

RETGERSITE, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, A NEW MINERAL*

CLIFFORD FRONDEL AND CHARLES PALACHE,
Harvard University, Cambridge, Mass.

ABSTRACT

The well-known artificial compound, tetragonal $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, is described from five natural occurrences: with morenosite and minasragrite at Minasragra, Peru; with annabergite at Cottonwood Canyon, Churchill Co., Nevada; at Lobenstein, Thuringia; at Lichtenberg, Bayreuth, Bavaria; and with ferroan chalcalthite at the Gap Nickel Mine, Lancaster Co., Pennsylvania. Tetragonal trapezohedral, with $a:c=1:2.7038$ (artificial; Scacchi, 1863); $a_0=6.765$ kX, $c_0=18.20$; $a_0:c_0=1:2.690$ (Minasragra). Uniaxial negative, with $O=1.510$, $E=1.486$ (natural). Crystals from Minasragra are short prismatic [001] with {001}, {110}, {011}, {012}, {112}; also found as fibrous aggregates and veinlets. Color blue-green. $G=2.04$ (Nevada). Cleavage {001} perfect, {110} in traces. Analysis gave: NiO 26.87, MgO 0.65, FeO 0.63, SO_3 30.32, H_2O [41.53], total [100.00] (Nevada). The name retgersite is proposed for the mineral in honor of J. W. Retgers (1856–1896), Dutch physical chemist and crystallographer.

Only four of the twenty-three reported natural occurrences of morenosite, orthorhombic $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, can be said definitely to be of that species.

INTRODUCTION

At least six different hydrates of nickel sulfate and an uncertain number of nickel oxysulfates have been synthesized (9, 12, 13). Several of these compounds have regions of stability which suggest that they might form under natural conditions, and one of them, the orthorhombic polymorph of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, is already known to mineralogists under the name morenosite. Most of the reported occurrences of morenosite are open to doubt as to the particular nickel sulfate represented, due to uncertainties as to the system of crystallization and the water content. A recent survey of the specimens of so-called morenosite in the Harvard collection verified the existence of morenosite in one instance and also proved the natural existence of the tetragonal polymorph of nickel sulfate hexahydrate. The latter substance, also known as blue- or alpha- $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, is described beyond under the name retgersite. The name is given after the Dutch physical chemist and chemical crystallographer Jan Willem Retgers (1856–1896). Retgers made numerous crystallographic studies of artificial salts with particular reference to their isomorphism and polymorphism. Retgers also made important contributions to mineralogical laboratory techniques, including the use of phosphorus as an index of refraction medium, the examination of detrital mineral grains by embedding techniques, and especially the development

* Contribution from the Department of Mineralogy and Petrography, Harvard University, No. 301.

and use of heavy liquids and melts for the measurement of specific gravity.

RETGERSITE, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$

The tetragonal polymorph of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ was first identified by the senior author as poorly formed, bluish green crystals incrusting a black coke-like mass of patronite from Minasragra, Peru. The crystals, which ranged up to about one millimeter in length, were too rough to permit accurate goniometric measurements but did afford sufficient data to establish the forms present as $\{001\}$, $\{110\}$, $\{011\}$, $\{012\}$ and $\{112\}$. The habit is shown in Fig. 1. An x -ray rotation photograph and 0-layer Weis-

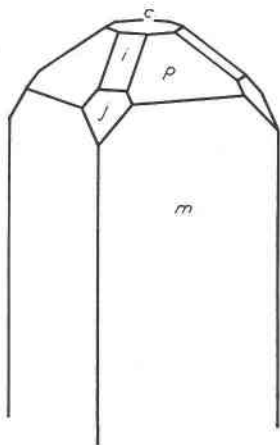


Fig. 1. Retgersite from Minasragra, Peru. Forms: $c\{001\}$, $m\{110\}$, $p\{112\}$, $j\{011\}$, $i\{012\}$.

senberg photograph taken about $[001]$ confirmed the tetragonal symmetry and afforded the cell dimensions given below in comparison with those obtained by a precision powder x -ray study of the artificial compound by Borghijs (2).

a_0	c_0
$6.765 \pm 0.02 \text{ kX}$	18.20 ± 0.05 (Minasragra)
6.776 ± 0.003	18.249 ± 0.009 (Artificial (2)).

