

## ALFREDSTELZNERITE: A NEW SPECIES OF CALCIUM BORATE HYDRATE FROM THE SANTA ROSA MINE, SALTA, NORTHWESTERN ARGENTINA

MIGUEL ANGEL GALLISKI<sup>§</sup>

*IANIGLA-CONICET, CCT-MENDOZA, Avda. Ruiz Leal s/n, Parque Gral. San Martín, C.C. 330 (5.500) Mendoza, Argentina*

MARK A. COOPER

*Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada*

MARÍA FLORENCIA MÁRQUEZ-ZAVALÍA

*IANIGLA-CONICET, CCT-MENDOZA, Avda. Ruiz Leal s/n, Parque Gral. San Martín, C.C. 330 (5.500) Mendoza, Argentina*

FRANK C. HAWTHORNE

*Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada*

### ABSTRACT

Alfredstelznerite is a new borate species of composition  $\text{Ca}_4(\text{H}_2\text{O})_4[\text{B}_4\text{O}_4(\text{OH})_6]_4(\text{H}_2\text{O})_{15}$ , discovered at the Santa Rosa mine, a Tertiary borate deposit in Sijes, Salta, northwestern Argentina. The mineral occurs as mm-sized white fibroradial aggregates consisting of fine acicular colorless crystals up to 30  $\mu\text{m}$  wide and up to 5 mm long, associated with colemanite, hydroboracite, ulexite, inyoite, gypsum and anhydrite, with minor meyerhofferite, nobleite, gowerite, inderborite, inderite, orpiment and realgar. The crystals of alfredstelznerite are euhedral, elongate along [001], with {010}, {hk0}, {100}, {hkl} and  $\{\bar{h}kl\}$  as common crystallographic forms. The cleavage is perfect parallel to {010}, the hardness is 2, the streak is white, the luster is vitreous to silky, the density in  $\text{g}/\text{cm}^3$  is 1.77(1)<sub>meas</sub> and 1.775<sub>calc</sub>. Alfredstelznerite is biaxial positive with  $\alpha = 1.476(3)$ ,  $\beta = 1.478(3)$ ,  $\gamma = 1.494(3)$ ,  $2V_{\text{calc}} = 39^\circ$  (for  $\lambda = 589$  nm); it has neither pleochroism nor dispersion. The optical orientation is  $X = \mathbf{b}$ ,  $Y = \mathbf{c}$ ,  $Z = \mathbf{a}$ ; the compatibility index is 0.022. Alfredstelznerite is orthorhombic, space group  $Pca2_1$ ,  $a$  12.161(2),  $b$  40.477(8),  $c$  10.1843(17) Å,  $V$  5013(3) Å<sup>3</sup>,  $Z = 4$ . The strongest six X-ray powder-diffraction lines [ $d$  in Å( $I$ )( $hkl$ )] are: 10.501(10)(120), 5.226(7)(201), 3.837(7)(222), 3.118(7b)(322), 2.612(6)(402) and 2.538(6)(004). Electron-probe microanalysis, combined with thermogravimetric analysis and crystal-structure refinement, gives the following ideal composition (in wt.%):  $\text{B}_2\text{O}_3$  41.57,  $\text{CaO}$  16.74,  $\text{H}_2\text{O}$  41.69. The empirical formula, normalized on the basis of 59 anions = 16  $\text{O}^{2-}$  + 24  $(\text{OH})^-$  + 19  $\text{H}_2\text{O}$ , gives  $\text{Ca}_{4.07}(\text{H}_2\text{O})_4[\text{B}_{3.99}\text{O}_4(\text{OH})_6]_4(\text{H}_2\text{O})_{15}$  or, ideally,  $\text{Ca}_4(\text{H}_2\text{O})_4[\text{B}_4\text{O}_4(\text{OH})_6]_4(\text{H}_2\text{O})_{15}$ .

*Keywords:* alfredstelznerite, new mineral species, borate, Sijes, Argentina.

