite–thérèsemagnanite has been determined from a sample collected at pillar 80 in the North mine, Cap Garonne, Var, France. The structure was refined to  $R_1 = 0.0693$  for 935 reflections with  $I > 2\sigma(I)$ . The mineral is isostructural with gordaite, forming a layered structure with an extensive hydrogen-bonding network. The possible polytypic relationship between gordaite, thérèsemagnanite and guarinoite is also discussed. The guarinoite formula  $(\text{Zn},\text{Co},\text{Ni})_6(\text{SO}_4)(\text{OH},\text{Cl})_{10}\cdot 5\text{H}_2\text{O}$  is also likely to be incorrect and is more likely to be  $\text{Na}(\text{Zn},\text{Co})_4(\text{SO}_4)(\text{OH})_6\text{Cl}\cdot 5\text{--}6\text{H}_2\text{O}$ , meaning that guarinoite is equivalent to Co-rich gordaite-2H and would not be a distinct mineral species.

**Keywords:** thérèsemagnanite, gordaite, Cap Garonne, crystal structure, polytype, solid solution, guarinoite

(Received 18 December 2018; accepted 14 January 2019; Accepted Manuscript online: 14 March 2019; Associate Editor: Anthony R Kampf)

### Introduction

Thérèsemagnanite was originally described as a new cobalt–zinc–nickel sulfate from the Cap Garonne mine, Var, Provence-Alpes-Côte d’Azur, France by Sarp (1993) with the formula  $(\text{Co},\text{Zn},\text{Ni})_6(\text{SO}_4)(\text{OH},\text{Cl})_{10}\cdot 8\text{H}_2\text{O}$ , but was redefined recently by Kasatkin *et al.* (2018) as  $\text{NaCo}_4(\text{SO}_4)(\text{OH})_6\text{Cl}\cdot 6\text{H}_2\text{O}$ ; the Co-analogue of gordaite. Unfortunately, Kasatkin *et al.* (2018) could not identify any crystals suitable for single-crystal analysis, however, during a systematic study looking for crystals of guarinoite and thérèsemagnanite in the North mine at Cap Garonne, we were able to find single crystals suitable for study. Here we report the crystal structure of Ni-rich gordaite–thérèsemagnanite near the triline, in order to shed light on the structure of thérèsemagnanite and the as yet unreported Ni-analogue of thérèsemagnanite and gordaite.

### Occurrence

The gordaite–thérèsemagnanite specimen studied was collected at pillar 80 in the North mine, Cap Garonne, Var, France (43° 4’53”N, 6°1’55”E). Pillar 80 is a long and straight mine wall exhibiting unusual mineralogy, dominated by copper, zinc, cobalt and nickel. The end of the wall includes a large cavity where 5 out of the 14 new species known at Cap Garonne have been found: geminite (Sarp and Perroud, 1990), guarinoite (Sarp, 1993), mahnertite (Sarp, 1996), pushcharovskite (Sarp and Sanz-Gysler, 1997) and thérèsemagnanite (Sarp, 1993). This specimen was collected as part of the systematic study of the mine mineralogy by

Association des Amis de la Mine de Cap Garonne (Favreau and Galea-Clolus, 2014; Mills *et al.*, 2014, 2015, 2017, 2018; Plášil *et al.*, 2018).

There are two different environments that co-exist in the cavity. The lower part of the cavity wall is comprised of a very compact quartz conglomerate, rich in tennantite, where acidic conditions may have existed for the formation of geminite and pushcharovskite. Other copper minerals are found in this environment, such as lavendulan, mahnertite, zdeněkite, atacamite, brochantite and olivenite. The upper part of the wall and the roof are made of a less compact conglomerate with malachite and cerussite, and the Zn–Co–Ni sulfates ktenasite, guarinoite and thérèsemagnanite. A thick, solid, fine-grained galena vein is located between the lower and upper part, with rare cavities hosting covellite, native sulphur (Kösters *et al.*, 2019) and anglesite. The specimen studied was found in a fracture of this galena vein.

Gordaite–thérèsemagnanite occurs as pale pink, vitreous hexagonal plates up to 0.2 mm in diameter, usually stacked as textbooks or organised as rosettes. The unusual thickness and size of the crystals in this specimen allowed for single-crystal studies to be conducted. The specimen studied has been deposited in the collections of Museums Victoria, registration number M54547.

