

## Hydrochlorborite from Antofagasta, Chile

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### Abstract

In 1966 crystals of hydrochlorborite were found in the Salar Carcote, Antofagasta Province, Chile. This is the second reported occurrence of the mineral.

Hydrochlorborite is monoclinic,  $2/m$ ; space group  $I2/a$  or  $Ia$ ;  $a=22.783$ ,  $b=8.745$ ,  $c=17.066\text{\AA}$ ,  $\beta=96.42^\circ$ ;  $a:b:c=2.605:1:1.952$ ; unit cell volume  $3376.9\text{\AA}^3$ ;  $Z=4$ ; cell content  $3\text{CaO}\cdot\text{CaCl}_2\cdot 4\text{B}_2\text{O}_3\cdot 22\text{H}_2\text{O}$ . Well-formed, colorless crystals with a maximum length of 13 mm show the forms:  $\{001\}$ ,  $\{110\}$ ,  $\{013\}$ ,  $\{112\}$ ,  $\{\bar{1}12\}$ ,  $\{211\}$ ,  $\{\bar{2}11\}$ . The strongest lines in the X-ray powder photograph are in  $\text{\AA}$ : 8.474(100), 6.005(24), 3.605(9), 2.798(8), 2.825(7).

Hydrochlorborite is optically (+);  $\alpha=1.499$ ,  $\beta=1.502$ ,  $\gamma=1.521$  (Na light);  $2V=45^\circ$ ;  $r<v$ ;  $Y=b$ ;  $Z\wedge c=25^\circ$ . Good  $\{001\}$  cleavage. Hardness  $2\frac{1}{2}$ . Specific gravity 1.852 (meas), 1.876 (calc).

Hydrochlorborite appears to be a seasonal mineral. Near-surface crystals formed during the dry season are dissolved with rising water table during the wet season.

### Introduction

Hydrochlorborite was described as a new mineral from China by Ch'ien and Chen (1965) and later by the same authors jointly with Ma and Liu (1965). The locality is not given. Quoting Michael Fleischer's translation from the Russian (1965), the occurrence is stated briefly as follows: "Tertiary boron-containing clayey rocks are widely distributed in some regions of China. During their study we found a new hydrous calcium chlor-borate, named hydrochlorborite from the composition. . . . often accompanied by ulexite, halite and a little gypsum, [it] occurs in saline crusts which coat the boron-containing clayey rocks." The present paper describes the second occurrence of the mineral.

### Occurrence

The hydrochlorborite used in this study was collected by Dr. K. R. Greenleaves in 1966 during his

investigation of ulexite deposits of northern Chile for Borax Consolidated Ltd. of London, England. The mineral was found in the Salar Carcote in northeast Antofagasta Province, about 20 km from the town of Ollague on the Bolivian border. The approximate latitude and longitude are  $21^\circ 20'S$  and  $68^\circ 10'W$ .

The hydrochlorborite, according to Greenleaves (written communication, 1969), was found near the northwest edge of the salar as euhedral crystals loosely included in a nearly continuous but irregular bed 15 cm thick. The crystal-containing layer was overlain by 20 cm of reddish, silty clay, with a thin surface coating of halite and underlain by a dark-gray to black organic clay. In 1966 the water table was 30 cm below the surface.

In April 1974 two of us (Aristarain and Hurlbut) visited the area with the hope of collecting additional material. Near the northwest shore, numerous pits made eight years earlier by Greenleaves were still

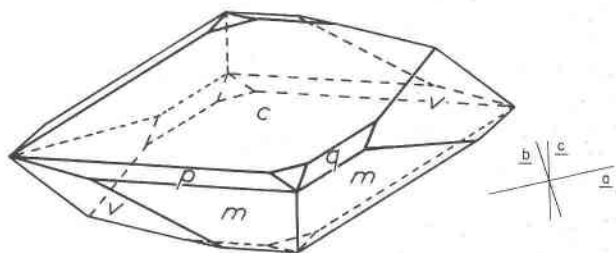


FIG. 1. Hydrochlorborite crystal shown in a nonconventional orientation to bring out the typical habit; *c* axis is vertical, *b* axis is essentially front-back, *a* axis is essentially right-left.

