

MINERALOGICAL STUDIES OF THE NITRATE DEPOSITS OF CHILE

IV. BRÜGGENITE, $\text{Ca}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$, A NEW SALINE MINERAL

By GEORGE E. ERICKSEN, MARY E. MROSE, and JOHN W. MARINENKO,
Washington, D.C.

Abstract.—Brüggerite, $\text{Ca}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$, is found in veins of high-purity soda niter in rhyolite tuff at Pampa Pique III, Oficina Lautaro, Chile, as long columnar anhedral crystals, as prismatic crystals, and as irregular anhedral crystals or encrusting masses. The mineral is colorless to bright yellow, and transparent to translucent, has vitreous luster and a hardness of about $3\frac{1}{2}$, is brittle, and has conchoidal fracture. It is biaxial and has variable optic angle and refractive indices, which were determined by the spindle-stage method. Refractive indices are as follows: $n_\alpha = 1.772-1.779$, $n_\beta = 1.795-1.802$, and $n_\gamma = 1.817-1.824$ (all ± 0.003); optic angle shows a range of $2V_Z = 86^\circ-96^\circ$; $Z = b$ and $X \wedge c = -47^\circ$; dispersion (Z) is $r < v$, moderate. Brüggerite is monoclinic, space group $P2_1/c$, with $a = 8.509 \pm 0.001$ Å, $b = 10.027 \pm 0.002$ Å, $c = 7.512 \pm 0.001$ Å, $\beta = 95^\circ 16.00' \pm 0.55'$, volume 638.2 Å³, $Z = 4$, $G(\text{calc}) = 4.244$, $G(\text{meas}) = 4.24 \pm 0.01$. The X-ray diffraction powder pattern of Brüggerite has the following strong lines (hkl , d_{hkl} Å): 031, 3.051 Å (100); 220, 3.238 Å (90); 200, 4.235 Å (80); 002, 3.739 Å (60); 012, 3.503 Å (60); 231, 2.522 Å (60). The composition was confirmed by chemical analyses.

The new mineral Brüggerite (pronounced brü-gĕn-äit) was discovered in a suite of saline minerals from nitrate deposits at Pampa Pique III, about a kilometer north of Oficina Lautaro (fig. 1) in the Taltal nitrate district of Chile. The material was collected in 1965 by Ericksen and his Chilean colleagues Fernando Munizaga and Mauricio Tabak of the Instituto de Investigaciones Geológicas. This area is the type locality for the minerals lautarite, $\text{Ca}(\text{IO}_3)_2$, and dietzeite, $\text{Ca}_2(\text{IO}_3)_2(\text{CrO}_4)$. Specimens of Brüggerite, which range from colorless to bright yellow, were first assumed to be lautarite and dietzeite, but X-ray powder diffraction studies showed them to be a distinct mineral species. Identification of the new mineral was made somewhat more difficult than usual because the published powder data for lautarite are actually those of Brüggerite, $\text{Ca}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$.

Pampa Pique III is a nitrate mine area that formerly supplied ore for treatment at the nearby nitrate plant at Oficina Lautaro. The area is within a closed depression, several hundred meters in diameter and 10–20 m deep, in a terrain of reddish to purplish rhyolite ash-flow tuff. This depression is one of several in this part of the Taltal district and may be an original feature dating from the time the tuff was deposited,

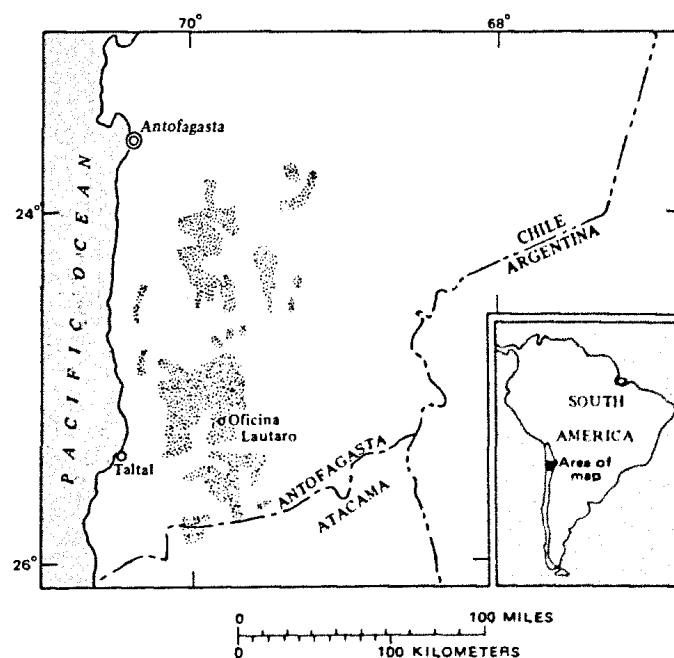


Figure 1.—Index map showing location of nitrate fields (stippled) in southern Antofagasta Province, Chile.

probably during the Pleistocene. However, the depression has been modified by wind deflation, the chief agent of erosion in this extremely dry region. Specimens for our study came from piles of nitrate ore and from veins in the tuff in the vicinity of a water well (Pique III) near the center and lowest part of the depression.

