

**2010-016**  
**CRANSWICKITE**

DEADLINE: 30 JUNE 2010

**2010-016 CRANSWICKITE**

MgSO<sub>4</sub>·4H<sub>2</sub>O

Monoclinic

Space group: *Cc*

*a* = 11.9172(4)

*b* = 5.1704(1)

*c* = 12.1880(3) Å

β = 117.538(2)°

*V* = 665.90(8) Å<sup>3</sup>

*Z* = 4

Ronald C. Peterson

Department of Geological Sciences and Geological Engineering, Queen's University

Kingston, Ontario, Canada, K7L 3N6

E-mail: peterson@geol.queensu.ca

**OCCURRENCE**

The mineral occurs as a filling in extensional veins in rock consisting of gypsum, illite and quartz, 1 km ESE of Calingasta, Argentina (31°20.351'S 69 23.546'W) at an elevation of 1540 m. In the vicinity are several small workings where miners have extracted magnesium sulfate, which is purified by dissolution of the ore in water and evaporation of the resulting solution

Associated minerals are starkeyite, hexahydrate, pentahydrate, kieserite, sanderite, gypsum, illite and quartz.

The fact that the mineral is observed as a vein filling indicates that at this locality it does not form by an evaporative process.

**APPEARANCE and PHYSICAL PROPERTIES**

X-ray diffraction analysis confirmed the presence of the new mineral cranswickite. The mineral occurs as very fine-grained, white, chalky material. In one instance, cranswickite was observed to fill a vein and exhibited a coarse, curved, fibrous morphology, suggesting that the mineral formed as the veins extended in width. There are 1-2 millimetre gypsum crystals in the rock adjacent to the magnesium sulfate veins.

Colour: white

Streak: white

Lustre: dull. translucent

Non-fluorescent

H (Mohs): estimated 2-3, as for starkeyite

Tenacity: not observable

Cleavage: not observable

Parting: not observable

Fracture: not observable

Density (meas.) = 1.917 g cm<sup>-3</sup> by Berman balance using toluene as immersion liquid

Density (calc.) = 1.919 g cm<sup>-3</sup> for MgSO<sub>4</sub>·4H<sub>2</sub>O

**OTHER PROPERTIES**

A sample of cranswickite (0.219 g) was heated to 450°C for 2 hours in air. The resulting weight loss (0.083 g) corresponding to H<sub>2</sub>O gives a water content of 37.90wt%.

The IR spectrum was recorded in air at room temperature using a Nicolet 320 FTIR spectrometer (32 scans, 4 cm<sup>-1</sup> resolution), and is shown in Figure 1, together with spectra of

**2010-016**  
**CRANSWICKITE**

liquid water and starkeyite for comparison. Discernable differences between the spectra of cranswickite and starkeyite are evident in the OH and SO stretching regions.  
In air.

**OPTICAL PROPERTIES**

The mineral is too fine-grained to perform optical measurements. Zayakina and Lazebnik (1999) report for unnamed mineral UM1999-28-SO:HMg  $\alpha' = 1.470$ ,  $\gamma' = 1.475$  (?biaxial); see Relation to other species, below.

**CHEMICAL DATA**

Table 1. Analytical data for cranswickite.

Sample	1/ppm	2/ppm	Average
Co/ppm	96.3	98.2	97.3
Mg/ppm	121000	123000	122000
Mn/ppm	442	450	446
Ni/ppm	596	613	605
S/ppm	161000	170000	165500
Zn/ppm	1350	1380	1365
H <sub>2</sub> O			37.90 wt%

Qualitative analysis by EDS showed no elements to be present other than Mg and S. H<sub>2</sub>O was determined by the Penfield method (see above) and its presence confirmed IR. Sulfate was also shown to be present by IR. Approximately 0.1 g of the mineral was weighed into a disposable SCP Science digitube and dissolved in 50 cm<sup>3</sup> of distilled water and contents analyzed by ICP-MS. Magnesium sulfate (certified ACS grade, MgSO<sub>4</sub>·7H<sub>2</sub>O) was analyzed in duplicate as a control. Analytical data are given in Table 1 for this solution.