### Experimental

#### Chemistry

Semi-quantitative chemical analyses of a crystal cluster from the specimen were performed on a JEOL 7001F FEG-SEM (energy-dispersive spectroscopy (EDS) mode, 20 kV, 3 nA and 6 µm beam diameter) at the Monash Centre for Electron Microscopy, Monash University, Australia. The scanning electron microscopy EDS method was used for semi-quantitative chemical analysis due

\*Author for correspondence: Stuart J. Mills, Email: [smills@museum.vic.gov.au](mailto:smills@museum.vic.gov.au)

Cite this article: Mills S.J., Missen O.P. and Favreau G. (2019) The crystal structure of Ni-rich gordaite–thérèsemagnanite from Cap Garonne, France. *Mineralogical Magazine* 83, 459–463. <https://doi.org/10.1180/mgm.2019.6>

**Table 1.** The average composition of gordaite–thérèsemaganite (23 analyses) determined by SEM–EDS\*.

| Element | Wt. % | Apfu  | Element | Wt. % | Apfu |
|---------|-------|-------|---------|-------|------|
| O       | 40.99 | 16.01 | Co      | 12.3  | 1.30 |
| Na      | 5.37  | 1.46  | Ni      | 10.2  | 1.09 |
| S       | 5.60  | 1.09  | Zn      | 15.1  | 1.44 |
| Cl      | 3.25  | 0.57  |         |       |      |
| K       | 0.21  | 0.03  | Total   | 93.0  |      |

\*H is not included. Apfu is atoms per formula unit, based on 23 non-H atoms.

to the hydrated nature of the mineral and its susceptibility to beam damage. Even gentle conditions in an electron microprobe caused burning of the sample. The standards used were: quartz (O and Si), albite (Na), pyrite (S), synthetic NaCl (Cl), synthetic KBr (K), Co metal (Co), Ni metal (Ni) and Zn metal (Zn). Results (Table 1) are recorded to only one decimal place for all elements, while H cannot be detected by EDS. Sodium is overestimated in the analyses due to the overlap between NaK $\alpha$  and ZnK $\alpha$ . The analyses for Co, Ni and Zn (Fig. 1) show a spread of values similar to those presented in fig. 6 in Kasatkin *et al.* (2018), where some points are Zn-dominant (18 points) and some Co-dominant (5 points), but with the average calculated Co:Ni:Zn ratio of 0.34:0.28:0.38. However, the Co:Zn average ratio is within error of each other given the uncertainties of the analytical method. The specimen studied shows more Ni than the samples of Kasatkin *et al.* (2018), suggesting that a Ni-dominant member of the gordaite group could also be found at Cap Garonne, probably at pillar 80.

**X-ray diffraction**

The single crystal X-ray diffraction experiment was carried out on the micro-focus macromolecular MX2 beamline at the Australian Synchrotron, part of ANSTO. A 10  $\mu\text{m} \times 10 \mu\text{m} \times 2 \mu\text{m}$  pale-pink single crystal (a fragment of a larger hexagonal plate) was selected from specimen M54547. Data were collected at 100 K by a Dectris EigerX 16M detector and monochromatic radiation with a wavelength of 0.71073 Å. After processing the data using XDS (Kabsch, 2010), XPREP (Bruker, 2001) and SADABS (Bruker, 2001), 10,670 reflections were integrated with a  $R_{\text{int}}$  of 0.1352. Structure solution in  $P\bar{3}$  was carried out by direct methods using SHELXT (Sheldrick, 2015a) and located all atoms. Structure refinement by full-matrix least-squares was implemented by SHELXL (Sheldrick, 2015b), using neutral atomic-scattering factors. Three reflections with calculated  $F_0/F_C$  errors >5.00 were omitted from the final refinement. All hydrogen atoms were located via calculation of the bond valence sums on the oxygen atoms, consideration of non-bonded O...O distances which might indicate the presence of hydrogen bonds, and careful inspection of the difference-Fourier maps. All hydrogen atoms were successfully located in this way. Hydrogen atoms were constrained softly to a distance of 0.90(2) Å and a  $U_{\text{eq}}$  1.5 times that of its corresponding oxygen atom. The Cl site refined to a final occupancy of 93% Cl and 7% OH. A difference peak located at (0, 0, 0.112, site occupancy factor = 1/3), 0.918 Å from the Cl/OH site may also indicate the presence of a partially occupied H atom. In the final stage of the refinement the Co:Ni:Zn ratio was fixed at 0.34:0.28:0.38 on the basis of the average chemical analyses. Details concerning data collection and structure refinement are provided