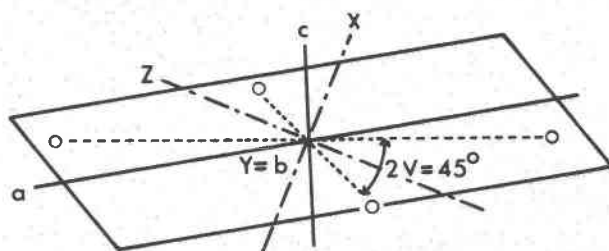


FIG. 2. Optical orientation of hydrochlorborite projected on (010).

TABLE 1. Angle table for hydrochlorborite from Chile

| Monoclinic; Prismatic $2/m$                             |                 |                |                 |                |                |                 |
|---|-----------------|----------------|-----------------|----------------|----------------|-----------------|
| $a:b:c = 2.605:1:1.952 \quad \beta = 96^\circ 42'$      |                 |                |                 |                |                |                 |
| $p_0:q_0:r_0 = 0.7491:1.938:1 \quad \mu = 83^\circ 18'$ |                 |                |                 |                |                |                 |
| $r_2:p_2:q_2 = 0.5160:0.3865:1$                         |                 |                |                 |                |                |                 |
| $p_{0'} = 0.7542, q_{0'} = 1.952, x_{0'} = 0.1175$      |                 |                |                 |                |                |                 |
| Form  | $\phi$          | $\rho$         | $\phi_2$        | $\rho_2 = B$   | C              | A               |
| $\underline{c}$ 001                                     | $90^\circ 00'$  | $6^\circ 42'$  | $83^\circ 18'$  | $90^\circ 00'$ | $0^\circ 00'$  | $83^\circ 18'$  |
| $\underline{m}$ 110                                     | $21^\circ 08'$  | $90^\circ 00'$ | $0^\circ 00'$   | $21^\circ 08'$ | $87^\circ 36'$ | $68^\circ 52'$  |
| $\underline{d}$ 013                                     | $10^\circ 14'$  | $33^\circ 28'$ | $83^\circ 18'$  | $57^\circ 08'$ | $32^\circ 52'$ | $84^\circ 23'$  |
| $\underline{p}$ 112                                     | $26^\circ 52'$  | $47^\circ 34'$ | $63^\circ 41'$  | $48^\circ 50'$ | $44^\circ 51'$ | $70^\circ 31'$  |
| $\underline{q}$ $\bar{1}12$                             | $-14^\circ 54'$ | $45^\circ 16'$ | $104^\circ 33'$ | $46^\circ 38'$ | $47^\circ 20'$ | $100^\circ 32'$ |
| $\underline{r}$ 211                                     | $39^\circ 48'$  | $68^\circ 31'$ | $31^\circ 36'$  | $44^\circ 22'$ | $64^\circ 21'$ | $53^\circ 27'$  |
| $\underline{v}$ $\bar{2}11$                             | $-35^\circ 29'$ | $67^\circ 21'$ | $144^\circ 17'$ | $41^\circ 16'$ | $71^\circ 19'$ | $122^\circ 23'$ |

TABLE 2. Unit-cell data for hydrochlorborite,  $3\text{CaO} \cdot \text{CaCl}_2 \cdot 4\text{B}_2\text{O}_3 \cdot 22\text{H}_2\text{O}$ , from Antofagasta, Chile

|                       |                     |                 |                           |
|-----------------------|---------------------|-----------------|---------------------------|
| $a$ (Å)               | 22.783(3)           | Mol. Weight     | 954.04                    |
| $b$                   | 8.745(1)            | Z               | 4                         |
| $c$                   | 17.066(1)           | Space Group     | $I2/a, Ia^*$              |
| $\beta$               | $96^\circ 42.3(4)'$ | sp. gr. (meas.) | $I.852(5)$                |
| $V$ (Å <sup>3</sup> ) | 3376.9(3)           | density (calc.) | $1.876 \text{ g cm}^{-3}$ |
| $a:b:c$               | 2.605:1:1.952       |                 |                           |

\*Morphology indicates  $I2/a$

visible, and new pits revealed the same succession of beds reported by him. However, no crystals of hydrochlorborite were found.

