THE AMERICAN MINERALOGIST, VOL. 48, NOVEMBER-DECEMBER, 1963

NICKELIFEROUS SERPENTINES, CHLORITES, AND RELATED MINERALS FOUND IN TWO LATERITIC ORES

J. W. Montoya and G. S. Baur

Abstract

The nickel-bearing serpentines, chlorites, and related mineral species found in laterite ores from California and New Caledonia were identified by detailed mineralogical, optical, chemical, *x*-ray diffraction, differential thermal, and infrared spectra analyses. Electron micrographs were prepared to define the morphology of each variety. The principal serpentine minerals were lizardite, clino-chrysotile, and antigorite. The minerals contained from 0.3 to 5.3 pct nickel. Electron micrographs of the lizardites showed tubular particle forms in some samples and minute plates in others.

Clino-chrysotile occurred chiefly as a component of natural mixtures with lizardite, antigorite, or chlorite. Clino-chrysotile exhibited a variety of tubular habits ranging from long splintery tubes and fibers to relatively short, broad, multiple tubes. Additionally, pure orthochrysotile was isolated and identified.

Nepouite, garnierite, nickel-bearing varieties of penninite, fibrous antigorite and septeamesite also were identified, isolated and described.

Introduction

Californian nickeliferous-laterite ores have been described by Jenkins (1953, 1954). However, little work has been done to identify the serpentine minerals present in these ores. Extensive geological studies were made on the New Caledonian laterites by LaCroix (1942), deChetelat (1947), and Caillère and Henin (1960). However, there appeared to be little agreement among these authors as to the nomenclature of the minerals present. In addition, non-nickel-bearing serpentines have been studied extensively by Faust and Fahey (1962).

This paper identifies, classifies and gives detailed descriptions of the optical, chemical and physical properties of the nickel-bearing serpentine and related minerals found in Californian and New Caledonian lateritic ores.

The serpentine nomenclature used in this paper is that of Whittaker and Zussman (1956), who classified the serpentines into three main groups: Chrysotile, lizardite and antigorite. Two major forms of chrysotile, clino-chrysotile and ortho-chrysotile, were recognized. Both forms exhibit a tubular morphology but are distinguished by differences in their *x*-ray diffraction patterns. The name lizardite was proposed for a one-layer ortho-serpentine mineral. The name antigorite was used to identify a serpentine mineral having platey morphology and a larger unit cell than chrysotile and lizardite.

The related minerals in the ores, penninite, septeamesite, nepouite and garnierite, were identified on the basis of chemical analyses and known *x*-ray diffraction data. The prefix "septe" was proposed by Nelson and Roy (1954) to distinguish chlorite minerals having a series of basal *x*-ray reflections due to a 7 Å interplanar spacing from more common chlorite which is characterized by a 14 Å periodicity.

Sample Descriptions

Materials for this study were selected from large representative lots of ore. Samples comprised minus $\frac{1}{4}$-inch serpentine fragments and limonitic fines.

The lateritic ore from Humboldt County, California, contained about 15 pct serpentine minerals including a trace of garnierite, 55 pct limonite, and over 30 pct forsterite and hypersthene. Small-to-minute quantities of maghemite concretions, chromite and biotite also were present.

New Caledonian lateritic ore was comprised of 60 pct serpentine and chlorite minerals including minute quantities of nepouite and garnierite; 25 pct limonite; and 15 pct actinolite, enstatite, forsterite and maghemite concretions. Traces of anorthite, tremolite asbestos and chromite were identified.

Laboratory Investigations

Samples of the lateritic ores were prepared for mineral identification by self-attritioning and washing to remove friable limonitic fines, which were discarded. Thereafter, the coarse fraction of each ore was hand sorted into various groups according to color and physical appearance. Each group then was crushed, screened and separated into appropriate specific gravity fractions from which specimens of relatively pure serpentine and related mineral species, as well as natural mixtures of these minerals, were selected for detailed study and analyses.

Mineralogical studies: The major serpentine mineral found in the two ores was lizardite. The other serpentine and related mineral species occurred in minor-to-trace quantities, generally as natural mixtures of two or more varieties. The distinguishing physical and optical properties of the serpentine and related mineral varieties found in the two ores are presented in Table 1.