Accurate morphological measurements were obtained by Scacchi (15) on artificial crystals, and an angle table for the known forms using his angles as given in Table 1. The original morphological cell of Scacchi is here turned 45° around $[001]$ to conform to the unit of the structure cell. The crystal structure of the compound has been described by Beevers and Lipson (1). Optically, the Minasragra mineral is uniaxial negative with $n_O = 1.510$ and $n_E = 1.486$, which compare closely with the indices

TABLE 1. ANGLE TABLE FOR RETGERSITE
 Tetragonal; trapezohedral—4 2 2
 $a:c=1:2.7038$; $p_0:r_0=2.7038:1$

	ϕ	ρ	Λ	M
<i>c</i> 001	—	0°00'	90°00'	90°00'
<i>m</i> 110	45°00'	90 00	45 00	90 00
<i>h</i> 013	0 00	42 01½	90 00	61 44½
<i>i</i> 012	0 00	53 30½	90 00	55 21½
<i>j</i> 011	0 00	69 42	90 00	48 27½
<i>o</i> 113	45 00	51 53	56 12	90 00
<i>p</i> 112	45 00	62 23½	51 12	90 00

$n_O=1.5109$ and $n_E=1.4873$ (for Na) obtained by the prism method of Topsøe and Christiansen (19) on artificial crystals. There is a good cleavage on {001} and traces of a cleavage, best seen on crushed grains under the microscope, on {110}. Sufficient material could not be obtained for a chemical analysis. The mineral occurs with morenosite, described beyond in more detail, and with blue efflorescent masses of minasragrite, $V_2H_2(SO_4)_3O_2 \cdot 15H_2O$. The latter substance unquestionably has formed at least in part since the specimen was collected but both the retgersite and morenosite appear to be original deposits. Both minerals presumably were formed ultimately by the oxidation of nickelian pyrite present in the ore-body.

Four additional natural occurrences of retgersite were found on specimens from other localities that had been labeled as of morenosite. The best of these comprised a foot-long mass of niccolite-bearing vein material from a mine in Cottonwood Canyon, Churchill County, Nevada, which was supplied for study through the interest of Mr. Hatfield Goudey of Yerington, Nevada. The geology of the deposit has been described by Ferguson (6). The specimen has been thoroughly oxidized and is crusted over and veined by apple-green, granular masses of annabergite and blue-green fibrous aggregates of retgersite. The retgersite is an original deposit, in part earlier formed than annabergite, and is not a dehydration product of morenosite. Optically, the retgersite is uniaxial negative with $n_O=1.510$ and $n_E=1.486$. The x-ray powder pattern checked that of artificial tetragonal $NiSO_4 \cdot 6H_2O$. The direction of the fiber axis is [001]. The specific gravity of a small compact grain was determined on the microbalance as 2.04, which compares to the values 2.064 and 2.074 obtained by Gossner (7) and Topsøe (18), respectively, on artificial crystals. A chemical analysis of this material is cited in Table 2. The Mg and part at least of the Fe^2 is present in substitution for Ni.

Retgersite also was identified as pale blue-green granular crusts and

TABLE 2. ANALYSIS OF RETGERSITE FROM COTTONWOOD CANYON, NEVADA

	1	2
NiO	26.87	28.42
MgO	0.65	
FeO	0.63	
SO ₃	30.32	30.46
H ₂ O	[41.53]	41.12
Total	[100.00]	100.00

1. Analysis by H. J. Hallowell, May, 1948. Analysis made on a cold water extract of material slightly admixed with limonite, quartz, and annabergite. The total iron is calculated as FeO, but is probably present in the mineral in part as admixed Fe₂O₃.

2. Theoretical composition, NiSO₄·6H₂O.

veinlets associated with fine-grained annabergite on a specimen labeled morenosite from Lichtenstein, Bayreuth, Bavaria. This is the type locality for the supposed variety of morenosite termed pyromeline by von Kobell (22). One cannot tell from the original description, however, whether his mineral was either retgersite or morenosite. Pyromeline was said on the basis of qualitative tests to contain a small amount of (AsO₄) in substitution for (SO₄) but this might well have been due to admixture of annabergite. Sufficient material was not available on the present specimen to permit an analysis. The indices of refraction of this material are practically identical with those of the pure artificial compound. Additional occurrences of retgersite were found as pale blue-green masses associated with annabergite on a specimen from Lobenstein, Thuringia, and with ferroan chalcantite on a specimen from the Gap Nickel Mine, Lancaster Co., Pennsylvania.

Systematic Relations and Synthesis. Retgersite is isostructural with the tetragonal polymorphs of the hexahydrated selenates of Ni and Zn. Some of the properties of these compounds are given in Table 3. Retgersite is the only known natural representative of the group. The monoclinic polymorph of NiSO₄·6H₂O has been prepared artificially and its crystallographic and optical properties have been described (8, 9). This compound, green in color, is formed from pure water solutions at temperatures over 53.3° C. and below this temperature rapidly inverts to the blue tetragonal polymorph. The occurrence of this unstable and relatively soluble (52.5 g. NiSO₄ in 100 g. water at 54.5°) monoclinic phase in nature seems very unlikely. The monoclinic zinc and magnesium analogues are stable under ordinary conditions, however, and occur in nature as the minerals bianchite and hexahydrate.