Undoubtedly the explanation for the lack of crystals is that in 1974 the water table stood only 15 cm below the surface, saturating the crystal-containing layer and dissolving the crystals. Ch'ien and Chen (1965) report that hydrochlorborite is insoluble in cold water; however, we found that it dissolves slowly in both pure water and in saline solutions. At room

TABLE 3. X-ray powder diffraction data for hydrochlorborite

| h k l | d(calc.)*<br>(Å) | d(obs.)**<br>(Å) | I   | h k l | d(calc.)*<br>(Å) | d(obs.)**<br>(Å) | I   | h k l | d(calc.)*<br>(Å) | d(obs.)**<br>(Å) | I   |
|-------|------------------|------------------|-----|-------|------------------|------------------|-----|-------|------------------|------------------|-----|
| 200   | 11.314           | ---              | --- | 321   | 3.739            | ---              | --- | 516   | 2.433            | 2.433            | 6   |
| 002   | 8.474            | 8.48             | 100 | 222   | 3.737            | 3.736            | 4   | 406   | 2.417            | ---              | --- |
| 110   | 8.157            | 8.18             | 6   | 114   | 3.697            | 3.703            | 6   | 910   | 2.416            | 2.416            | 3   |
| 011   | 7.772            | ---              | --- | 321   | 3.647            | 3.645            | 4   | 134   | 2.405            | ---              | --- |
| 202   | 7.198            | 7.20             | < 1 | 222   | 3.616            | ---              | --- | 525   | 2.405            | 2.405            | 3   |
| 211   | 6.572            | ---              | --- | 602   | 3.605            | 3.604            | 9   | 433   | 2.404            | ---              | --- |
| 202   | 6.432            | 6.43             | < 1 | 404   | 3.599            | ---              | --- | 226   | 2.369            | 2.369            | 6   |
| 211   | 6.252            | ---              | --- | 314   | 3.557            | 3.558            | 2   | 822   | 2.347            | ---              | --- |
| 112   | 6.005            | 6.01             | 24  | 420   | 3.460            | 3.462            | 2   | 714   | 2.347            | ---              | --- |
| 112   | 5.757            | 5.757            | 1   | 123   | 3.382            | 3.385            | 6   | 217   | 2.338            | 2.340            | 1   |
| 310   | 5.712            | ---              | --- | 611   | 3.324            | 3.323            | 1   | 813   | 2.331            | 2.332            | 1   |
| 400   | 5.657            | 5.658            | 1   | 422   | 3.286            | 3.289            | < 1 | 615   | 2.302            | 2.302            | 6   |
| 402   | 4.981            | ---              | --- | 404   | 3.216            | 3.216            | < 1 | 624   | 2.277            | 2.275            | < 1 |
| 312   | 4.943            | 4.934            | < 1 | 015   | 3.161            | 3.160            | 3   | 10-02 | 2.253            | 2.252            | < 1 |
| 013   | 4.745            | 4.739            | 1   | 521   | 3.138            | 3.136            | 2   | 417   | 2.248            | 2.248            | < 1 |
| 411   | 4.695            | ---              | --- | 514   | 3.080            | 3.079            | 5   | 525   | 2.217            | 2.217            | 2   |
| 312   | 4.553            | ---              | --- | 710   | 3.032            | 3.032            | 3   | 035   | 2.210            | 2.210            | 2   |
| 213   | 4.538            | ---              | --- | 224   | 3.002            | 3.003            | < 1 | 235   | 2.201            | 2.202            | 3   |
| 402   | 4.470            | 4.472            | 4   | 712   | 2.959            | 2.959            | < 1 | 040   | 2.186            | 2.186            | 7   |
| 411   | 4.461            | ---              | --- | 415   | 2.897            | 2.896            | 4   | 725   | 2.163            | ---              | --- |
| 020   | 4.372            | 4.379            | 4   | 224   | 2.878            | ---              | --- | 141   | 2.162            | 2.162            | 1   |
| 004   | 4.237            | ---              | --- | 031   | 2.873            | 2.876            | 5   | ---   | ---              | 2.143            | 1   |
| 213   | 4.231            | 4.230            | 1   | 006   | 2.825            | 2.825            | 7   | ---   | ---              | 2.128            | 5   |
| 121   | 4.184            | 4.179            | 1   | 231   | 2.798            | 2.798            | 8   | ---   | ---              | 2.116            | 4   |
| 121   | 4.140            | 4.140            | 6   | 424   | 2.779            | 2.779            | 3   | ---   | ---              | 2.091            | 4   |
| 204   | 4.130            | ---              | --- | 330   | 2.719            | 2.720            | 6   | ---   | ---              | 2.072            | 5   |
| 220   | 4.078            | 4.076            | 3   | 206   | 2.668            | 2.667            | 3   | ---   | ---              | 2.040            | 5   |
| 510   | 4.019            | ---              | --- | 604   | 2.666            | ---              | --- | ---   | ---              | 2.007            | 2   |
| 022   | 3.886            | 3.885            | 3   | 415   | 2.640            | 2.639            | 5   | ---   | ---              | 2.002            | 2   |
| 114   | 3.827            | ---              | --- | 811   | 2.613            | 2.611            | 4   | ---   | ---              | 1.996            | 2   |
| 413   | 3.825            | ---              | --- | ---   | ---              | ---              | --- | ---   | ---              | 1.967            | 2   |
| 204   | 3.824            | 3.824            | 6   | 325   | 2.601            | 2.602            | 5   | ---   | ---              | 1.962            | 2   |
| 512   | 3.787            | ---              | --- | 802   | 2.593            | 2.594            | 5   | ---   | ---              | 1.946            | 3   |
| 600   | 3.771            | 3.770            | 1   | 431   | 2.582            | 2.584            | 5   | ---   | ---              | 1.931            | < 1 |
| ---   | ---              | ---              | --- | 233   | 2.496            | 2.494            | < 1 | ---   | ---              | 1.925            | < 1 |
| ---   | ---              | ---              | --- | 316   | 2.448            | 2.449            | 6   | ---   | ---              | 1.912            | 2   |
| ---   | ---              | ---              | --- | ---   | ---              | ---              | --- | ---   | ---              | 1.906            | 2   |
| ---   | ---              | ---              | --- | ---   | ---              | ---              | --- | ---   | ---              | 1.891            | 3   |
| ---   | ---              | ---              | --- | ---   | ---              | ---              | --- | ---   | ---              | 1.888            | 3   |
| ---   | ---              | ---              | --- | ---   | ---              | ---              | --- | ---   | ---              | 1.870            | 1   |
| ---   | ---              | ---              | --- | ---   | ---              | ---              | --- | ---   | ---              | 1.865            | 1   |
| ---   | ---              | ---              | --- | ---   | ---              | ---              | --- | ---   | ---              | 1.848            | 2   |
| ---   | ---              | ---              | --- | ---   | ---              | ---              | --- | ---   | ---              | 1.841            | 6   |
| ---   | ---              | ---              | --- | ---   | ---              | ---              | --- | ---   | ---              | 1.809            | 2   |
| ---   | ---              | ---              | --- | ---   | ---              | ---              | --- | ---   | ---              | 1.798            | < 1 |
| ---   | ---              | ---              | --- | ---   | ---              | ---              | --- | ---   | ---              | 1.758            | < 1 |

