

## COALINGITE FROM THE MUSKOX INTRUSION, NORTHWEST TERRITORIES

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### ABSTRACT

Coalingite, a hydrous Mg-Fe<sup>3+</sup> oxide, discovered in 1965 in the New Idria serpentinite, California, occurs as fracture fillings in drill cores from the Muskox Intrusion, Northwest Territories. The Muskox coalingite contains more iron and significantly less carbon dioxide than the type material. The mineral is trigonal, with  $a = 3.1 \text{ \AA}$ ,  $c$  uncertain.

Muskox coalingite is believed to have formed *in situ* at room temperature during storage of the drill cores.

### INTRODUCTION

Coalingite was originally described by Mumpton, Jaffe, and Thompson (1965), who identified it in the surface weathering zone of the New Idria serpentinite, Fresno and San Benito Counties, California. The composition of the type material was found to be  $\text{Mg}_{10}\text{Fe}_2(\text{CO}_3)(\text{OH})_{24} \cdot 2\text{H}_2\text{O}$ . Coalingite has now been recognized in drill core from serpentinized portions of the Muskox Intrusion, a layered ultramafic body which outcrops in the Coppermine River area, Northwest Territories.

### OCCURRENCE

Preliminary descriptions of the geology of the Muskox Intrusion have been given by Smith (1962), and Smith and Kapp (1963). As part of the continuing study of the body, it was drilled for scientific purposes in the summer of 1963. Three vertical holes were bored into the intrusion and a total of 10,089 feet of diamond drilling was completed. The drilling project and core logs have been described in detail by Findlay and Smith (1965).

Coalingite has so far been recognized in the Muskox Intrusion only in specimens of drill core. Most of the mineral occurs in the core from the North hole, predominantly in the serpentinite unit extending from 2,364 to 3,271 feet (Findlay and Smith, 1965). Much, if not all, of the coalingite appears to have formed *in situ* in the cores within the five year interval since the cores were logged and stored. This is apparent from the fact that nearly all the coalingite is present in fractures in the core as very loose aggregates which do not have sufficient cohesion to withstand any movement (Fig. 1). Thus, pieces of core which were originally handled and stored in two-foot lengths have in many cases disintegrated into shorter pieces because the original cohesive material in the fractures has been replaced by noncohesive coalingite. This replacement required an expansion in volume which was sufficiently large that the fracture-filling ma-

terials were forced outwards and now commonly form ridges or rings which extend up to a millimeter beyond the main surface of undisturbed core. In a few cases the expansion was sufficient that it resulted in bowing or arching of the cores within their containers.

The formation of coalingite *in situ* is not without precedent. Mumpton *et al.* (1965, p. 1910) recognized that “. . . Results strongly indicate that coalingite is formed from pre-existing brucite in air, and in a matter of months”. In the Muskox drill core logs (Findlay and Smith, 1965), the pre-coalingite material is referred to as thin brown serpentine-magnetite veinlets (North hole, 2364–3271), and as reddish brown serpentine with hematite (North hole, 1571–1780). No brucite was found by X-ray dif-

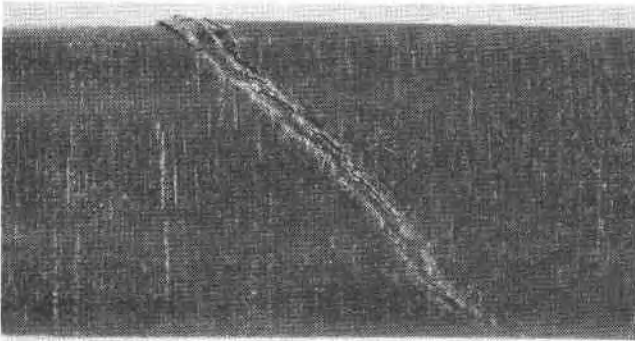


FIG. 1. Coalingite (white) at the margins of a serpentine veinlet in Muskox drill core (1 5/8 ins. diameter). The top of the core shows the expansion effects of coalingite growth whereas in the bottom portion the serpentine veinlet pinches out and the core is undisturbed.

fraction and thin-section studies of the cores. Rather, there is evidence that the Muskox coalingite was formed by *in situ* alteration of closely associated hydrous iron oxides and sulfides. A detailed study of the Muskox coalingite was also undertaken because the mineral differs from type coalingite in several important respects.

