Canadian Mineralogist
Vol. 24, pp. 689-693 (1986)

MINERALOGY OF HILGARDITE-4M FROM EVAPORITES IN NEW BRUNSWICK

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ABSTRACT

Hilgardite-4*M* occurs as euhedral crystals in the Salt Springs and Penobsquis evaporite deposits of New Brunswick. It is monoclinic, space group *Aa*, *a* 11.470(3), *b* 11.321(4), *c* 6.321(5) Å, β = 90.02 (7)°. The mineral is biaxial (+), α 1.623(2). β 1.628(2), γ 1.656(2). $2V$ (meas.) 34(2)°, $2V$ (calc.) 46°, $Y = b$, $Z\Lambda c = 1°$ (in the acute angle β). The measured and calculated densities are 2.67(3) and 2.676(2) g/cm^3, respectively. The crystals from New Brunswick are more complex morphologically than the type material from Louisiana, and the following forms have been identified: {010}, {100}, {160}, {140}, {110}, {011}, {111}, {322}, {211}, {231}, {522}, {31$\bar{1}$}, {52$\bar{2}$}, {23$\bar{1}$}, {32$\bar{2}$}, {13$\bar{1}$}, {12$\bar{2}$} and {3$\bar{2}$2}. Electron-microprobe analyses of three crystals showed no cations other than Ca and minor Sr. Some Sr-rich, platy crystals with values of Ca/(Ca + Sr) as low as 0.55 were also analyzed, but this material appears to be a triclinic polymorph of hilgardite-4*M*. The most Ca-rich sample gave the following analytical data: CaO 32.1, SrO 0.3, Cl 10.2, B_2O_3 (52.4), H_2O (5.4), sum 100.4, less O = Cl 2.3, total 98.1 wt.% (with B_2O_3 and water calculated to conform to the ideal formula, $Ca_2B_5O_9Cl{\bullet}H_2O$). TGA and evolved gas analysis of New Brunswick material gave 5.9 wt.% water and 17.4 wt% (HCl + other volatiles). Very similar results were obtained from the Louisiana material. The HCl probably is derived from the contents of channels in the zeolitic structure.

Keywords: hilgardite, hilgardite-4*M*, New Brunswick, new occurrence, evaporites.

SOMMAIRE

On trouve la hilgardite-4*M* en cristaux idiomorphes dans les gisements évaporitiques de Salt Springs et Penobsquis, au Nouveau-Brunswick. C'est une espèce monoclinique, groupe spatial *Aa*, *a* 11.470(3), *b* 11.321(4), *c* 6.321(5) Å, β 90.02(7)°. Elle est biaxe positive, α 1.623(2), β 1.628(2), γ 1.656(2), $2V$ 34(2)° (mesuré), 46° (calculé), $Y = b$, $Z\Lambda c = 1°$ dans l'angle aigu β. Les densités mesurée et calculée sont 2.67(3) et 2.676(2), respectivement. Les cristaux de ces localités sont plus complexes que ceux de la localité type en Louisiane; les formes suivantes ont été identifiées: {010}, {100}, {160}, {140}, {110}, {011}, {111}, {322}, {211}, {231}, {522}, {31$\bar{1}$}, {52$\bar{2}$}, {23$\bar{1}$}, {32$\bar{2}$}, {13$\bar{1}$}, {12$\bar{2}$}, et {3$\bar{2}$2}. Trois cristaux ont été analysés à la microsonde électronique; nul autre cation n'est présent que le calcium, sauf un peu de strontium. Certains cristaux en plaquettes, riches en Sr [le rapport Ca/(Ca + Sr) atteignant 0.55], ont aussi été analysés, mais ce matériau semble un polymorphe triclinique de la hilgardite-4*M*. L'échantillon le plus riche en Ca a donné: CaO 32.1, SrO 0.3, Cl 10.2, B_2O_3 (52.4), H_2O (5.4), somme 100.4, moins O = Cl 2.3, total 98.1% (en poids). Le B_2O_3 et l'eau sont calculés pour se conformer à la formule idéale $Ca_2B_5O_9Cl{\bullet}H_2O$. Une analyse thermogravimétrique et de gaz dégagé du matériau du Nouveau-Brunswick a donné 5.9% d'eau et 17.4% de HCl et autres composants volatils. Le matériau de Louisiane a donné des résultats très semblables. Le HCl se serait libéré des canaux de cette structure zéolitique.