The veins (fig. 2) contain extremely high-purity soda niter; chemical analysis of a sample of fibrous nitrate from this locality showed it to contain 99.8 percent NaNO_3 (Ericksen and Mrose, 1972, p. B48). Furthermore, the surface-leached zone of the veins is very shallow, commonly only 10 or 20 cm deep, in contrast with other areas where the leached zone is generally more than a meter deep.

The mineral is named for Juan Brügger M. (1887–1953), a leader in the study of Chilean geology. As a professor at the University of Chile he trained many of the Chilean geologists and mining engineers who are the leaders in the present mining



Figure 2.—Vein of fibrous to columnar soda niter, Pampa Pique III, Oficina Lautaro, Chile.

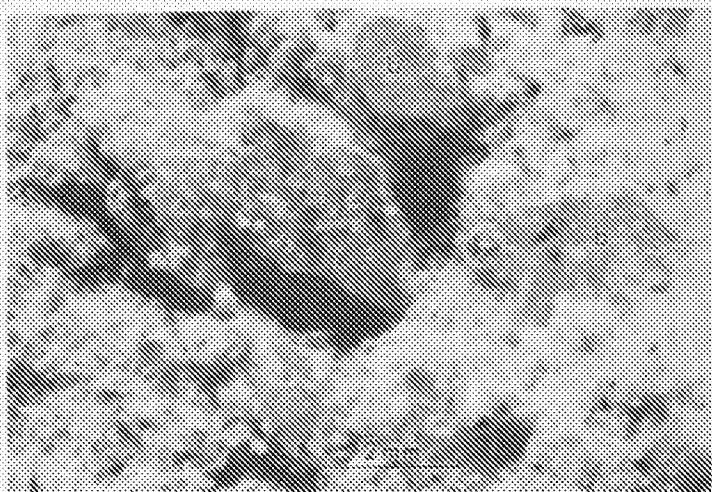


Figure 3.—Prismatic crystals of brüggerite (b) embedded in granular white soda niter, Pampa Pique III, Oficina Lautaro, Chile. Largest crystal shows diamond-shaped cross section about 4 mm in the longest dimension.

industry of Chile. His extensive bibliography covers many phases of Chilean geology and includes the first textbook on the geology of Chile. His descriptions of the nitrate deposits are among the most accurate that have been published.

The description and name of this new mineral were approved, in advance of publication, by the Commission on New Minerals and Mineral Names, I.M.A. A brief preliminary description of brüggerite appeared in an abstract (Mrose and others, 1971). Specimens of type material have been deposited in the mineral collection in the U.S. National Museum, Washington, D.C.; these consist of several small hand specimens, plus a vial containing approximately 10 g of purified crystalline material (USNM 122445).

OCCURRENCE AND ORIGIN

The brüggerite at Pampa Pique III occurs as thin columnar intergrowths in soda niter veins (fig. 2), as short subhedral prismatic crystals and encrusting masses, chiefly at margins of these veins, and as clusters of radiating prismatic crystals and impregnations in soft decomposed rhyolite tuff and gouge in the veins and the enclosing wall rock. The most spectacular specimens are those in which bright yellow brüggerite is intergrown with white fibrous to columnar soda niter that forms veins as much as 30 cm thick. The brüggerite in such veins occurs only in local patches that range from less than a centimeter to as much as 10 cm in longest dimension. Brüggerite may make up 50 percent or more of such patches. The thin columns of brüggerite are generally less than a millimeter across and less than 2 cm long. More rarely, the columns are as much as 5 cm long. Prismatic crystals occur as untruncated prisms as much as 1 cm long, showing a diamond-shaped cross section (fig. 3) as much as 6 mm in

longest dimension. They are either partly intergrown in clusters or are individual crystals in the granular soda niter or saline-cemented decomposed rhyolite at the vein boundary.

Other saline minerals associated with the brüggerite at Pampa Pique III are anhydrite, CaSO_4 , lautarite, $\text{Ca}(\text{IO}_3)_2$, hydroboracite, $\text{CaMgB}_6\text{O}_{14} \cdot 6\text{H}_2\text{O}$, and halite, NaCl . Dietzite was not found in our specimens, although Pampa Pique III is the type locality for this mineral (Osann, 1894, p. 588); we did identify it in specimens from this locality in the study collection of the U.S. National Museum, Washington, D.C. Anhydrite and halite are fairly abundant, lautarite is evidently less abundant than brüggerite, and hydroboracite is rare.

The brüggerite was deposited during at least two stages, first as an intergrowth with fibrous to columnar soda niter in veins and then in cavities at vein boundaries. The anhydrite formed earlier than the brüggerite and soda niter. Hydroboracite occurs in cavities in soda niter and therefore is younger than part of the brüggerite. Some of the crystalline lautarite and brüggerite are intimately associated, probably because of simultaneous crystallization of the two phases (see fig. 5) or partial alteration of one phase to the other after primary crystallization.

The source of the iodate is part of the broader problem of the origin of the nitrate deposits of Chile, a topic beyond the scope of this paper. Nevertheless, the association of abundant iodate minerals with the rhyolite tuffs of this region is unique and may indicate a genetic relation. The nitrate and the iodate minerals might have been deposited by thermal waters during the final phase of volcanic activity. Later, they might have migrated because of slow leaching by infrequent rain and might have been redeposited in veins lower in the depression. Alternatively, the iodine might have been supplied by atmospheric fallout, the ocean being the primary source.