Mg can substitute for Ni in retgersite, as indicated by the analysis of

the Nevada material, and at least a partial series extends from retgersite toward tetragonal $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$. There is no experimental proof of this at hand, however, and pure tetragonal $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ itself is not stable under ordinary conditions. It may be noted in this connection that a complete series extends between the orthorhombic compounds morenosite, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, and epsomite, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, as shown by Dufet (5) and by Hutton (10). Both Fe'' and Cu'' probably substitute only to a very small extent in retgersite. The observed limits of substitution of these elements in orthorhombic $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ are $\text{Cu}:\text{Ni} \sim 2:98$ and $\text{Fe}:\text{Ni} \sim 1:5$. Neither Fe'' or Cu'' form stable compounds in either the tetragonal or

TABLE 3. TETRAGONAL HEXAHYDRATED SULFATES AND SELENATES*

		$a:c$ (morph.)	a_0	c_0	nO (for Na)	nE
Retgersite	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	1:2.7038	6.776	18.249	1.5109	1.4873
(Artificial)	$\text{NiSeO}_4 \cdot 6\text{H}_2\text{O}$	1:2.5971			1.5393	1.5125
(Artificial)	$\text{ZnSeO}_4 \cdot 6\text{H}_2\text{O}$	1:2.6798			1.5291	1.5039
(Unstable)	$\text{CuSO}_4 \cdot 6\text{H}_2\text{O}$					
(Unstable)	$\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$					
(Unstable)	$\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$					

* Data summarized from Groth (8); cell dimensions of Borghijs (2).

monoclinic hexahydrate groups or in the orthorhombic heptahydrate group, although a metastable tetragonal modification of $\text{CuSO}_4 \cdot 6\text{H}_2\text{O}$ has been reported and the orthorhombic form of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ has been said on the basis of inconclusive evidence to exist in nature (the tauriscite of Volger (21)). Mn'' probably enters into a limited range of substitution for Ni in retgersite.

Retgersite can be synthesized by crystallization from pure water solution at temperatures between 31.5° , below which orthorhombic $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ is stable, and 53.3° , above which monoclinic $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ is stable. A dihydrate forms above about 118° . These transition temperatures are from the data of Steele and Johnson (17); slightly different values have been reported by others (see Seidell (17)), and metastable equilibria commonly occur. Retgersite also can crystallize at temperatures at least as low as 0° from solutions which contain an appropriate excess of free H_2SO_4 , as shown by Rohmer (14) and others. This factor may determine its formation in nature in place of morenosite. Under certain circumstances both retgersite and morenosite have been observed to crystallize simultaneously, one or the other of the two compounds being in metastable equilibrium.

MORENOSITE, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$

At least twenty-three different occurrences of morenosite have been reported in the literature by Laspeyres (11) and others. In only a few instances, however, have sufficient data been given to definitely prove the occurrence of the orthorhombic heptahydrate. Here may be mentioned the occurrence at Joachimstal, Bohemia, which Ulrich (20) established on the basis of optical measurements, and the occurrence in the Val Malenco, Lombardy, which was said by Cavinato (4) to be of orthorhombic crystals and which conformed on analysis to the heptahydrate. The original occurrence at Cape Hortegal, Galicia, Spain, described by Casares (3) also appears definitely to be of morenosite. Analytical evidence alone is not very satisfactory since the point at issue is the distinction between the hexahydrate and the heptahydrate. The difference in water content is small (41.12 and 44.90 weight per cent water, respectively), and decisive results would be difficult to obtain ordinarily since the material commonly occurs as fibrous or fine-grained efflorescences and contains hydrous impurities, notably annabergite. There also is the probability that part at least of the seventh molecule of water can be lost without breakdown of the orthorhombic structure, as in the case of the isostructural compound $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (epsomite).

In the course of the present work, morenosite was identified by its optical properties and *x*-ray powder diffraction pattern* as emerald-green crystals associated with minasragrite and retgersite on a specimen of patronite from Minasragra, Peru. The occurrence of morenosite at this locality has been remarked earlier by Schaller (16). The crystals were not suited for crystallographic measurement. The material is optically negative, with $n_X = 1.470$, $n_Y = 1.493$, $n_Z = 1.500$, $2V$ small and dispersion $r > v$. These data diverge slightly from those reported by Dufet (5) for the pure artificial salt: $n_X = 1.4693$, $n_Y = 1.4893$, $n_Z = 1.4923$ (for Na) with $2V = 41^\circ 54'$ (meas.) and $r > v$. A spectrographic examination revealed the presence of V in an amount of the order of a few tenths of a per cent.