The averaged analyses were normalized to S = 1 to give the empirical formula (Mg<sub>0.972</sub>Zn<sub>0.004</sub>Mn<sub>0.002</sub>Ni<sub>0.002</sub>)<sub>Σ0.980</sub>SO<sub>4</sub>·4.05H<sub>2</sub>O. The simplified formula is MgSO<sub>4</sub>·4H<sub>2</sub>O, which requires MgO 20.94, SO<sub>3</sub> 41.60, H<sub>2</sub>O 37.46, total 100.00 wt%.

CHEMICAL TESTS: soluble in water

**CRYSTALLOGRAPHY**

Single-crystal X-ray studies could not be carried out because of the small crystal size, but X-ray powder diffraction data were collected using a Panalytical X'pert Pro  $\theta$ - $\theta$  diffractometer. X-ray powder diffraction data (in Å for CuK $\alpha$ <sub>1</sub>) are given in Table 2. Unit cell parameters were refined from the powder data during the course of Rietveld refinement of the structure and are listed below.

Monoclinic                      Space group: *Cc*  
 $a = 11.9172(4)$                    $b = 5.1704(1)$                    $c = 12.1880(3)$  Å                   $\beta = 117.538(2)^\circ$   
 $V = 665.90(8)$  Å<sup>3</sup>                   $Z = 4$

**Crystal structure:**  $R = 0.0863$

Cranswickite is often intimately mixed with hexahydrite, starkeyite and/or kieserite. One sample contained no other phases and was used for further study. The sample was ground with a mortar and pestle, back-packed into a sample holder and scanned using a Panalytical X'pert Pro<sup>TM</sup> diffractometer equipped with a copper tube operating at 40 kV and 45 mA. An incident slit of 1/16°, a 1/8° anti-scatter slit and 0.02 rad Soller slits were used. A diffracted-

**2010-016**  
**CRANSWICKITE**

beam graphite monochromator (Johansson type Alpha-1 geometry) was used and the diffracted X-rays were detected with an X'celerator<sup>TM</sup> position-sensitive detector. Data were collected with an effective step size of  $0.017^\circ 2\theta$  and a 400 second counting time. Data were analyzed using the program EXPO2009 (Altomare *et al.*, 2009). The peaks were identified and indexed by N-TREOR (Altomare *et al.*, 2000) and the structure determined by direct methods using EXPO2009. The space group was determined to be *Cc* based on the unit cell dimensions and systematic absences observed. The resulting model was then refined using the program HIGHSCORE<sup>TM</sup> (Version 2.2; Panalytical, 2008). Background was modeled using a fourth order polynomial and a Pseudo-Voigt function was used to model peak shape. An overall isotropic atomic displacement parameter was refined and the hydrogen positions were not determined. Table 3 presents details of the Rietveld refinement and Table 4 lists final atom coordinates.

The structure of cranswickite consists of chains of alternating sulfate tetrahedra and magnesium-centred octahedra. Magnesium is coordinated by four water molecules and two sulfate oxygen atoms. This arrangement is the same as that observed in pentahydrate,  $\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$  (Baur and Rolin, 1972), chalcantite,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (Fisher, 1950) and siderotil  $\text{FeSO}_4 \cdot 5\text{H}_2\text{O}$  (Peterson *et al.*, 2003). The additional water molecule in pentahydrate, chalcantite and siderotil occurs between the chains, held in place by hydrogen bonds. All of these minerals have chains that are formed by the alternation of sulfate tetrahedra and magnesium-centred octahedra. The  $\text{S}-\text{M}^{2+}-\text{S}$  angles in all three structures are very close to  $180^\circ$ . The main difference in the three structures is the chain periodicity, which is 12.2 Å in cranswickite and 10.8 Å in pentahydrate and siderotil. This longer chain in the cranswickite structure also results in a larger  $\text{M}^{2+}-\text{S}-\text{M}^{2+}$  and  $\text{M}^{2+}-\text{O}-\text{S}$  angles. The structure of cranswickite is different than that of starkeyite,  $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$ , and rozenite,  $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ , where the sulfate tetrahedra and magnesium-containing octahedra share corners to make a four-membered ring instead of a chain (Baur, 1962, 1964). Sulfate tetrahedra are linked to the magnesium-centred octahedra in a *trans* fashion in cranswickite as opposed to a *cis* fashion in starkeyite.