PHYSICAL AND OPTICAL PROPERTIES

Individual crystals of brüggenite are colorless to bright yellow, transparent to translucent, and have a vitreous luster. The bright yellow of some brüggenite may be due to trace amounts of chromate (CrO_4^{2-}) as impurity, but small fragments and crystals of brüggenite that appear colorless are very pale yellow when grouped together, suggesting that the color is an inherent property of the mineral; synthetic crystals of brüggenite are also pale yellow. The powder and streak are white.

Brüggenite is brittle, has a hardness of 3½, lacks cleavage, and has conchoidal fracture. It does not fluoresce in either long- or short-wave ultraviolet light. The specific gravity, determined at 22°C on crystal fragments on the Bernier microbalance, using toluene as the immersion liquid, is 4.24 ± 0.01 (an average of six determinations), in excellent agreement with the value 4.24 ± 0.01 , determined by the pycnometer method at 25°C, for synthetic brüggenite; the density calculated for brüggenite from the X-ray data is 4.244 g cm^{-3} .

In transmitted light, brüggenite is colorless to very pale yellow and is nonpleochroic. The mineral is monoclinic, and synthetic prismatic crystals show orientation of $X/c = -47^\circ$, Z/b . The previously reported orientation (Mrose and others, 1971) is in error because determinations were made on natural columnar material that later proved not to have true crystal form. Dispersion (Z) is $r < v$, moderate.

The optic angle and refractive indices of both natural and synthetic brüggenite show considerable variation from grain to grain in apparently homogeneous material and even on different parts of a single grain or euhedral crystal (Ray E. Wilcox, written commun., 1973). Determinations of refractive indices were made on the spindle stage, using the focal masking technique, and by normal immersion method, using both sodium light and white light. Index oils were checked with a Leitz-Jelley-type microrefractometer at the times indices were measured. Optic angles were also measured on the spindle stage. Refractive indices for natural and synthetic brüggenite thus obtained are as follows: $n_x = 1.772\text{--}1.779$, $n_y = 1.795\text{--}1.802$, and $n_z = 1.817\text{--}1.824$ (all measurements accurate to ± 0.003); the optic angle shows a range of $2V_x = 86^\circ\text{--}96^\circ$. Twinning was not observed, although the columnar brüggenite that is intergrown with fibrous soda niter shows impressions of longitudinal twinning striae of crystals of the enclosing soda niter.

CRYSTALLOGRAPHY

Single-crystal X-ray data.—The unit-cell parameters of brüggenite from Pampa Pique III were first derived using Buerger precession techniques. Monoclinic cell constants and space group were obtained, using both nickel-filtered copper radiation and zirconium-filtered molybdenum radiation, with exposure times of approximately 72 h for the latter. The $0kl$,

hkl , $2kl$, $h0l$, $h2l$, and $h3l$ reciprocal lattice nets were photographed. The conditions limiting the possible reflections are $h0l: 2a$ and $0kl: k: 2a$, so that the space group $P2_1/c$ is thus uniquely defined. The cell data for the natural material, obtained by single-crystal techniques, are compared below with those derived from the X-ray diffraction powder data (table 1) by the least-squares refinement technique, using the digital computer program of Appleman and Evans (1973):

	Single-crystal data (precession method)	X-ray powder data (least-squares method)
Crystal system	Monoclinic	Monoclinic
$a(\text{\AA})$	8.505	8.509 ± 0.001
$b(\text{\AA})$	18.000	18.027 ± 0.002
$c(\text{\AA})$	7.498	7.512 ± 0.001
β	$90^\circ 20' \pm 10'$	$95^\circ 16.00' \pm 0.55'$
$a/b/c$	$0.47503:1:0.7490$	$0.8406:1:0.7492$
Space group	$P2_1/c$	$P2_1/c$
Cell volume	$634.9 \text{ \AA}^3$	$638.2 \text{ \AA}^3$
Cell contents	$4[\text{Ca}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}]$	$4[\text{Ca}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}]$
Density (calc)	4.267 g cm^{-3}	4.244 g cm^{-3}

X-ray powder data.—X-ray powder patterns were prepared for brüggenite from Pampa Pique III and for crystals of $\text{Ca}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$ synthesized during this study; the powder patterns of both are identical. Indexed X-ray powder data for brüggenite are listed in table 1. The powder data cited in the Powder Diffraction File (formerly ASTM) card 1-0306 for so-called synthetic lantarite (= synthetic brüggenite) are compared in table 1 with those of brüggenite of this study.

Morphology.—Most brüggenite occurs as anhedral crystals or microcrystalline masses. The anhedral crystals are long, thin, and columnar, elongated c , and are intergrown with fibrous to columnar soda niter crystals; these brüggenite crystals tend to have irregular rough striated faces that reflect the growth pattern of the soda niter. Faces on these crystals, limited to the prism zone, are distorted. Some may be true crystal faces; others clearly are not.

Prismatic crystals of brüggenite are as much as a centimeter long in the c direction and show a diamond-shaped cross section, as much as 6 mm long in the b direction (fig. 3). Interfacial angles measured with a petrographic microscope gave a ϕ angle of 60° for several of the diamond-shaped cross sections, which compares favorably with a calculated ϕ of $60^\circ 36'$ for the prism form $\{320\}$. None of the many synthetic crystals examined in the course of this study showed this form.

