

NICKELIAN EPSOMITE FROM NORTH AUCKLAND, NEW ZEALAND

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ABSTRACT

The optical and chemical properties of nickelian epsomite are described, and the physical constants are found to coincide with the appropriate curves in the epsomite-morenosite series. Attention is drawn to the deficiency in the water content, which, it is believed, results from the relatively loose nature of the bonds holding one of the molecules of water within the structure. The action of sulfuric acid derived from oxidizing pyrrhotite on serpentinite and pentlandite is suggested for the occurrence.

OCCURRENCE

The mineral described herein as nickelian epsomite was found as efflorescent patches of pale blue-green crystals on freshly broken surfaces of serpentinite in Gordon's Quarry, Kaukapakapa, about thirty miles northwest from Auckland City. The host rock is a serpentinite of the dunite type enclosing scattered, irregularly shaped grains of pentlandite-bearing pyrrhotite, and it is on these sulfidic areas that nickelian epsomite has crystallized. In the same quarry nickel-free epsomite¹ was also observed at other points on the serpentinite surface, but in these instances only traces of nickel were detected in the associated pyrrhotite.

Nickelian epsomite formed clusters of minute needle-like crystals that rarely exceeded 4 mm. in length, and averaged very much less; the areas covered by these efflorescences were about nine to twelve inches square.

CHEMICAL PROPERTIES

The mineral is very soluble in cold water to give a slightly acid solution with a very bitter and astringent taste, and qualitative chemical tests showed that magnesium, nickel, the sulfate radical, and water were the only constituents present; the absence of aluminum and particularly iron, is noteworthy. Water is evolved from the crystals very readily and the greater percentage of it is lost below 105° C. After heating to about 300° C. a pale yellow to greenish-yellow anhydrous powder remains.

An analysis of a very small quantity of the mineral, made by Mr. F. T. Seelye, is given in Table 1. In a second determination of total water by fusion with sodium carbonate (Gooch method) Mr. Seelye obtained a

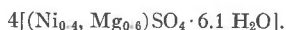
¹ Optics determined for this mineral are as follows: $\alpha=1.434$, $\beta=1.456$, $\gamma=1.461$; $\gamma-\alpha=0.027$. $2V=52^\circ$. Microchemical tests proved the absence of both iron and nickel.

TABLE 1. ANALYSIS OF NICKELIAN EPSOMITE

NiO		12.22%
MgO		9.81
SO ₃		33.05
H ₂ O	{ at 105° C. 38.78 }	44.92
	{ 105° - 225° C. 1.62 }	
	{ >225° C. 4.52* }	
		100.00%

* Determined by difference.

figure of 44.8 per cent. Since the heptahydrates of magnesium and nickel sulfates contain four molecules to the unit cell (Westenbrink, 1926; Cardoso, 1926) the analysis above may be recalculated and expressed approximately as follows:



PHYSICAL PROPERTIES

Aggregates of acicular crystals of nickelian epsomite are pale blue-green in color (16V in Radde's color scale), but individual crystals appear to be quite colorless when immersed in refractive index media. Crystals are elongated parallel to the Y vibration direction of the refractive index ellipsoid and in addition they show a marked flattening parallel to the plane containing the X and Y directions. Hence the majority of the crystals are positively elongated whereas only relatively few are found to be fast in that direction. The range of refractive indices determined by the immersion method in sodium light is as follows:

$$\begin{aligned} \alpha &= 1.446 - 1.448 \pm 0.002 \\ \beta &= 1.470 \\ \gamma &= 1.472 - 1.474 \\ \gamma - \alpha &= 0.026 \end{aligned}$$

Since the mineral readily loses water when it is heated it was not considered desirable to mount it in Canada balsam for immediate optic axial angle determination; instead a few needles were cemented in the cold state on a glass slip with clarite. The average of a number of measurements of the angle $2V$ was $47^\circ \pm 2^\circ$; there is a negative optic sign and no dispersion.

