THE AMERICAN MINERALOGIST, VOL. 51, MAY-JUNE, 1966

GASPEITE, (Ni, Mg, Fe) (CO_3), A NEW CARBONATE FROM THE GASPÉ PENINSULA, QUEBEC

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ABSTRACT

A new nickel carbonate mineral was found as a vein enclosed in siliceous dolomite in the Gaspé Peninsula, Quebec. Magnesium and to a lesser extent, iron, carbonates are in solid solution with the nickel carbonate. The name gaspeite has been selected for the nickel carbonate end member, the new mineral being designated as magnesian gaspeite. It occurs associated with small amounts of millerite, niccolite, annabergite and gersdorffite.

Magnesian gaspeite occurs as light green crystals up to 0.5 mm in length. The mineral is insoluble in water and very slowly soluble in nitric or hydrochloric acids. Its hardness is about 4.5 to 5; density 3.71 ± 0.01 g/cm^3; vitreous to dull luster; yellow-green streak; an uneven fracture; good rhombohedral cleavage. It is uniaxial negative, with $\omega = 1.83 \pm 0.01$ and $\epsilon = 1.61 \pm 0.01$; $\Delta = 0.22$.

X-ray analysis shows that the crystals are rhombohedral with the following characteristics: $a = 4.621 \pm 0.002$; $c = 14.93 \pm 0.02$ Å; $C = 3.231 \pm 0.006$; $a_{rh} = 5.65 \pm 0.02$ Å; $\alpha = 48° 18.3' \pm 5.5'$; volume 276.0 ± 0.9 Å^3; cell contents 3 $[(Ni_{0.98}Mg_{0.86}Fe_{0.16})(CO_3)_2]$ in the hexagonal unit. The strongest *x*-ray lines are: 2.741 (100); 1.692 (45); 3.543 (36); 2.098 (36); 1.932 (25); 2.317 Å (20).

Infrared absorptions occur at 7.00, 11.42 and 13.32 microns.

Chemical analysis of the purified mineral gave $NiO = 35.0\%$, $MgO = 17.3\%$, $FeO = 5.7\%$, $CO_2 = 42.0\%$, insoluble $= 1.8\%$, total $SiO_2 = 0.9\%$.

INTRODUCTION

An unusual light green mineral, occurring in a massive two-foot wide vein enclosed in a varicolored siliceous dolomite of Middle Silurian age, was found by the New Jersey Zinc Exploration Co. (Canada), Ltd., during an investigation of Lemieux Township, Gaspé Nord County, Gaspé Peninsula, Quebec, Canada.

The samples were submitted to the Research Department of The New Jersey Zinc Company at Palmerton, Pennsylvania, where *x*-ray, wet chemical, spectrographic, infrared, differential thermal analysis, and petrographic analyses suggested it to be a previously undescribed nickel, magnesium, iron carbonate. The name gaspeite has been selected for the nickel carbonate end member, the new mineral being designated as magnesian gaspeite. Its composition is $(Ni_{0.98}Mg_{0.86}Fe_{0.16})(CO_3)_2$.

OCCURRENCE

Magnesian gaspeite first was observed as a light green, massive rock occurring in a two-foot wide vein enclosed in a varicolored siliceous dolomite. The vein consists of essentially pure magnesian gaspeite with minor amounts of annabergite, magnesite and dolomite. Enclosed in the magnesian gaspeite are a small amount of serpentine and a (Cr, Al) spinel (5 to 10% and less than 5%, respectively). Well-formed crystals of millerite (NiS), niccolite (NiAs), annabergite ($Ni_3(AsO_4)_2 \cdot 8H_2O$), gersdorffite (NiAsS) and magnesite ($MgCO_3$) are found outside of the vein in the buff siliceous dolomite.

The vein did not crop out but was exposed by a bulldozer during road building operations in the area. The formation in which it occurs rests unconformably on the Shickshock Series, a hornblende-chlorite schist, of Cambrian or Precambrian age and is overlain by a quartzite of Middle Silurian age.

Serpentinized plugs of post Middle Silurian and pre-Middle Devonian age (McGerrigle, 1954) were intruded into the siliceous dolomite.