### SOMMAIRE

Nous décrivons l'alfredstelznerite, nouvelle espèce minérale; il s'agit d'un borate de composition  $\text{Ca}_4(\text{H}_2\text{O})_4[\text{B}_4\text{O}_4(\text{OH})_6]_4(\text{H}_2\text{O})_{15}$ , découvert à la mine Santa Rosa, un gisement de borates d'âge tertiaire à Sijes, Salta, dans le nord-ouest de l'Argentine. Le minéral se présente en agrégats millimétriques fibroradiés de cristaux aciculaires incolores atteignant une largeur de 30  $\mu\text{m}$  et une longueur de 5 mm; lui sont associés colemanite, hydroboracite, ulexite, inyoite, gypse et anhydrite, avec des quantités moindres de meyerhofferite, nobleite, gowerite, inderborite, inderite, orpiment et réalgar. Les cristaux d'alfredstelznerite sont idiomorphes, allongés selon [001], avec {010}, {hk0}, {100}, {hkl} et  $\{\bar{h}kl\}$  comme formes cristallographiques dominantes. Le clivage est parfait parallèle à {010}, la dureté est égale à 2, la rayure est blanche, l'éclat est vitreux à soyeux, et la densité est 1.77(1) (mesurée) et 1.775  $\text{g}/\text{cm}^3$  (calculée). L'alfredstelznerite est biaxe positive, avec  $\alpha = 1.476(3)$ ,  $\beta = 1.478(3)$ ,  $\gamma = 1.494(3)$ , et  $2V_{\text{calc}} = 39^\circ$  (pour  $\lambda = 589$  nm); elle ne montre ni pléochroïsme, ni dispersion. L'orientation optique est  $X = \mathbf{b}$ ,  $Y = \mathbf{c}$ ,  $Z = \mathbf{a}$ ; l'indice de compatibilité est égal à 0.022. L'alfredstelznerite est orthorhombique, groupe spatial  $Pca2_1$ ,  $a$  12.161(2),  $b$  40.477(8),  $c$  10.1843(17) Å,  $V$  5013(3) Å<sup>3</sup>,  $Z = 4$ . Les six raies les plus intenses du spectre de diffraction, méthode des poudres [ $d$  en Å( $I$ )

<sup>§</sup> E-mail address: galliski@lab.cricyt.edu.ar

(*hkl*) sont: 10.501(10)(120), 5.226(7)(201), 3.837(7)(222), 3.118(7b)(322), 2.612(6)(402) et 2.538(6)(004). Une analyse avec une microsonde électronique, une analyse thermogravimétrique et un affinement de la structure cristalline ont donné la composition idéale suivante, exprimée en % (poids): B<sub>2</sub>O<sub>3</sub> 41.57, CaO 16.74, H<sub>2</sub>O 41.69. La formule empirique, normalisée sur une base de 59 anions = 16 O<sup>2-</sup> + 24 (OH)<sup>-</sup> + 19 H<sub>2</sub>O, serait Ca<sub>4,07</sub>(H<sub>2</sub>O)<sub>4</sub> [B<sub>3,99</sub>O<sub>4</sub>(OH)<sub>6</sub>]<sub>4</sub> (H<sub>2</sub>O)<sub>15</sub> ou, de façon idéale, Ca<sub>4</sub>(H<sub>2</sub>O)<sub>4</sub> [B<sub>4</sub>O<sub>4</sub>(OH)<sub>6</sub>]<sub>4</sub> (H<sub>2</sub>O)<sub>15</sub>.

(Traduit par la Rédaction)

*Mots-clés*: alfredstelznerite, nouvelle espèce minérale, borate, Sijes, Argentine.

## INTRODUCTION

Alfredstelznerite is a new calcium borate mineral found in a borate deposit in northwestern Argentina. It was collected as a small sample measuring approximately 1.6 cm across. Powder X-ray diffraction showed a pattern different from any known mineral. Subsequent optical properties and electron-microprobe data showed that it is a new mineral species; its crystal structure was solved to determine the exact chemical composition.

