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# MINERALOGICAL STUDIES OF THE NITRATE DEPOSITS OF CHILE I. THE IDENTITY OF NITROGLAUBERITE WITH DARAPSKITE<sup>1</sup>

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#### Abstract

The validity of nitroglauberite, supposedly  $6NaNO_3 \cdot 2Na_2SO_4 \cdot 3H_2O$ , described and named as a new mineral by Domeyko in 1871 from the Reventon mine, Paposo region, Chile, has been questioned repeatedly. Examination was made of three museum specimens of alleged nitroglauberite; material from a specimen labeled "nitro sulfato de sodio" in the Domeyko Mineral Collection, Escuela Universitaria de Minas, La Serena, Chile, (perhaps type material) was found to be a mixture of darapskite and soda-niter. Recalculation of Domeyko's analysis of nitroglauberite, after deducting 40.23 percent NaNO<sub>3</sub>, gave a formula close to that of darapskite, Na<sub>3</sub>(NO<sub>3</sub>)(SO<sub>4</sub>)  $\cdot$  H<sub>2</sub>O. The optical data given by Larsen (1921) for nitroglauberite were made on a sample that is now shown to be trona.

Although the name nitroglauberite (1871) has priority over darapskite (1891), the description was incomplete and the composition assigned to it differed significantly from that of darapskite. Therefore, it is recommended that the name nitroglauberite be dropped.

## INTRODUCTION

In the course of the mineralogical study of darapskite from the nitrate deposits of Chile (Ericksen and Mrose, Amer. Mineral., in preparation) the validity of nitroglauberite as a mineral species was suspect. Investigations relating to this problem were carried out as part of a broad study of the Chilean nitrate deposits in cooperation with the Instituto de Investigaciones Geológicas of Chile. Our subsequent studies indicate that the material described as nitroglauberite by Domeyko (1871) consisted of a mixture of darapskite,  $Na_3(NO_3)(SO_4) \cdot H_2O$ , and soda-niter, NaNO<sub>3</sub>. Both minerals are known to occur as fibrous material in veins in nitrate ore, and as darapskite had not yet been described in 1871, Domeyko could easily have misidentified as a single mineral such an intimate mixture.

## NITROGLAUBERITE: ITS OCCURRENCE AND DESCRIPTION

Nitroglauberite, supposedly of composition  $6NaNO_3 \cdot 2Na_2SO_4 \cdot 3H_2O$ (=2[Na<sub>5</sub>(NO<sub>3</sub>)<sub>3</sub>(SO<sub>4</sub>)  $\cdot 1\frac{1}{2}H_2O$ ]), was described as a new mineral species by Domeyko (1871). Specimens of this new mineral had been collected by Dr. Schwartzemberg of Copiapó, Chile, from the south side of the hill, at the Reventon mine locality in the Paposo region of the Atacama Desert, Chile (Fig. 1). He sent these specimens to Domeyko for examination and study. Schwartzemberg had observed that these specimens con-

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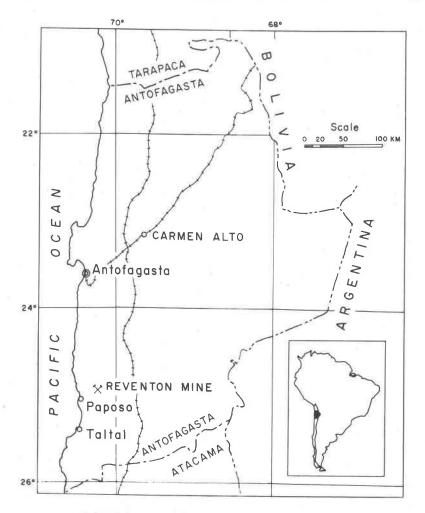


FIG. 1. Index map of the province of Antofagasta, Chile.

sisted of a natural nitrate mineral completely free of halite. Domeyko's chemical analysis of the mineral indicated that it was composed entirely of sodium nitrate (60.35%), sodium sulfate (33.90%), and water (5.75%), in the ratio 6:2:3, respectively. On the basis of these results Domeyko (1871) concluded that Schwartzemberg's mineral represented a new species and subsequently assigned to it the name nitroglauberite.