MINERAL SEPARATION

Magnesian gaspeite crystals were isolated by crushing the sample and separating the −100 to +150 mesh fraction on a Frantz isodynamic magnetic separator. It separated rather sharply between 0.40 and 0.45 ampere with cross slope and longitudinal slope of 15° and 30°, respectively. This fraction was further cleaned with methylene iodide (sp. gr. = 3.33). The heavy fraction was retained and one gram was submitted for chemical analysis.

PHYSICAL AND OPTICAL PROPERTIES

Magnesian gaspeite occurs as light green rhombohedral crystals up to 0.5 mm in length. The mineral has a vitreous to dull luster, yellow-green streak, and uneven fracture, and good rhombohedral cleavage $(10\bar{1}1)$. Its hardness is 4.5 to 5. The specific gravity of −100 to +150 mesh magnesian gaspeite crystals, determined by the pycnometer method using kerosene as the immersion liquid, is 3.71 ± 0.01; the calculated specific gravity is 3.748.

Magnesian gaspeite is light green in transmitted light. The indices of refraction, determined by the immersion method,[1] were $\omega = 1.83 \pm 0.01$ and $\epsilon = 1.61 \pm 0.01$; $\Delta = 0.22$. It is uniaxial negative.

INFRARED ABSORPTION ANALYSIS

An infrared spectrum of magnesian gaspeite was obtained with a Perkin-Elmer Recording Spectrophotometer Model 13, using sodium chloride optics. KBr pellets were prepared using 0.25 and 0.50 mg, respec-

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[1] High refractive index phosphorus-sulfur-methylene iodide liquids were used for determination of the ordinary ray (West, 1936).

tively, of fine powder in 500 mg of KBr. The experimental method was similar to that described by Adler and Kerr (1963).

The spectrum of magnesian gaspeite includes three major absorption bands ν_3, ν_2 and ν_4 at 7.00, 11.42 and 13.32 microns, respectively. A comparison of the spectrum of magnesian gaspeite and other selected calcite-group carbonates obtained by Adler and Kerr (1963) is given in Table 1.

An examination of Table 1 indicates that the infrared spectrum of magnesian gaspeite bears a closer resemblance to those of magnesite and smithsonite than to those of the other minerals of the calcite group.

DIFFERENTIAL THERMAL ANALYSIS

A DTA device, using 22-gauge chromel-alumel thermocouples, was employed in the analysis. The thermal reactions were recorded on a standard electronic millivolt recorder. Magnesian gaspeite was ground to −200 mesh to which 10% alundum was added. The heating rate varied from 6° to 15° C. per minute with alundum being used as a reference standard.

TABLE 1. COMPARISON OF THE INFRARED SPECTRUM OF MAGNESIAN GASPEITE WITH THOSE OF OTHER ANHYDROUS CARBONATES

Mineral	Locality	Wavelength (Microns)		
		ν_3	ν_2	ν_4
Magnesian Gaspeite	Gaspé Peninsula, Quebec, Canada	7.00	11.42	13.32
Magnesite	Tulare Co., California	6.86	11.28	13.35
Dolomite	Guanajuato, Mexico	6.95	11.35	13.72
Calcite	New Mexico	7.02	11.40	14.02
Smithsonite	Broken Hill, N.S. Wales	7.04	11.48	13.42
Siderite	Braundord, Germany	7.06	11.53	13.54
Rhodochrosite	Butte, Montana	7.07	11.54	13.75

The decomposition of magnesian gaspeite begins slowly at 520° C., reaches a peak at 690° C. and overlaps the exothermic peak representing the oxidation of ferrous to ferric iron. The latter reaches a peak at 735° C. Two unexplained, small exothermic peaks are present at 790° C. and 815° C., respectively.