#### Morphology

Habit: microcrystalline powder, curved fibres

Forms: not observable

Twinning: not observable

The *a:b:c* ratio calculated from the unit cell parameters is 2.305:1:2.357

#### NAME

The name is in honour of Lachlan M.D. Cranswick (1968–) who helped to develop and maintain the Collaborative Computational Project No. 14 in Powder and Small Molecule Single Crystal Diffraction (CCP14). The program used for the structure determination of cranswickite, EXPO2009, is listed by the CCP14 Project.

#### TYPE MATERIAL

The holotype is deposited at the Royal Ontario Museum, Toronto, accession number 55368. Part of the holotype is deposited at the Canadian Museum of Nature, Ottawa, catalogue number CMNMC 86134.

#### RELATION TO OTHER SPECIES

Cranswickite is dimorphous with starkeyite; Nickel and Strunz class 7.CB.

The mineral appears to be identical to unnamed mineral UM1999-28-SO:HMg; Unnamed 841; Unnamed 0841 (Smith and Nickel, 2007). Zayakina and Lazebnik

**2010-016**  
**CRANSWICKITE**

(1999) reported the occurrence of a mineral inferred to be a polymorph of starkeyite but with an inferred triclinic cell. Satisfactory elemental analyses were provided. Strongest lines in the powder X-ray trace [ $d/\text{\AA}(I_{\text{rel}})$ ], with corresponding peaks for cranswickite in bold for comparison, were 5.300(100) **5.284(100)**, 4.622(69) **4.621(33)**, 3.981(60) **3.983(25)**, 3.930(88) **3.940(49)**, 3.178(93) **3.176(50)**, 3.126(62) **3.127(24)**, 3.046(50) **3.042(20)**, and 2.576(62) **2.575(26)**.

**COMPATIBILITY**

Compatibility could not be calculated.

**REFERENCES**

- Altomare, A., Giacobozzo, C., Guagliardi, A., Moliterni, A.G.G., Rizzi, R. and Werner, P.-E. (2000) New techniques for indexing: *N-TREOR* in *EXPO*. *Journal of Applied Crystallography*, **33**, 1180-1186.
- Altomare, A., Camalli, M., Cuocci, C., Giacobozzo, C., Moliterni, A. and Rizzia, R. (2009) EXPO2009: structure solution by powder data in direct and reciprocal space. *Journal of Applied Crystallography*, **42**, 1197-1202.
- Baur, W.H. (1962) Zur kristallchemie der salzhydrate. Die kristallstrukturen von  $\text{MgSO}_4 \cdot 4(\text{H}_2\text{O})$  (leonhardtite) und  $\text{FeSO}_4 \cdot 4(\text{H}_2\text{O})$  (rozenite). *Acta Crystallographica*, **15**, 815-826.
- Baur, W.H. (1964) On the crystal chemistry of salt hydrates. Part 2. A neutron diffraction study of  $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$ . *Acta Crystallographica*, **17**, 863-869.
- Baur, W.H. and Rolin, J. L. (1972) Salt hydrates. IX. The comparison of the crystal structure of magnesium sulfate pentahydrate with copper sulfate pentahydrate and magnesium chromate pentahydrate. *Acta Crystallographica*, **B28**, 1448-1455.
- Fisher, D.J. (1950) Chalcantite by X-ray precession technique. *Geological Society of America Bulletin*, **61**, 1460.
- Peterson, R.C., Roeder, P.L. and Yousheng, Z. (2003) The atomic structure of siderotil,  $(\text{Fe,Cu})\text{SO}_4 \cdot 5(\text{H}_2\text{O})$ . *Canadian Mineralogist*, **41**, 671-676.
- Dorian G.W. Smith, D.G.W. and Nickel, E.H. (2007) A system of codification for unnamed minerals: report of the Subcommittee for Unnamed Minerals of the IMA Commission on New Minerals, Nomenclature and Classification. *Canadian Mineralogist*, **45**, 983-1055. (2007)
- Zayakina, N.V. and Lazebnik, K.A. (1999) Tetrahydrate magnesium sulfate from western Yakutiya. *Zapiski Vserossiskogo Mineralogicheskogo Obshchestva*, **128**, 99-101 (in Russian); Abstract: *American Mineralogist*, **85**, 1564 (2000).