Domeyko (1871, p. 46) characterized nitroglauberite as follows:

The mineral is a homogeneous mass; translucent white; small fragments are without color, transparent, have shiny glassy luster; structure is fibrous; fibers are thick prismatic,

straight, irregular; in part with randomly oriented crystals or crystals forming imperfect crosses parallel to crystal axes; irregular transverse fracture; not deliquescent or efflorescent; very soluble in water ...; very fusible, fusing at start of red color and losing  $5\frac{7}{10}$  of its weight. When dissolved in cold water, if not enough water is added to dissolve all the salt, it decomposes, forming large prismatic crystals of sodium sulfate decahydrate and the nitrate is dissolved. The same crystals also form when at  $40-50^{\circ}$  the quantity of water necessary to completely dissolve the salt is added and the solution is chilled.

The natural salt was discovered to have only traces of chloride (tested with AgNO<sub>3</sub>) . . .

On a later occasion Schwartzemberg sent Domeyko more than 20 kg of the same mineral from Paposo. In the second lot, in addition to fragments of "fibrous pure nitroglauberite identical to the sample analyzed," Domeyko (1871, p. 47) reported others of mixed material in which "at the sides of the lustrous (glassy) fibrous parts, one sees platy material, with thick, flat, white, less lustrous plates interlaced with the first (fibrous) material." Domeyko found that these heterogeneous samples in Schwartzemberg's second lot contained halite, less sulfate, less water, and a greater proportion of sodium nitrate than did those of the first lot.

No other occurrences or finds of nitroglauberite have since been recorded in the literature.

# VALIDITY OF NITROGLAUBERITE AS A MINERAL SPECIES

The existence of nitroglauberite as a valid mineral species was questioned as early as 1912. At that time Brendler (1912, p. 170) stated that "'Nitroglauberit' ist jedenfalls ein dichtes Gemenge von Darapskit und Natronsalpeter."

Later, on the basis of the results of his investigations in the system  $NaNO_3-Na_2SO_4-H_2O$  at 35°C, Foote (1925) concluded that the alleged mineral nitroglauberite does not exist, but is essentially a mixture of sodium nitrate and darapskite. Foote's experimental data only excluded the formation of this mineral below 35°C. Foote (1925) remarked that the formation of nitroglauberite at a higher temperature is precluded by the fact that, according to its alleged composition, the mineral contains somewhat more water than a mixture of sodium nitrate and darapskite would require; therefore, it should be formed, if at all, at a temperature below 35°C. Hamid (1926) also noted that the only double salt that exists in this same system at 25°C is darapskite; at 90°C the only stable phases he found in the system are the two anhydrous salts, sodium sulfate and sodium nitrate.

Dana (1892, p. 873) makes reference under nitroglauberite to an artificial salt having the composition  $2NaNO_3 \cdot 2Na_2SO_4 \cdot 3H_2O$ , a compound that had been synthesized and briefly described by Marignac (1857, p. 44-45). Later, de Schulten (1896) pointed out that the habit and interfacial angles of the crystals prepared by Marignac are in good agreement

|                   | Synthetic of Marignac             | Darapskite                               |
|-------------------|-----------------------------------|--|
|                   | Marignac (1857)<br>Weight Percent | Calculated Composition<br>Weight Percent |
| Na <sub>2</sub> O | 36.91                             | 37.94                                    |
| SO3               | 32.39                             | 32.67                                    |
| $N_2O_5$          | 21.23                             | 22.04                                    |
| $H_2O$            | 10.35                             | 7.35                                     |
| Total             | 100.88                            | 100.00                                   |

TABLE 1. ANALYSES OF DARAPSKITE

with those obtained for synthetic darapskite by Osann (1894). Recalculation of Marignac's chemical analysis by the present authors leads to the formula  $Na_3(NO_3)(SO_4) \cdot 1\frac{1}{2}H_2O$  which, except for a slight excess of water, is very close to that of darapskite,  $Na_3(NO_3)(SO_4) \cdot H_2O$ . See Table 1.

# "NITROGLAUBERITE" SPECIMENS

Specimens labelled nitroglauberite were located in three mineral collections: 1) Muséum National d'Histoire Naturelle in Paris; 2) U. S. National Museum in Washington, D. C. (USNM R5802); and 3) Domeyko Mineral Collection, Escuela Universitaria de Minas, La Serena, Chile. These were subjected to critical examination in order to evaluate the validity of nitroglauberite as a mineral species.