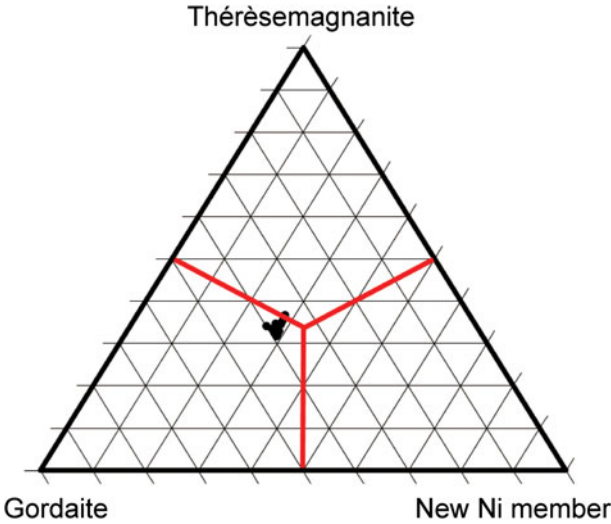


**Fig. 1.** Triangular diagram showing the Co:Zn:Ni proportions analysed in the gordaite–thérèsemaganite crystals (23 analyses). Plotted using Graham and Midgley (2000).

in Table 2. Fractional coordinates and atomic displacement parameters are provided in Tables 3 and 4, respectively. A bond-valence analysis is provided in Table 5, using the parameters of Gagné and Hawthorne (2015) for all ion–oxygen bonds except Na (Wood and Palenik, 1999) and H (Brown, 2002). The M1–Cl bond valence was calculated using the parameters of Brese and O’Keefe (1991).

**Table 2.** Summary of information relating to data collection and structure refinement of gordaite–thérèsemaganite.

|                                                                                         |                                                                                                                                         |
|-----------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------|
| <b>Crystal data</b>                                                                     |                                                                                                                                         |
| Ideal formula                                                                           | Na(Co <sub>0.34</sub> Ni <sub>0.28</sub> Zn <sub>0.38</sub> ) <sub>4</sub> (SO <sub>4</sub> )<br>(OH) <sub>6</sub> Cl·6H <sub>2</sub> O |
| Crystal system, space group                                                             | Trigonal, $P\bar{3}$                                                                                                                    |
| Temperature (K)                                                                         | 100(2)                                                                                                                                  |
| $a$ , $c$ (Å)                                                                           | 8.3260(12), 12.976(3)                                                                                                                   |
| $V$ (Å <sup>3</sup> )                                                                   | 779.0(3)                                                                                                                                |
| $Z$                                                                                     | 3                                                                                                                                       |
| Calculated density (g cm <sup>−3</sup> )                                                | 2.600                                                                                                                                   |
| Radiation type and wavelength (Å)                                                       | Synchrotron, $\lambda$ = 0.71073                                                                                                        |
| $\mu$ (mm <sup>−1</sup> )                                                               | 5.478                                                                                                                                   |
| Crystal dimensions (mm)                                                                 | 0.010 $\times$ 0.010 $\times$ 0.002                                                                                                     |
| Reflections for cell refinement                                                         | 223                                                                                                                                     |
| <b>Data collection</b>                                                                  |                                                                                                                                         |
| Crystal description                                                                     | Pale-pink fragment                                                                                                                      |
| Diffractometer                                                                          | Dectris EigerX 16M detector                                                                                                             |
| $\theta$ range (°)                                                                      | 1.569 to 26.331                                                                                                                         |
| Indices range of $h$ , $k$ , $l$                                                        | −10 $\leq h \leq$ 10, −10 $\leq k \leq$ 10, −16 $\leq l \leq$ 16                                                                        |
| Absorption correction                                                                   | SADABS (Bruker, 2001)                                                                                                                   |
| $T_{\text{min}}$ , $T_{\text{max}}$                                                     | 0.4323, 0.7464                                                                                                                          |
| No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections              | 10,670, 1072, 935                                                                                                                       |
| $R_{\text{int}}$                                                                        | 0.1352                                                                                                                                  |
| Data completeness to 25.242° $\theta$ (%)                                               | 99.8                                                                                                                                    |
| <b>Refinement</b>                                                                       |                                                                                                                                         |
| Number of reflections, parameters, restraints                                           | 1072, 89, 6                                                                                                                             |
| $R_1[I > 2\sigma(I)]$ , $R_2(\text{all})$                                               | 0.0693, 0.0746                                                                                                                          |
| $wR_2[I > 2\sigma(I)]$ , $wR_2(\text{all})$                                             | 0.1657, 0.1707                                                                                                                          |
| GoF ( $F^2$ )                                                                           | 1.095                                                                                                                                   |
| $\Delta\rho_{\text{min}}$ , $\Delta\rho_{\text{max}}$ (e <sup>−</sup> Å <sup>−3</sup> ) | −1.52, 4.55                                                                                                                             |