(Traduit par la Rédaction)

Mots-clés: hilgardite, hilgardite-4*M*, Nouveau-Brunswick, nouvelle localité, évaporites.

INTRODUCTION

Minerals of the hilgardite–tyretskite group are relatively rare and have been recognized in only a few occurrences. Hilgardite was first described by Hurlbut & Taylor (1937) from the Choctaw salt dome, Iberville Parish, Louisiana. Subsequently, parahil-

gardite, a triclinic polymorph, was described from the same locality by Hurlbut (1938). Braitsch (1959) described a mineral which he referred to as strontiohilgardite or 1*Tc*-strontiohilgardite from Germany. Kondrat'eva (1964) determined the crystal structure of a triclinic polymorph of the hydroxyl analogue of hilgardite and named it tyretskite. A mineral named Cl-tyretskite was described by Hodenberg & Kühn (1977) from salt deposits in Germany. Rumanova *et al.* (1977) solved the crystal structure of an unnamed "triclinic hilgardite" from the U.S.S.R. Hilgardite crystals were identified by Murowchick (1978) during mineralogical examination of drill cores recovered in the early stages of the exploration and development of some New Brunswick potash deposits. Crystal-structure determinations were carried out on hilgardite from Louisiana by Ghose & Wan (1979) and on parahilgardite by Wan & Ghose (1983). The confusion surrounding the nomenclature of the hilgardite–tyretskite group has been clarified by Ghose (1985). His system of nomenclature for these minerals was approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association.

According to the Ghose nomenclature, the name of the mineral described in this paper is hilgardite-4*M*.

Occurrence

A number of mineralogically interesting borate minerals occur in the potash deposits of southern New Brunswick. Roulston & Waugh (1981) described the general geology of the deposits and listed the various minerals found in each of them. Briefly, the potash and salt deposits are part of a thick sequence of Mississippian evaporites known as the Windsor Group. This sequence occurs in the Moncton subbasin, which is in the southwestern part of the northeasterly trending Fundy geosyncline. Two of the evaporite deposits, the Penobsquis and the Salt Springs, consist of a basal anhydrite, a lower halite member, a sylvite ore zone, a middle halite member, an upper anhydrite unit and an upper halite member. The majority of the borate minerals are found in the middle halite member. The borates are readily separated from the halite matrix by solution in water and include the following species: boracite, colemanite, hilgardite-4*M*, hydroboracite, priceite, szaibelyite, veatchite and volkovskite. This occurrence of volkovskite is presently under investigation.

General Appearance, Physical Data and Optical Data

The hilgardite-4*M* examined in this study occurs as isolated, almost equant, euhedral crystals up to 4 mm in size. Groups of subparallel euhedral crystals of a platy nature are much less common.

The crystals are colorless to slightly reddish brown and have a white streak. The mineral is transparent, has a vitreous lustre and is not discernibly fluorescent in either short-wave or long-wave ultraviolet radiation. The Mohs hardness is 5. Hilgardite-4*M* has a perfect cleavage on {010}, a good cleavage on {100}, and a conchoidal fracture. The density of five different euhedral crystals was measured using a Berman balance and toluene with the appropriate temperature-correction. The mean of these determinations is 2.67(3) g/cm^3, which compares favorably with the value 2.676(2) g/cm^3 calculated from the unit-cell parameters and the chemical composition according to the method outlined by Mandarino (1981b).

The indices of refraction of a polished section of one of the euhedral crystals were measured on a gem refractometer according to the method of Hurlbut (1984). A filter was used to transmit light of wavelength approximately 589 nm. The value of 2*V* and the orientation of the optical indicatrix were determined by means of a spindle stage using another crystal. The optical properties of hilgardite-4*M* from New Brunswick and Louisiana are compared in Table 1.