The specimen of nitroglauberite in the Paris museum had been listed as such in the catalogue of the mineral collection that had been compiled by Lacroix (1931); this specimen, re-labelled darapskite, was made available to us through the kindness of Mlle Simonne Caillère. It came from Carmen Alto, Chile, a railroad station in the nitrate fields northeast of Antofagasta (Fig. 1). Our examination of this specimen confirmed the presence of exceptionally fine platy crystals of darapskite; associated with these darapskite crystals were small amounts of halite and creamy white to pale orange, fine-grained aggregates which proved to be mixtures of quartz and feldspar.

The second specimen of so-called nitroglauberite (USNM R5802), labelled only Atacama, Chile (a specific locality not given), consisted of a vial containing the remaining fragments of material that had been studied optically by Larsen (1921). His optical determinations on this material have been recorded in the literature as being those for nitroglauberite. An X-ray powder diffraction pattern of Larsen's studied material proved it to be trona,  $Na_3H(CO_3)_2 \cdot 2H_2O$ . This is the first known recorded occurrence of trona in Chile. Table 2 compares Larsen's optical data for nitroglauberite (= trona) with those cited in the literature for trona from various localities. Consideration of the chemical composition of trona,  $Na_3H(CO_3)_2 \cdot 2H_2O$ , eliminates this mineral as having been described by Domeyko (1871) as nitroglauberite,  $6NaNO_3 \cdot 2Na_2(SO_4) \cdot$  $3H_2O$ .

A search for specimens of nitroglauberite in the Domeyko Mineral Collection at the Escuela Universitaria de Minas in La Serena was made

|                  | Nitroglauberite            | Trona                      | Trona                                 | Trona                      |  |
|------------------|----------------------------|----------------------------|---------------------------------------|----------------------------|--|
|                  | Atacama, Chile             | Sweetwater<br>County, Wyo. | Searles Lake,<br>Calif.               | Vesuvius, Italy            |  |
|                  | (Larsen, 1921)             | (Fahey, 1962)              | (Larsen, 1921)                        | (Larsen, 1921)             |  |
| Habit            | Stout laths                | _                          |                                       | Lath-shaped                |  |
| Optic sign       | Negative $(-)$             | Negative $(-)$             | Negative $(-)$                        | Negative $(-)$             |  |
| α                | $1.418 \pm 0.003$          | $1.417 \pm 0.002$          | $1.410 \pm 0.003$                     | $1.413 \pm 0.005$          |  |
| β                | $1.500 \pm 0.003$          | $1.494 \pm 0.002$          | $1.492 \pm 0.003$                     | $1.492 \pm 0.003$          |  |
| $\gamma$         | $1.543 \pm 0.003$          | $1.543 \pm 0.002$          | $1.542 \pm 0.003$                     | $1.538 \pm 0.003$          |  |
| 2V (meas.)       | $61^{\circ} \pm 5^{\circ}$ |                            | · · · · · · · · · · · · · · · · · · · | 3 <del></del>              |  |
| (calc.)          | $68^{\circ} \pm 3^{\circ}$ | 74°                        | $72^\circ \pm 5^\circ$                | $72^{\circ} \pm 5^{\circ}$ |  |
| Orientation      |                            |                            |                                       |                            |  |
| X                | elongation                 |                            |                                       | elongation                 |  |
| $\boldsymbol{Y}$ | ⊥ lath                     |                            |                                       | $\perp$ flat face          |  |
| Z                | ⊥ probable pf. clv.        |                            | nearly $\perp$ pf. clv.               | $\perp$ thin face          |  |
| Dispersion       | r < v, rather strong       | r < v                      | r < v, rather strong                  | 1.000                      |  |

Table 2. Comparison of Optical Properties of Nitroglauberite  $(=T_{RONA})$  and Trona

by Sr. Federico Peebles L. of the Instituto de Investigaciones Geológicas of Chile. Material labelled nitroglauberite was not found in this collection but Sr. Peebles did locate therein one specimen labelled "nitro sulfato de sodio" from the Reventon mine locality (the type locality of nitroglauberite). A small portion of the specimen was made available to us for study purposes. It contained two types of colorless, translucent, saline minerals: one, compact fibrous (thin columnar); the other, massive crystalline. The X-ray powder diffraction pattern of the former is that of darapskite; of the latter, that of soda-niter.