#### PROPERTIES

Coalingite in the New Idria serpentinite occurs as small (0.1 to 0.2 mm) brown mica-like platelets intimately intergrown with chrysotile and hydrocalcite. All analyses obtained by Mumpton *et al.* (1965) consequently contained variable amounts of chrysotile contamination.

Coalingite in the Muskox Intrusion drill cores is present as fillings of fractures of 1–2 mm width. The total amount of the mineral in the drill cores is of the order of 50 to 75 veinlets of 2 mm thickness in 1 5/8 inch

diameter (BX) core. Most of the coalinite occurs as (1) pale brownish aggregates of granular to somewhat elongate grains admixed with various impurities, and (2) as bundles of straw-colored fibers of up to 5 mm in length.

Under the microscope the brownish granular coalingite (1) shows two distinct habits, one of which is fibrous and gives optical figures which are uniaxial to biaxial negative with a small  $2V$  and  $\omega = 1.635$ . The second habit is one in which the grains are also elongate, but are platy rather than fibrous. In addition to a cleavage parallel to the elongation, these grains also show prominent cleavage traces either normal or inclined at about  $45^\circ$  to the elongation. Extinction and pleochroism are parallel or only slightly inclined to this cleavage direction, which is length slow (extinction in both the New Idria and MuskoX coalingite is commonly undulatory). These grains show marked pleochroism with  $\omega = 1.634$  (dark brown),  $\epsilon = 1.590$  (colorless). Both refractive indices, as well as the birefringence, are higher than those of the New Idria coalingite, for which  $\omega$  ranges from 1.588 to 1.606,  $\epsilon$  ranges from 1.560 to 1.575, but the birefringence is consistently about 0.03.

The bundles of straw-colored fibers (2) are generally length slow, but in every portion examined in immersion oil a few colorless individual grains or parts of a single fiber are length fast. The refractive indices of the main mass of yellow fibers are  $1.585 \pm 0.005$  to  $1.620 \pm 0.003$ .

For the new Idria coalingite, Mumpton *et al.* obtained a measured density of 2.32–2.33 g/cc; fibers of the MuskoX coalingite were found to have a density of  $2.42 \pm 0.03$  by suspension in heavy liquids.

TABLE 1. CHEMICAL ANALYSIS OF COALINGITE FROM THE MUSKOX INTRUSION  
Analyst: J.-L. Bouvier

	Wt. %	Recalc. to 100%	Mole ratios
MgO	42.9	45.30	8.13
MnO	1.0	1.06	0.11
FeO	0.7	0.74	0.08
Fe <sub>2</sub> O <sub>3</sub>	20.9	22.07	1.00
CO <sub>2</sub>	1.6	1.69	0.28
H <sub>2</sub> O	27.6	29.14	
	94.7	100.00	11.70
L.O.I. <sup>a</sup>	4.2		
	98.9		

<sup>a</sup> Total loss on ignition was 33.4%. Additional elements detected by optical spectrographic analysis are Si, Al (0.1–1.0); Sr, Cr, Zr, Ni (0.001–0.01); Cu <0.001%.