The mineral and the name were approved by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the IMA (IMA#2007–50). The name honors Dr. Alfred Wilhelm Stelzner (born 1840 in Dresden, Germany; died 1895 in Germany). During his career in Argentina between 1871 and 1874, he was the first Professor of Mineralogy at the University of Córdoba and founded the Museum of Mineralogy that today bears his name. On the basis of his papers on Argentinian geology, he is considered the real founder of the geological sciences in Argentina. He was professor at the Bergakademie of Freiberg and discovered famatinite and franckeite. Type material

is deposited at the Mineralogical Museum “Alfred Stelzner” of the Facultad de Ciencias Exactas Físicas y Naturales of the Universidad Nacional de Córdoba, Argentina, under the catalog number MS003266.

## OCCURRENCE

Alfredstelznerite was found as a white radial aggregate covering a cavity in a mudstone at the Santa Rosa mine, Sijes, Salta province, República Argentina. The Santa Rosa mine is a Tertiary playa-lake borate deposit located at 24°35'59" S, 66°39'26" W, 3890 meters above sea level in the high plateau of northwestern Argentina known as Puna (Fig. 1). This borate deposit is operated by Bórax Argentina S.A., and is in the Sijes district of the Pastos Grandes continental basin. The rocks exploited at the Santa Rosa mine are in the upper part of the sedimentary Pastos Grandes Group, in the Monte Amarillo and Monte Verde members of the late Miocene Sijes Formation (Alonso 1999). The deposit was studied by Russansky (1985, quoted in Alonso 1999) and consists of many beds of colemanite and hydroboracite intercalated in a folded playa-lake sedi-

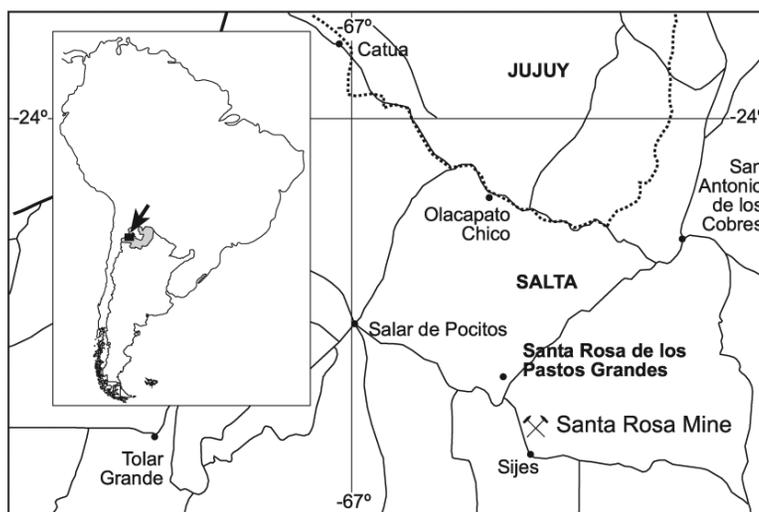


FIG. 1. Location map of the Santa Rosa mine.

mentary sequence dominated by mudstones, siltstones, sandstones, tuffs and evaporites. The mine is an open-pit quarry that exhibits several decimeter-thick beds containing colemanite (dominant) and hydroboracite (subordinate). In addition to the mined borates, ulexite and inyoite are abundant, and meyerhofferite, nobleite, gowerite and inderborite are rare; gypsum and anhydrite are common minerals, whereas orpiment and realgar are very rare (Russansky 1985, quoted in Alonso 1999). Inderite is also present in small nodules of prismatic crystals (M.A. Galliski, unpubl. data).

#### PHYSICAL AND OPTICAL PROPERTIES

Alfredstelznerite occurs as white sprays of acicular crystals in a cavity of fractured mudstone (Fig. 2). It is not intimately associated with other borates in the type specimen. The mineral was found immediately after the rainy season and it is of secondary origin. The individual crystals are colorless and transparent, the aggregates are white, and partly dehydrated crystals are translucent. The streak is white, and the luster changes from vitreous in individual crystals to slightly silky in some aggregates. Alfredstelznerite does not fluoresce under short- or long-wave ultraviolet light. The crystals are elongate along [001], up to 5 mm long and 30  $\mu\text{m}$  wide. The forms observed are {010} dominant, {hk0}, {100}, {hkl}, and  $\{\bar{h}kl\}$  (Fig. 3); crystals in some instances form parallel aggregates. The cleavage is perfect parallel to {010}, the fracture is irregular, and the mineral is brittle. The hardness is 2, the measured

density (with heavy liquids) is 1.77(1)  $\text{g}/\text{cm}^3$ , in accord with the calculated density, 1.775  $\text{g}/\text{cm}^3$ .

