THE AMERICAN MINERALOGIST, VOL. 55, SEPTEMBER–OCTOBER, 1970

MINERALOGICAL STUDIES OF THE NITRATE DEPOSITS OF CHILE. III. HUMBERSTONITE, $K_3Na_7Mg_2(SO_4)_6(NO_3)_2 \cdot 6H_2O$, A NEW SALINE MINERAL[1]

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ABSTRACT

Humberstonite, a new hydrous sulfate-nitrate of potassium, sodium, and magnesium, is found as a white powdery to compact layer, up to 40 cm thick, at several localities in the nitrate fields of northern Chile.

The powdery humberstonite consists of aggregates of thin, colorless, transparent, hexagonal-shaped crystals, up to 0.30 mm across. The crystals are trigonal, $R\bar{3}$; $a=10.900 \pm 0.001$ Å, $c=24.410 \pm 0.002$ Å, $Z=3$; $a_{rh}=10.286$ Å, $\alpha=64° 00'$, Z=1. The X-ray diffraction powder pattern has the following strong lines [$hk.l$, d (meas), I]: 20.5, 3.393 Å (100); 22.0, 2.724 Å (70); 00.3, 8.137 Å (60); 10.1, 8.802 Å (35); 11.3, 4.527 Å (35); 22.3, 2.583 Å (35). Precession photographs and the X-ray powder diffraction pattern indicate a structural relation to ungemachite. Crystals of humberstonite are platy $\{0001\}$; observed forms are $c\{0001\}$ and $r\{10\bar{1}1\}$. Hardness is about $2\frac{1}{2}$ and cleavage $\{0001\}$ is perfect. Humberstonite is soluble in water and insoluble in acetone and alcohol. The calculated density is 2.252 g/cm^3; measured specific gravity, 2.252 (pycnometer, at 25°C). Humberstonite is uniaxial negative with $\epsilon=1.436 \pm 0.002$ and $\omega=1.474 \pm 0.002$.

Chemical analysis (in percent) gave: SO_3 42.99, N_2O_5 9.14, Na_2O 18.43, K_2O 12.17, MgO 7.47, H_2O+9.78, H_2O-0.40; total 100.38. This leads to the formula $K_3Na_7Mg_2(SO_4)_6(NO_3)_2 \cdot 6H_2O$.

The name is for the chemist James Thomas Humberstone (1850–1939) who during his entire professional life worked to improve the recovery of the economic saline minerals of the Chilean nitrate deposits.

INTRODUCTION

Humberstonite is a widespread mineral of the nitrate fields in the Atacama Desert of northern Chile. The mineral is most abundant in near-surface layers where it is associated with varying amounts of other saline minerals such as bloedite, $Na_2Mg(SO_4)_2 \cdot 4H_2O$, and soda-niter, $NaNO_3$; it also occurs in small amounts in nitrate ore itself which is below the humberstonite-bearing layer. Humberstonite and niter (KNO_3) are the only two potassium-bearing minerals that have been recognized in the nitrate fields. The new mineral is one of two known sulfate-nitrate minerals; the other is darapskite, $Na_3(NO_3)(SO_4) \cdot H_2O$, a widespread mineral in the Chilean nitrate fields.

Humberstonite-rich sulfate layers have been mined for many years in the Taltal nitrate district, the source area of the material described here. This sulfate is treated together with nitrate ore to produce a potassium-bearing sodium nitrate product which commands a premium price as fertilizer.

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[1] Publication authorized by the Director, U. S. Geological Survey.

Humberstonite (pronounced hŭm′–börstŏnait) is named for James Thomas Humberstone, a chemist who is considered by many to be the father of the modern nitrate industry. Humberstone made many contributions to the technology involving the extraction of nitrate from the Chilean ores, the most important of which was his adaptation of the Shanks process (then used in England for the manufacture of sodium carbonate) to the extraction of $NaNO_3$ from nitrate ore. The new and more efficient process was tested in 1875 and the first Shanks plant was constructed in 1876. Soon most of the 100 nitrate plants of northern Chile had been converted to the Shanks process, producing most of the nitrate during the heyday of the Chilean nitrate industry, from this period until World War I. The description and name of this new mineral were approved by the Commission on New Minerals and Mineral Names, I.M.A. A brief description of humberstonite appeared in an abstract (Ericksen, Fahey, and Mrose, 1968). Specimen material and the purified material (analysis tube sample) were deposited in the U. S. National Museum, Washington, D. C. (USNM 120898).