The mean value of K_C for the three analyzed euhedral crystals is 0.231, and the value of K_P is 0.237. Therefore, the compatibility of the mean index

TABLE 1. OPTICAL PROPERTIES, DENSITY AND COMPATIBILITY INDEX OF HILGARDITE-4M

	New Brunswick (This study)	Louisiana (Hurlbut & Taylor 1937)
Optical Properties		
Biaxial (+)		
Refractive indices		
α	1.623(2)	1.630(2)
β	1.628(2)	1.636(2)
γ	1.656(2)	1.664(2)
2V (calc.)	46°	50°
2V (meas.)	34(2)°	35°
Orientation:		
	Y = b	Y = b
	Z:c = 1°	Z:c = 1.5°
Dispersion:	r > v, moderate	r > v, moderate
Density (g/cm^3)		
measured	2.67(3)	2.71
calculated	2.676(2)	2.71
Compatibility index	-0.026 (excellent)	-0.022 (excellent)

TABLE 2. TABLE OF ANGLES FOR HILGARDITE-4M FROM NEW BRUNSWICK

forms	phi	rho	forms	phi	rho
010	0°00'	90°00'	231	33 21	63 29
100	90 00	90 00	522	67 56	56 04
160	9 20	90 00	31$\bar{1}$	71 20	-60 11
140	13 52	90 00	52$\bar{2}$	67 56	-56 04
110	44 37	90 00	23$\bar{1}$	33 20	-63 29
011	00 02	29 10	32$\bar{2}$	55 57	-44 55
111	44 38	38 07	13$\bar{1}$	18 12	-60 26
322	55 58	44 56	12$\bar{2}$	26 14	-31 54
211	63 08	51 01	$\bar{3}$2$\bar{2}$	-55 58	-44 56

TABLE 3. UNIT-CELL PARAMETERS OF HILGARDITE-4M

Monoclinic, Space group: Aa, Z = 4

	New Brunswick (This study)	Louisiana (Ghose & Wan 1979)
a	11.470(3) Å	11.438(2) Å
b	11.321(4)	11.318(2)
c	6.321(5)	6.318(1)
β	90.02(7)°	90.06(1)°
V	820.8(7) Å^3	817.82(26) Å^3

TABLE 4. CHEMICAL ANALYTICAL DATA FOR HILGARDITE-4M

	Theor.	New Brunswick 1	2	3	Louisiana 4
CaO	33.82	32.1	31.3	31.9	35.14
SrO	....	0.3	1.5	0.6	.....
B_2O_3	52.48	(52.4)	(52.1)	(52.3)	50.22
Cl	10.69	10.2	10.2	10.3	10.59
H_2O	5.43	(5.4)	(5.4)	(5.4)	6.44
sum	102.41	(100.4)	(100.5)	(100.5)	102.39
- O=Cl	2.41	2.3	2.3	2.3	2.39
Total	100.00	(98.1)	(98.2)	(98.2)	100.00

Notes: 1. Analyses 1 through 3 are for euhedral crystals from New Brunswick. 2. Analyses 1 and 2 are from the same crystal with 2 representing the highest SrO value fro the Sr-rich areas. This crystal has a boracite core. 3. Analysis 4 is for Louisiana material (Hurlbut & Taylor 1937). 4. B_2O_3 and H_2O contents are calculated for the ideal formula in analyses 1 through 3. 5. The analytical data for analysis 4 was recalculated to 100 % after subtracting 1.89 % insoluble residue.

of refraction, the calculated density and the chemical composition is -0.026, *i.e.*, excellent on the scale proposed by Mandarino (1979, 1981a). For the data given by Hurlbut & Taylor (1937) for crystals from Louisiana, the values of K_C and K_P are, respectively, 0.232 and 0.243, so that the compatibility is -0.043 or good. However, the density given by Hurlbut & Taylor (1937) was calculated for the old formula. Using the density calculated from the formula and unit-cell parameters given by Ghose & Wan (1979), the value of K_P is 0.237, so that the compatibility of the Louisiana hilgardite-4*M* is -0.022 or excellent.