Under the polarizing microscope, alfredstelznerite is biaxial positive. Its indices of refraction (measured with light of wavelength 589 nm) are  $\alpha$  1.476(3),  $\beta$  1.478(3),  $\gamma$  1.494(3),  $2V_{(\text{calc})} = 39^\circ$ . The mineral shows neither pleochroism nor dispersion. The optical orientation is  $X = \mathbf{b}$ ,  $Y = \mathbf{c}$ ,  $Z = \mathbf{a}$ . The compatibility index is 0.022, excellent (Mandarino 1981).

#### CHEMICAL COMPOSITION

A chemical analysis was done with a Cameca SX 100 electron microprobe operating in wavelength-dispersion mode with colemanite as an internal standard. Data were reduced using the PAP routine of Pouchou & Pichoir (1984, 1985). Electron-beam conditions were optimized (8 kV, 6 nA, 20  $\mu\text{m}$  beam) so as to maintain reasonably high and stable count-rates for both Ca and B during analysis. Alfredstelznerite dehydrates very easily, producing white and translucent crystals with a damaged structure (resulting in degraded diffraction patterns) and diminished amounts of  $\text{H}_2\text{O}$  in the altered material. Thus the values of CaO and  $\text{B}_2\text{O}_3$  determined by electron-microprobe analysis are much too high, as the (initially transparent) crystals analyzed lost  $\text{H}_2\text{O}$  in the high vacuum of the microprobe, enhancing the amounts of CaO and  $\text{B}_2\text{O}_3$  in the material actually analyzed and resulting in an excess total (122.8 wt.%) if 19  $\text{H}_2\text{O}$  groups from the structure determination are assumed to be present (Table 1). A 100% analytical total

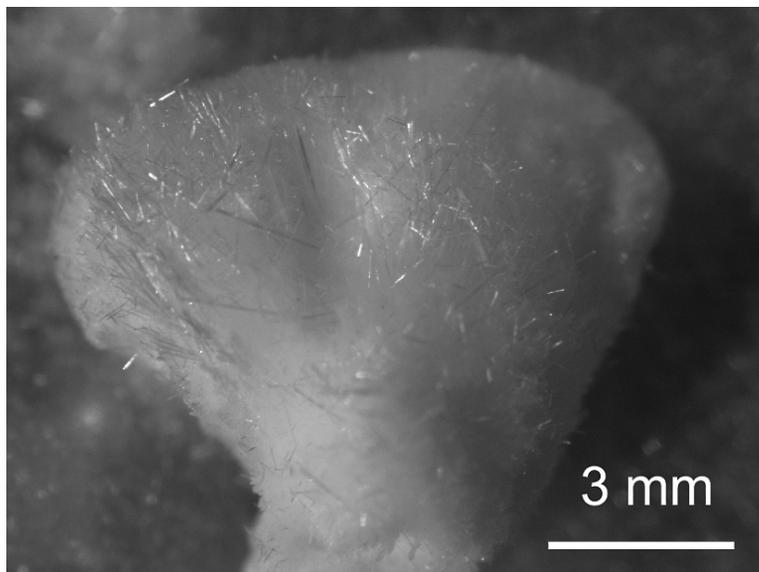


FIG. 2. An aggregate of acicular crystals of alfredstelznerite.

for dehydrated alfredstelznerite gives 5.2 H<sub>2</sub>O groups in this altered material. The H<sub>2</sub>O content, derived from a thermogravimetric analysis, is 37.0 wt.%, slightly lower than the ideal value of 41.7% (assuming 19 H<sub>2</sub>O), possibly suggesting that the bulk sample used for TGA contained a small fraction of partly dehydrated alfredstelznerite. Despite this complication of dehydration in alfredstelznerite, the ratio of Ca to B is still the same