\*All calculated hkl's listed for  $d_{hkl} \geq 3.500\text{Å}$ . All  $d_{hkl} \geq 2.150\text{Å}$  are indexed. Indices and d(calc.) from the least-squares analysis of X-ray powder data using the digital computer program of Appleman and Evans (1973).

\*\*X-ray diffractometer conditions are: Chart No. X-3707; Cu/Ni radiation,  $\lambda_{CuK\alpha_1} = 1.540598\text{Å}$ ; Si used as internal standard; scanned at  $\frac{1}{2}^\circ 2\theta$  per minute.

Plus additional lines all with  $I \leq 5$

temperature a 2 mm crystal dissolves completely in a saturated sodium chloride solution (similar to salar brine) in approximately four hours. These observations and the association with ulexite and halite suggest that hydrochlorborite is a seasonal mineral present in ulexite playa deposits only in the dry season. It must be looked for near the fringes of salars at the shorelines of the temporary wet-season ponds. It is here that boron and calcium are most frequently found and where chlorine is always present.

**Crystallography**

*Morphology*

In the description of hydrochlorborite from China, it is stated that the mineral usually is in dense masses

and that the development of crystal forms is poor. Since neither single-crystal X-ray data nor the crystal system were given, the description presumably was made from fine-grained mineral. In contrast, the mineral from Chile is in well-formed, untwinned crystals all of the same habit (Fig. 1). The maximum length of the crystals available for this study is 9 mm, but the largest crystals found were 13 mm long. Many crystals were etched and dull, but a few have faces of sufficient quality to give reasonably good reflections on the optical goniometer. Although there is good agreement between the crystallographic constants calculated from the morphology with those derived from unit-cell measurements, the latter are consid-

TABLE 4. Optical properties of hydrochlorborite

|                 | Antofagasta,<br>Chile                          | China<br>Ch'ien and Chen (1965) |
|-----------------|--|---------------------------------|
| $\alpha$        | 1.499(1)*                                      | 1.5008(1)                       |
| $\beta$         | 1.502(1)                                       | 1.5036(1)                       |
| $\gamma$        | 1.521(1)                                       | 1.5199(1)                       |
| $\gamma-\alpha$ | 0.022  | 0.0191                          |
| 2V (meas.)      | 45°  | 45° 48'                         |
| Sign            | Positive                                       | Positive                        |
| Dispersion      | $r < v$  | ---                             |
| Orientation     | $\bar{X} \wedge c = 25^\circ$<br>$Y = \bar{b}$ | ---                             |

\*Na light

ered better and were used in calculating the angles given in Table 1.