One fair cleavage was noted normal to the direction of prominent flattening, (010) cleavage, and a poor cleavage, probably (011), was seen to bevel the ends of the acicular crystals in a number of instances. Details of the optic orientation are shown diagrammatically in Fig. 1.

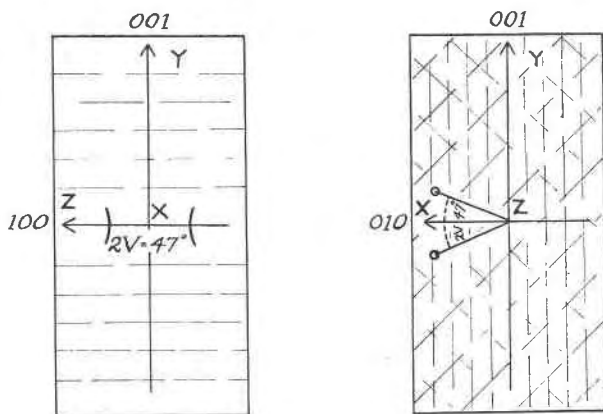


FIG. 1. Optical orientation of nickelian epsomite.

DISCUSSION OF PROPERTIES

There are two significant points in connection with this mineral that require comment, and it is necessary that they should be considered at the same time.

(a) The number of water molecules is less than the theoretical figure for a heptahydrate formula, but distinctly above that required for the hexahydrate, and

(b) In spite of the low figure for water the physical constants correspond almost exactly with those that would be expected for an intermediate member of the epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$)-morenosite ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$) series.

Few analyses of either morenosite or any intermediate members of the epsomite-morenosite series appear in the literature available to the writer, and even fewer are accompanied by refractive index data. However deficiency in water appears to be a feature of a number of these analyses; for example the formula $\text{NiSO}_4 \cdot 6.5 \text{H}_2\text{O}$ was derived from an analysis of morenosite from Valtournanche by Cavinato (1938), and in an epsomite² from Rakos,³ Slovakia, Zsivny (1915) also found water to be slightly less than the normal seven molecules. Again Simpson (1920) has described cobaltian epsomite from Parkerville, West Australia, with only 5.7 molecules of water, whereas Walker and Parsons (1927) have found that the compositions of crystals of magnesium sulfate from lake

² Since 1.78 per cent of MnO was found therein the mineral is probably the variety fauserite.

³ Formerly Rákospány in Hungary.

deposits near Oroville, Washington, and from Ashcroft, British Columbia, show a range of from six to seven molecules of water depending upon atmospheric conditions. On the other hand, a few analyses of