Four small, terminated, apparently euhedral crystals of natural brüggenite, of long prismatic habit (length:width:thickness, approximately 0.5 mm:0.15 mm:0.10 mm) were measured on the optical goniometer. The interfacial angles obtained for the four hkl faces in the prism zone were not consistent with those of a prism form; these faces undoubtedly resulted from growth control effected by the fibrous soda niter. Forms observed on these crystals were $h\{010\}$, as very narrow faces, and the clinodome, $w\{011\}$.

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lkl , $2kl$, $h0l$, $h2l$, and $h3l$ reciprocal lattice nets were photographed. The conditions limiting the possible reflections are $h0l:l=2n$ and $0k0:k=2n$, so that the space group $P2_1/c$ is thus uniquely defined. The cell data for the natural material, obtained by single-crystal techniques, are compared below with those derived from the X-ray diffraction powder data (table 1) by the least-squares refinement technique, using the digital computer program of Appleman and Evans (1973):

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β	$95^\circ 20' \pm 10'$	$95^\circ 16.00' \pm 0.55'$
$a:b:c$	$0.8505:1:0.7498$	$0.8486:1:0.7492$
Space group	$P2_1/c$	$P2_1/c$
Cell volume	$634.9 \text{ \AA}^3$	$638.2 \text{ \AA}^3$
Cell contents	$4[\text{Ca}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}]$	$4[\text{Ca}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}]$
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Table 1.—X-ray diffraction powder data for brüggeneite, $\text{Ca}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$ [Monoclinic, $P2_1/c$; $a=8.509 \pm 0.001$ Å, $b=10.027 \pm 0.002$ Å, $c=7.512 \pm 0.001$ Å, $\beta=95^\circ 16.00' \pm 0.55'$]

Pampa Pique III, Oficina Lautaro, Chile "Lautarite" (PDF 1-0386) = synthetic brüggeneite						Pampa Pique III, Oficina Lautaro, Chile "Lautarite" (PDF 1-0386) = synthetic brüggeneite					
hkl	Calculated ¹	Measured ²		Measured ³		hkl	Calculated ¹	Measured ²		Measured ³	
	d(Å)	d(Å)	I ⁴	d(Å)	I		d(Å)	d(Å)	I ⁴	d(Å)	I
100	8.473					023	2.233	2.233	18	2.23	13
110	6.472	6.475	7	6.7	7	302	2.161				
011	5.996	5.996	35	6.0	27	240	2.157	2.157	13		
111	5.073					330	2.157				
020	5.013	5.011	50	5.1	33	322	2.136	2.135	5		
111	4.733	4.733	7			400	2.118	2.118	35	2.12	27
120	4.315					232	2.093	2.093	7		
200	4.237	4.235	80	4.27	100	410	2.073	2.072	5		
021	4.165	4.167	5			142	2.046				
210	3.902					223	2.046	2.045	35	2.04	23
121	3.815	3.814	5			411	2.045				
002	3.740	3.739	60	3.75	30	142	1.9986	1.9987	11	2.00	3
211	3.587	3.587	18			051	1.9369	1.9368	35	1.95	20
102	3.544					223	1.9114	1.9113	18		
012	3.504	3.503	60	3.51	27	104	1.8625	1.8635	25		
211	3.346	3.345	50	3.35	23	014	1.8384	1.8388	35	1.85	20
112	3.341							1.7964	25		
102	3.311							1.7768	60	1.78	42
220	3.236	3.238	90	3.24	67			1.7737	60		
112	3.144							1.7476	60	1.75	42
130	3.109							1.7104	30	1.71	13
031	3.051	3.051	100	3.04	100			1.6929	7		
221	3.049							1.6716	42	1.67	23
022	2.998	2.998	42					1.6320	35	1.63	13
202	2.941	2.940	30					1.5982	18	1.60	13
131	2.906							1.5801	9		
221	2.897							1.5655	13	1.56	13
122	2.894	2.894	7					1.5435	7		
131	2.837							1.5285	13		
300	2.824							1.5122	13		
212	2.822	2.820	18	2.83	7			1.4940	13	1.49	7
122	2.763							1.4775	13		
310	2.719	2.718	18					1.4573	18		
202	2.684	2.685	35	2.69	33			1.4512	18	1.45	13
311	2.631							1.4323	13		
230	2.624							1.4130	18	1.41	17
212	2.593	2.592	18	2.59	7			1.3990	18		
222	2.537							1.3640	18	1.36	13
231	2.521	2.522	60	2.53	50			1.3478	11		
032	2.492	2.491	7					1.3320	11		
231	2.433	2.431	35	2.43	27			1.3147	13		
132	2.431							1.3026	11		
013	2.420	2.420	7					1.3002	11		
321	2.395	2.395	7					1.2850	13		
222	2.366	2.366	50	2.37	30			1.2725	11		
312	2.298	2.298	13	2.30	7						

¹ All possible calculated d's listed for $d \geq 2.521$ Å; calculated d's, ≤ 2.520 Å and ≥ 1.8000 Å, listed only for those observed.