## CHEMICAL ANALYSIS

A chemical analysis of the straw-colored fibrous coalingite was obtained from material purified by separation in heavy liquids and centrifuging in carbon tetrachloride. It was noted during this procedure that the coalingite had acquired a peculiar unpleasant odor reminiscent of stale boiled cabbage. After washing five to ten times with distilled water and then with alcohol, the material was dried and chemically analyzed. It appears, however, that a considerable amount of extraneous liquid must have been adsorbed by the fibrous mass of coalingite. This was first evident from the excessive weight loss obtained by thermogravimetric analysis and was subsequently confirmed by a determination of the loss on ignition. A test for chlorine using silver nitrate gave positive results on the analytical remnant, but no reaction was obtained from material which had not been treated with the separating liquids. Furthermore, as the X-ray powder diffraction pattern of the analyzed coalingite is identical to that of the untreated material, the excessive weight loss found by ignition can be fairly conclusively attributed to adsorption of the separatory liquids. In view of the strong halogen reaction obtained, the contaminating liquid is presumably largely carbon tetrachloride. After deduction of this and recalculating to 100 percent, the analysis of the MuskoX coalingite yields the formula  $Mg_{8.31}Fe_2(CO_3)_{0.38}(OH)_{22.06} \cdot H_{1.35}O_{1.51}$ . The formula is clearly irrational but was calculated on the basis of two atoms of ferric iron so that direct comparison could be easily made with the type coalingite:  $Mg_{10}Fe_2CO_3(OH)_{24} \cdot 2H_2O$ .

The MuskoX coalingite thus has substantially lower molecular ratios of Mg and  $CO_3$  than does the New Idria material. These differences are not believed to be the result of sample contamination or analytical error, but are taken as an indication that coalingite is nonstoichiometric and also quite variable in composition. This variability probably occurs for all components in the formula, just as Allman and Lohse (1966) have established for sjögrenite, the hexagonal polymorph of pyroaurite. In sjögrenite, approximately 20 to 40 percent of the magnesium can be replaced by ferric iron, with charge equalization taking place by addition of interlayer  $(OH)^-$  or  $\frac{1}{2}(CO_3)^{2-}$ . The remainder of the interlayer space is filled with water of hydration.

Coalingite is thus chemically very similar to minerals of the sjögrenite and pyroaurite groups, but differs most notably in its higher proportion of magnesium. The MuskoX coalingite is also characterized by its very low  $CO_3$  content; this suggests that in the coalingite structure  $(OH)^-$  may play a more extensive role for charge balance than it does in the pyroaurite-type minerals.

## X-RAY DATA

X-ray powder data for the New Idria and Muskox coalingites are given in Table 2. Patterns of material from the Muskox cores show small variations both in cell dimensions and in the intensities of some of the weaker lines. The agreement with the New Idria X-ray data is nevertheless relatively good despite the known chemical differences. Mumpton *et al.* (1965) obtained consistently reproducible X-ray patterns from the New Idria coalingite; however, they also noted that one small hand specimen gave a pattern in which the peaks were significantly shifted from their standard position. They temporarily designated this material as "coalingite-K" and postulated that it was a compositional variant of "normal" coalingite. This hypothesis would appear to be most reasonable in view of the compositional variability thus far established for coalingite.

There were indications from the preliminary single crystal study reported in Mumpton *et al.* (1965) that coalingite was hexagonal, but attempts at indexing the powder pattern were largely unsuccessful. Attempts at obtaining single crystal data from the Muskox coalingite were likewise not completely successful, but precession photographs of one fragment showed it to be trigonal (*P*) with  $a = 3.12 \text{ \AA}$ . On zero level precession films with  $c^*$  vertical, only three spots can be clearly seen along the  $c^*$  axis (using Cu radiation). These have spacings of 6.1, 4.3, and 2.5  $\text{\AA}$ . The separation between the first two spots indicates that  $c$  is at least 15  $\text{\AA}$ , but to index all three spots satisfactorily,  $c$  must be at least 30  $\text{\AA}$ . The indices based on  $c = 30 \text{ \AA}$  are as follows:  $005 = 6.00$ ,  $007 = 4.29$ ,  $00.12 = 2.50 \text{ \AA}$ . Films obtained with  $hk0$  as the precession axis show no mirror planes, whereas films obtained with  $010$  as the precession axis show a mirror plane parallel to  $c$ . All diffraction spots having an  $l$ -index are somewhat diffuse and show streaking parallel to the  $c$ -axis. Another feature is that, with  $\text{CuK}\alpha$  radiation, the distance between successive spots is either  $\sim 6.5 \text{ mm}$  or  $\sim 9 \text{ mm}$ . Furthermore, the spots occur in a repeat pattern as follows: 6.5, 6.5, 9, 6.5, 6.5, 9. In other words, the spots in the  $c$ -direction follow a repeat of AAB, AAB, AAB. The streakiness and cyclical repetition presumably indicate a long-range ordering phenomenon.