**AUTHORS' REMARKS**

Nil

**CHAIRMAN'S REMARKS**

Nil

**2010-016**  
**CRANSWICKITE**

Table 2. Powder X-ray data for cranswickite.

<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> (calc.)	<i>I</i> (calc. %)	<i>d</i> (obs. %)	<i>I</i> (obs.)
0	0	2	5.404	3	5.387	3
2	0	0	<b>5.284</b>	100	5.259	100
1	1	-1	<b>4.621</b>	33	4.603	29
1	1	1	<b>3.983</b>	25	3.970	22
1	1	-2	<b>3.940</b>	49	3.927	46
1	1	2	3.214	10	3.206	8
1	1	-3	<b>3.176</b>	50	3.168	45
3	1	-1	<b>3.127</b>	24	3.118	22
2	0	2	3.124	3		
3	1	-2	3.106	6		
2	0	-4	3.042	20	3.035	17
4	0	-2	2.978	12	2.971	10
3	1	0	2.911	17	2.904	12
3	1	-3	2.861	7	2.855	5
0	0	4	2.702	5	2.696	3
3	1	1	<b>2.575</b>	26	2.570	23
1	1	-4	2.574	7		
3	1	-5	2.179	4	2.177	3
2	2	-3	2.162	5	2.160	3
5	1	-1	2.088	4	2.086	2
5	1	-4	2.057	3	2.055	1
2	2	2	1.992	13	1.990	7
5	1	0	1.956	5		
4	2	-2	<b>1.952</b>	22	1.952	14
5	1	-5	1.914	3	1.912	2
3	1	-6	1.888	9	1.887	4
1	1	5	1.823	4	1.820	2
1	1	-6	1.808	5	1.804	2
2	2	-5	1.772	3	1.771	1
6	0	0	1.761	5		
5	1	-6	1.750	3	1.760	2
3	1	-7	1.650	3	1.649	2
4	2	2	1.597	4	1.597	2
6	2	-2	1.563	5	1.564	2

**2010-016**  
**CRANSWICKITE**

Table 3. Rietveld refinement details for cranswickite.

$a/\text{\AA}$	11.9172(4)
$b/\text{\AA}$	5.1704(1)
$c/\text{\AA}$	12.1880(3)
$\beta/^\circ$	117.538(2)
$V/\text{\AA}^3$	665.90(8)
$R_{\text{exp}}$	0.0863
$R_{\text{p}}$	0.0835
$R_{\text{wp}}$	0.1107
GOF	1.64
$R_{\text{Bragg}}$	0.0330
$U$	0.57
$V$	-0.11
$W$	0.023
$B_{\text{iso}}$	0.96(4)

Table 4. Final atom coordinates for cranswickite.