Humberstonite is probably the same mineral that Wetzel (1928) described and provisionally named Chile-loeweite because of its presumed relation to loeweite, $Na_4Mg_2(SO_4)_4 \cdot H_2O$. Although neither specimens of type Chile-loeweite nor specimens so labelled could be located in museum collections, Wetzel's description indicates that the habit (small hexagonal plates), refractive indices ($\epsilon = 1.434$, $\omega = 1.470$), and specific gravity (2.153) are essentially the same as those of humberstonite. The chemical composition of Chile-loeweite-bearing material, analyzed by Wetzel (1928) and cited in column 7 of Table 1, is similar to that of humberstonite (column 2, Table 1). Wetzel considered Chile-loeweite to be nitrate-free, yielding the formula $K_2Na_4Mg_2(SO_4)_5 \cdot 5H_2O$, after deduction of supposed nitrate-contaminating minerals, soda-niter and darapskite. The field occurrence of Chile-loeweite and humberstonite, as a white sulfate layer, is also similar; Wetzel collected his Chile-loeweite-bearing specimen from a sulfate layer in the vicinity of Oficina Alemania, the source of our analyzed sample of humberstonite.

A new name, humberstonite, was proposed for our mineral because 1) the chemical composition differs significantly from that assigned to Chile-loeweite by Wetzel (1928); 2) the mineral is crystallographically unrelated to loeweite; 3) Chile-loeweite was only a provisional name. The name Chile-loeweite should be abandoned.

The humberstonite-bearing material for the present study was collected by Ericksen during field studies on the Chilean nitrate deposits (1961–1964). This material was first recognized as containing a possible new mineral in the course of mineralogical studies by Mrose and Ericksen

TABLE 1. CHEMICAL ANALYSES OF PURE HUMBERSTONITE COMPARED WITH IMPURE HUMBERSTONITE-BEARING MATERIAL FROM THE NITRATE FIELDS

	Composition in weight percent						
	1	2	3	4	5	6	7
SO_3	42.32	42.99	42.38	34.67	27.21	15.79	43.43
N_2O_5	9.52	9.14	8.64	8.48	12.04	8.74	8.73
Na_2O	19.11	18.43	n.d.	n.d.	n.d.	n.d.	20.51
K_2O	12.45	12.17	12.14	11.74	9.03	4.82	10.83
MgO	7.08	7.47	6.96	5.87	5.26	3.42	7.15
CaO			n.d.	0.94	1.12	1.96	
H_2O (+110°C)	9.52	9.78	10.01	n.d.	n.d.	n.d.	9.05[a]
H_2O (−110°C)		0.40					0.23[a]
Insol.			0.42	8.92	7.66	46.9	
Total	100.00	100.38					99.93

1. Calculated composition of humberstonite, $K_3Na_7Mg_2(SO_4)_6(NO_3)_2 \cdot 6H_2O$.

2. Purified humberstonite from Oficina Alemania, Chile. ($NaNO_3$ leached with acetone; bulk sample contained 17.5 percent $NaNO_3$). Analyst, Joseph J. Fahey.

3. Selected high-purity natural humberstonite from Officina María Elena, Chile. Analysis, courtesy of Anglo-Lautaro Nitrate Corp.

4. Bulk sample of powdery humberstonite-bearing material from Officina María Elena, Chile. Analysis, courtesy of Anglo-Lautaro Nitrate Corp.

5. Bulk sample of hard humberstonite-bearing material from Oficina María Elena, Chile. (Same prospect pit as No. 4). Analysis, courtesy of Anglo-Lautaro Nitrate Corp.

6. Saline-cemented regolith underlying humberstonite-bearing material from Officina María Elena, Chile (Same pit as No. 4 and No. 5). Analysis, courtesy of Anglo-Lautaro Nitrate Corp.

7. Analysis from Wetzel (1928, p. 388) of sulfate layer, assumed to consist mainly of Chile-loeweite [$K_2Na_4Mg_2(SO_4)_5 \cdot H_2O$], soda-niter, and/or darapskite.

[a] Water determined at +115°C and −115°C.

in 1963. Purification of the natural material and the chemical analysis were made by Fahey.

OCCURRENCE

Humberstonite-bearing layers are most extensive in the Taltal nitrate district, being thickest (as much as 40 cm) and most widespread in the vicinity of Oficina Alemania (Fig. 1). Such layers also are found at many other places in the district. The loose covering of the nitrate fields of this district contain isolated pods, thin lenses, and discontinuous thin irregular humberstonite-bearing layers. Thick layers, similar to those near Oficina Alemania, also were found about 10 kilometers west of Oficina María Elena (Fig. 1) and isolated thin layers and pods of humberstonite, in several places in the nearby nitrate fields. In contrast, the very exten-

