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HYDRATED SULFATES IN THE SYDNEY COALFIELD OF CAPE BRETON, NOVA SCOTIA. II. PYRITE AND ITS ALTERATION PRODUCTS

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ABSTRACT

Repeated observations made on hydrated sulfates from coal mines in the Sydney coalfield (Cape Breton) and on the alteration products of the samples over time suggest a regenerative cycle of the hydrated sulfates. Assuming an Al-and-Mg-rich sedimentary environment, we propose the following paragenesis: pyrite, melanterite, fibroferrite, and aluminocopiapite and related minerals. Pyrite also alters directly to aluminocopiapite and to fibroferrite, and fibroferrite to rhomboclase. Sideronatrite and melanterite were investigated by TGA in a dry nitrogen atmosphere. The main end-products of sideronatrite decomposition are thenardite and hematite.

SOMMAIRE

Des observations répétées, faites sur les sulfates hydratés des mines du bassin houiller de Sydney (Cap Breton) et sur l'altération des échantillons avec le temps, semblent indiquer un cycle regénérateur de ces sulfates. Dans l'hypothèse d'un milieu sédimentaire riche en Al et Mg, nous proposons la séquence paragénétique suivante: pyrite, mélantérite, fibroferrite, aluminocopiapite et minéraux connexes. On observe aussi les altérations directes pyrite → aluminocopiapite, pyrite → fibroferrite → rhomboclase. Le comportement de la sidéronatrite et de la mélantérite a été étudié par ATG dans l'azote sec. La sidéronatrite se décompose surtout en thénardite + hématite.

(Traduit par la Rédaction)

INTRODUCTION

Zodrow & McCandlish (1978a) described the occurrence of some hydrated sulfates in the Sydney coalfield as a first step in an environmental study. The present paper reports on observed alteration products of pyrite and on dehydration and thermal decomposition of sideronatrite and melanterite.

The Sydney coalfield, situated in the northeastern part of Cape Breton, forms the southeastern border of a deformed basin assumed to be of Carboniferous age (Bell 1938). The basin trends northeast into the Atlantic Ocean. Coal measures in the basin outcrop along the Atlantic coast in an east-west belt, but synclinal-anticlinal structures on-shore modify this trend, locally quite substantially. Samples were collected exclusively from the Cape Breton Development Corporation's #26 Colliery, 1–B mine, Glace Bay, and Prince Colliery at Point Aconi.

ANALYTICAL PROCEDURES

Identification of hydrated sulfates by means of X-ray diffraction (XRD) analysis is sometimes difficult because of continuous changes in water content, such as occur in fibroferrite, or because of dehydration to another phase. Samples were hand-picked under a binocular microscope to remove contaminants. Sample numbers of the type 978GM–201, shortened to 201, are accession and catalogue numbers of the Nova Scotia Museum in Halifax, Nova Scotia.

All minerals and final phases obtained from TGA were identified by XRD comparison with J.C.P.D.S. standards. The final phases of TGA of fibroferrite (221) and sideronatrite ($233^{c,d}$) were exposed to Ni-filtered Cu*K*α radiation. All other hydrated sulfates were exposed to Fe-filtered Co*K*α radiation. The humidity was not controlled during XRD analysis. Minor amounts of other unidentified phases are present in most mineral samples, but the X-ray lines are of low intensities and cannot readily be matched with known minerals.

Standard techniques were used for the chemical analysis of mineral samples, *i.e.*, SO_4 was done by gravimetric analysis, heavy metals by atomic absorption, Na and K were determined by flame photometry and ferrous iron by titration. Care was exercised to analyze samples "as received" to prevent possible loss of coordinated water. Plasma spectroscopy was used to study trace elements in certain samples.

TGA curves were obtained on a DuPont 961 Thermogravimetric Analyzer equipped with a platinum pan. This apparatus also permitted the simultaneous recording of DTG (derivative thermogravimetry) curves. The heating rate was 10°C/min in a flowing nitrogen atmosphere at 50 ml/min. Pre-TGA purging of samples in the TGA apparatus was performed at the temperatures indicated in the tables.

SIDERONATRITE

Interpretation of XRD and chemical data

The occurrence of sideronatrite $Na_2Fe(SO_4)_2(OH)\cdot 3H_2O$ in #26 Colliery, 1–B mine, is much more widespread than originally reported by Zodrow & McCandlish (1978a), but amounts at the various locations are small. The mineral also was discovered at Point Aconi, Cape Breton, on a coal-seam outcrop.