X-RAY POWDER DATA

An *x*-ray powder diffraction pattern of magnesian gaspeite was taken in a 114.59-mm diameter Debye-Scherrer camera with nickel-filtered

TABLE 2. X-RAY POWDER DATA FOR MAGNESIAN GASPEITE

		Calculated	Measured	
(1) hkl	(2) $h_rk_rl_r$	(3) d_{hkl}	(4) d_{hkl}	(5) I
01.2	110	3.527	3.543	36
10.4	211	2.730	2.741	100
00.6	222	2.488	2.495	3
11.0	$10\bar{1}$	2.311	2.317	20
11.3	210	2.096	2.098	36
20.2	200	1.933	1.932	25
02.4	220	1.764	1.766	10
01.8	332	1.691	1.692	45
21.1	$20\bar{1}$	1.505	1.506	4
12.2	$21\bar{1}$	1.483	1.485	10
21.4	310	1.402	1.401	9
20.8	422	1.365	1.366	3
11.9	432	1.348	1.349	2
12.5	320	1.349		
03.0	$11\bar{2}$	1.334	1.337	11
00.12	444	1.244	1.242	3
02.10	$44\bar{2}$	1.197	1.195	2
30.6	411	1.176	1.176	5
03.6	330			
22.0	$20\bar{2}$	1.155	1.156	2
13.4	$32\bar{1}$	1.064	1.064	5
22.6	420	1.048	1.048	3
40.4	400	0.966	0.967	3
31.8	512	0.954	0.954	4
23.2	$31\bar{2}$	0.911	0.910	4
32.4	$41\bar{1}$	0.892	0.892	1
04.8	440	0.882	0.882	2
14.0	$21\bar{3}$	0.873	0.874	2
32.7	520	0.843	0.844	2
23.8	530	0.824	0.824	2
41.6	510			
14.6	$43\bar{1}$			

copper radiation ($\lambda = 1.5418$ Å). In making spacing measurements, film shrinkage and camera radius errors were taken into account by using the Straumanis film mount and correction procedures. The interplanar spacings and intensities for the observed lines are given in Table 2, columns 4 and 5. The intensities were visually estimated by comparison with a calibrated intensity strip.

Hexagonal cell constants, $a = 4.621 \pm 0.002$ and $c = 14.93 \pm 0.02$ Å, were determined from

$$1/2\left[\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right]$$

extrapolations using reflections in the range 40° to 62°. Interplanar spacings calculated from the *x*-ray cell constants on a digital computer are listed in Table 2, column 3.

Comparison of Magnesian Gaspeite, $MgCO_3$, $NiCO_3$ and a Hypothetical Solid Solution $Ni_{0.50}$, $Mg_{0.50}$

A comparison of the optical and crystallographic data for magnesian gaspeite with those of $MgCO_3$ and $NiCO_3$ (Graf, 1961; Isaacs, 1963) shows the remarkable similarity of magnesian gaspeite to those two compounds (Table 3, columns 1, 3, and 4). The physical constants for a hypothetical solid solution of $Ni_{0.50}$, $Mg_{0.50}$ were predicted by taking them midway between those of $MgCO_3$ and $NiCO_3$ (Table 3, column 2). A comparison of the a_0 and c_0 values shows that the values for magnesian

Table 3. Comparison of Magnesian Gaspeite, $MgCO_3$, $NiCO_3$ and Theoretical $Ni_{0.50}Mg_{0.50}$

Locality Reference	(1) Magnesian Gaspeite Gaspé, Quebec, Canada Present Paper	(2) $Ni_{0.50}Mg_{0.50}$ Calculated[1] Present Paper	(3) Magnesite $MgCO_3$ Synthetic Graf (1961)	(4) Gaspeite $NiCO_3$ Synthetic Graf (1961) Isaacs (1963)
Optical Constants				
ω	1.83	1.815	1.700	1.930
ε	1.61	1.615	1.509	1.721
Δ	0.22	0.200	0.191	0.209
Cell Constants (Å)				
a	4.621 ± 0.002	4.6152	4.6330	4.5975
c	14.93 ± 0.02	14.889	15.016	14.723
$C=c_0/a_0$	3.231 ± 0.006	3.2261	3.2411	3.2024
a_{rh}	5.65 ± 0.02	5.6273	5.6752	5.5795
α	48°18.3′±5.5′	48° 25.3′	48° 10.9′	48° 39.7′
Volume Å³ (Hexagonal)	276.00 ± 0.90			
Density-g/cc				
Calculated	3.748	3.67		
Observed	3.71 ± 0.01		2.96	4.388

[1] Hypothetical solid solution with physical constants midway between those of the two end members.

gaspeite are close to those given for $Ni_{0.50}$, $Mg_{0.50}$ being between those given for $Ni_{0.50}$, $Mg_{0.50}$ and $MgCO_3$.

