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## THE HYDROUS NICKEL-MAGNESIUM SILICATES— THE GARNIERITE GROUP<sup>1,2</sup>

GEORGE T. FAUST, *U.S. Geological Survey, Washington, D. C.*

### ABSTRACT

The hydrous nickel-magnesium silicates are one of the most poorly understood mineral groups. A principal member of this group was originally described by Professor Martin H. Klaproth in 1788 as "grüner Chrysopraserde". He found this clay mineral, now called pimeleite, to be the coloring matter of the gem material chrysoprase from the famous locality at Kosemütz, near Frankenstein in Silesia, Germany. Nickel analogues of the polymorphs of the serpentine-group, chrysotile, lizardite and antigorite are the most abundant members of the group. In addition, schuchardite, nickel chlorite; nickel-exchanged vermiculites; nickeloan talc; and nickeloan sepiolite have been observed in natural deposits. Other minerals described as hydrous nickel-magnesium silicates are shown by chemical, DTA, optical and x-ray powder diffraction studies to be either pimeleite or nickel serpentine-group minerals or mixtures. Thus, genthite is a mixture of 20 per cent pimeleite and 80 per cent nickeloan serpentine-group mineral; röttisite is pimeleite; de saulesite is pimeleite; revdanskite is chiefly pimeleite; garnierite, nepouite, noumeite are mixtures of pimeleite, nickel serpentine-group minerals and other minerals. The tie-lines nickel serpentine-group minerals-pimeleite, and pimeleite-quartz are established in this study.

The hydrous nickel-magnesium silicates<sup>3</sup> constitute one of the oldest mineralogical families. Its first member from Silesia was named "grüner Chrysopraserde" in 1788 by Professor Martin H. Klaproth, then assessor in pharmacy in the Obercollegii Medicii in Berlin. The relationships within this group are still one of the most poorly understood among the assemblages in the mineral kingdom. This is despite the auspicious occasion of the rediscovery of the gem material chrysoprase in Silesia in 1740 by an officer of the Prussian Army and its subsequent control by Frederick The Great (1712–1786). The king used the output of the quarries and mines to adorn his palace, San Souci, at Potsdam. Feuchtwanger (1859, p. 294) writes: ". . . At the royal palace of Potsdam, in Prussia, are two tables of chrysoprase, the plates of which are three feet

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<sup>2</sup> Publication authorized by the Director, U.S. Geological Survey.

<sup>3</sup> The experimental work on which this address is based is in preparation for publication by the U.S. Geological Survey.

long, two feet broad and two inches thick. . . ." The excellent quality of the chrysoprase from the type locality in Silesia is attested to by the many treatises on gemology. The deposits were worked in the fourteenth century and part of their production was used in the liturgical decoration of churches in Austria and Germany. The type occurrence of these minerals at Kosemütz in Silesia is a hydrothermal replacement of gabbroic and ultrabasic intrusions into the gneisses of the Eulenmassiv. Frankenstein, the center of the former nickel industry, is located approximately 40 miles south southwest of Breslau. The serpentinized intrusives all lie within about six miles of Frankenstein and west of the village of Kosemütz, southwest of Gläserndorf and west of Baumgarten at Grochau. The geology of the region has been described by Beyschlag and Krusch (1913), Bederke (1929) and Cloos (1953). Briefly the relations are as follows: the Eulengebirge, a Precambrian massif composed of gneisses, and called the Eulenmassiv, contains intrusions of ultrabasic and gabbroic rocks of Ordovician age (Erich Bederke, pers. comm.). These intrusions all lie in the border zone of the Eulenmassif. The Eulenmassif and the Innersudetische Mulde are separated by a border fault. The Innersudetische Mulde is a basin filled with Carboniferous, Permian, Triassic, and Cretaceous sediments. The ultrabasic and gabbroic rocks were hydrothermally serpentinized subsequent to their intrusion.

Grüner chrysopraserde is a constituent of the semiprecious stone known as chrysoprase. Figure 1 shows a colored photograph of the massive brecciated chrysoprase from Silesia and three cabochons cut from similar material and illustrates clearly the variations in the tone of the color. When the cut and polished chrysoprase looks grayish the color is called "Prussian gray" in the gem trade. This color change arises from dehydration during overheating in the polishing process.

Prior to Klaproth's investigations, chrysoprase had been regarded as an apple-green colored quartz. Typical of the early notions concerning the coloring agent of chrysoprase and of the chrysoprase-earth is that of Bergrath Johann G. Lehmann of Berlin (1761), who considered the pigmentation to be due to the "iron part" of the material. Professor Balthazar Sage of Paris (1786) opined that the color of chrysoprase was due to cobalt, and Director Franz Achard of Berlin (1779), claimed it was due to the presence of "iron-earths" and copper oxide.