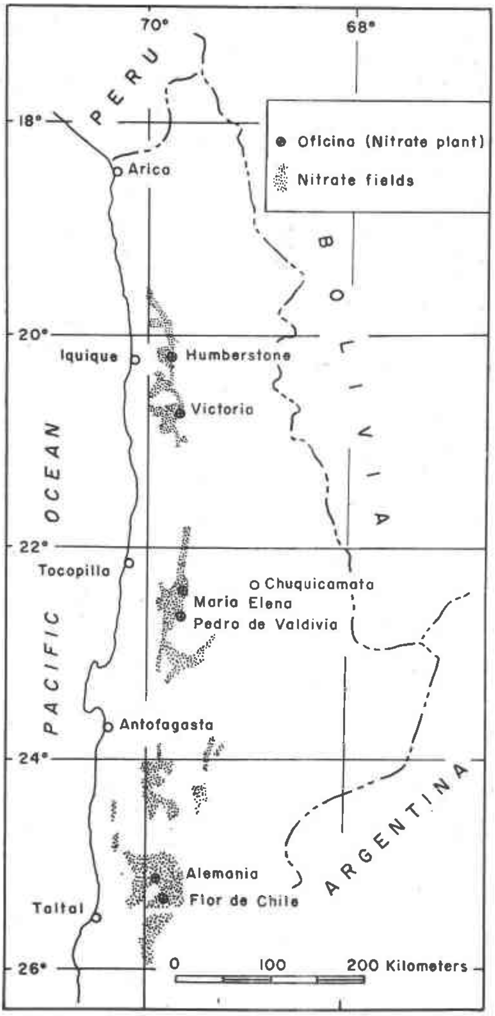

Fig. 1. Index map of Chilean nitrate fields.

sive sulfate layers in the nitrate fields to the southeast of the city of Antofagasta and north of the Taltal fields (Fig. 1), which appear to be the same as those of Oficina Alemania, consist chiefly of thenardite, Na_2SO_4, and bloedite, having little or no humberstonite.

The humberstonite-bearing layers are highly irregular in thickness, pinching and swelling from a few centimeters to a maximum of about 40 centimeters. The more persistent layers that have been mined are gen-

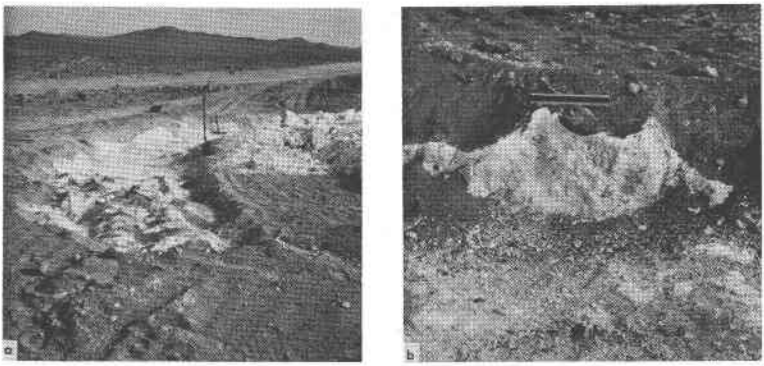

Fig. 2 (a) Humberstonite layer (white) in strip-mine area, Oficina Alemania, Taltal district. (b) Scalloped surface of humberstonite layer, same locality.

erally 20 to 30 cm thick. They are covered with 10 to 40 cm of loose regolith or soil (Fig. 2A) which locally contains considerable amounts of powdery to granular gypsum and small amounts of other saline minerals, or by a friable porous material consisting mainly of silt and sand held together by a meshwork of gypsum crystals. The surface of the humberstonite layer commonly has a scalloped appearance, as shown in Figure 2B. The layer generally rests on hard saline-cemented regolith that contains humberstonite and other saline minerals, including soda-niter. The undersurface of the sulfate layer is also irregular.

The naturally occurring humberstonite consists of hard and soft material but most abundant is a friable granular material that easily crumbles to a powder in the hand. Hard material occurs as lumps in the friable material and locally as an irregular but relatively continuous layer below the friable material. It is very fine grained to vitreous and breaks with a conchoidal fracture. This hard material may generally contain less humberstonite than the softer material with which it is associated, as indicated by the analyses of these two types (columns 4 and 5, Table 1). More analyses, however, are needed to demonstrate such variations in composition.

The humberstonite layers probably formed as the result of slow leaching of nitrate ore, with downward migration of the more soluble salines, such as soda-niter and halite, and concentration of less soluble sulfates, including gypsum, in the surface zone. The relation of the hard and soft materials indicates that the hard material formed first, perhaps as a gel-like substance; and the soft, from it by desiccation and recrystallization under the extremely arid conditions prevailing in the Atacama Desert.

The layers vary considerably in mineralogical composition. Some consist of nearly pure humberstonite; others, principally of sulfate minerals such as bloedite, thenardite, and gypsum. The purest humberstonite encountered in the present study came from the vicinity of Oficina Alemania and Oficina María Elena (Fig. 1), regions where the nitrate ore in nearby fields is relatively high in potassium (commonly 1 to 3 percent K). More typical nitrate ore contains less than 1 percent potassium. The humberstonite-rich layers generally contain several percent of soda-niter, but little or no halite, which is of comparable solubility and which is generally more abundant than soda-niter in nitrate ore and saline-cemented soils of the region.