## Physical and Chemical Considerations

The physical and chemical properties ascribed to nitroglauberite are listed in Table 3 for comparison with those of darapskite; they are virNITROGLAUBERITE WITH DARAPSKITE

| Locality               | Nitroglauberite<br>(Domeyko, 1871)  | Darapskite<br>(Ericksen and Mrose, in prep.<br>Taltal nitrate district, Chile |  |
|------------------------|-------------------------------------|---|--|
|                        | Paposo region, Chile                |   |  |
| Habit                  | Thick prismatic; platy              | Long prismatic; platy   |  |
| Color                  | Colorless to white                  | Colorless   |  |
| Luster                 | Glassy                              | Vitreous  |  |
| Diaphaneity            | Transparent to translucent          | Transparent to translucent  |  |
| Solubility             | Very soluble in water               | Easily soluble in water   |  |
| Fusibility             | Very fusible                        | Easily fusible  |  |
| Reaction in atmosphere | Not deliquescent or<br>efflorescent | Not deliquescent or<br>efflorescent   |  |

TABLE 3. COMPARISON OF THE PROPERTIES OF NITROGLAUBERITE AND DARAPSKITE

tually the same for the two minerals and present strong support for the identity of nitroglauberite with darapskite.

Comparison of the chemical analysis of nitroglauberite (Domeyko, 1871) with the calculated composition of darapskite (Table 4, columns 1 and 2) does not support the contention that the two minerals are identical. As will be shown, it is probable that the nitroglauberite of Dr. Schwartzemberg is a mixture of darapskite and soda-niter, minerals that are abundant in the nearby nitrate fields.

| ×.                | Darapskite<br>(Calculated<br>Composition) | Nitroglauberite<br>(Domeyko, 1871)ª         | Nitroglauberite<br>(after deducting<br>40.23% NaNO <sub>3</sub> ) <sup>b</sup> | Atomic Ratios<br>to 8 oxygens |
|-------------------|---|---|--|-------------------------------|
| Oxides            | (1)                                       | (2)   | (3)  | (4)                           |
| Na <sub>2</sub> O | 37.94                                     | 36.80                                       | 37.02  | Na 2.88                       |
| $N_2O_5$          | 22.04                                     | 38.34                                       | 21.39  | N 0.95                        |
| $SO_3$            | 32.67                                     | 19.11                                       | 31.97  | S 0.96                        |
| $H_2O$            | 7.35                                      | 5.75  | 9.62   | Н 2.57                        |
| Total             | 100.00                                    | 100.00                                      | 100.00   |                               |
| Formula           | $Na_3(NO_3)(SO_4) \cdot H_2O$             | $Na_5(NO_3)_3(SO_4)\cdot 1\tfrac{1}{2}H_2O$ | (Empirical): Na <sub>3</sub>   | $(NO_3)(SO_4) \cdot H_2$      |

TABLE 4. COMPARISON OF CHEMICAL COMPOSITION OF NITROGLAUBERITE AND DARAPSKITE

 $^a$  Domeyko's analysis (NaNO\_3 60.35%, Na\_2SO\_4 33.90%, H\_2O 5.75%) recalculated to oxides by present authors.

 $^{b}$  Recalculated to 100 percent after deducting the equivalent of  $4(NaNO_{3})$  in weight percent from original analysis.