² Camera diameter, 114.59 mm; Ni-filtered Cu radiation ($\lambda_{\text{CuK}\alpha} = 1.5418$ Å); internal standard, CaF_2 . Lower limit measurable for 2θ is approximately 6.0° (14.7 Å).

³ Camera diameter, 16 in.; Zr-filtered Mo radiation ($\lambda_{\text{MoK}\alpha} = 0.709$ Å). Intensities were obtained by comparison with calibrated strips.

⁴ Intensities estimated visually by direct comparison with a calibrated intensity filmstrip of successive step-line exposures related to each other by a factor of $\sqrt{2}$.

Several well-formed, doubly-terminated crystals of synthetic brüggenite (fig. 4) were examined and measured on a goniometer. Crystals synthesized at 50°C are short prismatic, nearly equidimensional; those at 60°C, are long prismatic parallel to *c* (length:width:thickness averaging 1.0 mm:0.5 mm:0.25 mm). All the brüggenite crystals synthesized in this study are simple, having only three measurable forms: $\{010\}$, $m\{110\}$, and $\infty\{011\}$. The form $m\{110\}$ is dominant; $\{101\}$ is generally very narrow. General forms $\{hkl\}$ were not found on any of the many crystals examined. The absence of any positive piezoelectric response by the Giebe-Schiebe apparatus and the unequivocal space group $P2_1/c$ supports our assumption that the crystal class for brüggenite is prismatic, $2/m$.

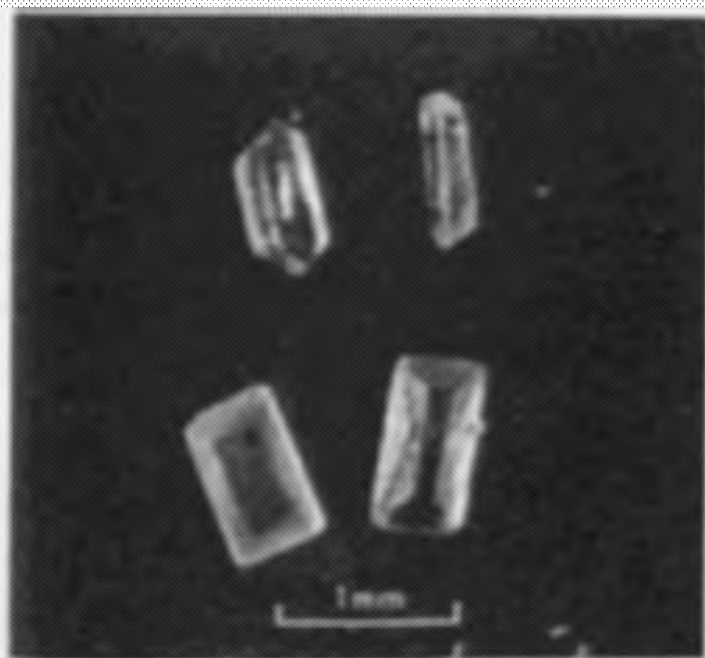


Figure 4.—Prismatic crystals of synthetic brüggenite, synthesized at 50°C.

The angles and axial ratios for the observed forms of brüggenite, calculated from the crystallographic data cited in table 1, are given in table 2.

Table 2.—Angle table for brüggenite from Pampa Pique III, Oficina Lautaro, Chile

[Calculated from X-ray data in table 1]

Monoclinic, prismatic— $2/m$

$$a:b:c = 0.8486:1.07492; \beta = 95^\circ 16'; p_a:q_a:r_a = 0.8929:0.7460:1; \\ r_a/p_a:q_a = 1.3465:1.1834; \mu = 84^\circ 44'; \\ p_a' = 0.8966, q_a' = 0.7492, r_a' = 0.8922$$

Form	ϕ	ρ	ϕ_2	$\rho_2 = B$	C	A
$\{010\}$	$0^\circ 00'$	$90^\circ 00'$		$0^\circ 00'$	$90^\circ 00'$	$90^\circ 00'$
$\infty\{011\}$	$7^\circ 01'$	$37^\circ 03'$	$84^\circ 44'$	$53^\circ 16' 1/2''$	$36^\circ 43' 1/2''$	$85^\circ 47'$
$m\{110\}$	$49^\circ 45'$	$90^\circ 00'$	$0^\circ 00'$	$46^\circ 48'$	$85^\circ 59'$	$46^\circ 12'$

Crystal-structure analysis.—The crystal structures of brüggenite, lautarite, and $\text{Ca}(\text{IO}_3)_2 \cdot 6\text{H}_2\text{O}$ have been determined in the laboratories of the U.S. Geological Survey (unpub. data, 1973).

CHEMICAL PROPERTIES

Chemical analysis.—Material for chemical analysis was leached from specimens of nitrate ore from Pampa Pique III; from this concentrate only crystal fragments, free of visible inclusions, were handpicked for the analysis sample. X-ray patterns of selected fragments of this material indicated a mixture of brüggenite and lautarite. Attempts to separate brüggenite from lautarite in Clerici solution were unsuccessful, because both minerals reacted with this liquid.