PHYSICAL AND OPTICAL PROPERTIES

Humberstonite occurs as massive, compact to loose aggregates of thin, colorless and transparent, euhedral crystals, hexagonal in outline, and platy {0001} (Fig. 3). Examination of the crushed aggregates under the binocular microscope (200X) showed crystals mostly less than 0.10 mm in diameter, very uniform and distinctly rhombohedral in habit; crystals as much as 0.30 mm in diameter have been observed. The mineral is brittle; hardness is about $2\frac{1}{2}$; it has perfect cleavage {0001} and irregular fracture; luster is vitreous. The specific gravity, determined at 25°C by the pycnometer method (Fahey, 1961) is 2.252; density calculated from the X-ray data is 2.252 g/cm^3. The mineral does not fluoresce in either long- or short-wave ultraviolet radiation.

Optically, humberstonite is uniaxial negative (−) with $\epsilon = 1.436 \pm 0.002$ and $\omega = 1.474 \pm 0.002$. Twinning has not been observed.

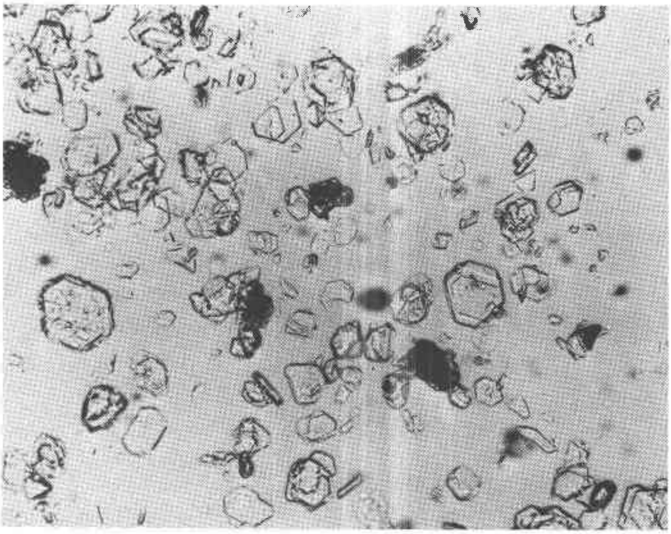

Fig. 3. Photomicrograph of humberstonite crystals (×110).

CRYSTALLOGRAPHY

Morphology. Although minute in size, crystals of humberstonite give excellent basal reflections on the two-circle optical goniometer; the truncating faces give fair to very good signals and fall into three radial zones, clearly revealing a three-fold symmetry axis and an inversion center. From goniometry the dominant forms were identified as $c\{0001\}$ and $r\{10\bar{1}1\}$. Two of the largest crystals that were examined (approximately 0.3 mm in diameter) possessed several extremely narrow, almost line, faces in the radial zones; although these did not permit accurate goniometric measurements leading to positive identification of the forms, their positions in the $[h0\bar{h}l]$ and $[0h\bar{h}l]$ zones suggested that they are positive and negative rhombohedrons of the second and third order.

The morphology of these two large humberstonite crystals, as well as the absence of piezoelectric effects, as determined with the Giebe-Scheibe apparatus, is consistent with the presence of a center of symmetry and indicates that the crystal class is rhombohedral, $\bar{3}$.

X-ray Powder Data. X-ray powder diffraction patterns of humberstonite from Oficina Alemania, Chile, and its synthetic equivalent, $K_3Na_7Mg_2(SO_4)_6(NO_3)_2 \cdot 6H_2O$, were taken with a Debye-Scherrer powder camera (114.59 mm diameter) using the Straumanis and Wilson techniques with Cu/Ni radiation ($\lambda CuK\alpha = 1.5418$ Å) and Cr/V radiation ($\lambda CrK\alpha = 2.2909$ Å). Film measurements were corrected for expansion. All interplanar spacings and intensities for the observed lines of natural and synthetic humberstonite are listed in Table 2, together with calculated values; the intensities of the observed lines were estimated visually by comparison with a calibrated intensity strip. Interplanar spacings for humberstonite and synthetic $K_3Na_7Mg_2(SO_4)_6(NO_3)_2 \cdot 6H_2O$ were calculated from the refined X-ray cell parameters (Table 2) down to the value of $d = 1.2000$.

Single-crystal X-ray Data. Precession photographs of two crystals of humberstonite, each approximately 0.15 mm in diameter, revealed that the mineral has trigonal symmetry, with $R3$ and $R\bar{3}$ as the two possible space groups. From morphological evidence $R\bar{3}$ is preferred.

Preliminary unit-cell constants obtained from single-crystal precession photographs were refined (Table 2) by a least-squares analysis (Evans *et al.*, 1963), using all the observed powder diffraction data of both natural and synthetic humberstonite.