Professor Klaproth, the discoverer of the five elements uranium, zirconium, titanium, strontium, and cerium, attacked the problem with that singular attention to pertinent detail of an experimentalist of the first order. He noted that the test used by Bergrath Lehmann, while it did show the presence of iron in the mineral, did not prove that iron was the coloring agent. Klaproth further discerned that the observations of Sage



FIG. 1. Massive chrysoprase from the deposits near Frankenstein, Silesia, Germany. U.S. National Museum No. 81980. Three cabochons cut from similar material. The center stone is catalogue No. 1424, the two outside stones are catalogue No. 1425 in the U.S. National Museum.



FIG. 2. "Grüner Chrysopraserde" of Klaproth, 1788—now called pimelite. From deposits in the vicinity of Frankenstein, Silesia, Germany. U.S. National Museum No. R4700.



and Achard were inconclusive. The analytical procedures used by Klaproth embodied those of analytical chemistry and its close ally assaying. These procedures along with the names of the chemicals used as reagents—"schwefelleber, flüchtiges Alkali, phlogistirtem Alkali, and Gallapfeltinctur"<sup>1</sup> suggest an almost alchemical atmosphere with consequent imperfect separations but Klaproth got the right answer on two scores—the cause of the color and the discovery of a new mineral.

Klaproth examined a suite of specimens from the mines and quarries at Kosemütz and he suspected, as Lehmann had previously hinted, that the coloring agent of the gemstone "chrysoprase" was the fine-grained green

TABLE 1. CHEMICAL ANALYSES OF GRÜNER CHRYSOPRASERDE AND CHRYSOPRASE FROM KOSEMÜTZ, UPPER SILESIA, GERMANY BY MARTIN H. KLAPROTH IN 1788

Grüner Chrysopraserde		Chrysoprase (a green-colored quartz)			
Kieselerde	85 grains	SiO <sub>2</sub>	35.00%	288.50 grains	96.17%
Alaumerde	12 grains	Al <sub>2</sub> O <sub>3</sub>	5.00	.25	.08
Bittersalzerde	3 grains	MgO	1.25	trace	.01 ± <sup>1</sup>
Kalkerde	1 grain	CaO	0.41	2.50	.83
Eisenkalk	11 grains	FeO	4.58	.25	.08
Nickelkalk	37.50 grains	NiO	15.63	3.00	1.00
Verlust	91.50 grains	Loss in weight	38.13	5.50	1.83
240.00 grains ( $\frac{1}{2}$ ounce)			100.00	300.00 grains	100.00

<sup>1</sup> Estimated from Klaproth's statement as present "but never more than  $\frac{1}{8}$  of a per cent."

earthy mineral which is intimately associated with it. This material is shown in Fig. 2. He also noted in his specimens the presence of quartz, hornstone, chalcedony, opal, asbestos, talc and earths of various kinds. To test his theory of the coloring agent and to identify it he chose two kinds of material for analysis—of the first he writes:

"Amongst the different modifications of the fine shiny, greasy-to-the-feel, crude chryso-praserde which accompanies the chrysoprase, I chose that for investigation which marks itself—through its uniform apple-green color—as the purest and least contaminated by heterogeneous parts."

Klaproth (1788, p. 44) made a number of analyses of this mineral and records one made on a half-ounce of the substance which is given in Table 1. The value for total water of 38 per cent is high for montmoril-

<sup>1</sup> In modern terminology these are potassium sulfide, ammonia, and tincture of tannic acid.

lonites, which usually contain approximately 25 per cent. But interlayer water contents of 35 per cent and more have been attained in the hydration studies on montmorillonites of Hofmann and Bilke (1936). We may infer, therefore, that Klaproth analyzed his material shortly after washing to free it from impurities and before it had dried to approach an equilibrium with the humidity of the laboratory. This chemical analysis was unique and differentiated the mineral clearly from all known species. Further, the color could be definitely attributed to the nickel content of the clay mineral.

For the second sample he selected chrysoprase itself and his analysis performed on a sample weighing 300 grains is given in Table 1. Klaproth's comments (1788, p. 43, 44) are as follows:

"These determined proportions of the constituents agree well with the results of many of my investigations. Nevertheless, I admit willingly that in some experiments small differences, chiefly in the content of nickel and iron may occur, since the green color of the chrysoprase often varies; likewise, I have found appreciable traces of MgO, however, never more than one-eighth of a per cent."

This analysis coupled with Klaproth's visual observations clearly shows that the color in chrysoprase is due to the green nickel clay mineral "grüner chrysopraserde". He further confirmed the presence of nickel in both materials by obtaining through chemical separations and subsequent reduction a "Nickelkönig" (nickel button).

Klaproth's investigation should have left little doubt as to the identity of the pigmenting substance in chrysoprase, yet as late as 1932, E. S. Dana in his "Textbook of Mineralogy" (revised by W. E. Ford) writes "An apple-green chalcedony, the color being due to nickel oxide" and does not mention either Chrysopraserde or its modern equivalent, pimeleite. Professor Frondel in Volume III of the seventh edition of "The System of Mineralogy" sets the matter straight.