**Table 3.** Atom coordinates, site occupancies and atomic displacement parameters ( $\text{\AA}^2$ ) for gordaite-thérèsemagnanite.

| Atom | $x/a$          | $y/b$         | $z/c$       | $U_{eq}$   | $U^{11}$   | $U^{22}$   | $U^{33}$   | $U^{23}$    | $U^{13}$    | $U^{12}$   |
|------|----------------|---------------|-------------|------------|------------|------------|------------|-------------|-------------|------------|
| M1*  | 0              | 0             | 0.36131(9)  | 0.0128(4)  | 0.0072(4)  | 0.0072(4)  | 0.0239(7)  | 0           | 0           | 0.0036(2)  |
| M2*  | −0.13022(9)    | 0.28578(9)    | 0.49769(5)  | 0.0161(4)  | 0.0092(5)  | 0.0084(5)  | 0.0301(6)  | −0.0001(2)  | −0.0015(2)  | 0.0040(3)  |
| Na1  | $\frac{1}{3}$  | $\frac{2}{3}$ | 0.9141(3)   | 0.0226(9)  | 0.0184(13) | 0.0184(13) | 0.031(2)   | 0           | 0           | 0.0092(6)  |
| S1   | $-\frac{1}{3}$ | $\frac{1}{3}$ | 0.72418(19) | 0.0175(6)  | 0.0134(7)  | 0.0134(7)  | 0.0258(12) | 0           | 0           | 0.0067(4)  |
| Cl** | 0              | 0             | 0.18484(19) | 0.0189(12) | 0.0156(13) | 0.0156(13) | 0.0256(17) | 0           | 0           | 0.0078(6)  |
| O1   | $-\frac{1}{3}$ | $\frac{1}{3}$ | 0.6073(6)   | 0.0209(16) | 0.016(2)   | 0.016(2)   | 0.031(4)   | 0           | 0           | 0.0079(11) |
| O2   | −0.3730(5)     | 0.1059(5)     | 0.4283(4)   | 0.0156(10) | 0.012(2)   | 0.0094(19) | 0.025(2)   | 0.0023(14)  | 0.0010(14)  | 0.0048(15) |
| O3   | 0.0556(5)      | 0.2463(5)     | 0.4074(4)   | 0.0172(10) | 0.011(2)   | 0.010(2)   | 0.030(3)   | −0.0003(14) | −0.0011(14) | 0.0045(15) |
| O4   | −0.1733(6)     | 0.5059(6)     | 0.7607(3)   | 0.0214(9)  | 0.018(2)   | 0.014(2)   | 0.031(2)   | −0.0009(16) | −0.0026(16) | 0.0078(16) |
| OW1  | 0.1236(6)      | 0.4397(6)     | 0.7922(4)   | 0.0247(10) | 0.017(2)   | 0.020(2)   | 0.037(3)   | −0.0006(18) | −0.0020(17) | 0.010(2)   |
| OW2  | 0.6074(6)      | 0.7802(6)     | 1.0240(4)   | 0.0249(10) | 0.022(2)   | 0.022(2)   | 0.029(2)   | −0.0015(18) | −0.0021(17) | 0.0104(19) |
| H1   | 0.580(12)      | 0.756(12)     | 1.091(2)    | 0.037      |            |            |            |             |             |            |
| H2   | 0.578(11)      | 0.766(13)     | 0.957(2)    | 0.037      |            |            |            |             |             |            |
| H3   | 0.196(10)      | 0.451(13)     | 0.847(4)    | 0.037      |            |            |            |             |             |            |
| H4   | 0.016(6)       | 0.436(12)     | 0.779(7)    | 0.037      |            |            |            |             |             |            |
| H5   | 0.116(10)      | 0.330(9)      | 0.356(5)    | 0.037      |            |            |            |             |             |            |
| H6   | −0.398(11)     | 0.121(12)     | 0.363(3)    | 0.037      |            |            |            |             |             |            |

\* Occupancies for M sites fixed to 34% Co, 28% Ni and 38% Zn.