TABLE 1. CHEMICAL COMPOSITION OF ALFREDSTELZNERITE

	EMPA <sup>1</sup> 19H <sub>2</sub> O	EMPA <sup>2</sup> 5.17H <sub>2</sub> O	IDEAL <sup>1</sup> 19H <sub>2</sub> O
B <sub>2</sub> O <sub>3</sub> wt.%	50.8	50.8	41.57
CaO	20.9	20.9	16.74
H <sub>2</sub> O	51.1	28.3	41.69
Total	122.8	100	100
B <i>apfu</i>	15.96	15.95	16
Ca	4.07	4.07	4
OH	24	24	24
H <sub>2</sub> O	19	5.17	19

The chemical data (EPMA) were acquired with an electron microprobe, <sup>1</sup> assuming 19 (H<sub>2</sub>O), as established from the structure determination (Cooper *et al.* 2010). <sup>2</sup> Amount of H<sub>2</sub>O obtained by difference.

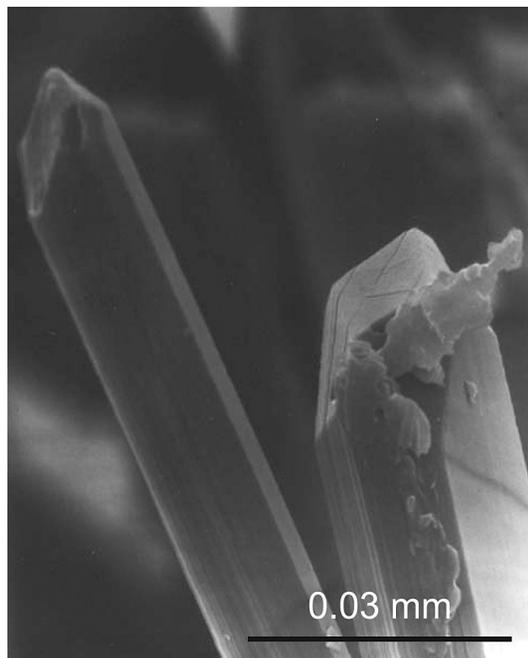


FIG. 3. Prismatic to acicular crystals of alfredstelznerite elongate along [001], showing the common crystallographic forms and {010} cleavage.

(even though the absolute amounts are enhanced), and hence the formula can be calculated using this ratio and the results of crystal-structure analysis, including the number of H<sub>2</sub>O groups in the unit cell. Alfredstelznerite dissolves slowly in warm water, is soluble in HCl, and

TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR ALFREDSTELZNERITE

<i>l</i> <sub>est.</sub>	<i>d</i> <sub>meas</sub> (Å)	<i>d</i> <sub>calc</sub> (Å)	<i>h</i>	<i>k</i>	<i>l</i>	<i>l</i> <sub>est.</sub>	<i>d</i> <sub>meas</sub> (Å)	<i>d</i> <sub>calc</sub> (Å)	<i>h</i>	<i>k</i>	<i>l</i>
1	11.678	11.658	1	1	0	6	2.538	2.546	0	0	4
10	10.501	10.437	1	2	0	"	"	2.534	2	14	1
5	9.992	10.142	0	4	0	"	"	2.530	4	4	2
5	8.975	9.047	1	3	0	<1	2.469	2.469	0	4	4
3	7.711	7.792	1	4	0	2	2.403	2.405	3	11	2
2	7.329	7.289	1	2	1	"	"	2.404	3	13	1
1b	6.836	6.763	1	3	1	"	"	2.402	2	15	1
"	"	6.751	1	5	0	4	2.351	2.349	2	0	4
1b	6.172	6.188	1	4	1	1b	2.272	2.288	2	4	4
1	5.680	5.627	1	5	1	"	"	2.287	4	11	1
7	5.226	5.224	2	0	1	"	"	2.282	1	17	1
6b	4.623	4.644	2	4	1	"	"	2.281	2	16	1
1b	4.144	4.134	2	6	1	"	"	2.257	1	13	3
7	3.837	3.835	2	2	2	1b	2.199	2.211	4	4	3
1b	3.669	3.688	0	11	0	"	"	2.192	5	7	1
"	"	3.644	2	4	2	1b	2.132	2.142	5	9	0
1b	3.333	3.335	1	11	1	"	"	2.130	4	13	1
1	3.179	3.178	1	3	3	"	"	2.128	1	17	2
7b	3.118	3.135	3	2	2	"	"	2.127	3	11	3
"	"	3.121	0	13	0	<1b	2.065	2.069	4	8	3
"	"	3.112	1	4	3	"	"	2.065	1	11	4
"	"	3.094	2	8	2	1	1.994	1.999	3	13	3
"	"	3.089	3	3	2	"	"	1.990	6	0	1
4	3.025	3.023	1	13	0	4b	1.942	1.953	4	0	4
1	2.966	2.965	2	0	3	"	"	1.952	6	4	1
5	2.893	2.896	2	3	3	"	"	1.947	1	13	4
"	"	2.898	1	13	1	"	"	1.944	4	2	4
3	2.844	2.846	2	4	3	"	"	1.931	2	0	5
6	2.612	2.612	4	0	2	"	"	1.928	1	17	3
"	"	"	"	"	"	1b	1.683	1.681	5	17	1