Crystallographic Data

Morphologically, the euhedral hilgardite-4*M* crystals from New Brunswick are much more complex than those described by Hurlbut & Taylor (1937). A total of eighteen forms have been identified by an optical goniometric study. They are: {010}, {100}, {160}, {140}, {110}, {011}, {111}, {322}, {211}, {231}, {52$\bar{2}$}, {31$\bar{1}$}, {52$\bar{2}$}, {23$\bar{1}$}, {32$\bar{2}$}, {13$\bar{1}$}, {12$\bar{2}$} and {3$\bar{2}\bar{2}$}. Table 2, an angle table, contains a list of these forms and the phi and rho angles calculated from the refined unit-cell parameters.

A single-crystal precession study confirmed the space group *Aa* given by Ghose & Wan (1979). The unit-cell parameters were refined from the X-ray powder-diffraction data obtained from a Debye-Scherrer film produced in an internally calibrated camera with a diameter of 114.6 mm using Cu$K\alpha$ X radiation. The unit-cell data obtained in this study are compared to those given by Ghose & Wan (1979) for material from Louisiana in Table 3. The X-ray powder-diffraction data do not differ significantly from those given in the JCPDS Powder Diffraction File (Card 11-404).

Chemical Data

Electron-microprobe analyses were carried out on

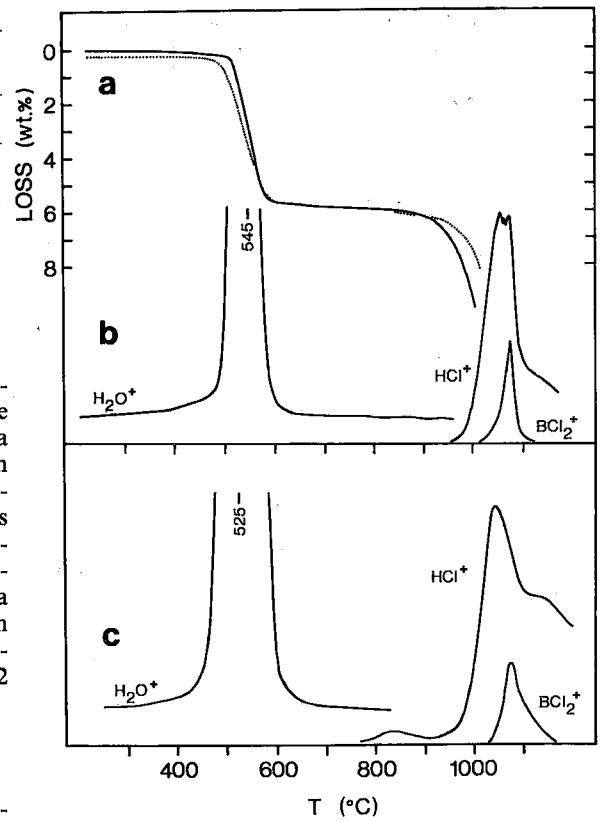

FIG. 1. Thermogravimetric curves (a) and evolved gas curves (b, c) for hilgardite-4*M*. a. Weight-loss curves (_____ New Brunswick, 5.33 mg) and (..... Louisiana, 10.63 mg). b, c. Evolved gas curves for New Brunswick (b) hilgardite-4*M* and Louisiana (c) hilgardite-4*M*. Ordinate: ion peak-height, with H_2O^+ curve for Louisiana sample reduced ×0.5 relative to other curves. Masses monitored: HCl^+ = 36 atomic mass units, BCl_2^+ = 81 atomic mass units.