\*\* Occupancy refined to Cl 0.93(3) and O (as OH) 0.07(3)

**Table 4.** Bond lengths ( $\text{\AA}$ ) for gordaite-thérèsemagnanite\*.

|          |          |        |          |           |          |
|----------|----------|--------|----------|-----------|----------|
| M1–O3 ×3 | 1.956(4) | M2–O2  | 2.028(4) | Na–OW1 ×3 | 2.413(5) |
| M1–Cl    | 2.290(3) | M2–O2  | 2.053(4) | Na–OW2 ×3 | 2.444(5) |
| <M1–φ>   | 2.040    | M2–O2  | 2.073(4) | <Na–O> ×3 | 2.429    |
|          |          | M2–O3  | 2.094(4) |           |          |
|          |          | M2–O3  | 2.116(4) | S1–O4 ×3  | 1.466(4) |
|          |          | M2–O1  | 2.389(5) | S1–O1     | 1.517(8) |
|          |          | <M2–O> | 2.126    | <S–O>     | 1.479    |

| Hydrogen bonding |                         |                           |                           |           |
|------------------|-------------------------|---------------------------|---------------------------|-----------|
| Donor O          | d(D–H) ( $\text{\AA}$ ) | d(H···A) ( $\text{\AA}$ ) | d(D···A) ( $\text{\AA}$ ) | <DHA> (°) |
| O2–H6            | 0.89(2)                 | 2.13(6)                   | 2.892(7)                  | 144(8)    |
| O3–H5            | 0.91(2)                 | 1.94(3)                   | 2.820(6)                  | 163(8)    |
| O3–H5            | 0.91(2)                 | 2.51(8)                   | 3.089(4)                  | 122(7)    |
| OW1–H4           | 0.90(2)                 | 1.95(3)                   | 2.819(6)                  | 163(8)    |
| OW1–H4           | 0.90(2)                 | 2.56(6)                   | 3.251(6)                  | 134(7)    |
| OW2–H1           | 0.90(2)                 | 2.02(2)                   | 2.918(6)                  | 175(8)    |

\*Occupancies for M sites fixed to 34% Co, 28% Ni and 38% Zn; occupancy for Cl site refined to 93% Cl and 7% OH.

### Structure description

The structure of the gordaite-thérèsemagnanite from Cap Garonne (Figs 2 and 3) is very similar to those reported for gordaite (Adiwidjaja *et al.*, 1997; Zhu *et al.*, 1997 – although only the former study located H atoms on the H<sub>2</sub>O group oxygen atoms), with the only main difference noted in the hydrogen bonding. The structure is layered parallel to {001}, with a brucite-like

sheet formed from edge-sharing  $[M2(OH)_5O]^{3-}$  octahedra. Each octahedron is surrounded by six others, but one-seventh of the octahedral sites are vacant, providing three corner-linking O3 sites for two  $[M1(OH)_3Cl]^{2-}$  tetrahedra to be bonded to the layer, one above and one below the sheet. SO<sub>4</sub> tetrahedra are corner-linked to one-third of the  $[M2(OH)_5O]^{3-}$  octahedra, also pointing both above and below the sheet. To compensate for the overall negative charge of the  $[M1(OH)_3Cl]^{2-}$  tetrahedra,  $[M2(OH)_5O]^{3-}$  octahedra and SO<sub>4</sub> tetrahedra, isolated Na(H<sub>2</sub>O)<sub>6</sub> octahedra are found between the layers. Hydrogen bonding is integral in linking the layers together along [001].

The hydrogen bonding network is similar to that described by Adiwidjaja *et al.* (1997). Identical H bonds are seen connecting the channel H<sub>2</sub>O groups to SO<sub>4</sub> oxygen atoms, and from sheet OH groups to channel H<sub>2</sub>O oxygen atoms. The main difference is that no H bonds in our structure are oriented towards the Cl anions or between adjacent Na(H<sub>2</sub>O)<sub>6</sub> octahedra. Instead, the H bonds are more typically oriented towards other H<sub>2</sub>O groups (Fig. 2).

The structure has a superficial resemblance to the sulfate members of the hydrotalcite supergroup (Mills *et al.*, 2012), however, in hydrotalcites SO<sub>4</sub> tetrahedra do not bond directly onto the brucite layer. Therefore, the gordaite-thérèsemagnanite structure is more closely related to minerals such as spangolite, Cu<sub>6</sub>Al(OH)<sub>12</sub>(SO<sub>4</sub>)Cl·3H<sub>2</sub>O (Hawthorne *et al.*, 1993) and jaborite, Ni<sub>1–x</sub>Co<sub>x</sub><sup>3+</sup>(OH)<sub>2–x</sub>(SO<sub>4</sub>)<sub>x</sub>·nH<sub>2</sub>O (Bindi *et al.*, 2015) where the SO<sub>4</sub> tetrahedra bond directly to the layer.