The pattern was generated with a 114.6-mm Debye-Scherrer powder camera with a Gandolfi attachment using Ni-filtered Cu radiation ( $\lambda\text{CuK}\alpha = 1.54178 \text{ \AA}$ ). Intensities estimated visually, b = broad. Not corrected for shrinkage, no internal standard. A calculated powder-diffraction pattern from the structure was used to aid indexing. Indexed on a cell of dimensions *a* 12.172(14), *b* 40.57(5), *c* 10.184(10) Å.

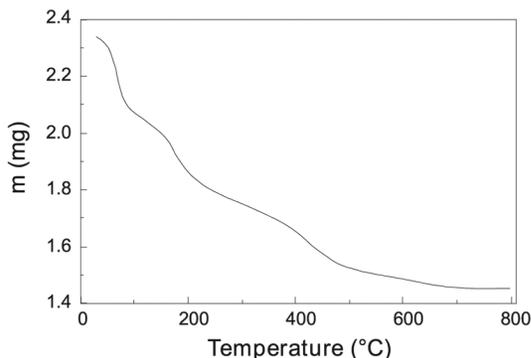


FIG. 4. TGA curve of alfredstelznerite.

that solution colors a flame yellowish green, as is typical of boron-bearing minerals.

### Thermogravimetric analysis

Thermogravimetric analysis was done on an initial sample of 2.304 mg using Shimadzu TGA-51 equipment with a heating rate of 5°C/min. and  $\Delta T = 22\text{--}1000^\circ\text{C}$  in a  $\text{N}_2$  atmosphere with a flow rate of 50 mL/min. Figure 4 shows the curve of dehydration.

### Infrared spectrum

The infrared spectrum of alfredstelznerite mixed in a pellet of KBr was obtained in a Nicolet Protege 460 spectrometer (Fig. 5). A digital version of the spectrum is available from the Depository of Unpublished Data, on the MAC website [document Alfredstelznerite CM48\_123]. The spectrum shows a broad minimum at  $\sim 3450\text{ cm}^{-1}$  assigned to various  $\text{H}_2\text{O}$  stretching modes and consistent with the presence of a major amount of  $\text{H}_2\text{O}$  in the mineral, and in accord with the weak absorption at  $\sim 1630\text{ cm}^{-1}$ , which may be assigned to

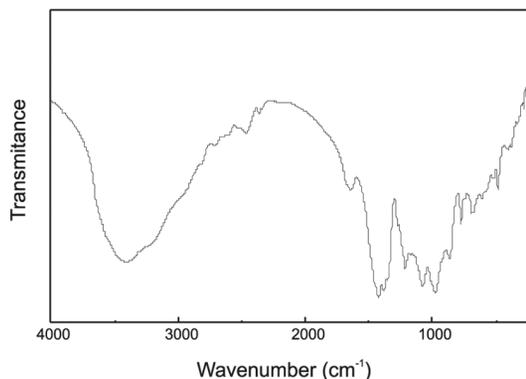


FIG. 5. Infrared spectrum of alfredstelznerite.

the H–O–H bending mode. There are strong absorptions in the region  $1500\text{--}1000\text{ cm}^{-1}$ , which may be assigned to B–O stretching modes. They are in accord with the presence of borate groups in the structure.