#### X-ray data

Unit-cell dimensions were determined from precession photographs (Mo radiation, Zr filter) with  $a$  and  $b$  precession axes for zero-, first-, and second-layer photographs. The extinctions in these photographs ( $hkl$  for  $h+k+l=2n$  only;  $h0l$ ,  $h$  and  $l=2n$ ; and  $0k0$ ,  $k=2n$ ) lead to space groups  $I2/a$  or  $Ia$ . However, the form development argues in favor of  $I2/a$ . The cell dimensions, given in Table 2, were refined by least-squares analysis of the X-ray powder data using the digital computer program of Appleman and Evans (1973). The X-ray powder data are given in Table 3.

#### Physical and optical properties

Hydrochlorborite is brittle with a single good cleavage {001}; elsewhere it breaks with a conchoidal fracture. It is colorless with a vitreous luster and is nonfluorescent. Many crystals, free from inclusions, are transparent, but some contain small amounts of clay from the bed in which they grew. The hardness is  $2\frac{1}{2}$ . The specific gravity at 25°C, measured both by suspension in bromoform-acetone and by the Berman balance, is 1.852(5). Ch'ien and Chen (1965) report a specific gravity of 1.83 for the Chinese material.

The optical properties and the optical orientation are summarized in Table 4.

#### Chemical composition

For the present study 300 mg of transparent crystals were used for a chemical analysis performed by

TABLE 5. Chemical analyses of hydrochlorborite

|                               | Salar Carcote,<br>Antofagasta, Chile |                     |                            | China  | Calculated<br>Composition |
|-------------------------------|--------------------------------------|---------------------|----------------------------|--------|---------------------------|
|                               | Wt. %*                               | Recalcd.<br>to 100% | Atomic<br>Ratio<br>(B=8)** | Wt. %† | Wt. %††                   |
| CaO                           | 24.0                                 | 23.92               | Ca 4.08                    | 23.31  | 23.52                     |
| MgO                           | 0.01                                 | 0.01                | Mg --                      | --     | --                        |
| FeO                           | 0.04                                 | 0.04                | Fe --                      | --     | --                        |
| B <sub>2</sub> O <sub>3</sub> | 29.2                                 | 29.10               | B 8.00                     | 29.50  | 29.19                     |
| Cl                            | 7.2                                  | 7.18                | Cl 1.94                    | 7.62   | 7.43                      |
| H <sub>2</sub> O              | 41.5                                 | 41.36               | H 43.94<br>O 37.09         | 41.91  | 41.54                     |
| Total                         | 101.95                               | 101.61              |                            | 102.34 | 101.68                    |
| Cl <sub>2</sub> = 0           | 1.62                                 | 1.61                |                            | 1.72   | 1.68                      |
|                               | 100.33                               | 100.00              |                            | 100.62 | 100.00                    |

\*Jun Ito, Harvard University, *analyst*. A spectrographic analysis indicates traces of Sr, Mn, V, Al, and Si.  
\*\*Corresponding to the formula  $3.12\text{CaO} \cdot 0.97\text{CaCl}_2 \cdot 4\text{B}_2\text{O}_3 \cdot 21.97\text{H}_2\text{O}$ .  
†Chang-Mei Chang, *analyst*.  
††For  $3\text{CaO} \cdot \text{CaCl}_2 \cdot 4\text{B}_2\text{O}_3 \cdot 22\text{H}_2\text{O}$ .

Dr. Jun Ito of Harvard University. The results are given in Table 5 with the analysis made by Ch'ien and Chen (1965) on massive material for comparison. Based on eight boron atoms, the oxide formula obtained from the analysis closely approximates  $3\text{CaO} \cdot \text{CaCl}_2 \cdot 4\text{B}_2\text{O}_3 \cdot 22\text{H}_2\text{O}$ , thus confirming the results of the original description.

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