The specific gravity of the entire sample (500 mg) was determined by Joseph J. Fahey of the U.S. Geological Survey by pycnometer method; the value obtained, 4.397, indicated that approximately two-thirds of the sample was brüggenite, $\text{Ca}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$, and one-third lautarite, $\text{Ca}(\text{IO}_3)_2$. The chemical analysis of this 500-mg mixture is given in column 1 of table 3; the recalculated chemical analysis (col. 2 of table 3), obtained by deducting the insoluble matter, CO_2 , and lautarite, is in good agreement with the theoretical composition, $\text{Ca}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$, and with the analysis of crystals of brüggenite synthesized in the course of this study, also cited in table 3.

The determinations of the chemical components (table 3), except for CO_2 and SrO , were by standard methods cited by Hillebrand, Lundell, Bright, and Hoffman (1953). Carbonate carbon was determined by gas chromatography after acid evolution (Marinenko and May, 1970); SrO was determined by atomic absorption.

Spectrographic analysis.—Prior to chemical analysis, a sample of columnar fragments of brüggenite from Pampa Pique III was submitted for semiquantitative spectrographic analysis. The spectrogram obtained by Joseph L. Harris of the U.S. Geological Survey gave the results shown below (values are reported to the nearest number in series 1, 0.7, 0.5, 0.3, 0.2, 0.15, 0.1, and so forth, which represent approximate midpoints of group data on a geometric scale):

Weight percent	Parts per million
Ca.....>10	Sr.....2000
Si.....1	Ca.....200
Na......63	B.....100
Mg......007	Ba.....70
Fe......0007	Cr.....30
Al.....(°)	Mo.....20
	V.....7
	Mn.....1

° Detected, but below limit of determination.

Note.—Looked for, not found: As, Au, Be, Bi, Cd, Ce, Co, Cr, Cu, Fe, Hf, In, K, La, Li, Nb, Ni, P, Pb, Pd, Pt, Rb, Sb, Se, Sn, Ta, Te, Th, Ti, Tl, U, W, Y, Yb, Zn, Zr.

Table 3.—Chemical analyses of brüggerite, $\text{Ca}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$, and its synthetic equivalent

[Analyst: John W. Marinenko]

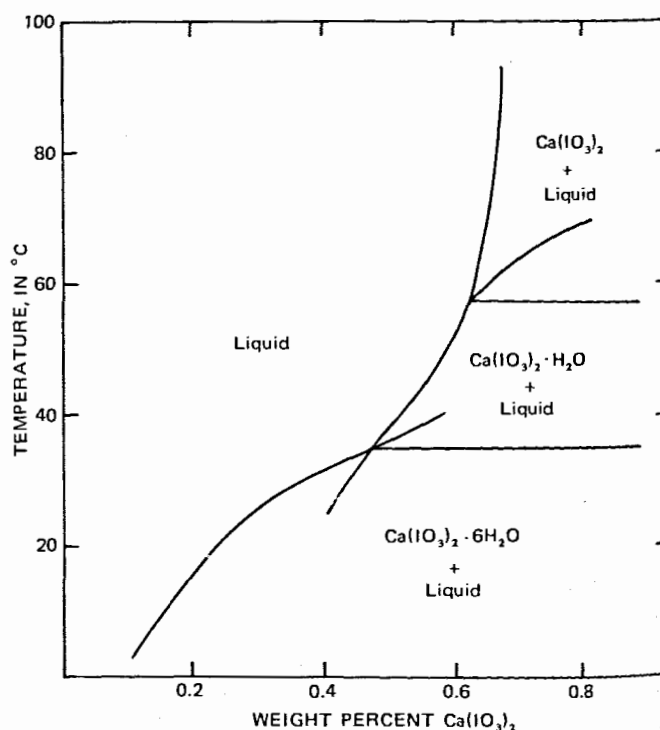
	Brüggerite		Synthetic equivalent		Theoretical composition for $\text{Ca}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$	Cations on the basis of seven oxygens		
	Weight percent	Recalculated ¹	Weight percent	Recalculated ²	Weight percent	Brüggerite	Synthetic equivalent	
CaO	14.2	14.1	14.2	14.1	13.75	Ca } 1.1	1.0	
SrO	0.4	0.4				Sr } 2.0		
I ₂ O ₅	81.7	81.4	80.6	81.4	81.83	I 2.0	2.0	
H ₂ O	2.8	4.1	4.4	4.5	4.42	H 1.9	2.0	
CO ₂	<0.1		³ 0.13					
Insoluble residue. ⁴	0.3		<0.1					
Total	99.4	100.0	99.3	100.0	100.00			

¹ Recalculated to 100.0 after deducting insoluble, CO₂, and 33¹/₃ percent lautarite.² Recalculated to 100.0 after deducting insoluble, and CO₂ as CaCO₃.³ Sample contained a small amount of CaCO₃ (used in the synthesis) as an impurity.⁴ Insoluble residue in (1:1) HCl.

Synthesis.—Brüggerite is readily synthesized. It was prepared during this study by initially adding a 0.2 molal solution of iodic acid (HIO₃) to 9.5 g of reagent-grade calcium carbonate (CaCO₃). When effervescence ceased, the filtrate was carefully decanted, passed through very fine filter paper, and then held in an oven (50°–80°C) in a covered vessel until crystallization took place. Well-formed transparent doubly-terminated crystals of brüggerite were thus formed (fig. 4). They were dried between filter papers, washed successively with methyl alcohol and acetone, and air dried at room temperature. The chemical analysis of these synthetic crystals (table 3) confirmed that the composition was $\text{Ca}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$. X-ray powder patterns for the synthetic crystals and naturally occurring brüggerite show them to be identical.