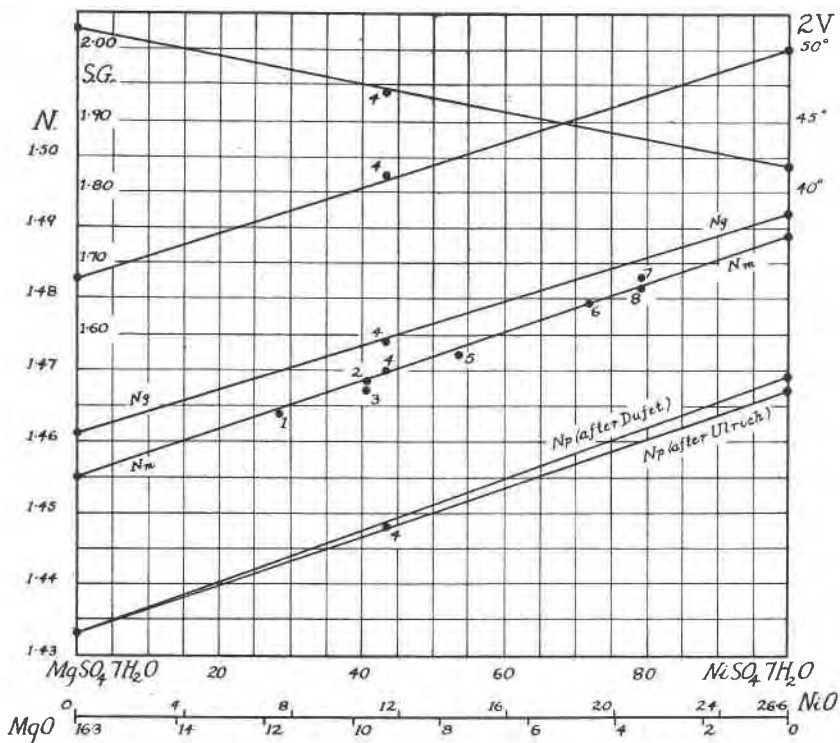


FIG. 2. Variations in composition and physical properties in the epsomite-morenosite series.

Key to analyses in Fig. 2:

1. 71.65 per cent $MgSO_4 \cdot 7H_2O$. Dufet (1878), compound no. 1.
2. 59.3 per cent $MgSO_4 \cdot 7H_2O$. Dufet (*loc. cit.*), compound no. 2; β calculated.
3. As in 2, but β observed.
4. Data for Kaukapakapa mineral.
5. 46.1 per cent $MgSO_4 \cdot 7H_2O$. Dufet (*loc. cit.*), compound no. 3.
6. 28.05 per cent $MgSO_4 \cdot 7H_2O$. Dufet (*loc. cit.*), compound no. 4.
7. 20.9 per cent $MgSO_4 \cdot 7H_2O$. Dufet (*loc. cit.*), compound no. 5; β observed.
8. As in 7, but β calculated.

members of the epsomite-morenosite series are available that give no indication of any deficiency in the number of molecules of water (Ulrich, 1921; Kokta, 1930), and in some instances the analyses are unsatisfac-

tory in that water has been determined only by difference (Jirkovsky, 1928, pp. 59–60).

In view of the care taken to determine the full amount of water and also the ease with which nickel and magnesium sulfates yield water, it might be suggested that the deficiency in the case of the New Zealand mineral at least, is to be attributed to the presence of an intermediate member of a hexahydrate solid solution series. Certainly a lower hydrate of magnesium sulfate, though rare, does occur in nature, *viz.* hexahydrate, and it might be expected to form an ionic substitution series with the corresponding hexhydrate of nickel sulfate,⁴ but the optical properties, particularly optic orientation, of this compound would be distinct enough from those recorded for the New Zealand mineral to permit differentiation.

In Fig. 2 of this paper curves for the variation of refractive indices, optic axial angle, and specific gravity with composition in the epsomite-morenosite series have been drawn up. The data for epsomite⁵ are those quoted by Winchell (1933) and Larsen and Berman (1934), whereas in the case of morenosite the values for α , β , γ , and $2V$ are those determined by Dufet (1878, p. 882) for the pure salt. It should be noted that other determinations for the nickel salt made by Topsoe and Christiansen (*vide* Ulrich, 1921, p. 124) gave a distinctly lower figure for the refractive index of the X vibration direction, *viz.* 1.4669, than that recorded by Dufet; this value is represented by the lowermost point for morenosite on the N_p line. Dufet's determinations, both observed and calculated, of the refractive indices for the Y vibration direction in a number of the synthetic intermediate members of the series have been plotted in Fig. 2, and a straight line variation results.

When the analysis of the New Zealand mineral is recalculated to seven molecules of water and the physical constants plotted on Fig. 2, coincidence is such that the existence of a member of a hexahydrate solid solution series therein seems to be out of the question. Further, careful inspection of the material when mounted in an oil of refractive index 1.470 did not reveal the existence of a second, but distinct, crystalline phase. It would seem then that the loss of a small percentage of water from the heptahydrate does not necessarily cause any appreciable variation in the optical properties characteristic of members of that series;

⁴ $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ is dimorphous, crystallizing from solution at about 35° C. in tetragonal forms, or at about 60° C. in the monoclinic system.