STRUCTURAL RELATION TO UNGEMACHITE

Humberstonite, $K_3Na_7Mg_2(SO_4)_6(NO_3)_2 \cdot 6H_2O$, has a c/a ratio of

Table 2. X-ray Diffraction Powder Data for Humberstonite, $K_3Na_7Mg_2(SO_4)_6(NO_3)_2 \cdot 6H_2O$

	Oficina Alemania, Chile Trigonal, $R\bar{3}$: $a = 10.900 \pm 0.001$, $c = 24.410 \pm 0.002$ Å			Synthetic Trigonal, $R\bar{3}$: $a = 10.896 \pm 0.001$, $c = 24.401 \pm 0.001$ Å		
$hk \cdot l$	Measured[2]		Calculated[1]	Measured[3]		Calculated[1]
	d(Å)	I[4]	d(Å)	d(Å)	I[4]	d(Å)
10.1	8.80	35	8.805	8.81	30	8.801
00.3	8.14	60	8.137	8.13	60	8.134
01.2	7.47	25	7.467	7.47	21	7.464
11.0	5.45	9	5.450	5.45	11	5.448
10.4	5.13	4	5.125	5.13	6	5.123
02.1	4.64	9	4.634	4.64	11	4.632
11.3	4.53	35	4.528	4.52	30	4.527
20.2	4.40	18	4.402	4.40	11	4.401
01.5	—	—	4.336	—	—	4.335
00.6	4.07	25	4.068	4.06	30	4.067
02.4	3.73	25	3.734	3.73	30	3.732
21.1	3.53	3	3.530	3.53	4	3.529
12.2	—	—	3.425	3.42	8	3.423
20.5	3.39	100	3.393	3.39	100	3.392
10.7	3.27	6	3.271	3.27	8	3.270
11.6	—	—	3.260	—	—	3.259
30.0	3.15	4	3.147	3.15	6	3.145
21.4	3.08	6	3.080	3.08	8	3.179
30.3	2.933	6	2.935	2.933	9	2.934
01.8	2.903	25	2.903	2.903	21	2.902
12.5	2.880	25	2.881	2.880	21	2.880
02.7	2.805	11	2.805	2.805	15	2.804
22.0	2.724	70	2.725	2.724	85	2.724
00.9	—	—	2.712	—	—	2.711
13.1	—	—	2.603	—	—	2.602
22.3	2.583	35	2.584	2.584	42	2.583
20.8	—	—	2.562	—	—	2.562
31.2	2.558	18	2.560	2.559	11	2.559

[1] All possible calculated d's listed for $d \geq 2.000$; calculated d's ≤ 1.999 listed only for those measured.

[2] Camera diameter, 114.59 mm; Ni-filtered Cu radiation, ($\lambda CuK\alpha = 1.5418$ Å). Measurements corrected for expansion. Lower limit measurable for 2θ, approximately 6.5° (14 Å).

[3] Camera diameter, 114.59 mm; V-filtered Cr radiation, ($\lambda CrK\alpha = 2.2909$ Å). Measurements corrected for expansion. Lower limit measurable for 2θ, approximately 6.5° (20 Å). D = diffuse.

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

TABLE 2.—(*Continued*)

	Oficina Alemania, Chile Trigonal, $R3$: $a=10.900\pm0.001$, $c=24.410\pm0.002$ Å			Synthetic Trigonal $R\bar{3}$: $a=10.896\pm0.001$, $c=24.401\pm0.001$ Å		
$hk\cdot l$	Measured[2]		Calculated[1]	Measured[3]		Calculated[1]
	d(Å)	I[4]	d(Å)	d(Å)	I[4]	d(Å)
21.7	—	—	2.494	—	—	2.493
30.6	2.488	13	2.489	2.489	13	2.488
11.9	—	—	2.428	—	—	2.427
13.4	2.406	11	2.406	2.405	8	2.405
10.10	2.363	9	2.363	2.363	6	2.362
40.1	—	—	2.349	—	—	2.348
12.8	—	—	2.319	—	—	2.318
04.2	2.317	9	2.317	2.315	7	2.316
31.5	—	—	2.307	—	—	2.306
22.6	—	—	2.264	—	—	2.263
40.4	2.200	21	2.201	2.199	21	2.200
02.10	—	—	2.168	—	—	2.167
01.11	2.160	4	2.160	2.161	2	2.159
32.1	—	—	2.157	—	—	2.156
23.2	—	—	2.132	—	—	2.132
04.5	2.125	6	2.125	2.125	6	2.124
13.7	—	—	2.094	—	—	2.093
14.0	2.060	9	2.060	2.059	6	2.059
30.9	2.055	9	2.054	2.054	6	2.054
32.4	—	—	2.041	—	—	2.040
00.12	2.035	11	2.034	2.033	7	2.033
21.10	—	—	2.015	—	—	2.014
20.11	—	—	2.008	—	—	2.007
41.3	1.9966	3	1.9970	1.9970	4	1.9962
23.5	—	—	1.9796	1.9786	2	1.9789
40.7	1.9539	2	1.9545	—	—	1.9538
22.9	1.9217	4	1.9224	1.9221	4	1.9217
11.12	1.9056	3	1.9058	1.9064	4	1.9051
50.2	1.8661	35	1.8658	1.8666	30	1.8661
41.6	1.8379	6	1.8378	1.8368	8	1.8371
05.4	1.8030	2	1.8037	—	—	1.8030
24.1	1.7785	3	1.7792	1.7855	1	1.7847
42.2	1.7649	6	1.7652	1.7657	6	1.7654
02.13	1.7422	3	1.7447	1.7421	2	1.7441
24.4	1.7105	3	1.7123	1.7107	2	1.7117
31.11	1.6930	2	1.6928	1.6927	2	1.6922
15.2	—	—	1.6793	1.6769	8	1.6787
42.5	1.6766	5	1.6756	—	—	1.6750
05.7	1.6598	5	1.6603	1.6595	4	1.6597
41.9	1.6434	3	1.6405	1.6430	2	1.6399