X-ray powder data recorded for a compound synthesized and characterized as $\text{Ca}(\text{IO}_3)_2 \cdot n\text{H}_2\text{O}$ by Kaplan (1966) in his efforts to prepare lautarite, $\text{Ca}(\text{IO}_3)_2$, using various methods, are in good agreement with those for brüggerite.

Solubility data.—The three known phases (fig. 5) in the system $\text{Ca}(\text{IO}_3)_2\text{--H}_2\text{O}$ ($T < 100^\circ\text{C}$; $P = 1$ bar) include the minerals lautarite and brüggerite, which occur together in the Chilean nitrate deposits, and $\text{Ca}(\text{IO}_3)_2 \cdot 6\text{H}_2\text{O}$ which has not yet been found as a mineral. Solubility data presented by Hill and Brown in 1931 show $\text{Ca}(\text{IO}_3)_2$ to be the high-temperature phase ($T \geq 57.5^\circ\text{C}$), $\text{Ca}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$ the intermediate phase ($T = 35^\circ\text{--}57.5^\circ\text{C}$), and $\text{Ca}(\text{IO}_3)_2 \cdot 6\text{H}_2\text{O}$ the low-temperature phase ($T \leq 35^\circ\text{C}$). Furthermore, $\text{Ca}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$ forms metastably in the temperature ranges of $25^\circ\text{--}35^\circ\text{C}$ and $57.5^\circ\text{--}70^\circ\text{C}$, and $\text{Ca}(\text{IO}_3)_2 \cdot 6\text{H}_2\text{O}$ in the range $35^\circ\text{--}40^\circ\text{C}$, as indicated in figure 5. The presence of lautarite and brüggerite in the nitrate deposits, which probably formed at an average temperature of less than 25°C ($P = 1$ bar), probably indicates that their stability temperatures were

Figure 5.—The system $\text{Ca}(\text{IO}_3)_2\text{--H}_2\text{O}$. (From Hill and Brown, 1931, p. 4319)

depressed by other salines present in the crystallizing solutions. $\text{Ca}(\text{IO}_3)_2 \cdot 6\text{H}_2\text{O}$, which readily desiccates to $\text{Ca}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$ in air at room temperature, either did not form in these solutions, which is most likely, or, if formed, became unstable as the newly formed nitrate caliche dried.

Brüggerite is readily soluble in hot water ($\approx 100^\circ\text{C}$) but only slowly soluble in cold water ($\approx 22^\circ\text{C}$). It is readily soluble in dilute to concentrated hot HCl and HNO₃ and in moderately concentrated (1:1) to concentrated cold HCl and HNO₃.

Brüggerite is less soluble in dilute (1:10) cold HCl and only slightly soluble in HNO₃ of similar concentration. It is only slightly soluble in sulfuric acid, decomposing and forming a precipitate of gypsum (CaSO₄·2H₂O). It is insoluble in organic solvents such as alcohol, acetone, and xylol.

Pyrognostics.—Before the blowpipe, brüggerite is infusible. When heated in an open platinum crucible just below red heat, brüggerite gives off water and violet vapors of iodine; the crystals turn light reddish brown, minute cracks appear, and some exfoliation takes place. This material gives an X-ray powder pattern of an unidentified phase, possibly Ca₅(IO₆)₂. At red heat in the open platinum crucible, iodine vapors are given off and the brüggerite crystals turn white and decrepitate; this residue has the X-ray powder pattern of CaO. When heated in a closed tube at red heat, brüggerite first gives off water; almost immediately thereafter, copious violet vapors of iodine deposit shining black rhomboidal crystals of iodine on the walls of the upper end of the tube.

Thermogravimetric analysis.—A thermogravimetric trace (fig. 6) of brüggerite was made by Frederick O. Simon, U.S. Geological Survey, using a 100-mg sample and a thermogravimetric balance that automatically records the weight of the sample as the temperature rises (4°C/min in air) to a maximum of 1,000°C. The trace shows a loss (table 3) of most or all of the water (≈5 percent) between the temperatures of 210° and 240°C. The remaining material, consisting