Specimens obtained from the Californian deposit contained a nickel-bearing lizardite and small quantities of clino-chrysotile and fibrous antigorite. Minute grains of garnierite also were identified.

Specimens obtained from the New Caledonian deposit consisted

Table 1. Optical and Physical Properties of Serpentines, Chlorites, and Related Species

Mineral	Color	Refractive index	Habit
Lizardite			
California	Yellow-green	1.575	Plates
New Caledonia	do.	1.575–1.580	Do.
Clino-chrysotile			
California	Light- to dark-green	1.570–1.580	Do.
New Caledonia	Light-green	1.565–1.575	Plates
Ortho-chrysotile			
New Caledonia	Gray-green	1.570–1.575	Do.
Antigorite			
California	White	1.565	Fibers
New Caledonia	Light- to dark-green	1.565–1.575	Do.
Related species			
New Caledonia septeamesite	Light-green	1.540–1.560	Cryptocrystalline
New Caledonia penninite	Yellow- to dark-green	1.590	Plates
New Caledonia nepouite	Bright- to blue-green	1.620–1.630	Fibers
California garnierite	Light- to yellow-green	1.545–1.570	Cryptocrystalline
New Caledonia garnierite	do.	1.580–1.610	Do.

mainly of nickeliferous lizardite. Nickel-bearing clino-chrysotile and penninite were present in minor quantities generally as natural mixtures in combination with each other and/or with lizardite. Ortho-chrysotile, septeamesite, nepouite and garnierite occurred in small amounts as isolated grains. A few grains of impure antigorite were identified.

Chemical studies: The chemical analyses of the serpentine minerals are presented in Table 2. The percentages given in this table represent average values obtained by analyzing a number of fragments. Similar chemical analyses of the New Caledonian chlorites, nepouite and garnierite are shown in Table 3. The chemical analyses of the serpentines agree fairly well with the literature (Faust and Fahey, 1962), except for the substitution of variable amounts of nickel for magnesium. The analysis of nepouite is in close agreement with that of nepouite published by Alekseeva and Godlevsky (1937). Garnierite, according to Dana (1914), has a variable composition, especially with respect to the mutual replacement of nickel and magnesium. This variability of chemical com-

TABLE 2. CHEMICAL ANALYSES OF SERPENTINE MINERALS

Mineral	Analysis, pct								
	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	Cr_2O_3	NiO	LOI	
								400° C.	900° C.[1]
Lizardite									
California	40.8	0.2	7.2	1.3	34.3	n.d.[2]	2.0	3.5	10.6
New Caledonia	38.3	.6	6.8	1.5	33.3	0.2	4.3	3.1	11.3
Clino-chrysotile									
New Caledonia	41.3	1.0	3.4	n.d.[2]	34.4	0.1	5.3	2.1	11.7
Antigorite									
California	39.6	1.0	5.9	n.d.[2]	39.9	n.d.[2]	.3	.5	11.9

[1] Difference between loss on ignition at 400° and 900° C.

[2] Not determined.

position also is reflected in the variability of the optical character (Table 1).

X-Ray diffraction studies: Identification of the serpentines, chlorites and related species was based in part on *x*-ray diffraction data. Lizardite, clino-chrysotile, ortho-chrysotile and antigorite were identified using *x*-ray data compiled by Whittaker and Zussman (1956). Septeamesite, penninite, nepouite and garnierite were identified by comparison with ASTM *x*-ray diffraction data.

TABLE 3. CHEMICAL ANALYSES OF NEW CALEDONIAN CHLORITES AND RELATED MINERALS

Mineral	Analysis, pct									
	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	Cr_2O_3	NiO	LOI	
									400° C.	900° C[1]
Septeamesite	30.9	26.7	0.9	n.d.[2]	21.4	n.d.[2]	trace	3.6	4.8	10.6
Penninite	32.7	14.5	3.8	2.5	29.6	n.d.[2]	0.3	3.2	1.7	11.1
Nepouite	33.8	4.1	1.3	n.d.[2]	13.5	trace	.1	34.8	1.6	10.6
Garnierite	46.7	<1.0	1.4	n.d.[2]	19.9	1.6	n.d.[2]	14.5	3.0	11.2

[1] Difference between loss on ignition at 400° C.