Because of the unusual results obtained from the Muskox coalingite an effort was made to obtain single crystal data from the New Idria mineral for comparative purposes. One crystal of poor quality was obtained and examined by precession methods using Mo and Cu radiation. The films confirm the trigonal symmetry and  $a$ -dimension found for the Muskox coalingite, but the poor quality of the films containing  $c^*$  does not permit further comparisons. It should be noted, however, that the

TABLE 2. X-RAY POWDER DIFFRACTION PATTERNS OF NEW IDRIA AND MUSKOX COALINGITES

New Idria, Calif. (Mumpton <i>et al.</i> , 1965) <sup>a</sup>		Muskox			
$I/I_0$	$d(\text{\AA})$	$I/I_0^b$	$d(\text{\AA})$	$I/I_0^c$	$d(\text{\AA})$
4 B	13.4			1	13.2
				$\frac{1}{2}$	7.83
5	6.05	4 B	6.0	3	6.05
1	4.75	2	4.74	1	4.75
				$\frac{1}{2}$	4.62
8	4.20	8	4.24	10	4.26
3	2.67	2	2.68	$< \frac{1}{2}$	2.68
$\frac{1}{2}$	2.62				
1 B	2.52	$\frac{1}{2}$ B	2.48		
10	2.34	10	2.34	2	2.34
		$< \frac{1}{2}$	2.14		
3	1.884	1B	1.885		
		$\frac{1}{2}$	1.792		
3	1.767	2	1.769	$\frac{1}{2}$	} v. broad 1.79 to 1.73
3	1.712	1 B	1.719		
		$< \frac{1}{2}$	1.580		
5	1.558	4	1.559	$< \frac{1}{2}$	1.561
1	1.509	$\frac{1}{2}$	1.509		
		$< \frac{1}{2}$	1.488		
1	1.462	$\frac{1}{2}$	1.465		
$\frac{1}{2}$	1.430	$< \frac{1}{2}$	1.430		
		$< \frac{1}{2}$	1.369		
		$< \frac{1}{2}$	1.373		
		$< \frac{1}{2}$	1.350		
$\frac{1}{2}$	1.313	1 B	1.315		
1	1.298	1	1.298		
		$\frac{1}{2}$	1.171		
		$\frac{1}{2}$	1.158		
		$< \frac{1}{2}$	1.022		
		$< \frac{1}{2}$ B	1.010		
1 B	0.998	2	0.999		

<sup>a</sup> 114.6 mm camera,  $\text{CuK}\alpha$  radiation.

<sup>b</sup> 57.3 mm camera,  $\text{FeK}\alpha$  radiation.

<sup>c</sup> Diffractometer,  $\text{CuK}\alpha$  radiation. Strong orientation effect.

distribution and proximity of the cyclical AAB spots on the Muskox coalingite films require that  $c$  be larger than  $30 \text{ \AA}$ . Likewise, cell dimensions significantly larger than  $a=3.1$  and  $c=30 \text{ \AA}$  are required to index the X-ray powder diffraction pattern, but the uncertainty in  $c$  precludes a meaningful assignment of indices at this stage.