**Table 5.** Bond-valence sums (in valence units) for gordaite-thérèsemagnanite, (A) indicates an accepted hydrogen bond.

|      | M1*        | M2*              | Na1        | S1         | H1       | H2   | H3   | H4             | H5       | H6       | Σ    |
|------|------------|------------------|------------|------------|----------|------|------|----------------|----------|----------|------|
| Cl** | 0.45       |                  |            |            |          |      |      |                |          |          | 0.45 |
| O1   |            | 0.16             |            |            |          |      |      |                | 0.08 (A) |          | 1.60 |
| O2   |            | 0.40, 0.38, 0.36 |            |            |          |      |      |                |          | 1.06     | 2.21 |
| O3   | 0.49 (×3↓) | 0.34, 0.32       |            |            |          |      |      |                | 0.99     |          | 2.15 |
| O4   |            |                  |            | 1.56 (×3↓) | 0.17 (A) |      |      | 0.20, 0.07 (A) | 0.20 (A) |          | 2.20 |
| OW1  |            |                  | 0.17 (×3↓) |            |          |      | 1.03 | 1.03           |          |          | 2.22 |
| OW2  |            |                  | 0.16 (×3↓) |            | 1.03     | 1.03 |      |                |          | 0.15 (A) | 2.35 |
| Σ    | 1.903      | 1.973            | 0.98       | 6.05       | 1.03     | 1.03 | 1.03 | 1.03           | 0.99     | 1.06     |      |

\* 34% Co, 28% Ni and 38% Zn; \*\* 93% Cl and 7% OH

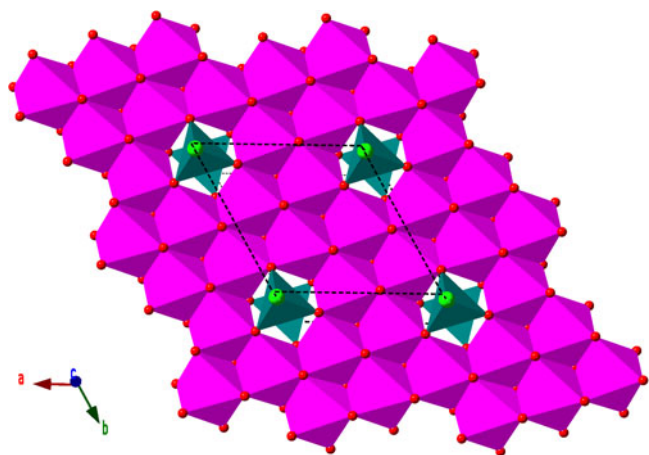


**Fig. 2.** One sheet of gordaite-thérèsemagnanite viewed down [001].  $[M2(OH)_5O]^{3-}$  octahedra are in magenta,  $[M1(OH)_3Cl]^{2-}$  tetrahedra in dark cyan, O atoms in red, Cl atoms in bright green. H atoms are not shown for clarity.

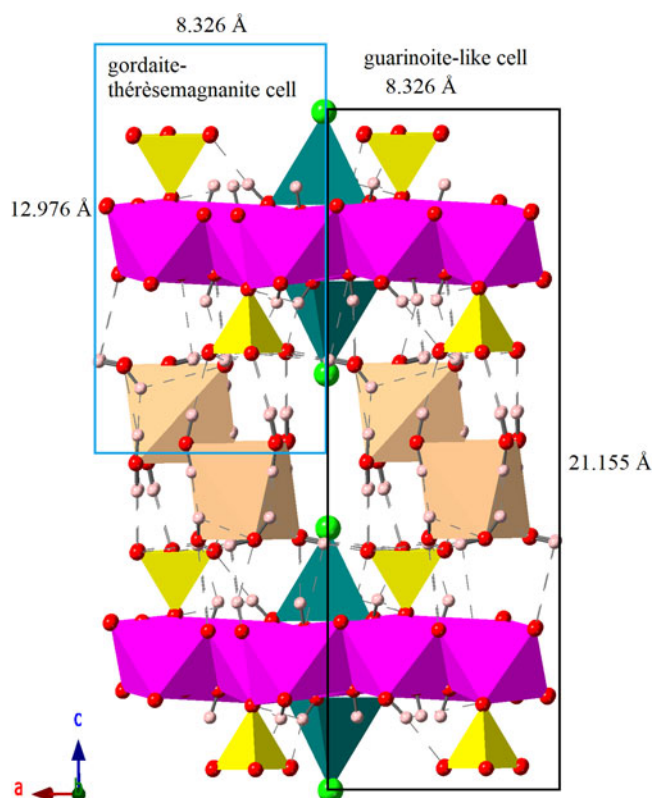


**Fig. 3.** The structure of gordaite-thérèsemagnanite viewed down [010]. Colour scheme is as above, with  $SO_4$  tetrahedra in yellow,  $Na(H_2O)_6$  octahedra in pale orange and H atoms in pale pink. H bonds are shown as dashed lines.