[2] Not determined.

X-ray diffraction data for the serpentines, chlorites, nepouite and garnierites are presented in Tables 4 and 5. The specimen of California garnierite used was contaminated with serpentine and quartz. Many of the peaks in the *x*-ray pattern shown are due to or have been intensified

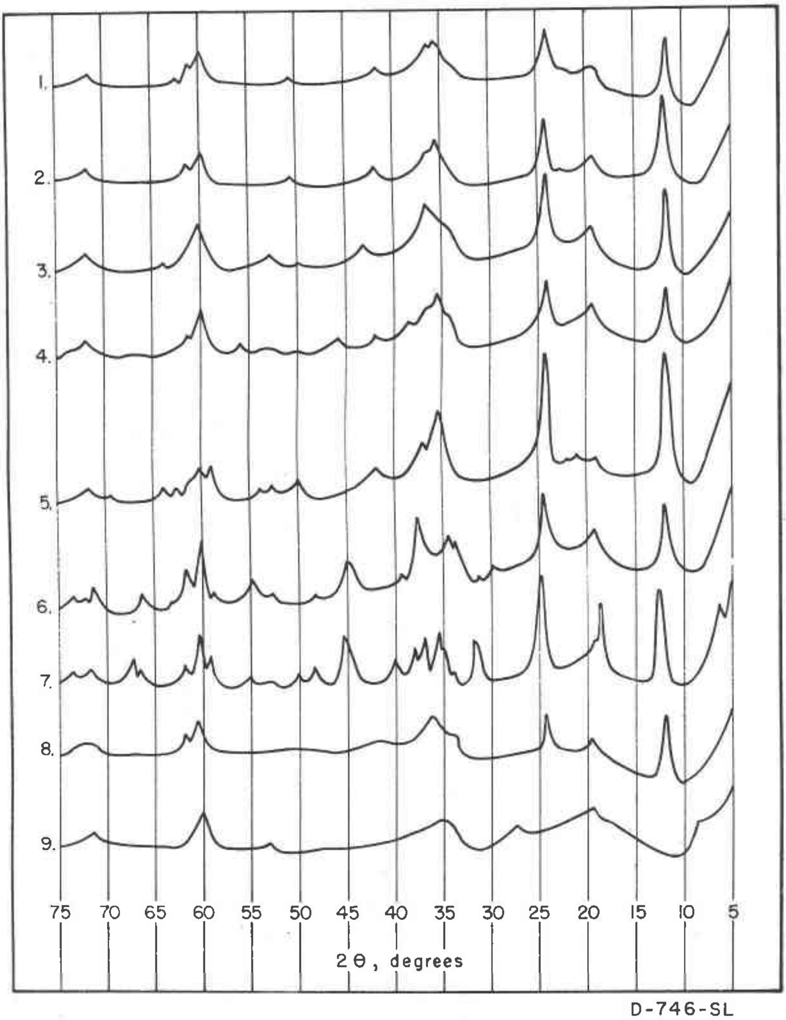

FIG. 1. Smoothed powder diffraction patterns for serpentines, chlorites, nepouite, and garnierite. (1) California lizardite, (2) New Caledonia lizardite, (3) New Caledonia clinochrysotile, (4) New Caledonia orthochrysotile, (5) California antigorite, (6) septeamesite, (7) penninite, (8) nepouite, (9) New Caledonia garnierite.

by the presence of the serpentine impurity in the sample. If the reflections suspected as due to the presence of serpentine are ignored, the data agree fairly well with that of ASTM card No. 2-0060 as well as with that of Alekseeva and Godlevsky (1937). Copper Kα radiation was used. The diffractometer patterns are reproduced as Fig. 1.