The name chrysoprase, like so many very ancient or old names for precious stones was apparently applied to several yellowish-green gems including beryl, but gradually it became limited to the apple-green colored quartz and chalcedony. The name comes from the Greek for golden χρυσός and a leek πράσον (Smith, 1958; Chester, 1896).

In 1797, Klaproth reaffirmed this name, grüner chrysopraserde, in his textbook. The systematist Dietrick L. G. Karsten (1800), however, in his mineralogische Tabellen accepted Klaproth's definition and description of the species but found the name unsuitable and renamed it pimeleite from the Greek word for fat, πιμελή, in allusion to its appearance. The name, pimeleite, was thus established for this species. It was quickly accepted and was used by Meinelcke in his classic treatise of 1805 entitled: "Über den Chrysopras und die denselben begleitenden Fossilien in

Schlesien" where he developed a spider-web type diagram showing the affinity of pimelite and its associates.

Carl Schmidt (1844), a student in the laboratory of Professor Heinrich Rose, analyzed a specimen of pimelite but he made the mistake of drying his specimen on a water bath, thus, removing the interlayer water of the clay mineral and found only 5.23 per cent of water. This led him to the erroneous conclusion that pimelite was merely a water-bearing talc or meerschaum. Professor Glocker (1845) of Breslau University suggested that the name be changed to alipidite from the Greek word for not greasy, *ἀλιπής*. Despite these two ill-advised sorties, the name pimelite has held to the present day.

TABLE 2. CHEMICAL ANALYSIS OF PIMELITE FROM KOSEMÜTZ,  
UPPER SILESIA, GERMANY

SiO <sub>2</sub>	= 47.20
Al <sub>2</sub> O <sub>3</sub>	= .22
Fe <sub>2</sub> O <sub>3</sub>	= .20
MgO	= 11.42
NiO	= 27.66
CaO	= .16
H <sub>2</sub> O+	9.38
H <sub>2</sub> O	= 3.64
	99.88

Analyst: Sarah Berthold

This analysis is incomplete, in that the results for the alkalis are not available as of February, 1966.

Over the years since Klaproth's discovery, new analyses of pimelite from the Silesian locality have been made and a striking feature of these analyses is the variation in the proportions of NiO, MgO, FeO, and Al<sub>2</sub>O<sub>3</sub>. Klaproth noted the inverse relation between NiO and the sum  $\Sigma(\text{MgO} + \text{FeO})$ . The alumina content originally was given as 5.00 per cent and ranged down to 0.30. For two clays, low in nickel, the alumina was high, ranging from 14 to 23 per cent. This variation led Beyschlag and Krusch (1913) to observe that the samples with high alumina content were not pimelites. Spangenberg (1938) restudied pimelite and states that no essential alumina or ferric oxide is present. The specimen examined in this study, at the U.S. Geological Survey, has been analyzed by my colleague, Sarah Berthold, and her analysis is given in Table 2. The results bear out the conclusions of earlier workers that neither alumina nor ferric iron are essential in the pimelite from Kosemütz, Silesia.

Pimelite has been considered a clay mineral for a long time. If we

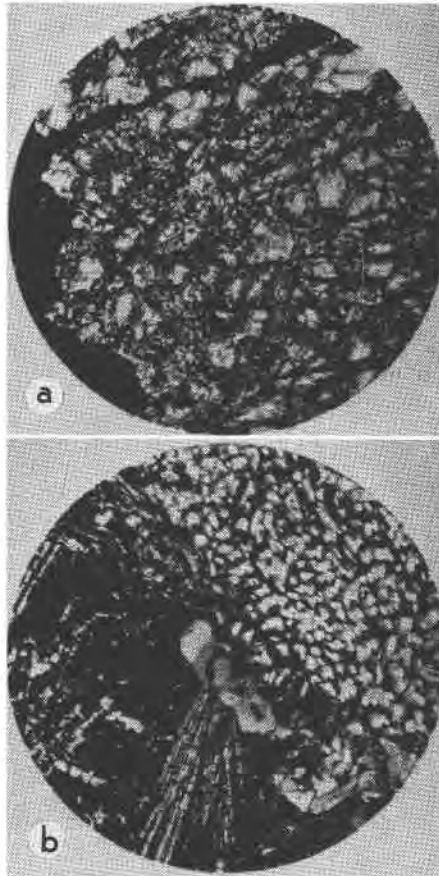


FIG. 3(a). Thin section of pimelite under crossed polars and magnified 60X. Apparent birefringence .014 to .025. Locality: deposits near Frankenstein, Silesia, Germany. Reproduced from Beyschlag and Krusch (1913).