On standing in the open in dry air, crystals of morenosite generally dehydrate rapidly to the tetragonal hexahydrate, retgersite. This was verified by the writers on several artificial preparations. The product formed, however, varies considerably with circumstances. One artificial preparation, crystallized from a water solution containing a little HCl, proved to be stable under ordinary conditions. Further, the natural morenosite from Minasragra had partially effloresced during the thirty years or so that it had been contained in the collection, but the dehydration product

* X-ray powder data for the hydrated nickel sulfates are given by Hammel (9), in the *ASTM* card file, and for $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ by Borghijs (2).

proved to be not the hexahydrate but a mixture of several lower hydrates. Morenosite does not lose water if it is kept in a sealed, tightly packed container. It may be noted that orthorhombic $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (epsomite), with which morenosite is isostructural, dehydrates to the monoclinic polymorph of $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ (hexahydrate) and not to the tetragonal phase as in the case of morenosite. The tetragonal phase of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ retgersite, apparently is stable in dry air at room temperature. Finely ground artificial preparations did not lose weight on standing in the open air for a period of weeks. A few large crystals of this substance that had been exposed to direct sunlight were observed to break down very slowly to a yellow-green product, probably $\text{NiSO}_4 \cdot \text{H}_2\text{O}$. The decomposition began at a few isolated spots, and the areas of the yellow green substance were rimmed by an intermediate zone of a pale bluish green material probably consisting of $\text{NiSO}_4 \cdot 2\text{H}_2\text{O}$.

REFERENCES

1. BEEVERS, C. A., AND LIPSON, H., *Zeit. Kryst.*, **83**, 123 (1932).
2. BORGHIS, L., *Natuurwet. Tijdschr.*, **19**, 115 (1937).
3. CASARES, D. A., cited by ALCIBAR, A. M., *Revista Minera*, Madrid, 176 (1851).
4. CAVINATO, A., *Atti R. Accad. Lincei, Rend.*, Cl. Sci., Rome, ser. 6, **25**, 399 (1937).
5. DUFET, H., *Compt. rend.*, **86**, 880 (1878) and *Bull. Soc. Min.*, **1**, 58 (1878).
6. FERGUSON, H. G., *Univ. Nevada Bull.*, **33**, No. 5 (1939).
7. GOSSNER, B., *Ber. deutsch. Chem. Ges.*, **40**, 2374 (1907).
8. GROTH, P., *Chemische Kryst.*, **2**, 423, 426, 428 (1908).
9. HAMMEL, F., *Ann. Chim.*, ser. 11, **11**, 247 (1939).
10. HUTTON, C. O., *Am. Mineral.*, **32**, 553 (1947).
11. LASPEYRES, H., *Verhandl. naturhist. Ver. Bonn*, **50**, 255 (1893). See also HUDSON, F. S., *Bull. Univ. Calif. Dept. Geol.*, **13**, 175 (1922); JOHNSTON, R.A.A., *Canada Dept. Mines, Geol. Surv.*, Mem. **74**, 162 (1915); HINTZE, C., *Handbuch der Min.*, **1**, Pt. 3B, 4354 (1929); and COLEMAN, A. P., *Canada Dept. Mines, Mines Branch*, Rept. **170** (1913).
12. MELLOR, J. W., *A Comp. Treatise on Inorg. Chem.*, **15**, 453 (1936).
13. PASCAL, P., *Traité de Chim. Min.*, **10**, 155 (1935).
14. ROHMER, R., *Ann. Chim.*, ser. 11, **11**, 611 (1939).
15. SCACCHI, A., *Atti R. Accad. Sci. Napoli*, **1**, no. 11 (1863).
16. SCHALLER, W. T., *J. Wash. Acad. Sci.*, **7**, 501 (1917).
17. SEIDELL, A., *Solubilities of Inorg. Compounds*, New York, 3rd ed., 1347 (1940); also STEELE, B. D. and JOHNSON, F. M. G., *J. Chem. Soc. London*, **85**, 116 (1904).
18. TOPSØE, H. F. A., *Archiv. sci. phys. nat. Geneve*, ser. 2, **45**, 223 (1872).
19. TOPSØE, H. F. A., AND CHRISTIANSEN, C., *Ann. Chim. Phys.*, ser. 5, **1**, 63 (1874).
20. ULRICH, F., *Casopis Musea Ceskeho, Prague*, **95**, 123 (1921).
21. VOLGER, G. H. O., *Jahrb. Min.*, 152 (1855).
22. VON KOBELL, F., *J. prakt. Chem.*, **58**, 44 (1853).