Metasideronatrite $Na_4Fe_2(SO_4)_4(OH)_2\cdot 3H_2O$ was identified by XRD of sideronatrite samples which were exposed to atmospheric conditions for about seven months. Other samples of sideronatrite (sample series 234), stored in containers with mine air for four days, showed no evidence of dehydration to metasideronatrite (transfer from the containers to the X-ray apparatus was carried out with minimum time loss). Contrary to reports by Palache *et al.* (1957, p. 604), metasideronatrite evidently may form naturally by dehydration of sideronatrite. The unit cell and other crystallographic data for metasideronatrite are discussed by Finney (1973).

Thirty m south of the up-cast air shaft (Zodrow & McCandlish 1978a, Fig. 4), sideronatrite and aluminocopiapite(?) appear intermixed (312 to 318). This mixture has an unusual greenish tint.

TABLE 1. QUANTITATIVE ANALYSES OF SIDERONATRITE FROM #26 COLLIERY, 1-B MINE, GLACE BAY, N.S.

	Theoretical	239[a]	240[a]	241[a]
Na	12.59	10.1	9.3	9.4
Fe^{3+}	15.30	15.43	15.78	14.18
SO_4^{2-}	52.63	48.45	52.14	50.95
Mg	nil	0.12	0.11	0.12
Ca	nil	0.005	0.003	0.004
K	nil	0.015	0.015	0.015
Total (less H_2O and OH)	80.52	74.12	77.35	74.67

Plasma spectrographic analysis of sample 653-1:

Al	1100 ppm	Mn	100 ppm	Si	100 ppm
As	400	Mo	20	Sn	5
Ba	10	Ni	20	Ti	10
Ca	1200	P	70	V	10
Cr	30	Pb	100	Zn	10
Cu	50	Sb	100		

[a] Analyzed "as is" on April 13, 1978.

TABLE 2. SUMMARY RESULTS OF TGA IN A DRY N_2 ATMOSPHERE FOR SIDERONATRITE FROM #26 COLLIERY, 1-B MINE, GLACE BAY, N.S.

	assumed loss	cumulative % wt loss theoret.	cumulative % wt loss measured*	Temp (°C) DTG
Initial phase: sideronatrite				
Assumed transitional phases:				
$\frac{1}{2}Na_2Fe(SO_4)_2(OH).3H_2O$	$1\frac{1}{2}H_2O$	7.4	8.0**	25
$\frac{1}{2}Na_4Fe_2(SO_4)_4(OH)_2.3H_2O$	$\frac{1}{2}H_2O$	9.9	9.7(9.3**)	93(25)
$\frac{1}{2}Na_4Fe_2(SO_4)_4(OH)_2.2H_2O$	$1H_2O$	14.8	14.4(13.6)	289(285)
$\frac{1}{2}Na_4Fe_2(SO_4)_4(OH)_2$	$\frac{1}{2}H_2O$	17.3	18.6(16.8)	423(450)
$\frac{1}{2}Na_4Fe_2O(SO_4)_4$	$\frac{1}{2}SO_3$	28.2	29.0(25.6)	668(725)
$\frac{1}{2}Na_4Fe_2O_2(SO_4)_3$	$\frac{1}{2}SO_3$	39.2	40.6(38.6)	912(940)
Final phases as in Table 3: $Na_2SO_4 + Fe_2O_3$				

Analyst: J. Wiltshire; sample 653-1[b], analyzed Nov. 1, 1977.

*Weights at intermediate stages taken at the minima in the DTG curves. Values in parentheses are from a duplicate run (Table 3).

**Observed weight loss during purging of the TGA apparatus at 25°C in a dry N_2 atmosphere flowing at 50 ml/min.

The interpretation of chemical analyses of sideronatrite (Table 1) is complicated by the presence of minor amounts of unidentified contaminants. The greatest problem lies with unidentified substitutions for sodium and, to a lesser extent, possible substitutions for Fe and SO_4. Variations in amounts of water of crystallization as a source of error in the analyses are ruled out by TGA results (Table 2); these show a maximum loss of 18.6% at the completion of the dehydration process at 423°C. Plasma spectrographic analysis of sample 653–1 showed no high concentration of trace elements (Table 1). The possibility exists that nitrates, carbonates and borates may substitute for SO_4. Amounts of insoluble residue associated with the samples were judged to be negligible at the time of analysis.