FIG. 3(b). Thin section of a vein of chrysoprase under crossed polars and magnified 60X. Chrysoprase vein (chiefly light-colored material) lies in the approximate position of NNW to ESE. The dark material is serpentine and contains laths of actinolite. Locality: deposits near Frankenstein, Silesia, Germany. Reproduced from Beyschlag and Krusch (1913).

examine the photomicrographs of pimelite made by Beyschlag and Krusch in 1913 in terms of our present knowledge of the montmorillonite group we can readily see that pimelite behaves optically as expected. Figure 3a shows pimelite with a measured apparent birefringence of 0.014 to 0.025. Figure 3b shows a vein of chrysoprase, chiefly pimelite, associated with almost isotropic-appearing serpentine and lath-like



crystals of actinolite. Both photomicrographs were taken with crossed polars and at 60 $\times$  magnification.

X-ray powder diffraction study in this investigation establishes the fact that the pimeelite from Kosemütz is definitely a member of the montmorillonite group. This had previously been suggested by Kurt Spangenberg (1938) in an unusually perceptive study of this group of minerals. On the basis of chemical studies, x-ray powder diffraction studies and differential thermal analyses pimeelite is confirmed and established as a phase in the system NiO-MgO-SiO<sub>2</sub>-H<sub>2</sub>O.

It is noteworthy that pimeelite, discovered in 1788, was the first mineral of the presently constituted montmorillonite group to be adequately described. It antedates the species montmorillonite of Salvétat (1847) by 59 years.

The second hydrous nickel-magnesium silicate to be considered here is actually a group of phases—the nickel analogues of the polymorphous members of the serpentine-group including antigorite. The occurrence of nickel in these minerals has been known for a long time. The following have been observed: “Nickel chrysotile”, “nickel-lizardite”, and “nickel antigorite”. These names are given in quotes because descriptions and new names, where applicable, are reserved for a later paper. Nickeliferous chrysotile has been frequently observed and described from many serpentinized dunites and peridotites—it probably is the most abundant hydrous-nickeliferous magnesium silicate. Nickeliferous antigorite, while apparently not quite so abundant, has been recorded from many localities. In this study, nickeliferous lizardite has been found.

The two “phases”—pimeelite and the “nickel serpentine-group”—have been discussed first because it is possible to interpret materials such as genthite, garnierite, röttisite, de saulesite, etc., by comparing the parallel relations for the nickel-poor part of the system H<sub>2</sub>O-MgO-NiO-SiO<sub>2</sub> with those of the nickel-rich part of the system. The tie-line stevensite-serpentine group minerals was established previously in the U.S. Geological Survey (Faust and Fahey, 1962) and it was shown that specimens of deweylite (gymnrite) were actually a mixture of two phases—the end members defining the tie-line. This observation makes possible the interpretation of the nickel-rich members of the system H<sub>2</sub>O-NiO-MgO-SiO<sub>2</sub>, whose nomenclature is in a hopeless state of confusion.

In 1851, Professor Frederick A. Genth of the University of Pennsylvania published a description of a mineral he named nickel-gymnrite. The journal in which he published his study is rather inaccessible—Keller and Tiedemann's *nordamerikanischer Monatsbericht für Natur-und Heilkunde*. The mineral was found at Texas, Lancaster County, Pennsylvania, and Fig. 4 shows a specimen which fits exactly his description of nickel-

gymnite coating chromite. Genth's analysis is shown in Table 3. When the pimelite analysis is adjusted to the water content of Genth's nickel-gymnite it is found that pimelite is richer in silica and poorer in the "RO" group than nickel-gymnite. Genth's description of hand specimens is as good today as when it was written—amorphous, grape-like clusters, stalactitic, dense, occasionally reniform. Hardness 3–4, specific gravity at 16° C. = 2.409, brittle. Fracture uneven to conchoidal. Opaque to translucent. Waxy luster. Apple-green to verdigris and possessing a greenish-white streak. Had subsequent investigators heeded this careful description and his accompanying chemical tests, the confusion in nomenclature which followed would not have taken place. Dana (1867) renamed the species *genthite* and drew it to the attention of the scientific world at this time. Genth (1875, 117B–118B) accepted Dana's renaming of the species.

TABLE 3. GENTHITE (NICKEL-GYMNITE) FROM TEXAS, LANCASTER COUNTY, PENNSYLVANIA. DESCRIBED BY FREDERICK A. GENTH (1851)

SiO <sub>2</sub>	35.36%
FeO	.24
MgO	14.60
CaO	.26
NiO	30.64
H <sub>2</sub> O(±)	19.09
	100.19

Analyst: F. A. Genth.

Although the hand specimen description of genthite is good, it is just a coincidence of nature, for genthite is not a single mineral species but actually a fine-grained mixture of pimelite and a nickeloan serpentine-group mineral. X-ray diffraction, chemical and other studies show that the type genthite is actually a mixture of pimelite and nickeloan serpentine in the proportion of about 20% pimelite to 80% nickeloan serpentine. The separation here defines the phases present but gives no indication of the distribution of Ni ions between these two phases. Based on the study of a large number of specimens and particularly the paragenetic position of the phases, pimelite and nickeloan serpentine, we may conclude that most of the nickel ions are in the pimelite member of the mixture.