⁵ The value of 1.751 given by Ford (1932) for the specific gravity of epsomite appears to be an error; it should also be noted that the heptahydrate of magnesium sulfate is dimorphous and the specific gravity of the normal orthorhombic form is 1.677, whereas the figure for the monoclinic modification is 1.691 (Doelter and Leitmeier, 1929, p. 20).

or alternatively, since loss of water is almost invariably found to cause a rise in the refractive indices of minerals, loss of water from nickelian epsomite, while still retaining orthorhombic disphenoidal symmetry of the stable heptahydrate, does not bring about any easily measurable rise in the value of the refractive indices. Any pronounced change in optical properties then is only to be expected when one molecule of water has been removed, and the salt recrystallizes with monoclinic (or possibly tetragonal) symmetry of the true hexahydrate.

In an ionic compound such as $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, six of the water molecules are in octahedral groups surrounding each nickel ion, but the seventh is isolated and is linked not to cations, but instead to oxygen ions of the SO_4 groups, and to other water molecules (*vide* Beevers and Schwartz, 1935). The function of the first six water molecules is clearly to co-ordinate the cations and to promote a stable structure by enlargement of the effective radius of the cations, whereas the position of the seventh water molecule appears to be of less importance but it is certainly more vital than the role of water in zeolites, since it is accommodated in small cavities in the structure and has developed hydrogen bonds. It is suggested therefore, that the structure of nickelian epsomite could retain its stability, even after the loss of some of the "seventh" water molecules, and although this would result in a deficiency of water, the heptahydrate symmetry would be retained.

ORIGIN OF EPSOMITE

The close association of the two sulfates, nickelian epsomite and epsomite, with pyrrhotite clearly suggests that the sulfide has been a vital factor in their formation, and there seems to be little doubt that the processes that have been formative here are similar to those that produced heavy efflorescences of morenosite on pyrrhotite-pentlandite ores at Sudbury (Coleman, 1913, p. 20). Processes that involve oxidation of pyrrhotite to give ferric sulfate and sulfuric acid are well known and need no elaboration here; the sulfuric acid so derived has apparently reacted with the readily soluble serpentinite and with the pentlandite in the pyrrhotite giving sulfates of nickel, magnesium, and iron. It is assumed that the primary nickel is confined to the sulfide since qualitative tests indicate that only strong traces of nickel occur in the serpentinite itself.

The virtual absence of iron from these salts in view of its relative abundance in the source materials is interesting. However, the separation of iron from nickel during oxidation of sulfide ores is well known (Emons, 1917, p. 460), and arises solely from the rapidity with which

ferrous sulfate is oxidized to basic ferric sulfate, and ultimately hydrolyzed to limonitic products; on the other hand, nickelous salts are stable and do not oxidize or hydrolyze in air as iron compounds do. Thus iron will remain behind near its source whereas nickel is removed in solution and permitted to crystallize in forms uncontaminated by iron; magnesium will behave in a similar manner to that of nickel.

NOMENCLATURE

According to Mellor (1936, p. 454) the heptahydrate of nickel sulfate was termed pyromieline by F. von Kobell, but Casares' name—morenosita—after St. Moreno, has definite priority. Later Pisani (*vide* Doelter and Leitmeier, 1929, p. 612) gave the name pyromeline to a stalactitic mineral from Zermatt which was an intermediate member of the $\text{MgSO}_4 \cdot 7\text{H}_2\text{O} \cdot \text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ series with a composition similar to, but slightly richer in nickel than, the New Zealand mineral described herein. Therefore, in view of possible ambiguity the term pyromeline should not be employed but instead the terms nickelian epsomite and magnesian morenosite should be used to denote intermediate members of the series.

ACKNOWLEDGMENT

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