Although Zodrow & McCandlish (1978a) reported that the occurrence of sideronatrite from Cape Breton was the first in North America, the mineral had been found previously in the

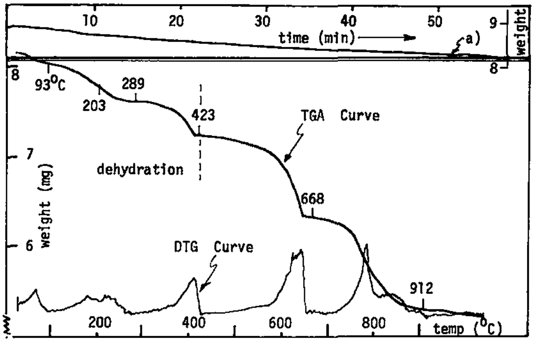


FIG. 1. TGA and DTG curves of sideronatrite. Curve a) shows initial weight loss at 25°C. Results are summarized in Table 2.

Kramer borate district, California (Morgan & Erd 1969).

Interpretation of TGA and DTG results

The dehydration of sideronatrite (Fig. 1) exhibits four distinct stages and is complete at about 423°C (Table 2). The first stage, which yields metasideronatrite, occurs spontaneously on exposure to the dry nitrogen atmosphere in the TGA apparatus. This result is consistent with the reported formation of metasideronatrite by drying sideronatrite over sulfuric acid (Palache *et al.* 1957, p. 604).

The TGA of sideronatrite gives hematite and a polymorph of thenardite (Na_2SO_4) as end products; in samples 233[c,d] (Table 3), the presence of minor zeta iron oxide (ζ-hematite) is suggested by additional *d* values in the XRD data (written comm., J. D. Grice 1978). As an independent check, sideronatrite sample 653–1[b] (Table 2) was heated in a tube furnace under a stream of dry nitrogen. XRD data were obtained from intermediate products: (1) at 125° and at 350°C, no identification was possible because of broad peaks and low absolute intensities; (2) at 500°C, sharp, well-defined peaks of $3Na_2SO_4 \cdot Fe_2(SO_4)_3$; (3) at 700° and at 900°C, hematite and thenardite.

TABLE 3. INTERPRETATION OF DEHYDRATION BEHAVIOR OF SIDERONATRITE IN A PURGING DRY N_2 ATMOSPHERE DURING pre-TGA AND TGA

Assumed process	cumulative % wt loss				
	theoret.	653-1[a]	653-1[b]	233[c]	233[d]
$Na_2Fe(SO_4)_2(OH).3H_2O$					
$½Na_4Fe_2(SO_4)_4(OH)_2.3H_2O$	7.4	nil	8.0 (8.1)*	nil	nil
$½Na_4Fe_2(SO_4)_4(OH)_2.2H_2O$	9.9	9.3 (6.1)	9.7 (2.0)	9.2 (7.1)	nil
$½Na_4Fe_2(SO_4)_4(OH)_2$	14.8	13.6 (6.8)	14.4 (2.7)	14.2 (4.0)	14.8 (0)
$½Na_4Fe_2O(SO_4)_4$	17.3	16.8 (2.9)	18.6 (7.5)	18.3 (5.8)	19.4 (12.1)
$½Na_4Fe_2O_2(SO_4)_3$	28.2	25.6 (9.2)	29.0 (2.8)	27.7 (1.8)	28.5 (1.1)
$Na_2SO_4 + Fe_2O_3$	39.2	38.6 (1.5)	40.6 (3.6)	39.9 (1.8)	41.1 (4.8)

Conditions of samples prior to analysis

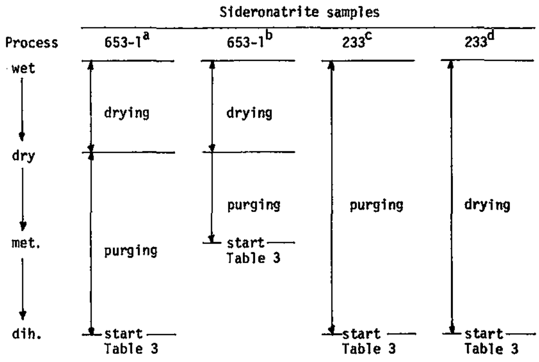
[a] dried in atmosphere for 15 weeks; collected June 23, analyzed Oct. 18, 1977.

[b] dried in atmosphere for 17 weeks; collected June 23, analyzed Nov. 1, 1977.

[c] analyzed 24 hrs after collection, March 9, 1978. Assumed to have contained 7% admixed water.

[d] analyzed after drying in atmosphere for 10 days; collected March 9, 1978. Assumed to have dehydrated in atmosphere to the dihydrate $Na_4Fe_2(SO_4)_4(OH)_2.2H_2O$.