TABLE 2.—(*Continued*)

	Oficina Alemania, Chile Trigonal, $R\bar{3}$: $a=10.900\pm0.001$, $c=24.410\pm0.002$ Å			Synthetic Trigonal, $R\bar{3}$: $a=10.896\pm0.001$, $c=24.401\pm0.001$ Å		
hk·l	Measured[2]		Calculated[1]	Measured[3]		Calculated[1]
	d(Å)	*I*[4]	*d*(Å)	*d*(Å)	*I*[4]	*d*(Å)
22.12	—	—	1.6301	1.6289	2	1.6295
00.15	1.6287	3	1.6273	—	—	1.6267
15.5	1.6027	2	1.6016	1.6028	2	1.6010
60.0	1.5746	9	1.5733	1.5746	11	1.5727
42.8	1.5401	15	1.5401	1.5400	8	1.5395
52.3	1.4871	3	1.4862	1.4867	4	1.4856
40.13	1.4691	2	1.4694	1.4688	2	1.4688
31.14	1.4507	2	1.4512	1.4507	1	1.4507
24.10	1.4407	2	1.4403	1.4407	1	1.4398
43.7	1.4178	3	1.4179	1.4177	4	1.4173
22.15	1.3968	4	1.3972	1.3971	4	1.3967
61.5	1.3813	2	1.3808	1.3811	3	1.3803
44.0	1.3628	9	1.3625	1.3627	11	1.3620
44.3	1.3440	2	1.3438	1.3441	2D	1.3433

Plus seven additional weak lines with $I \leq 4$.

2.239, close to that of the rare mineral ungemachite, $K_3Na_8Fe^{3+}(SO_4)^6(OH)_2\cdot 10H_2O$ (Peacock and Bandy, 1938), which has a c/a ratio of 2.290. Their crystallographic data, compared in Table 3, are remarkably close. In addition, both minerals have similar crystal habit, have perfect cleavage parallel to (0001), are readily soluble in water, and give X-ray powder patterns that indicate that they must be structurally related. Although humberstonite and ungemachite do not have the same type of chemical formula, as used in the strictest sense of the term, the evidence presented above suggests that these minerals, though not isostructural, must possess strikingly similar structural configurations.

The formulas assigned to ungemachite (see Table 3) are based on the only reported chemical analysis (Peacock and Bandy, 1938). Material available on museum specimens is insufficient for a new chemical analysis. Crystals of ungemachite, averaging 1 mm, and as much as 1.5 mm, in diameter, were synthesized in large quantity by Mrose for investigation of the chemical and structural relations of humberstonite and ungemachite. The physical and optical properties, X-ray crystallography, and chemistry of synthetic ungemachite are being investigated.

TABLE 3. CRYSTALLOGRAPHIC DATA COMPARED FOR HUMBERSTONITE AND UNGEMACHITE

	Humberstonite: Present Study	Ungemachite: Peacock and Bandy (1938)[a]	
Locality	Oficina Alemania, Chile	Chuquicamata, Chile	
Symmetry	Hexagonal-*R*; rhombohedral-$\bar{3}$	Hexagonal-*R*; rhombohedral-$\bar{3}$	
Cell Constants			
a	10.900 ± 0.001 Å	10.86 ± 0.02 Å	
c	24.410 ± 0.002 Å	24.87 ± 0.05 Å	
c/a	2.239	2.290	
$a^{2\text{rh}}$	10.286 Å	10.39 ± 0.02 Å	
α	64°00′	63°00′	
Space Group	$R\bar{3}$	$R\bar{3}$	
Volume (hex.)	2512 Å^3	2540 Å^3	
Cell Contents	$3[K_3Na_7Mg_2(SO_4)_6(NO_3)_2 \cdot 6H_2O]$	$3[K_3Na_8Fe^{3+}(SO_4)_6(OH)_2 \cdot 10H_2O]^b$	$3[K_3Na_9Fe^{+3}(SO_4)_6(OH)_3 \cdot 9H_2O]^c$
Density (calc.)	2.252 gcm^{-3}	2.251 gcm^{-3d}	2.294 gcm^{-3d}
(obs.)	2.252 (at 25° C)	2.287	2.287

[a] Cell constants recalculated from kX to Å units by present authors.

[b] Formula suggested by Berman (Peacock and Bandy, 1938).

[c] Formula suggested by Frondel (Palache *et al.*, p. 596–597, 1951)

[d] Calculated by present authors.