TABLE 4. *X*-RAY DIFFRACTION DATA FOR LIZARDITES AND CHRYSOTILES

Lizardite				Clino-chrysotile New Caledonia		Ortho-chrysotile New Caledonia	
California		New Caledonia					
dÅ	I/I_0	dÅ	I/I_0	dÅ	I/I_0	dÅ	I/I_0
7.19	75	7.25	100	7.25	85	7.25	00
4.53	45	4.55	15	4.57	25	4.55	45
3.90	<5	3.91	5	2.583	25	2.605	50
3.63	100	3.65	60	3.66	100	3.65	100
2.493	70	2.499	35	2.486	40	2.499	85
2.453	60	2.447	20	2.440	65	2.460	60
2.154	20	2.145	15	2.092	15	2.336	35
1.792	10	1.789	5	1.823	10	2.149	10
1.540	40	1.536	20	1.739	15	1.971	20
1.504	20	1.502	10	1.534	45	1.816	5[1]
1.310	20[1]	1.310	10[1]	1.470	10	1.723	15[1]
						1.641	15
				1.315	20	1.538	65
						1.509	30
						1.310	25[1]

[1] Broad peak.

Differential thermal analysis studies: Differential thermal analyses were made on selected serpentine and chlorite specimens. The curves are shown in Fig. 2. The general shape of the curves agreed with those obtained on similar minerals by Faust and Fahey (1962), Nelson and Roy (1954) and Brindley and Ali (1950). No differential thermal data were available on nepouite. The samples were heated 12° C. per minute in an air atmosphere. In all samples, the differential thermal analyses showed a strong endothermic reaction between 600° and 750° C., which was due to dehydration and destruction of crystal structure. Nickeliferous lizardite, clino-chrysotile, septeamesite and penninite showed evidence of an additional weak endothermic reaction near 800° C. All varieties tested exhibited a strong exothermic reaction due to the formation of forsterite

TABLE 5. *X*-RAY DIFFRACTION DATA FOR ANTIGORITE, SEPTEAMESITE, PENNINITE, NEPOUITE, AND GARNIERITE

Antigorite California		Septeamesite, New Caledonia		Penninite, New Caledonia		Nepouite, New Caledonia		Garnierite			
								California		New Caledonia	
dÅ	I/I_0	dÅ	I/I_0	dÅ	I/I_0	dÅ	I/I_0	dÅ	I/I_0	dÅ	I/I_0
7.19	95			14.2	55			10.4	100^1	10.0	35^1
4.59	10	7.19	80	7.13	90	7.25	100	7.4	75^2		
				4.74	70			6.4	10		
4.13	10	4.60	40	4.62	10	4.55	35	5.0	10		
4.00	5	3.59	100	3.57	100	3.62	100	4.6	100^1	4.57	100^1
3.60	100	2.96	5								
2.527	30			2.838	25						
2.421	15							3.68	50^2		
2.210	<5	2.650	50			2.642	40				
2.154	10	2.583	55	2.583	20			3.22	10^1	3.24	55^1
1.816	5			2.540	30	2.479	60^1	2.65	$75^{1,2}$	2.650	65^1
				2.440	25			2.45	$75^{1,2}$	2.460	65^1
1.732	5	2.384	80	2.378	15						
1.562	10	2.257	15	2.252	10			2.11	$<5^{1,2}$		
1.536	10					2.149	15	1.73	10^1	1.729	15^1
1.513	5	2.009	35	2.004	25			1.53	$100^{1,2}$	1.531	80
1.502	5	1.886	15	1.886	10			1.32	$100^{1,2}$	1.315	35^1
1.478	5			1.823	5						
		1.726	10	1.742	5						
1.450	5	1.665	25	1.660	5						
1.315	5	1.569	15	1.564	15						
		1.534	60	1.541	25	1.529	60				
		1.502	20	1.504	10	1.500	30				
		1.405	15	1.416	5						
				1.396	15						
		1.322	20	1.318	10	1.303	25^1				
		1.287	15	1.290	10						
		1.215	5	1.223	5						

[1] Broad peak.

[2] Peaks due to or augmented by the presence of serpentine minerals.

and/or enstatite between 750° and 850° C., with the exception of New Caledonian septeamesite and nepouite, which exhibited weak reactions in this temperature range.