Two hydrous nickel silicates found in the Hanns-Georg mine in the village of Röttis in Vogtland, Saxony, were named röttisite and connarite by the Saxon mineralogist August Breithaupt in 1859. Röttisite (Fig. 5) has now been examined by x-ray powder diffraction methods and found



FIG. 4. Nickel-gymnite of Genth (1851), later called genthite by Dana (1867), coating chromite from the Wood's chrome mine near Texas, Little Britain Township, Lancaster County, Pennsylvania. U.S. National Museum No. 82525.



FIG. 5. Röttisite of Breithaupt (1859) from the Hanns-Georg mine in the village of Röttis, in Vogtland, Saxony, Germany. U.S. National Museum No. 80404.



to give the pattern of pimeleite. Material answering to this description of connarite, as given by Breithaupt and by Dana, in the collections of the U.S. National Museum, yields an  $x$ -ray powder diffraction pattern unlike that of any of the known hydrous-nickel silicates. It is under continued study in our laboratory and it may be a mixture. Spangenberg (1938) classified it as a member of the schuchardite group (nickel chlorite).

De saulesite, a hydrous nickel-magnesium silicate, was described by Koenig (1889) from the zinc deposits of Franklin, New Jersey. A specimen of de saulesite, selected for this study by the late Professor Harry Berman from the mineral collection at Harvard University, yielded an excellent pattern of pimeleite when examined by  $x$ -ray powder diffraction methods.

The discovery of a hydrous nickel-magnesium silicate at Revdansk, a locality in the Ural Mountains, Russia, was made by Hans Rudolph Hermann, Director of the Mineral Water Institute in Moscow, in 1867, and he named it Revdanskite. A specimen of this mineral coated with cryptocrystalline quartz, supplied to the U.S. National Museum by the Mining and Metallurgical Laboratory of the Institute of Economic Mineralogy at Leningrad, was examined by  $x$ -ray powder diffraction methods and found to consist of quartz with pimeleite.

In 1867, Jules Garnier, a French geologist, published his significant studies on the geology of New Caledonia and on the basis of a qualitative analysis by Professor Edouard Jannettaz announced the discovery of nickel. Seven years thereafter followed a lengthy series of papers by various authors in which claims were made for new species at this locality, garniérite, népouite, nouméite, noumeaite. All of these can be identified with existing minerals. The confusion introduced into the nomenclature of the group of hydrous nickel-magnesium silicates based on the mineralogy of the deposit at New Caledonia is unusually large.  $X$ -ray powder diffraction analyses and DTA studies show that most of the specimens from this island consist of a mixture of pimeleite and a serpentine-group mineral.

About 1864, sheepherders discovered the ore deposits on Nickel Mountain, about five miles northwest of Riddle, in Douglas County, Oregon. Their true character as nickel ores was recognized about 1881 by W. Q. Brown of Riddle. These ores have been studied by a large number of scientists and engineers and are under detailed study by the staff of the Hanna Mining Company today. Pecora, Hobbs and Murata (1949) studied the mineralogy of these deposits and recognized that the so-called garnierite was an inhomogeneous material consisting of ". . . three hydro-silicates analogous in structure to serpentine, deweylite and pimeleite." They further made the excellent suggestion that "The name garnierite is

on a par with other such 'mineral mixture' names as limonite, bauxite, and 'manganese wad'. . . . Retention of the name garnierite as a general-field term serves a very useful purpose among economic geologists." This suggestion is followed here.

Hydrous nickel-magnesium silicates have been described from many other localities: North Carolina, Brazil, Cuba, the West Indies, India, Madagascar and elsewhere.

The garnierite group as defined here, following and extending the usage of Pecora *et al.* includes all hydrous nickel-magnesium silicates. This broad definition necessitates some mention of the lesser abundant species: schuchardite, the nickel chlorite; nickel-exchanged vermiculites; nickeloan talc, and nickeloan sepiolites.

Schuchardite was described as a chlorite by Professor Albrecht Schrauf of Vienna in 1882. In naming the species he gave two analyses by his student candidate Starkl. Starkl (1883) later published dehydration data for his specimen and noted that the powdered mineral is only slightly attacked by hydrochloric acid. The analytical data for schuchardite are inconclusive; they do not fall near to the composition of the serpentine group where they would be expected to be situated but suggest admixture with pimelite. That schuchardite is nickel-rich chlorite rests upon the *x*-ray studies of Spangenberg (1938) and of Schüller (1956).