### X-RAY CRYSTALLOGRAPHY

Powder X-ray-diffraction data were obtained on a carefully selected transparent crystal with Ni-filtered  $\text{CuK}\alpha$  radiation ( $\lambda = 1.54178\text{ \AA}$ ) using a Debye–Scherrer camera of 114.6 mm diameter with a Gandolfi attachment. The intensities were estimated visually, and the data were not corrected for film shrinkage. The calculated powder pattern generated from the refined crystal-structure was used to aid indexing. The results are given in Table 2.

### RELATION TO OTHER SPECIES

Alfredstelznerite is characterized by the cluster  $[\text{B}_4\text{O}_4(\text{OH})_6]$ ; this cluster does not occur in any other borate mineral (Hawthorne *et al.* 2002), and hence this mineral is structurally and chemically unique (Cooper *et al.* 2010). Hydrated Ca borate minerals (with no additional cations) based on borate clusters are listed in Table 3; note that meyerhofferite and inyoite occur in association with alfredstelznerite. Of all the hydrated Ca borate cluster minerals (with no additional cations), alfredstelznerite contains the most complex borate cluster, has the lowest density, and the greatest content of interstitial ( $\text{H}_2\text{O}$ ) groups.

### ACKNOWLEDGEMENTS

The Argentinian authors are very grateful to the staff of Bórax Argentina S.A., especially to geologist R. Gutiérrez, for authorizing their visit to the Santa Rosa mine. Dr. J.C. Oyarzábal is acknowledged for providing the infrared and thermogravimetric data. The authors thank Dr. Joel D. Grice for his careful review and Robert F. Martin for his editorial comments. Grants from CONICET of Argentina to Miguel A. Galliski and

TABLE 3. HYDRATED Ca BORATE-CLUSTER MINERALS (WITHOUT ADDITIONAL CATIONS)

Name	Formula	Cluster [7]	$\text{H}_2\text{O}/$ anions %	$(\text{H}_2\text{O})_{\text{interstitial}}/$ $(\text{H}_2\text{O})_{\text{total}}$ %	$\sigma_{\text{calc}}$	Ref.
Nifontovite	$\text{Ca}_3(\text{H}_2\text{O})_2 [\text{B}_3\text{O}_3(\text{OH})_2]_2$	<3□>	10	—	2.34	[1]
Olshanskyite	$\text{Ca}_2(\text{OH})(\text{H}_2\text{O}) [\text{B}_2\text{O}_3(\text{OH})_4]$	<3□>	9	—	2.20	[2]
Meyerhofferite	$\text{Ca}(\text{H}_2\text{O}) [\text{B}_2\text{O}_3(\text{OH})_3]$	< $\Delta 2$ □>	11	—	2.12	[3]
Pentahydroborite	$\text{Ca}(\text{H}_2\text{O}) [\text{B}_2\text{O}(\text{OH})_6] (\text{H}_2\text{O})$	<2□>	22	50	2.02	[4]
Inyoite	$\text{Ca}(\text{H}_2\text{O})_3 [\text{B}_2\text{O}_3(\text{OH})_3] (\text{H}_2\text{O})$	< $\Delta 2$ □>	33	25	1.87	[5]
Alfredstelznerite	$\text{Ca}_4(\text{H}_2\text{O})_4 [\text{B}_4\text{O}_4(\text{OH})_6]_4 (\text{H}_2\text{O})_{15}$	< $\Delta 2$ □> $\Delta$	32	79	1.78	[6]

[1] Simonov *et al.* (1978), [2] Callegari *et al.* (2001), [3] Burns & Hawthorne (1993), [4] Kazanskaya *et al.* (1977), [5] Rumanova & Genkina (1981), [6] this study, [7] Burns *et al.* (1995).

from NSERC (Discovery and Infrastructure Grants) and CFI (Innovation Grants) to Frank C. Hawthorne financed the research.