Thermal reaction studies: Supplemental studies were made to correlate the reactions detected by DTA with phase changes that occurred in these minerals upon heating. Individual samples were heated in air for 30 minutes at various temperatures ranging from 500° to 1,000° C. The heat-treated samples then were examined by *x*-ray diffraction analyses to identify the different phases formed. The pertinent findings are summarized in Table 6.

Temperatures at which the serpentine and chlorite minerals decomposed and then recrystallized to form forsterite varied. All minerals studied however, formed enstatite between 750° and 850° C. Except for antigorite all heat-treated minerals exhibited an amorphous phase before the formation of forsterite. Antigorite apparently decomposed simultaneously with the formation of forsterite. Septeamesite transformed to sapphirine in addition to forsterite between 750° and 800° C., and to forsterite, enstatite and a spinel-type structure above 800° C.

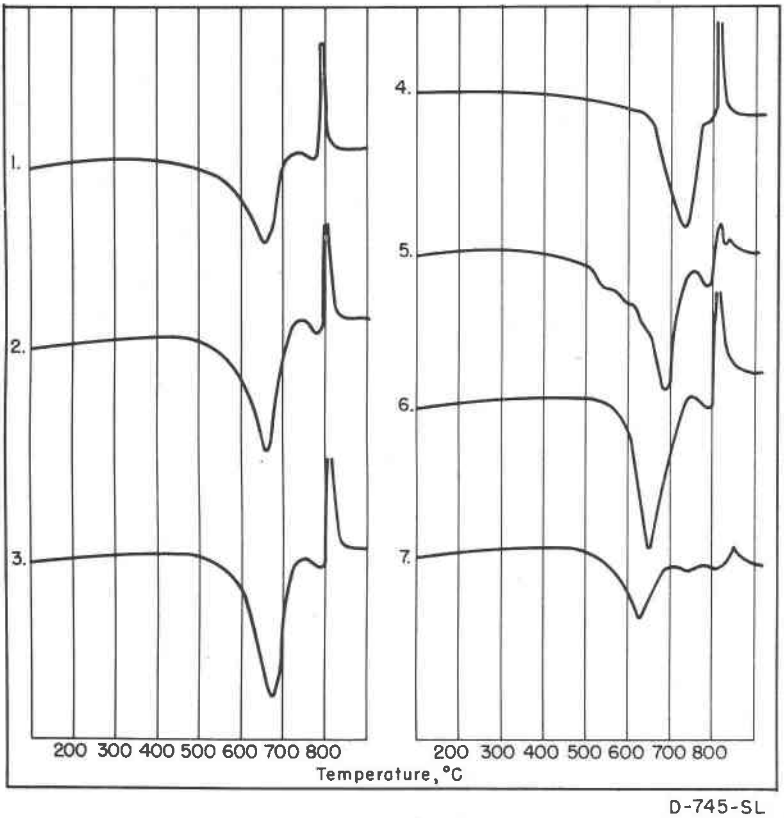

FIG. 2. DTA curves for serpentines, chlorites, and nepouite. (1) California lizardite, (2) New Caledonia lizardite, (3) New Caledonia clino-chrysotile, (4) California antigorite, (5) septeamesite, (6) penninite, (7) nepouite.

The chlorites, when heat treated, retained or developed a symmetry associated with the 14.7 Å and 2.8 Å interplanar spacings. In heat-treated penninite, the chlorite structure collapsed except for this symmetry. The 14.7 Å and 2.8 Å reflections increased in intensity as the sample was

TABLE 6. PHASE CHANGES ON HEATING PRODUCED IN SERPENTINES AND CHLORITES

Mineral	Temperature of phase change, ° C.		
	Decomposition of serpentine lattice	Forsterite formation	Enstatite formation
Lizardite			
California	550–600	700–750	750–800
New Caledonia	550–600	750–800	750–800
Clino-chrysotile			
New Caledonia	550–600	750–800	750–800
Antigorite			
California	600–650	600–650	800–850
Chlorite			
New Caledonia septeamesite	700–750	750–800	800–850
New Caledonia penninite	650–700	750–800	750–800

heated until forsterite formed (about 750° C.), at which temperature they disappeared. The high temperature form of septeamesite, represented by weak reflections due to 14.7 Å and 2.8 Å interplanar spacings, appeared at about 500° C. These peaks also disappeared with the formation of forsterite.