Atom	Wyckoff site	$x/a$	$y/b$	$z/c$
S1	4a	0.011(1)	0.6867(4)	0.753(1)
Mg	4a	0	0	0
O1	4a	0.114(1)	0.507(2)	0.796(2)
O2	4a	0.508(1)	0.632(2)	0.155(1)
O3	4a	0.892(1)	0.717(3)	0.007(2)
O4	4a	0.362(2)	0.732(3)	0.881(2)
O5	4a	0.876(1)	0.526(2)	0.709(2)
O6	4a	0.168(1)	0.760(3)	0.132(2)
O7	4a	0.641(1)	0.795(3)	0.012(2)
O8	4a	0.038(1)	0.848(2)	0.862(1)

2010-016  
CRANSWICKITE

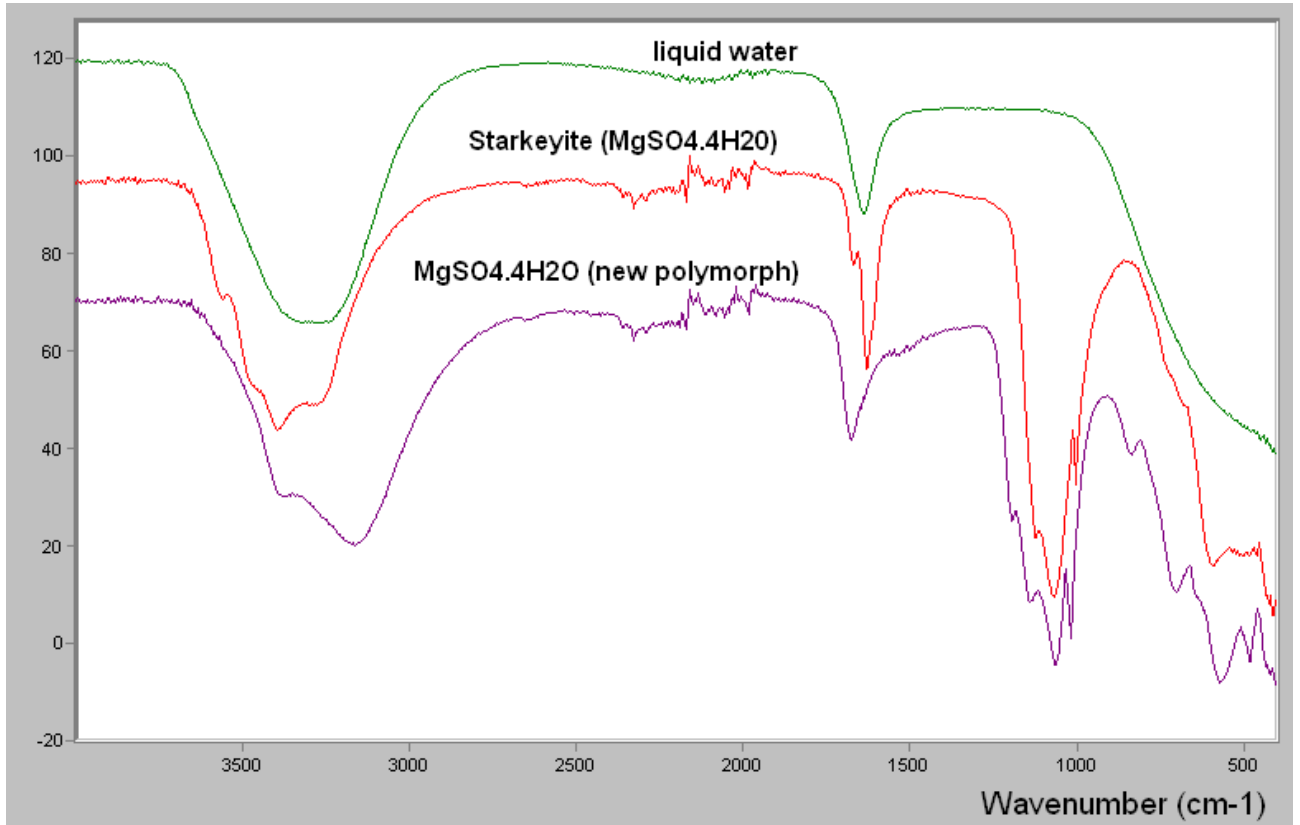


Figure 1. IR spectra of liquid water, starkeyite and cranswickite (new polymorph).

CONFIDENTIAL INFORMATION