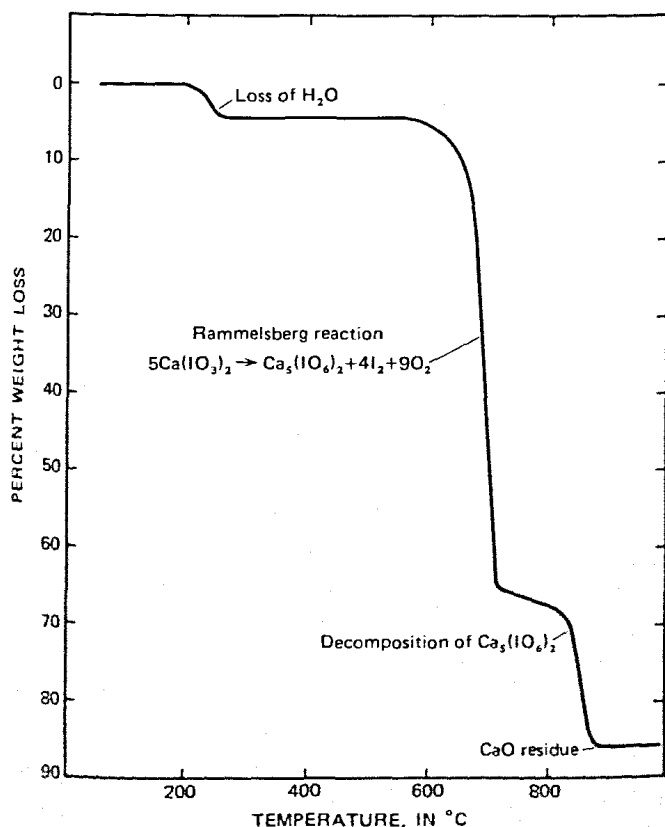


Figure 6.—Thermogravimetric trace for brüggerite, Ca(IO₃)₂·H₂O, showing progressive decomposition to CaO upon heating.

of Ca(IO₃)₂, then decomposes in two steps: (1) Between about 550° and 710°C, there is a weight loss due to loss of iodine and oxygen by the Rammelsberg reaction (Duval, 1953, p. 155): $5\text{Ca}(\text{IO}_3)_2 \rightarrow \text{Ca}_5(\text{IO}_6)_2 + 4\text{I}_2 + 9\text{O}_2$, and (2) at about 710°C, a strong inflection in the curve indicates that Ca₅(IO₆)₂ begins to decompose, releasing additional oxygen and the remaining iodine. Decomposition is completed at about 875°C, leaving a residue of CaO equivalent to about 14 percent of the original sample.

Infrared analysis.—Infrared traces of brüggerite from Pampa Pique III, and its synthetic equivalent, for the region 4000–200 cm⁻¹, are shown in figure 7; the principal absorption bands are listed in table 4. For comparison, the infrared frequencies for the IO₃ ion and for H₂O reported for the compound Ca(IO₃)₂·6H₂O by Miller and Wilkins (1952) and Miller, Carlson, Bentley, and Jones (1960) also are shown in table 4.

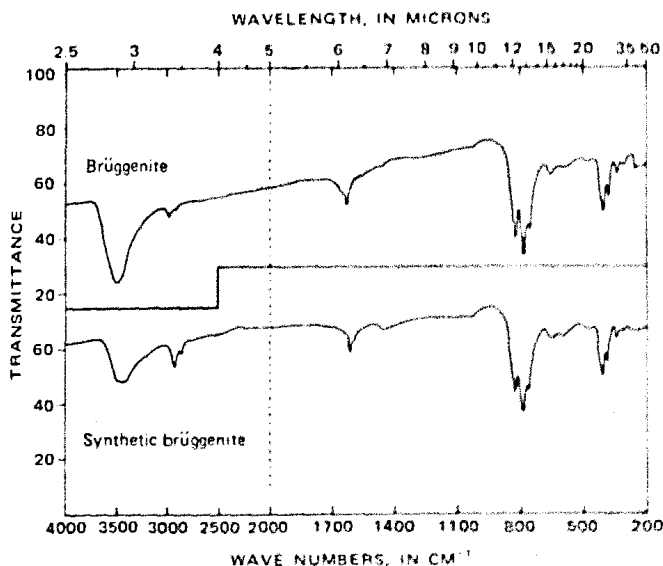


Figure 7.—Infrared traces of natural and synthetic brüggerite.

Table 4.—Infrared frequencies (cm⁻¹) for H₂O and IO₃⁻ in brüggerite, Ca(IO₃)₂·H₂O, compared with those for Ca(IO₃)₂·6H₂O

	[Intensities: s, strong; m, medium; w, weak]					
	H ₂ O		IO ₃ ⁻			
	ν _s ¹	ν ₂	ν ₁	ν ₂	ν ₃	ν ₄
Brüggerite	3500 s	1625 m	750 s	380 m	820 s	335 w
	2975 m		780 s	400 m		
Ca(IO ₃) ₂ ·6H ₂ O ²	3350 m	1610 w	748 m	397 m	817 s	335 m
	3450 m		760 m	367 m		
			775 s			

¹ ν_s = stretching mode (ν₁ and ν₂).

² Frequencies from Miller and Wilkins (1952, p. 1258); Miller, Carlson, Bentley, and Jones (1960, p. 217).

The infrared curves were made by Irving A. Breger, U.S. Geological Survey, with a Perkin-Elmer Model 621

spectrophotometer, utilizing KBr disks consisting of a mixture of 0.500 mg $\text{Ca}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$ and 300 mg KBr. The absorption bands (table 4) were identified by comparison of the spectra shown in figure 7 with spectra of iodate compounds (NaIO_3 , KIO_3 , and $\text{Ca}(\text{IO}_3)_2 \cdot 6\text{H}_2\text{O}$) presented by Miller and Wilkins (1952) and Miller, Carlson, Bentley, and Jones (1960). Vibrational modes (ν) for the IO_3 ion were assigned by comparison with the fundamental vibrational frequencies listed by Nakamoto (1963, p. 87); those for H_2O were assigned by comparison with spectra by Adler (1965).

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