Infrared studies: Infrared absorption spectra were recorded on the nickeliferous serpentines, chlorites, nepouite, and garnierite as an aid in distinguishing the different varieties. The spectra for the 9 to 11 micron-wavelength range are presented in Fig. 3.

Samples were mixed with potassium bromide and hand ground under alcohol to prevent lattice destruction and then pressed into disks. Measurements were made using sodium chloride optics.

Although the serpentines and chlorites gave somewhat similar absorption spectra, differences in the position, shape, and intensity of the peaks enabled the varieties to be distinguished from one another. The results agreed generally with those of Brindley and Zussman (1959) and Tuddenham and Lyon (1959).

Electron microscope studies: The morphology of the serpentines, chlorites, nepouite and garnierite was determined by the electron microscope.

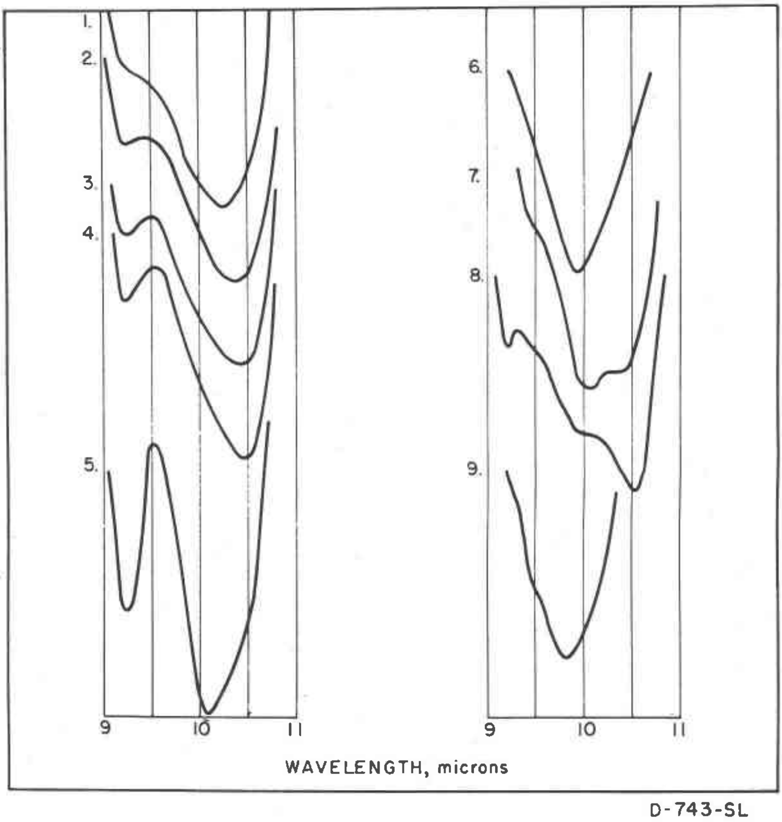

FIG. 3. Infrared curves for serpentines, chlorites, nepouite, and garnierite. (1) California lizardite, (2) New Caledonia lizardite, (3) New Caledonia clino-chrysotile, (4) New Caledonia ortho-chrysotile, (5) California antigorite, (6) septeamesite, (7) penninite, (8) nepouite, (9) garnierite.

1) *Lizardites*

Californian lizardite exhibited a tubular morphology, whereas New Caledonian lizardite consisted of plate-like particles similar to those of lizardite from Snarum, Norway, photographed by Zussman *et al.* (1957). Comparison of the x-ray pattern of the California lizardite with the x-ray data on chrysotile compiled by Whittaker and Zussman (1956) demonstrates the tubular California lizardite is neither ortho- nor clino-chrysotile. Although the California lizardite could be mistaken for poorly developed antigorite, its tubular habit and the DTA and infrared data rule out this possibility.