## REFERENCES

- ALONSO, R.N. (1999): Boratos terciarios de la Puna, Jujuy, Salta y Catamarca. In Recursos Minerales de la República Argentina (E. Zappettini, ed.). *Instituto de Geología y Recursos Minerales SEGEMAR, Anales* **35**, 1779-1826.
- BURNS, P.C., GRICE, J.D. & HAWTHORNE, F.C. (1995): Borate minerals. I. Polyhedral clusters and fundamental building blocks. *Can. Mineral.* **33**, 1131-1151.
- BURNS, P.C. & HAWTHORNE, F.C. (1993): Hydrogen bonding in meyerhofferite: an X-ray and structure energy study. *Can. Mineral.* **31**, 305-312.
- CALLEGARI, A., MAZZI, F. & TADINI, C. (2001): The crystal structure of olshanskyite. *Can. Mineral.* **39**, 137-144.
- COOPER, M.A., HAWTHORNE, F.C., GALLISKI, M.A. & MÁRQUEZ-ZAVALÍA, M.F. (2010): The crystal structure of alfredstelnzerite,  $\text{Ca}_4(\text{H}_2\text{O})_4 [\text{B}_4\text{O}_4(\text{OH})_6]_4 (\text{H}_2\text{O})_{15}$ , a complex hydroxy-hydrated calcium borate mineral. *Can. Mineral.* **48**, 129-138.
- HAWTHORNE, F.C. BURNS, P.C. & GRICE, J.D. (2002): The crystal chemistry of boron. In *Boron: Mineralogy, Petrology and Geochemistry* (E.S.Grew & L.M.Anovitz, eds.). *Rev. Mineral.* **33**, 41-116.
- KAZANSKAYA, E.V., CHEMODINA, T.N., EGOROV-TISMENKO, YU.K., SIMONOV, M.A. & BELOV, N.V. (1977): Refined crystal structure of pentahydroborite  $\text{Ca}[(\text{B}_2\text{O}(\text{OH})_6)_2 \cdot 2\text{H}_2\text{O}]$ . *Sov. Phys. Crystallogr.* **22**, 35-36.
- MANDARINO, J.A. (1981): The Gladstone–Dale relationship. IV. The compatibility concept and its application. *Can. Mineral.* **19**, 441-450.
- POUCHOU, J.L. & PICOIR, F. (1984): A new model for quantitative analysis. A. Application to the analysis of homogeneous samples. *Recherche Aérosp.* **5**, 47-65.
- POUCHOU, J.L. & PICOIR, F. (1985): “PAP” ( $\phi\rho Z$ ) correction procedure for improved quantitative microanalysis. In *Microbeam Analysis* (J. T. Armstrong, ed.). San Francisco Press, San Francisco, California (104-106).
- RUMANOVA, I.M. & GENKINA, E.A. (1981): Precise structure of inyoite  $\text{Ca}(\text{H}_2\text{O})_3 (\text{B}_3\text{O}_3(\text{OH})_5) (\text{H}_2\text{O})$ . *Latvijas PSR Zinatnu Akademijas Vestis, Khimijas Serija* **6**, 643-653.
- RUSSANSKY, J. (1985): *Estudio Geológico-Económico de la mina de boratos Santa Rosa 1 y 2, Depto. Los Andes, Salta*. Tesis Doctoral N° 448, Facultad de Ciencias Naturales y Museo, La Plata, Argentina.
- SIMONOV, M.A., EGOROV-TISMENKO, YU.K., KAZANSKAYA, E.V., BELOKONEVA, E.L. & BELOV, N.V. (1978): Hydrogen bonds in the crystal structure of the nifontovite  $\text{Ca}_3[(\text{B}_3\text{O}_3(\text{OH})_6)_2 \cdot 2\text{H}_2\text{O}]$ . *Sov. Phys. Dokl.* **23**, 159-161.

Received July 18, 2008, revised manuscript accepted November 14, 2009.