If Domeyko's formula for nitroglauberite, 6NaNO<sub>3</sub> · 2Na<sub>2</sub>SO<sub>4</sub> · 3H<sub>2</sub>O, is recast to read  $2[Na_5(NO_3)_3(SO_4) \cdot 1\frac{1}{2}H_2O]$  and then compared with that of darapskite,  $2[Na_3(NO_3)(SO_4) \cdot H_2O]$ , the nitroglauberite formula differs from the darapskite formula only by containing four molecules more of NaNO<sub>3</sub> and one molecule more of H<sub>2</sub>O; this slight excess of water could easily have resulted from analytical error. Recalculation of Domeyko's original analysis of nitroglauberite (NaNO<sub>3</sub>, 60.35; Na<sub>2</sub>SO<sub>4</sub>, 33.90; and H<sub>2</sub>O, 5.75%), after deducting therefrom 40.23 percent NaNO<sub>3</sub> (equivalent to 4[NaNO<sub>3</sub>] in weight percent) and then converting to oxides, leads to the results tabulated in column 3 of Table 4. The atomic ratios, based on 8 oxygens, given in column 4 (Table 4) are close to the empirical formula for darapskite, Na<sub>3</sub>(NO<sub>3</sub>)(SO<sub>4</sub>) · H<sub>2</sub>O. This strongly supports our supposition, as well as that stated by Brendler (1912) and Foote (1925), that the original sample of so-called nitroglauberite analyzed actually represented a mixture of darapskite and soda-niter. In support of our theoretical calculation of the mineral composition of nitroglauberite, a solution containing 402.3 mg NaNO<sub>3</sub> and 598.7 mg synthetic darapskite was made and slowly evaporated at room temperature (20-25°C); the first crystallization product consisted of large, colorless, prismatic crystals of darapskite; later, crystals of soda-niter formed and upon completion of evaporation remained admixed with darapskite crystals.

### CONCLUSIONS

The results of our investigations corroborate the statements of Brendler (1912) and Foote (1925) that so-called nitroglauberite represents a mixture of two minerals, darapskite and soda-niter. Although the name nitroglauberite has priority, the description of this mineral was incomplete and the formula derived from the chemical analysis such that when Dietze (1891) described darapskite, he did not relate the identity of his new mineral to that previously described as nitroglauberite (Domeyko, 1871). Because the characterization of darapskite is so well-defined (Dietze, 1891), its description and name, though later than that of nitroglauberite, should be retained. We recommended that nitroglauberite be deleted from the list of accepted mineral species; this recommendation has been accepted by vote of the Commission on New Minerals and Mineral Names, I.M.A. (Michael Fleischer, Chairman of the Commission, written comm., 1967).

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National Museum (Washington, D. C.); and Sr. Federico Peebles L., Instituto de Investigaciones Geológicas of Chile (Santiago, Chile).

### References

- BRENDLER, WOLFGANG (1912) Mineralien-Sammlungen; ein Hand- und Hilfsbuch für Anlage und Instandhaltung mineralogischer Sammlungen, Vol. II. Wilhelm Engelmann, Leipzig, 699 pp.
- DANA, EDWARD SALISBURY (1892) System of Mineralogy 6th ed. John Wiley and Sons, New York 1134, pp.

DIETZE, AUGUST (1891) Einige neue chilenische Mineralien. Z. Kristallogr., 19, 443-451.

- DOMEYKO, IGNACIO (1871) Mineralojia, 2nd ed.: Tercer apéndice al reino mineral de Chile i de las repúblicas vecinas. Imprenta Nacional, Santiago de Chile, 64 pp.
- FAHEY, JOSEPH J. (1962) Saline minerals of the Green River Formation. U. S. Geol. Surv. Prof. Pap. 405, 50 pp.

FOOTE, H. W. (1925) The system sodium nitrate-sodium sulphate-water, and the minerals darapskite and nitroglauberite. *Amer. J. Sci.*, 9, 441–447.

HAMID, MOHAMMED ABDUL (1926) Heterogeneous equilibria between the sulphates and nitrates of sodium and potassium and their aqueous solutions. Part I. The ternary system. J. Chem. Soc., 128, 199-205.

LACROIX A. (1931) Collection de Minéralogie du Muséum National D'Histoire Naturelle. Masson et Cie, Paris, 136 pp.

LARSEN, ESPER S. (1921) The microscopic determination of the non-opaque minerals. U. S. Geol. Surv. Bull., 679, 294 pp.

MARIGNAC, C. (1857) Sur les formes cristallines et la composition chimique de divers sels. Ann. Mines, ser. 5, 12, 1-74.

OSANN, A. (1894) Kristallographische Untersuchung einiger neuer chilenischer Mineralien: Z. Kristallogr., 23, 584–586.

DE SCHULTEN, A. (1896) Sur la reproduction artificielle de la darapskite. Bull. Soc. Fr. Minéral. Cristallogr., 19, 161-164.

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