2) *Clino-chrysotile*

Relatively pure clino-chrysotile and clino-chrysotile-antigorite mixtures in New Caledonian samples occurred as relatively long, thin splintery tubes and fibers. Some of the fibers appeared to have curled edges. Clino-chrysotile mixed with penninite or with lizardite occurred as thin splintery tubes and fibers and as relatively short, broad multiple tubes (tube-in-tubes). The multiple tubes consisted of progressively larger tubes similar to a telescope, or of a broad tube enclosing a longer, thinner tube that projects at both ends.

3) *Ortho-chrysotile*

The ortho-chrysotile from New Caledonia exhibited a tubular morphology similar to the New Caledonian clino-chrysotile, but the tubes were somewhat shorter.

4) *Antigorites*

Californian and New Caledonian fibrous antigorites occurred as broad laths.

5) *Septeamesite, penninite and nepouite*

New Caledonian septeamesite, penninite, and nepouite occurred as plates. Septeamesite occurred as minute, irregularly shaped platey particles. Penninite plates were large and broad. Nepouite plates were somewhat smaller than the penninite plates and appeared to be hexagonal in outline.

ACKNOWLEDGMENTS

The authors wish to thank B. H. Clemmons, Jr., Research Director, and the staff of the Salt Lake City Metallurgy Research Center of the Bureau of Mines, for their assistance, especially that of R. G. Anderson, for the differential thermal analyses; K. R. Farley, for the infrared spectra; and M. R. Howcroft, for the chemical analyses.

REFERENCES

ALEKSEEVA, E. F. AND M. N. GODLEVSKY (1937) X-ray studies of nickel hydrosilicates. *Mem. Soc. Russe Mineral.*, Ser. 2, **66,** 51–106.

BRINDLEY, G. W. AND S. Z. ALI (1950) X-ray study of thermal transformations in some magnesian chlorite minerals. *Acta Cryst.*, **3,** 25–30.

——— AND J. ZUSSMAN (1959) Infrared adsorption data for serpentine minerals. *Am. Mineral.* **44,** 185–188.

CAILLÈRE, S. AND M. S. HENIN (1960) Étude minéralogique de certains minérals de nickel dits "nickel coocolat." *Silicate Industriels*, **25,** 293–296.

DANA, E. S. (1914) *A System of Mineralogy.* John Wiley & Sons, Inc., 6th Ed., New York, N. Y., pp. 676–677.

DE CHETELAT, E. (1947) La genèse et l'evolution des gisements de nickel de la Nouvelle-Caledonie. *Soc. Geol. France. Bull. ser. 5*, **17,** 105–160.

Faust, G. T. and J. J. Fahey (1962) The serpentine-group minerals. *U. S. Geol. Survey Prof. Paper* **384-A.**

Jenkins, Olaf P. (1953) Serpentine in California. *Mineral Info. Serv., State of California,* **6,** 1–4.

——— (1954) Nickel in California. *Mineral Info. Serv., State of California,* **7,** 1–5.

La Croix, A. (1942) Les peridotites de la Nouvelle, Caledonie; leurs serpentines et leur gîtes de nickel et de cobalt; les gabbros qui les accompagnent. *Acad. Sci. Paris Mem.* **66,** 1–143.

Nelson, Bruce W. and Rustum Roy (1954) New data on the composition and identification of chlorites. *Second Natl. Conf. Clays Clay Minerals, Nat'l. Acad. Sci. Pub.,* Pp. 327, 335–348.

Tuddenham, W. M. and R. J. P. Lyon (1959) Relation of infrared spectra and chemical analysis in the chlorite mineral series. *Anal. Chem.* **31,** 377–380.

Whittaker, E. J. W. and J. Zussman (1956) The characterization of serpentine minerals by X-ray diffraction. *Mineral. Mag.* **31,** 107–126.

Zussman, J., G. W. Brindley and J. J. Comer, (1957) Electron diffraction studies of serpentine minerals. *Am. Mineral.* **42,** 133–153.

Manuscript received, April 8, 1963; accepted for publication, July 2, 1963.