The similarity of the crystallographic data for magnesian gaspeite, $MgCO_3$, and $NiCO_3$, and the similar ionic size of nickel, magnesium, and iron suggests that all three have the same calcite-type structure.

The optical properties and density of magnesian gaspeite (Table 3, column 1) are close to those predicted for a hypothetical solid solution of $Ni_{0.50}$ and $Mg_{0.50}$.

CHEMISTRY

A qualitative spectrographic analysis is as follows:

	Approximate Order of Magnitude
Ni	10% or more
Mg	10%
Si and Fe	1%
Al, Mn, Cr, Tl	0.01–0.1%
Ti	0.01%
Pb, Co	0.001–0.01%
B	0.001%
Cu, Sn, Mo	0.0001%

The chemical analysis of purified magnesian gaspeite is as follows: 35.0% NiO, 17.3% MgO, 5.7% FeO, 42.0% CO_2 by ignition and absorption, 41.5% ignition loss, 1.8% insoluble, 0.9% total SiO_2. It is known from *x*-ray data that a small amount of serpentine is present. The silica has therefore been assigned to serpentine with its equivalent magnesia. The remaining magnesia, the nickel and the iron, were calculated as carbonates as shown in Table 4. CO_2 equivalent to the metal values, 42.0%, is in good agreement with CO_2 by ignition and absorption, 42.0%, and the ignition loss, 41.5%. Ignition loss is all CO_2 except about 0.3% equiv-

TABLE 4. COMPOSITION OF ANALYZED MAGNESIAN GASPEITE AND OF EQUIVALENT PURE CARBONATE

Analyzed Sample		Equivalent Carbonates		
	Weight %		Weight %	Mol %
$H_4Mg_3Si_2O_9$	2.1			
MgO	16.4	$MgCO_3$	34.3	42.6
NiO	35.0	$NiCO_3$	55.6	49.1
FeO	5.7	$FeCO_3$	9.1	8.3
CO_2	42.0			
Totals	101.2		99.0	100.0

alent water from the serpentine. The usual method of CO_2 analysis, by evolution with acid, absorption, and weighing could not be used here because of the extremely slow reaction of magnesian gaspeite with mineral acids.

The formula of magnesian gaspeite derived from the analysis is $(Ni_{0.98} Mg_{0.86} Fe_{0.16}) (CO_3)_2$. From the similar ion sizes of the three metals it is reasonable to suppose that variation in composition is possible and that this is one member of a solid solution series.

DISCUSSION

Chu-siang, *et al.* (1964) have described a series of magnesium-nickel carbonates from the oxidized zone of a nickeliferous copper sulfide deposit in an arid region of China. The NiO content varies from 0.77 to 29.31% with the molal per cent of nickel always less than magnesium. Their data suggest that these nickeliferous magnesites are part of a solid solution series. A summary of the reported physical properties of the 29.31% NiO carbonate is as follows: $\omega = 1.728$; $\epsilon = 1.534$; $d = 3.36$ g/cc; $a = 4.637 \pm 0.001$; and $c = 15.004 \pm 0.001$ Å. These values, very close to those of magnesite, are not the values expected for magnesite containing 29.31% NiO.

Isaacs (1963) synthesized a series of Ni-Mg carbonates and found complete solid solubility between the end members at 450° C. Recently Goldsmith and Northrup (1965), using different methods, reported that a miscibility gap exists in the $MgCO_3$-$NiCO_3$ system up to at least 750° C.

The optical, crystallographic and density values of magnesian gaspeite with 35.0% NiO are close to those expected from a solid solution of the two end members and suggest that a solid solution series does exist between $MgCO_3$ and $NiCO_3$.

ACKNOWLEDGMENTS

The writers express appreciation to other members of The New Jersey Zinc Company who gave assistance during the course of the investigation and in the preparation of the manuscript.

The name gaspeite has been accepted for the mineral with Ni > Mg by the Commission on New Minerals and Mineral Names, IMA, which also recommends that the name hoshiite (= nickeloan magnesite) be dropped.

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Manuscript received, October 20, 1965; accepted for publication, January 18, 1966.