## INFRARED SPECTRUM

The infrared spectrum of coalingite from New Idria was shown by Mumpton *et al.* (1965) to closely resemble the spectra of hydrotalcite and sjögrenite. Their coalingite showed the strong absorption bands of water in the 2.5 to 3.0 micron region, and two relatively strong bands at 6.5 and 7.1 microns attributable to carbonate stretching vibrations.

The relatively uncomplicated spectrum of the type coalingite is duplicated by the MuskoX material; the principal difference is that the MuskoX mineral shows only extremely weak absorption for the CO<sub>2</sub> bands.

## THERMAL BEHAVIOR

Both static and dynamic heating methods were used in the study of the thermal behavior of the MuskoX coalingite. For the static heating tests, powdered coalingite was put into a silica glass tube open at one end, and the tube was heated at atmospheric pressure in a Tuttle-type cold-seal bomb using a well-known commercially available apparatus constructed for hydrothermal experimentation. Differential thermal and thermogravimetric curves of the MuskoX coalingite were obtained at heating rates of 12°C/min and 6°C/min respectively.

Detectable weight losses on the thermogravimetric curve occur almost immediately above room temperature. A 6.0 percent weight loss was recorded up to 260°C, which is the approximate point at which the main breakdown of the mineral begins. The total weight loss up to 800°C was 33.1 percent, of which 29.2 percent is water and carbon dioxide, the remainder being the previously mentioned adsorbed liquid (CCl<sub>4</sub>?) used in the concentration process. The end product at 800°C is the periclase phase also reported by Mumpton *et al.* as the final compound formed in the thermal decomposition of the New Idria coalingite.

The DTA curve of the MuskoX coalingite is similar to that reported for the New Idria material, but there are differences in some of the details. This is shown in Figure 2, where a schematic DTA curve of the New Idria mineral adapted from Mumpton *et al.* is also given for comparative purposes. One of the principal differences appears in the resolution of the endotherms at the shoulders of the main peak which in the MuskoX coalingite has its maximum at approximately 375°C in air. A second DTA curve, which was run in a CO<sub>2</sub> atmosphere on another portion of the same concentrate, shows that there are at least three, and probably four reactions occurring in this region.

The processes involved in the generation of all the endotherms of the MuskoX and New Idria coalingites are not well understood. However, the thermal behavior of the latter mineral was carefully studied by Mumpton *et al.*, who established the following decomposition scheme: coalin-

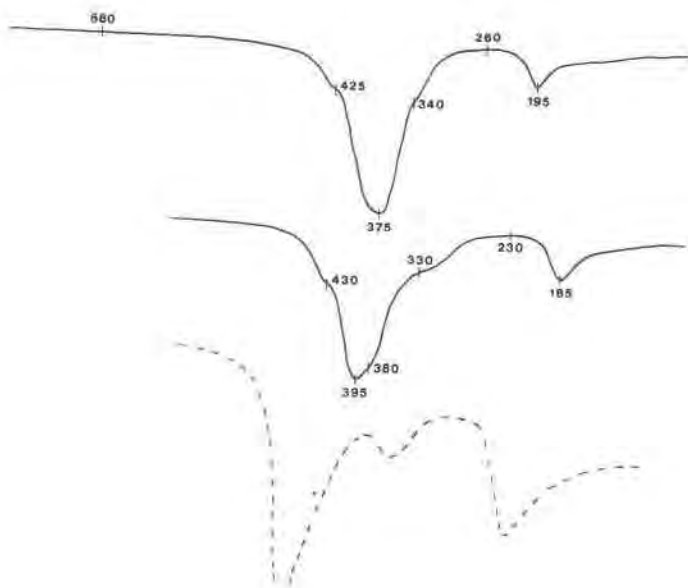


FIG 2. Differential thermal curves of MuskoX coalingite heated in air (top) and in a  $\text{CO}_2$  atmosphere (middle). The bottom (dashed) schematic curve is that of coalingite from the New Idria serpentinite.