Analyst: J. Wiltshire. *Quantities in brackets represent errors: (Theoretical - Measured)/Theoretical with units in percentages.



met.= $Na_4Fe_2(SO_4)_4(OH)_2.3H_2O$

dih.= $Na_4Fe_2(SO_4)_4(OH)_2.2H_2O$

drying took place in atmospheric conditions.

FIG. 2. Graphical illustration of dehydration behavior of samples of sideronatrite or related products during pre-TGA in a dry N_2 atmosphere or in atmospheric conditions. Refer to Table 3.

Metasideronatrite is not always observed as a transitional product during TGA. Moisture content of the sample immediately prior to analysis apparently determines the shape of the "a) curve" and the variation at the start of the TGA curve (Fig. 1). In a purging dry N_2 atmosphere at 22–25°C, sideronatrite apparently can form either metasideronatrite or dihydrate. Interpretation of TGA data for sample 233[d] (Table 3) indicates that dihydrate may form by exposing sideronatrite to atmospheric conditions (Fig. 2).

The large range of error in Tables 2 and 3 of up to 12.1% is explained in two ways: 1) high-temperature phases were not considered, and 2) formation of transitional species different from those assumed, *e.g.*, $3Na_2SO_4 \cdot Fe(SO_4)_3$ at 500°C.

MELANTERITE AND ASSOCIATED HYDRATED SULFATES

Chemical composition and TGA of melanterite

Chemical analyses of melanterite are given in Table 4. Our attempts to classify melanterite by a subjective color index seem to have no substantiated chemical basis, for there are no observed significant chemical differences either in the major or minor elements.

The TGA curve of melanterite is shown in Figure 3; $FeSO_4 \cdot 4H_2O$ formed at 40°C in a

TABLE 4. ANALYSES OF MELANTERITE AND EPSOMITE FROM VARIOUS LOCATIONS IN #26 COLLIERY, 1-B MINE, GLACE BAY, N.S.

Melanterite[a]:		white	green	green	yellow	Epsomite	
	Theoret.	2-2	2-6	2-9	2-10	Theoret.	5
Total Fe:	20.10	19.61	19.82	19.95	19.33	nil	1.91
Fe^{3+}	nil	0.56[b]	n.f.[c]	n.f.	n.f.	nil	n.f.
Fe^{2+}	20.10	19.05	19.82	19.95	19.33	nil	1.91
SO_4^{2-}	34.55	34.39	34.97	33.78	33.70	38.97	45.12
Mg	nil	0.02	0.04	0.03	0.11	9.87	9.88
Ca	nil	0.03	0.02	0.02	0.08	nil	1.03
Na	nil	0.05	0.03	0.02	0.03	nil	0.04
Cu ppm	nil	10	86	22	69	nil	14
Co	nil	16	28	14	90	nil	80
Ni	nil	24	50	20	98	nil	114
Mn	nil	439	92	43	215	nil	6100
Zn	nil	16	20	16	20	nil	60
U[d]	nil	from 0.02 to 0.28				nil	n.a.[e]
Total (less H_2O or OH)	54.65	54.10	54.88	53.80	53.25	48.84	57.98[f]

[a] Subjective color index. [b] Nonstoichiometric mineral possibility or two phases, one of which is due to oxidation forming, for example, $Fe(OH)SO_4$.

[c] Not found. [d] By the neutron activation method. [e] Not analyzed

[f] Fits the mineral hexahydrite better.

TABLE 5. QUANTITATIVE ANALYSES OF HALOTRICHITE AND FIBROFERRITE FROM #26 COLLIERY, 1-B MINE, GLACE BAY, N.S.

	Halotrichite			Fibroferrite	
	Theoret.	214[a]	247[b]	Theoret.	219[c]
Total Fe:	6.43	7.72	3.23	21.57	21.25
Fe^{3+}	nil	nil	nil	21.57	21.25
Fe^{2+}	6.43	7.72	3.23	nil	nil
Mg	nil	0.72	1.74	nil	0.04
Al	6.22	4.55	5.22	nil	0.07
SO_4^{2-}	44.25	42.22	41.92	37.10	37.78
Na ppm	nil	127	54	nil	256
Ca	nil	50	55	nil	190
Cu	nil	24	72	nil	30
Ni	nil	81	180	nil	74
Zn	nil	58	1425	nil	22
Total (less H_2O and OH)	56.90	55.21	52.11	58.67	59.14

[a] Location: site #5; [b] Location: site #7 minus 8 m; from sedimentary rocks stratigraphically above the Phalen seam.