Nickel-exchanged vermiculite was described by Ross and Shannon (1926) from Webster, North Carolina. Based on the field relationship and the chemistry of the minerals involved, Ross, Shannon, and Gonyer (1928) suggested "That the nickel as it was set free from the weathering dunite has been fixed in the vermiculite-bearing veins by the chemical process called base-exchange." This mineral presents a controversial problem in nomenclature because the position of the nickel ions in the structure is almost entirely in cation exchange positions in the crystal structure. It cannot, therefore, be correctly called nickel vermiculite. It is best called nickel-exchanged vermiculite.

Nickeloan talc has been known for more than a hundred years because the presence of very small amounts of nickel was reported by the early chemical analysts. A few talcs containing noteworthy amounts of nickel oxide are on record.

Nickeloan sepiolites have been reported by a number of scientists. Percy H. Walker (1888) reported a nickel sepiolite from Webster, North Carolina, but the physical description fits pimelite and the chemical analysis could be interpreted as pimelite admixed with one of the silica minerals. Professor Alfred La Croix (1943) lists four analyses of nickeloan sepiolites, but his microscopic studies show an extensive development of veinlets of quartz traversing the sepiolite. This observation suggests

caution in accepting the identification—for a mixture of pimelite and 10% silica would yield an analysis closely resembling theoretical sepiolite. There is no reason, however, to doubt that some of the nickeloan sepiolites reported occurring naturally are bona fide phases.

To set the mineral phases, delineated in this study, into a proper frame of reference they are considered compositionally with respect to the system  $\text{H}_2\text{O-NiO-MgO-SiO}_2$ .

The quaternary system  $\text{H}_2\text{O-NiO-MgO-SiO}_2$  has been shown to contain at least five natural quaternary phases—pimelite, the nickel serpentine-group minerals, schuchardite (nickel chlorite), nickel talc, and nickel sepiolite. The two bounding natural ternary systems  $\text{H}_2\text{O-NiO-SiO}_2$  and  $\text{H}_2\text{O-MgO-SiO}_2$  have been shown to have a one-to-one correspondence with respect to these phases. The natural phases indicate complete solid solution relations between corresponding phases.

The location of the phases in the system  $\text{H}_2\text{O-MgO-SiO}_2$  are shown in Fig. 6 which is a diagram based on weight per cent. In a mole per cent diagram the points in the two systems  $\text{H}_2\text{O-MgO-SiO}_2$  and  $\text{H}_2\text{O-NiO-SiO}_2$  would coincide.

The tie-line between serpentine-group mineral and stevensite has its equivalent in the tie-line “nickel serpentine-group mineral” and pimelite.

From crystal chemical considerations the complete replaceability of Mg for Ni or vice versa arises from the very close agreement of their ionic radii,  $\text{Mg}^{2+} = 0.66 \text{ \AA}$  and  $\text{Ni}^{2+} = 0.69 \text{ \AA}$ .

The arithmetical closeness of the chemical compositions of serpentine-group minerals and stevensite and their very frequent association in fine-grained admixtures have led many workers to consider both of these phases as members of the serpentine-group and to attempt to fit them into a generalized formula. Although this assumption of earlier investigators is not correct, Faust and Fahey (1962) found that it was fortunately a very useful one because it permitted them to dissect out the admixtures of phases. To do this they calculated all the analyses to the generalized serpentine formula  $\text{Mg}_6\text{Si}_4\text{O}_{10}(\text{OH})_8$  by setting the positive valence equivalent to 28. From this the ions in octahedral and tetrahedral coordination were obtained. All the metallic ions have to occupy octahedral or tetrahedral sites. From a knowledge of the chemical analyses of natural and synthetic phases and of the determination of the crystal structure of the serpentine-group minerals, all silicon ions are placed into tetrahedral sites. If there are insufficient silicon ions, then Al ions, if necessary  $\text{Fe}^{3+}$  ions, are transferred to tetrahedral sites in order to bring the sum to 4.00. The remaining metallic ions are assigned to octahedral sites. If the silicon ions exceed 4.00, they are retained in tetrahedral sites. The values for the ions in octahedral sites and those in tetrahedral sites are then plotted