gite  $\rightarrow$  dehydrate I  $\rightarrow$  dehydrate II  $\rightarrow$  periclase. All these phases have distinctive X-ray powder patterns. Dehydrate I was found to form at  $120^\circ\text{C}$  by loss of water from coalingite, but the reaction is reversible, and in the presence of water or water vapor the dehydrated material can revert to coalingite. On further heating, a phase change to dehydrate II occurs at  $255\text{--}275^\circ\text{C}$  without any accompanying weight loss. At  $320^\circ\text{C}$  the remainder of the  $\text{H}_2\text{O}$  and  $\text{CO}_2$  are lost, the product being an anhydrous periclase phase.

Because of the known reversibility of the reaction coalingite  $\rightarrow$  dehydrate I, in several of the experiments with MuskoX coalingite the samples were quenched with a compressed air spray and given short X-ray exposures so that the total elapsed time after heating was less than an hour. The results of the static heating experiments are summarized in Table 3. Most notable is the lack of detection of the dehydrate I and dehydrate II phases, that is, there is an apparent breakdown of coalingite directly to the periclase phase at  $275 \pm 15^\circ\text{C}$ . The absence or undetected rapid reversibility of the expected dehydrate phases is perhaps a reflection of the nonstoichiometric composition and lower proportion of carbonate in the MuskoX coalingite. It may be that the strength with which the  $\text{H}_2\text{O}$



TABLE 3. THERMAL DECOMPOSITION OF MUSKOX COALINGITE

Sample 1			Sample 2			Sample 3		
Time (hr)	Temp. (°C)	Ident. <sup>a</sup>	Time	Temp.	Ident.	Time	Temp.	Ident.
16	147	C	20	136	C	118	268	C+P
22	170	C	43	162	C	47	274	P
24	187	C	21	185	C			
23	206	C	20	216	C			
43	224	C	20	246	C			
25	246	C	19	276	C			
21	267	C	23	315	P			

<sup>a</sup> From 57.3 mm X-ray films, FeK $\alpha$  radiation. C=coalingite, P=periclase.

molecules are held in the coalingite structure is variable, and they can be withdrawn with or without an attendant structural collapse.

The apparent absence of the "dehydrate II" phase in the heated Muscox material could be explained by assuming that the phase in this case is stable in an extremely narrow temperature range. This is possible, but unlikely. On the other hand, Mumpton *et al.* demonstrated that the formation of "dehydrate II" from the New Idria coalingite is the result of a CO<sub>2</sub> rearrangement without any accompanying weight loss. Because of the significantly lower carbonate content of the Muscox coalingite, the possibility of a structurally stable compound equivalent to dehydrate II being formed is less likely; consequently, the decomposition of coalingite to periclase is direct and the reaction takes place at lower temperatures.

The only clearly recognizable change in X-ray films obtained from the heated coalingite is a shift toward an increase in unit cell volume. Although most of the diffraction lines show no appreciable shift, the line at  $d=4.24$  Å (Table 2) increased to  $d=4.30$  Å at 127°C, and to  $d=4.36$  Å at 246°C. Other than suggesting that the expansion is the result of structural disorder which progressively increases on heating, little can be said about this unexpected behavior at this time.

The New Idria and Muscox coalingites show significant differences in their physical and chemical properties. As far as can be determined, however, the minerals do not recognizably differ in the gross features of their X-ray diffraction properties.

