MINERALOGY OF HILGARDITE-4M FROM EVAPORITES IN NEW BRUNSWICK

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ABSTRACT

Hilgardite-4M occurs as euhedral crystals in the Salt Springs and Penobsquis evaporite deposits of New Brunswick. It is monoclinic, space group \( \text{Aa}, a \ 11.470(3), b \ 11.321(4), c \ 6.321(5) \ \text{Å}, \beta \ = \ 90.02(7)^\circ \). The mineral is biaxial (+), \( a = 1.623(2), \beta = 1.628(2), \gamma = 1.656(2), 2V (\text{meas.}) \ 34(2)^\circ, 2V (\text{calc.}) \ 46^\circ, Y = b, ZAc = 1^\circ \) (in the acute angle \( \beta \)). The measured and calculated densities are 2.67(3) and 2.676(3) 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\}, \{311\}, \{522\}, \{231\}, \{322\}, \{131\}, \{122\} and \{322\}. Electron-microprobe analyses of three crystals showed no cations other than Ca and minor Sr. Some Sr-rich, platy crystals with values of \( \text{Ca}/(\text{Ca} + \text{Sr}) \) as low as 0.55 were also analyzed, but this material appears to be a triclinic polymorph of hilgardite-4M. The most Ca-rich sample gave the following analytical data: \( \text{CaO} \ 32.1, \ \text{SrO} \ 0.3, \ \text{Cl} \ 10.2, \ \text{B}_2\text{O}_3 \ (52.4), \ \text{H}_2\text{O} \ (5.4) \), sum 100.4, less \( \text{O} = \text{Cl} + 2.3, \text{total} 98.1\% \) (with \( \text{B}_2\text{O}_3 \) and water calculated to conform to the ideal formula, \( \text{Ca}_2\text{B}_2\text{O}_5\text{Cl} + \text{H}_2\text{O} \)). TGA and evolved gas analysis of New Brunswick material gave 5.9 wt.% water and 17.4 wt.% (\( \text{HCl} + \text{other volatiles} \)). 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-4M, New Brunswick, new occurrence, evaporites.

INTRODUCTION

Minerals of the hilgardite-tytresetkite 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 stron- 
tiohilgardite or 1Tc–strontiohilgardite from Germa-
ny. Kondrat’eva (1964) determined the crystal struc-
ture 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 Ger-
many. 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 examina-

 tion of drill cores recovered in the early stages of 

 the exploration and development of some New Brun-

 swick potash deposits. Crystal-structure determina-

 tions were carried out on hilgardite from Louisiana 

 by Ghose & Wan (1979) and on parahilgardite by 

 Wan & Ghose (1983). The confusion surrounding the 

 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-4M.

 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 vari-

 ous 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 sub-

 basin, which is in the southwestern part of the north-

 easterly 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 mem-

 ber, 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-4M, hydroboracite, priceite, 

 szaielyite, veatchite and volkovskite. This occur-

 rence of volkovskite is presently under investigation.

 General Appearance, Physical Data and 
 Optical Data

 The hilgardite-4M examined in this study occurs 

 as isolated, almost equant, euhedral crystals up to 

 4 mm in size. Groups of subparallel euhedral crys-

 tals 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 fluores-

 cent in either short-wave or long-wave ultraviolet 

 radiation. The Mohs hardness is 5. Hilgardite-4M 

 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 Ber-

 man balance and toluene with the appropriate 

 temperature-correction. The mean of these determi-

 nations is 2.67(3) g/cm³, which compares favorably 

 with the value 2.676(2) g/cm³ 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 2V 

 and the orientation of the optical indicatrix were 

 determined by means of a spindle stage using another 

 crystal. The optical properties of hilgardite-4M 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 (Harlous & Taylor 1937) |
| Optical Properties | | |
| Biaxial (±) | | |
| Refractive indices | | |
| α | 1.623(2) | 1.630(2) |
| β | 1.628(2) | 1.636(2) |
| γ | 1.686(2) | 1.694(2) |
| 2V (calc.) | 46° | 56° |
| 2V (meas.) | 34°(2)° | 36° |
| Orientation: | | |
| Y = b | Y = b | |
| Zic = 1° | Zic = 5° | |
| Dispersions: | r > v, moderate | r > v, moderate |
| Density (g/cm³) measured | 2.673(2) | 2.71 |
| calculated | 2.676(2) | 2.71 |
| Compatibility index | -0.086 | -0.022 |