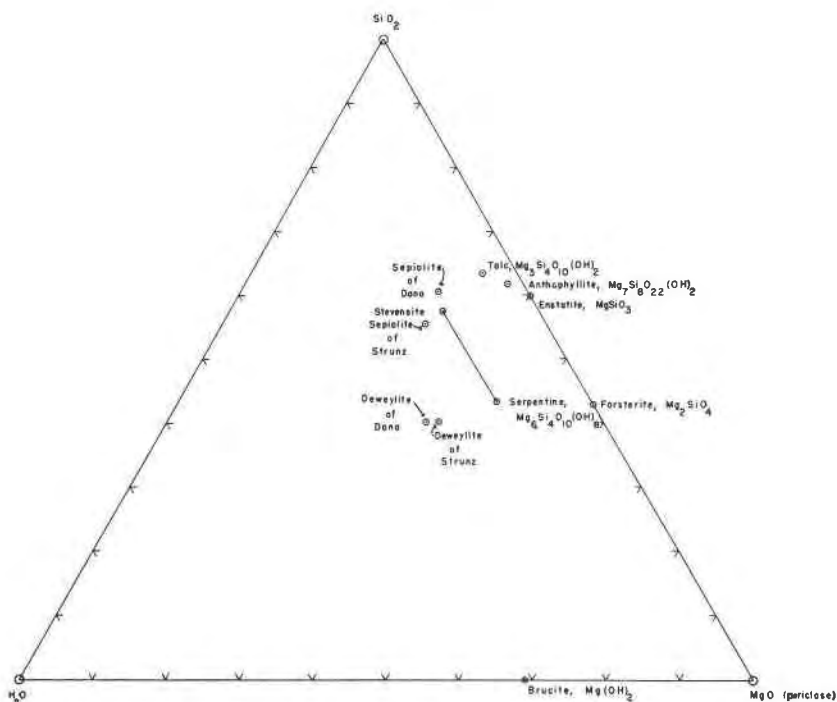


FIG. 6. Location of the phases and the mixture deweyllite in the ternary system  $\text{H}_2\text{O}$ - $\text{MgO}$ - $\text{SiO}_2$ . The diagram is in terms of weight percent. For the analogous system  $\text{H}_2\text{O}$ - $\text{NiO}$ - $\text{SiO}_2$  the compositions would all be shifted towards the RO component because of the higher molecular weight of NiO. In a mole percent diagram the points in the two systems would coincide.

against one another. Serpentine-group minerals cluster about the point

$$\sum_{\text{oct. ions}} = 6.00 \quad \text{and} \quad \sum_{\text{tet. ions}} = 4.00;$$

while the stevensites cluster about

$$\sum_{\text{oct. ions}} = 3.82 \quad \text{and} \quad \sum_{\text{tet. ions}} = 5.09.$$

The mixtures of these two phases are scattered along and astride the tie-line. The treatment of the similar data for the hydrous nickel-magnesium silicates shows an identical behavior. The graph (Fig. 7) contains the plots of 110 analyses of garnierite-group minerals taken mostly from the literature. It is at once apparent that there is a bias to the data in that all points lie on or below the tie-line. This is also true for the serpentine-group minerals and this suggests that for many of the analyses the silica is slightly too low. The reason for this may be inherent in the application



of the standard methods of analyzing silicates to the serpentine- and garnierite-group minerals which are relatively low in the  $R_2O_3$  group. In the filtrate from the silica there remains a small amount of unrecovered silica (usually about 1 to 3 mg). This is coprecipitated and subsequently measured with the  $R_2O_3$  group in the usual silicate analysis but in the serpentine- and garnierite-group minerals the  $R_2O_3$  is not sufficiently large to entrap the silica which is thereby lost.

To show the effect of common impurities in garnierite deposits upon the calculation of the analyses, hypothetical formulas were calculated for mixtures of 90 per cent pimelite and 10 per cent respectively of gibbsite, goethite, hematite, magnetite, quartz, and andesine and these are plotted on Fig. 7.

It is at once apparent that most of the hydrous nickel-magnesium silicates lie on or astride the tie-line nickel serpentine-group mineral to pimelite. Since pimelites are frequently associated with silica-group minerals, the tie-line has been continued to a point representing the admixture of 90 per cent pimelite and 10 per cent quartz. The alignment of some of the analyses suggests contamination by opal or quartz. The tie-lines serpentine-group minerals-pimelite and pimelite-silica minerals are established in this system. The mixture chrysoprase is located near the silica end of the later tie-line.

The nickel-exchanged vermiculities are a very difficult group to understand. The plot shown here is only a skirmish into the quinary system with alumina. The analyses of phlogopite and other micas, such as eastonite, from magnesium-rich parageneses, and of a natural mixture of serpentine and phlogopite were calculated to the generalized serpentine-group formula as previously, and are plotted as squares along the tie-line. Similarly, various vermiculites and nickel-exchanged vermiculites are plotted below the serpentine-group minerals. Since some of the nickel-exchanged vermiculites are admixed with pimelite, the chemical analysis of pimelite has been likewise put into the generalized serpentine-group with  $\Sigma_{tet} = 4.00$  by shifting silica to octahedral sites in order to show this admixed relationship. For any particular sample, microscopic examination or analysis by  $x$ -ray or DTA or chemical methods should readily disclose the impurities.

In summary, the confusion in the nomenclature of this group of minerals has been caused by

(1) failure to study carefully the previous literature; (2) the use of impure materials for analysis; and (3) the analysis of samples dried on a steambath.