CHEMICAL PROPERTIES

Microscopic and X-ray diffraction powder studies showed humberstonite-rich material to be eighty to ninety percent pure, with soda-niter the only other mineral present in more than trace quantities. Preparation of a humberstonite sample free of soda-niter posed a serious problem. Efforts to separate the humberstonite from the soda-niter by means of a heavy liquid were not successful. It was found experimentally that humberstonite is insoluble in acetone, whereas soda-niter is very slowly soluble. By repeated treatment with acetone over a ten-month period it was possible to completely remove the soda-niter.

A humberstonite-rich sample that initially weighed three hundred grams was sieved; the fraction that passed the 200 mesh sieve contained the smallest percentage of soda-niter; this fraction (approximately 40 grams) was used in the preparation of a purified sample for the chemical analysis. An X-ray powder diffraction pattern taken of the acetone-treated sample showed no trace of lines attributable to soda-niter.

The chemical analysis of the purified humberstonite sample is cited in Table 1 (column 2), as well as the calculated composition of humberstonite, $K_3Na_7Mg_2(SO_4)_6(NO_3)_2 \cdot 6H_2O$, and analyses of natural humberstonite-bearing material from several localities. Slight differences in the analysis of purified material and the calculated composition of humberstonite are considered to be due largely to the presence of kieserite, $MgSO_4 \cdot H_2O$, which was found in the unpurified material.

A microspectrochemical analysis of handpicked crystals of humberstonite from Oficina Alemania was made by Claude E. Waring of the U. S. Geological Survey. The major cations found present were K, Na, and Mg; also present were trace amounts of Ca, Si, Cu, and Fe. Greater amounts and a wider variety of contaminating elements and ions present in natural humberstonite-bearing material (Table 4) are probably due to several admixed saline minerals as well as fine rock particles.

Humberstonite is readily soluble in water, about one gram dissolving in five milliliters, but is insoluble in acetone and alcohol.

When heated in a closed tube, humberstonite first gives off its water; upon further heating, brown fumes of oxide of nitrogen are released and fill the tube. Weight losses due to these changes are shown by the loss on heating curve (Fig. 4): nearly all the water is lost between 110° and 130°C, and nitrogen oxide, between 460° and 590°C. At about 700°C differential melting occurs and magnesium oxide remains in the solid phase in a melt of alkali sulfates. Quantitative analysis of the magnesium oxide indicated that it is stoichiometrically equivalent to the nitrate in the analyzed humberstonite.

Laboratory tests showed that at room temperature (20°–25°C) hum-

Table 4. Trace Elements and Ions in Humberstonite-Bearing Material, Oficina María Elena (Chile)

[Data, obtained by spectrographic and wet chemical analyses, furnished by Roy E. Cameron, Jet Propulsion Laboratory, California Institute of Technology]

Element or Ion	Wt. Percent	Element or Ion	Wt. Percent
Ca	0.49	B	0.018
Si	.29	NH_4	.0052
Al	.24	Ti	.0044
Fe	.078	Cr	.0044
Cl	.06	I	.003
CO_3	.055	NO_2	.0002
PO_4	.043	Cu	.00057

berstonite crystallizes from water solutions in which the relative amounts of the component ions differ from their formula weights. Solutions of natural humberstonite-rich material from several localities (contaminated with an estimated 5 to 20 percent of soda-niter) and of a stoichiometric mixture of chemical reagents were evaporated. Picromerite,

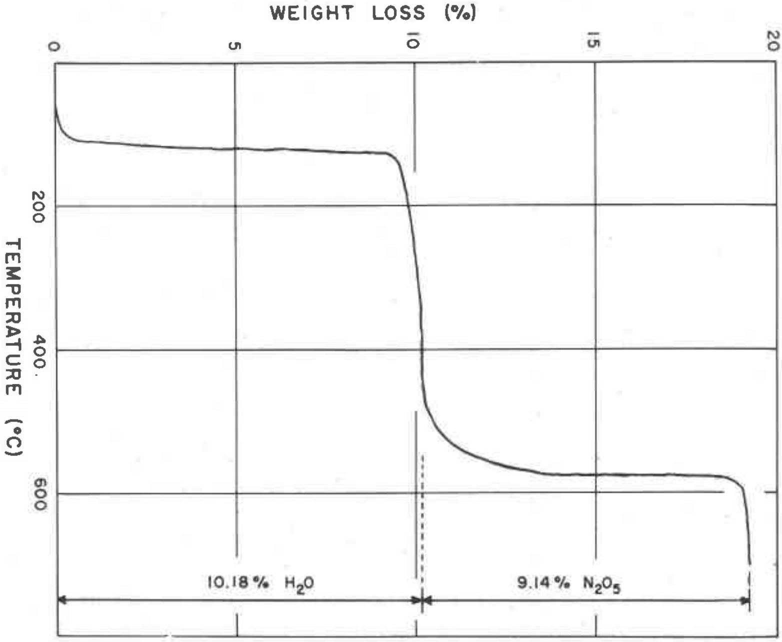

Fig. 4. Weight-loss heating curve of humberstonite.