#### ORIGIN

Mumpton *et al.* (1965) and Mumpton and Thompson (1966) have shown that iron-rich brucite in the New Idria serpentinite is oxidized and converted *in situ* to coalingite and pyroaurite. Examination of the

Muskox cores and coalingite veinlets shows that small amounts of coalingite have formed by alteration of pre-existing oxides, and larger amounts have formed from the peculiar fibrous iron sulfide described below. Some of the straw-colored coalingite fibres are in fact pseudomorphs of the sulfide mineral. Although the details of the chemical processes involved in the evolution of coalingite from the sulfide are not precisely understood, it should be mentioned that no sulfur-bearing mineral residues are present and sulfur was not detected in coalingite by X-ray spectroscopy. The peculiar odor originally emitted by the coalingite concentrate may be an indication that excess sulfur is dissipated in a gaseous form.

For the main bulk of the coalingite, there is no direct evidence as to the nature of the original fracture-filling material. Thus, although brucite has not been found in the cores, the possibility that it was originally present in some of the fractures cannot be unequivocally excluded.

#### FIBROUS IRON SULFIDE

The detection of this mineral in the drill cores came about through its common association with coalingite (Fig. 3). The unaltered sulfide itself is hardly conspicuous because it occurs in fractures less than a millimeter thick as black, metallic veinlets which megascopically resemble the magnetite veinlets common in many portions of the cores.

The X-ray powder pattern of the fibrous sulfide is simple and without anomalous line broadening. The first four diffraction lines are as follows: 10.9(6), 5.45(10), 1.83(3), 1.55(1) Å. Electron microprobe analysis by A. G. Plant gave Fe 48, Mg 8, Mn <0.5, S 23 weight percent. Cr, Co, Ni,

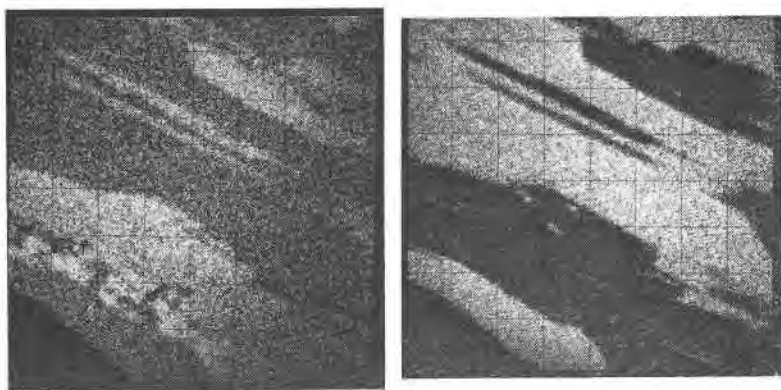


FIG. 3. X-ray scanning micrographs of Muskox coalingite and associated fibrous sulfide. Left: magnesium X-ray image showing relatively high Mg content of coalingite (light grey) as compared to the sulfide (darker grey). Right: sulfur X-ray image of the same area. Black areas are coalingite.

Ca, Cu, As, Pb, Al, and Si were not detected. The sulfide does not effervesce in acetic or dilute hydrochloric acid, and hence the remaining 21 percent required to bring the analytical total to 100 percent is assumed to be H<sub>2</sub>O. If it is further assumed that part of the iron is trivalent, then the formula corresponds approximately to  $3\text{FeS} \cdot 2(\text{Mg, Fe}^{3+})(\text{OH})_{2+n}$ , where  $n$  is the additional hydroxyl required to balance the ferric iron. Additional speculation is not attempted in view of the limited data available.

## ACKNOWLEDGMENTS

The writer is grateful to D. G. Fong, A. G. Plant, J.-L. Bouvier, F. Hill and F. J. Cooke of the Geological Survey, and to J. F. Rowland of the Mines Branch for their assistance in various aspects of the study. The D.T.A. and T.G.A. curves of coalingite were kindly prepared by R. H. Lake and the infrared curve of coalingite was obtained through the courtesy of A. H. Gillieson, both of the Mines Branch, Ottawa. The writer is most grateful to R. J. Traill and F. A. Mumpton for critical reading of the manuscript.

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*Manuscript received, July 15, 1968; accepted for publication September 27, 1968.*