In selecting the names to be retained in the description of the hydrous-nickel-magnesium silicates, we follow a dictum laid down long ago in

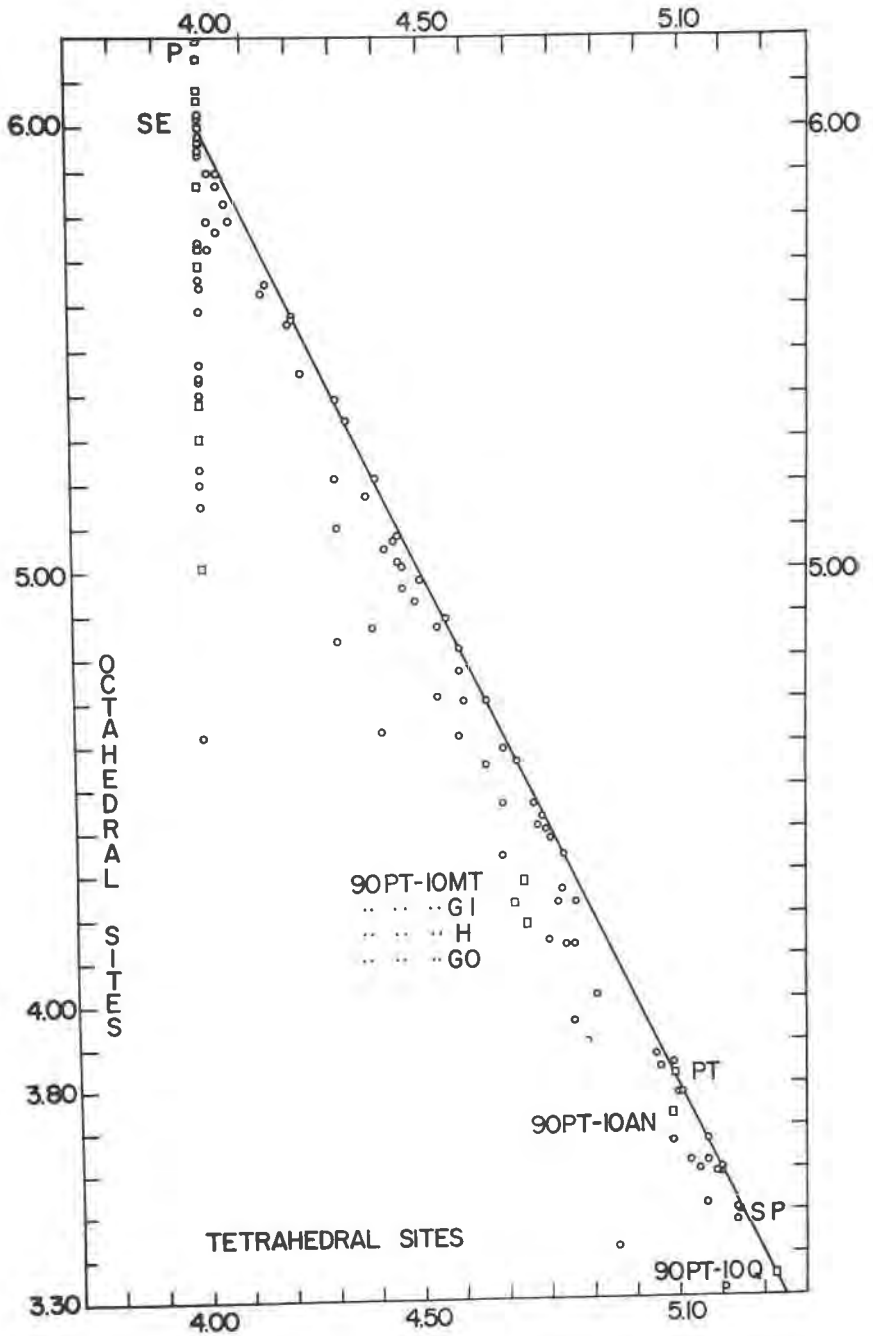


FIG. 7. The relation between the ions in octahedral sites and those in tetrahedral sites calculated from 110 chemical analyses of hydrous nickel-magnesium silicates, taken from the literature, is plotted in terms of cartesian coordinates. The tie-line theoretical serpentine-group minerals (SE) to theoretical pimeilite (PT) is extended to theoretical sepiolite (SP). All analyses have been computed to the generalized serpentine-group formula  $Mg_6Si_4O_{10}(OH)_8$  to facilitate comparison. Similarly, synthetic mixtures of various possible contaminants have been computed and plotted as squares to aid in the interpretation of the natural mixtures—these are for 90 percent pimeilite plus 10 percent contaminant. Designated 90PT-10MT (magnetite); 90PT-10GI (gibbsite); 90PT-10H (hematite); 90PT-10GO (goethite); 90PT-10AN (andesine) and 90PT-10Q (quartz). The points for 90PT-10H and 90PT-10GI are coincident. Letter P (top) locates phlogopite.



another discipline by Luther of Halle-Wittenberg: “Quod bonum est tenebimus”—that which is good we shall retain.

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