TABLE 5. TGA/EGA DATA FOR HILGARDITE-4M

	1	2	3
Sample Weight (mg)	8.02	5.33	10.630
Loss in vacuum (wt. %)	<0.6	not detectable	0.2
Temperature Interval #1	350-645°C	300-670°C	380-650°C
Peak	532°C	app. 540°C	525.°C
Loss (wt. %)	5.9	5.8	5.55
Temperature Interval #2	645-1090°C	670-1090°C	650-1215°C
Peak	1060°C	1075°C	1050°C
Loss (wt. %)	17.4	16.8	17.7

Notes: Samples 1 and 2 are from New Brunswick. Sample 3 is from Louisiana.

three euhedral crystals. The analyses were done with an ARL–SEMQ electron microprobe utilizing an operating voltage of 15 kV and a sample current of 0.025 μA, measured on brass. After checking for homogeneity with a small beam-spot, samples were analyzed with a 60-μm beam spot. Wavelength-dispersion scans indicated the absence of other elements with atomic numbers greater than 11. The analytical data were obtained using the following standards: celestine (Sr), hornblende (Fe, Mg), NaCl (Cl), synthetic wollastonite (Ca) and microcline (K), and corrected using a modified version of the MAGIC–4 program. The analytical data are given in Table 4. The B_2O_3 and H_2O contents were calculated from the ideal formula. It can be seen that the euhedral crystals have compositions close to the ideal formula, $Ca_2B_5O_9Cl{\bullet}H_2O$, with little substitution of Sr for Ca. Some platy material, on the other hand, shows substantial substitution of Sr for Ca, with values of the Ca/(Ca + Sr) ratio ranging from 0.97 to 0.55. Electron-microprobe results suggest that this material is hilgardite-4*M* or one of its polymorphs. An X-ray powder-diffraction pattern of one of the crystals with high Sr, removed from the section after electron-microprobe analysis,is similar to that of the triclinic mineral described by Rumanova *et al.* (1977) and probably is hilgardite-1*Tc*. Further study of this Sr-rich, platy material from New Brunswick is under way.

Thermal Analysis

Two samples of New Brunswick hilgardite-4*M* (8.02 and 5.33 mg) and one sample from Louisiana (10.63 mg) were subjected to simultaneous thermogravimetric and evolved gas analyses (TGA/EGA) using a Mettler TA–1 Thermoanalyzer in conjunction with an Inficon IQ 200 quadrupole mass-spectrometer. Typical results are shown in Figure 1 and in Table 5. After being subjected to a high vacuum for several hours at room temperature, the samples showed weight losses of less than 0.6 wt. %. Results were consistent for all three samples. With a heating rate of 10°C/minute *in vacuo*, two major losses in weight occurred. The first loss, ranging from 5.55 to 5.9 wt. %, peaked at approximately 530°C; the evolved gas analysis showed that it was due to H_2O. This loss is slightly higher than the loss of H_2O predicted (5.30 wt. %) from the ideal formula.

The second loss, ranging from 16.8 to 17.7 wt. %, is difficult to interpret. It peaked at approximately 1060°C and is marked by the evolution of abundant HCl. However, simultaneous detection of a significant quantity of BCl_n molecular fragments, as well as of $CaCl_n$ and possibly BO_n fragments, indicated the evolution of additional volatile species. This prevented a quantitative determination of the evolved HCl. These results raise the question of the source of the excess hydrogen. Ghose & Wan (1979) showed that the Louisiana hilgardite-4*M* has a zeolite-type crystal structure composed of an open three-dimensional borate framework with large open channels parallel to the *a* and *c* axes (the two channels have diameters of 6 and 5 Å, respectively). The HCl may be derived from these channels, but the manner in which it is produced is, as yet, unknown. These channels probably also account for the slight excess of H_2O over the theoretical amount.

Acknowledgements

The authors are grateful to the late Mr. R. C. Staveley, who was partly responsible for initiating this study. We thank Mr. B. D. Sturman, who kindly measured the optic axial angle of one of the hilgardite-4*M* crystals from New Brunswick. It is a pleasure to dedicate this paper to Prof. R. B. Ferguson on the occasion of his retirement. The authors, along with many other mineralogists, have benefitted from his research.

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Received August 28, 1985, revised manuscript accepted November 1, 1986.