$K_2Mg(SO_4)_2 \cdot 6H_2O$, was the first substance to crystallize from these solutions, followed by darapskite, and finally, humberstonite. As each successive mineral formed, crystals of the earlier mineral became corroded, indicating reaction with the solution in response to its changing composition. These reactions, however, were slow and evaporation, over periods of as long as 2 to 3 weeks, still yielded residues containing all three minerals.

INFRARED CHARACTERISTICS

The infrared spectrum (Fig. 5) was made under the direction of Irving A. Breger of the U. S. Geological Survey. The instrument used was a Perkin-Elmer model 21 spectrophotometer with NaCl optics. The spectrum was made of a pellet consisting of 1 milligram of handpicked humberstonite crystals in 300 milligrams of KBr, prepared at room temperature and analyzed against a reference 300-milligram pellet of KBr, also prepared at room temperature. The sample was also analyzed at 110°C, giving a spectrum almost identical to that shown in Figure 5. The two traces differ only in slight shifting of some of the absorption peaks, probably due to slight expansion of the crystal lattice upon heating.

For comparison, Figure 5 also shows the infrared spectrum of darapskite (Ericksen and Mrose, 1970), the only other known sulfate-nitrate mineral.

The infrared absorption peaks for humberstonite (Table 5) were identified with the aid of information about infrared spectra of sulfates and

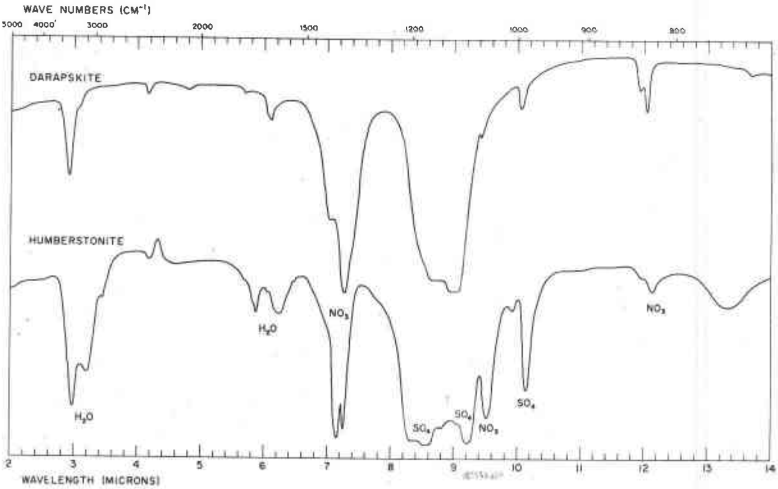

Fig. 5. Infrared traces of humberstonite and darapskite.

TABLE 5. ABSORPTION WAVELENGTHS FOR INFRARED SPECTRUM OF HUMBERSTONITE SHOWN IN FIGURE 6

H_2O		NO_3				SO_4	
ν_s[1]	ν_b[2]	ν_1	ν_2	ν_3	ν_4	ν_1	ν_3
2.98 (3350)	5.86 (1708)	9.51 (1052)	12.12 (825)	7.15 (1400)	13.32 (751)	10.13 (986)	8.33 (1201)
3.19 (3130)	6.24 (1603)			7.25 (1380)			8.55 (1168)
							9.22 (1085)

[1] ν_s = stretching mode (ν_1 and ν_3)
[2] ν_b = in-plane bending mode (ν_2)

nitrates that have been reported in the literature (Adler, 1965; Adler and Kerr, 1965; and Weir and Lippincott, 1961).

ACKNOWLEDGMENTS

We are grateful to the Anglo-Lautaro Nitrate Corporation, owner of Oficina María Elena, and the Compañia Salitrera Iquique, owner of Oficina Alemania, for information and hospitality during field work. Oficina María Elena made several special analyses of samples of humberstonite-bearing material. Special acknowledgment is given to the late Frank T. Humberstone, who like his father, James T. Humberstone, for whom humberstonite is named, was an important and well-loved figure of the nitrate industry. He gave much first-hand information about the nitrate deposits that has been invaluable to our studies. It was his suggestion that the final *e* in the name Humberstone be dropped from the mineral name to make it more easily pronounceable in Spanish. His death in 1966 ended the long and intimate association of the Humberstone family with the Chilean nitrate industry.

Our thanks are extended to these colleagues at the U. S. Geological Survey for their assistance in our study: to Irving A. Breger, for the infrared analyses and assistance in the interpretation of their curves; to Judith Konnert, for the unit-cell refinements; to Frederick Simon, for thermogravimetric analyses and curves of purified and natural humberstonite that supplemented the weight-loss curve; and to Claude E. Waring, for the microspectrochemical analysis. We also thank Roy E. Cameron, Jet Propulsion Laboratory, California Institute of Technology, for the spectrographic and wet chemical data presented in Table 4.

The investigation on which this work is based was carried out in cooperation with the Instituto de Investigaciones Geológicas of Chile.

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Manuscript received, October 3, 1969; accepted for publication, February 5, 1970.