### Comment on relationship to guarinoite

Sarp (1993) described guarinoite as ideally  $(Zn,Co,Ni)_6(SO_4)(OH,Cl)_{10} \cdot 5H_2O$  and thérèsemagnanite as  $(Co,Zn,Ni)_6(SO_4)(OH,Cl)_{10} \cdot 8H_2O$ , with the unit cells  $a = 8.344(4)$  and  $c = 21.59(2)$  Å and  $a = 8.363(8)$  and  $c = 26.18(17)$  Å for guarinoite and thérèsemagnanite, respectively. We note that the  $a$  axis and chemistry reported by Sarp are very similar.

The correct unit cell for thérèsemagnanite is actually half of that originally reported:  $a = 8.3260(12)$  and  $c = 12.976(3)$  Å.

Given that the crystal structure is similar to hydrotalcite super-group minerals, it is reasonable to suggest that the gordaite crystal structure may also be polytypic. If we consider the gordaite-thérèsemagnanite crystal structure has one layer (i.e.  $1T$ ), and then we take two layers and draw the unit cell from Cl atom to Cl atom we get the parameters  $a \approx 8.34$  and  $c \approx 21.16$  Å (Fig. 3). This unit cell would then match that reported by Sarp (1993) and would be considered the  $2H$  polytype. It is also possible that there could be a loss of  $\sim 1 H_2O$  in the structure, corresponding to a  $\sim 1$  Å decrease in  $c$ . If this is correct, then the guarinoite formula reported by Sarp (1993) is also likely to be incorrect and is more likely to be  $Na(Zn,Co)_4(SO_4)(OH)_6Cl \cdot \sim 5-6H_2O$ . That would, therefore, mean guarinoite is equivalent to Co-rich gordaite- $2H$  and would not be a distinct mineral species.

We were not able to find a suitable crystal for single-crystal analysis on the type specimen of guarinoite (Natural History Museum of Geneva, specimen 435/85). Any analyses with  $Co > Zn$  and the unit cell parameters  $a \approx 8.34$  and  $c \approx 21.16$  Å would be considered thérèsemagnanite- $2H$ .

**Acknowledgements.** This research was undertaken in part using the MX2 beamline at the Australian Synchrotron, part of ANSTO, and made use of the Australian Cancer Research Foundation (ACRF) detector. The authors acknowledge use of the facilities and the assistance of Nick McDougall and Xi-Ya Fang at the Monash Centre for Electron Microscopy. Support funding has also been provided to OPM by an Australian Government Research Training Program (RTP) Scholarship. We would like to thank Jakub Plášil, Peter Leverett and Nikita Chukanov for providing helpful comments on the manuscript.

**Supplementary material.** To view supplementary material for this article, please visit <https://doi.org/10.1180/mgm.2019.6>

### References

- Adiwidjaja G., Friese K., Klaska K.-H. and Schlüter J. (1997) The crystal structure of gordaite  $NaZn_4(SO_4)(OH)_6Cl \cdot 6H_2O$ . *Zeitschrift für Kristallographie*, **212**, 704–707.
- Breese N.E. and O'Keeffe M. (1991) Bond-valence parameters for solids. *Acta Crystallographica*, **B47**, 192–197.
- Bindi L., Christy A.G., Mills S.J., Ciriotti M.E. and Bittarello E. (2015) New compositional and structural data validate the status of jaborite. *The Canadian Mineralogist*, **53**, 791–802.
- Brown I.D. (2002) *The Chemical Bond in Inorganic Chemistry*. Oxford University Press, UK.
- Bruker (2001) *SADABS and XPRED*. Bruker AXS Inc., Madison, WI, USA.
- Favreau G. and Galea-Clolus V. (2014) *Cap Garonne*. Association Française de Microminéralogie, France, 320 pp.
- Gagné O.C. and Hawthorne F.C. (2015) Comprehensive derivation of bond-valence parameters for ion pairs involving oxygen. *Acta Crystallographica*, **B71**, 562–578.
- Graham D.J. and Midgley N.G. (2000) Graphical representation of particle shape using triangular diagrams: an Excel spreadsheet method. *Earth Surface Processes and Landforms*, **25**, 1473–1477.
- Hawthorne F.C., Kimata M. and Eby R.K. (1993) The crystal structure of spangolite, a complex copper sulfate sheet mineral. *American Mineralogist*, **78**, 649–652.
- Kabsch W. (2010) XDS. *Acta Crystallographica*, **D66**, 125–132.
- Kasatkin A.V., Plášil J., Škoda R., Belakovskiy D.I., Marty J., Meisser N. and Pekov I.V. (2018) Redefinition of thérèsemagnanite,  $NaCo_4(SO_4)(OH)_6Cl \cdot 6H_2O$ : new data and relationship to 'cobaltogordaite'. *Mineralogical Magazine*, **82**, 159–170.
- Kösters J., Galéa-Clolus V., Clolus P., Heying B. and Pöttgen R. (2019) Orthorhombic sulfur from Cap Garonne, Mine du Pradet. *Zeitschrift für Naturforschung B*, **74**, 5–8.