| Table 2. Table of Angles for Hilgardite-4M from New Brunswick |
|-----------------------------------------------|-----------------------------------------------|
| Forms | φ | ρ | Forms | φ | ρ |
| 010 | 0°00’ | 90°00’ | 231 | 33 21 | 63 29 |
| 010 | 90 00 | 90 00 | 522 | 67 56 | 56 04 |
| 160 | 9 20 | 90 00 | 311 | 71 20 | 60 11 |
| 140 | 13 52 | 90 00 | 532 | 67 56 | 56 04 |
| 110 | 44 37 | 90 00 | 231 | 33 20 | 63 29 |
| 011 | 00 02 | 29 10 | 325 | 55 57 | -96 15 |
| 111 | 44 38 | 38 07 | 137 | 18 12 | 60 26 |
| 322 | 56 58 | 44 56 | 122 | 25 14 | -31 54 |
| 211 | 63 08 | 51 01 | 325 | -55 58 | 44 56 |
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TABLE 3. UNIT-CELL PARAMETERS OF HILGARDITE-4M

<table>
<thead>
<tr>
<th></th>
<th>New Brunswick</th>
<th>Louisiana (Ghose &amp; Wan 1979)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>11.470(3)</td>
<td>11.438(2)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>11.321(4)</td>
<td>11.318(2)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>6.321(5)</td>
<td>6.318(1)</td>
</tr>
<tr>
<td>β (°)</td>
<td>90.02(7)</td>
<td>90.06(1)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>820.8(7)</td>
<td>817.82(26)</td>
</tr>
</tbody>
</table>

A single-crystal precession study confirmed the space group $Aa$, $Z = 4$ 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 CuKα 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).

TABLE 4. CHEMICAL ANALYTICAL DATA FOR HILGARDITE-4M

<table>
<thead>
<tr>
<th></th>
<th>New Brunswick</th>
<th>Louisiana</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theor.</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>CaO</td>
<td>33.82</td>
<td>31.9</td>
</tr>
<tr>
<td>SrO</td>
<td>10.69</td>
<td>10.3</td>
</tr>
<tr>
<td>$B_2O_3$</td>
<td>52.48</td>
<td>52.3</td>
</tr>
<tr>
<td>Cl</td>
<td>5.43</td>
<td>5.4</td>
</tr>
<tr>
<td>H2O</td>
<td>5.43</td>
<td>5.4</td>
</tr>
</tbody>
</table>

Electron-microprobe analyses were carried out on

Morphologically, the euhedral hilgardite-4M 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}, {522}, {311}, {522}, {231}, {322}, [131], [122], and [322]. Table 2, an angle table, contains a list of these forms and the phi and rho angles calculated from the refined unit-cell parameters.

CHEMICAL DATA

Electron-microprobe analyses were carried out on

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 from 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 H2O 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-4M is -0.022 or excellent.

CRYSTALLOGRAPHIC DATA

Morphologically, the euhedral hilgardite-4M 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}, {522}, {311}, {522}, {231}, {322}, [131], [122], and [322]. Table 2, an angle table, contains a list of these forms and the phi and rho angles calculated from the refined unit-cell parameters.

FIG. 1. Thermogravimetric curves (a) and evolved gas curves (b, c) for hilgardite-4M. a. Weight-loss curves (New Brunswick, 5.33 mg) and (Louisiana, 10.63 mg). b, c. Evolved gas curves for New Brunswick (b) hilgardite-4M and Louisiana (c) hilgardite-4M. Ordinate: ion peak-height, with H2O+ 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

<table>
<thead>
<tr>
<th>Sample Weight (mg)</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loss in vacuum (wt. %)</td>
<td>0.6</td>
<td>5.33</td>
<td>10.63</td>
</tr>
<tr>
<td>Temperature Interval #1</td>
<td>350-545°C</td>
<td>300-670°C</td>
<td>380-650°C</td>
</tr>
<tr>
<td>Peak</td>
<td>532°C</td>
<td>app. 540°C</td>
<td>525°C</td>
</tr>
<tr>
<td>Temperature Interval #2</td>
<td>645-1090°C</td>
<td>670-1090°C</td>
<td>650-1215°C</td>
</tr>
<tr>
<td>Peak</td>
<td>1060°C</td>
<td>1075°C</td>
<td>1050°C</td>
</tr>
<tr>
<td>Loss (wt. %)</td>
<td>17.4</td>
<td>16.8</td>
<td>17.7</td>
</tr>
</tbody>
</table>

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

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 THERMAL ANALYSIS

Two samples of New Brunswick hilgardite-4M (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 H₂O. This loss is slightly higher than the loss of H₂O 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 BCl₄ molecular fragments, as well as of CaCl₂ and possibly BO₃ 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-4M 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 H₂O 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-4M 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 benefited from his research.

REFERENCES


GHOSE, S. (1985): A new nomenclature for the borate minerals in the hilgardite (Ca₂B₅O₉Cl·H₂O)-tyretskite (Ca₂B₅O₉(OH)·H₂O) group. Amer. Mineral. 70, 636-637.


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