- Mills S.J., Christy A.G., Colombo F. and Price J.R. (2015) The crystal structure of cyanotrichite. *Mineralogical Magazine*, **79**, 321–335.
- Mills S.J., Christy A.G., Génin J.-M., Kameda T. and Colombo F. (2012) Nomenclature of the hydrotalcite supergroup: natural layered double hydroxides. *Mineralogical Magazine*, **76**, 1289–1336.
- Mills S.J., Christy A.G., Schnyder C., Favreau G. and Price J.R. (2014) The crystal structure of camerolaite and structural variation in the cyanotrichite family of merotypes. *Mineralogical Magazine*, **78**, 1527–1552.
- Mills S.J., Christy A.G., Favreau G. and Galea-Clolus V. (2017) Multidimensional structural variation in the cyanotrichite family of merotypes: camerolaite-3b-F-1. *Acta Crystallographica*, **B73**, 950–955.
- Mills S.J., Christy A.G. and Favreau G. (2018) The crystal structure of ceruleite,  $\text{CuAl}_4[\text{AsO}_4]_2(\text{OH})_8(\text{H}_2\text{O})_4$ , from Cap Garonne, France. *Mineralogical Magazine*, **82**, 181–187.
- Plášil J., Petříček V., Mills S.J., Favreau G. and Galea-Clolus V. (2018) Zippeite from Cap Garonne, France: an example of reticular twinning. *Zeitschrift für Kristallographie – Crystalline Materials*, **233**, 861–865.
- Sarp H. (1993) Guarinoite  $(\text{Zn}, \text{Co}, \text{Ni})_6(\text{SO}_4)(\text{OH}, \text{Cl})_{10} \cdot 5\text{H}_2\text{O}$  et thérèsemagnanite  $(\text{Co}, \text{Zn}, \text{Ni})_6(\text{SO}_4)(\text{OH}, \text{Cl})_{10} \cdot 8\text{H}_2\text{O}$ , deux nouveaux minéraux de la mine de Cap Garonne, Var, France. *Archives de Science Genève*, **46**, 37–44.
- Sarp H. (1996) Mahnertite,  $(\text{Na}, \text{Ca})\text{Cu}(\text{AsO}_4)_4\text{Cl} \cdot 5\text{H}_2\text{O}$ , a new mineral from the Cap Garonne Mine, Var France. *Archives de Science Genève*, **49**, 119–124.
- Sarp H. and Sanz-Gysler J. (1997) Pushcharovskite,  $\text{Cu}(\text{AsO}_3)(\text{OH}) \cdot \text{H}_2\text{O}$ , a new mineral from Cap Garonne (Var, France). *Archives de Science Genève*, **50**, 177–186.
- Sarp H. and Perroud P. (1990) La geminite,  $\text{Cu}_2\text{As}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ , un nouveau minéral de la mine de Cap Garonne, Var, France. *Schweizerische Mineralogische und Petrographische Mitteilungen*, **70**, 309–314.
- Sheldrick G.M. (2015a) SHELXT – integrated space-group and crystal-structure determination. *Acta Crystallographica*, **A71**, 3–8.
- Sheldrick G.M. (2015b) Crystal structure refinement with SHELXL. *Acta Crystallographica*, **C71**, 3–8.
- Wood R.M. and Palenik G.J. (1999) Bond valence sums in coordination chemistry. Sodium–oxygen complexes. *Inorganic Chemistry*, **38**, 3926–3930.
- Zhu L., Seff K., Witzke T. and Nasdala L. (1997) Crystal structure of  $\text{Zn}_4\text{Na}(\text{OH})_6\text{SO}_4\text{Cl} \cdot 6\text{H}_2\text{O}$ , *Journal of Chemical Crystallography*, **27**, 325–329.