[c] Location: site #7; refer to Zodrow and McCandlish (1978a, Fig. 4).

dry N_2 atmosphere decomposed on further heating to the monohydrate and to the anhydrous compound. The pentahydrate, siderotil, was not detected. Additional heating resulted in a weight loss consistent with that reported by Gallagher *et al.* (1970), with evolution of SO_2 and SO_3. The end product is assumed to be hematite.

Alterations of melanterite in #26 Colliery

Fibroferrite $FeSO_4(OH)\cdot 5H_2O$ "grew" on a melanterite crystal (653–2–9, Table 4) stored in a glass vial. Examination of other samples in the collection revealed also that fibroferrite formed directly from melanterite. On revisiting #26 Colliery, 1–B mine on 1 March 1978, it was observed that melanterite had almost disappeared from the coal faces and associated detritus, except for some isolated occurrences near certain sample sites (*e.g.*, #1,3) (Zodrow & McCandlish 1978a). Instead, a mineral (fibroferrite) had appeared that resembles vermiculite in crystal habit and is olive green when wet. Had we not visited #26 Colliery previously, melanterite would have escaped our notice. Experiments show that fibroferrite reacts with water (hydrolysis) with an attendant pH decrease to about 2.6. The hydrolysate is white and orthorhombic. Diffractometer traces closely correspond to those of fibroferrite. Reports by Winchell (1951) that fibroferrite dissolves in water are not consistent with our observations.

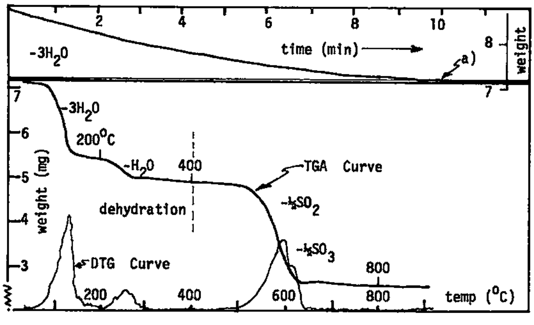


FIG. 3. TGA and DTG curves of melanterite. Curve a) shows initial weight loss at 40°C.

Thermogravimetric analysis of fibroferrite shows that a weight loss of about 68.7% occurs by heating to 690°C; the average of two analyses place the value at 67.97%, assuming a calculated value of 4.16 for the number of water molecules in sample 221 (Table 5). The end product of fibroferrite breakdown at 1000°C is hematite. The chemical analysis of fibroferrite (Table 5) suggests less than 5 water molecules (H_2O by difference), in agreement with that in Palache *et al.* (1957). However, water loss differs in that our fibroferrite samples dehydrated completely at about 450°C. Cocco (1952) showed a total H_2O loss of 35.24% to 280°C, with 23.15% occurring at 100°C. The dehydration temperatures of fibroferrite, sideronatrite and melanterite are similar according to our work.

A yellow mineral, which seems to grow as an alteration product directly on fibroferrite,

TABLE 6. CHEMICAL ANALYSES OF RHOMBOCLASE AND ALUMINOCOPIAPITE SAMPLES FROM THE PRINCE AND #26 COLLIERY, 1-B MINES, CAPE BRETON COALFIELD, N.S.

Rhomboclase			Aluminocopiapite		
	Theoret.	203a*	203a-moist*	202a-7days*	349**
Fe	17.39	19.63	20.03(21.41)+	14.29(16.39)	18.10(18.98)
Mg	nil	0.05	0.16	1.20	1.60
Al	nil	0.42	0.33	2.02	0.08
SO_4^{2-}	61.09	58.74	52.02(46.37)	48.13(48.17)	47.47(47.10)
Na ppm	nil	338	274	212	235
Ca	nil	205	269	148	2235
K	nil	202	201	80	100
Cu	nil	70	61	274	24
Mn	nil	410	347	2581	1647
Zn	nil	1641	1380	245	36
Total (less H_2O and OH)	78.48	78.84	72.54	65.64	67.25

*Collected from the Prince mine near the portal of #4 slope. **Collected from #26 Colliery, 1-B mine. +Values in brackets are based on $Fe_{1-x}Mg_xFe_{4(1-y)}Al_4(SO_4)_6(OH)_2 \cdot 20H_2O$ with molecular weight 1249.914 - 31.535x - 115.462y.

is identified as aluminocopiapite (Table 6, sample 349). Some samples of fibroferrite (341) stored in the laboratory are altering to what appears to be aluminocopiapite.

Changes in melanterite in the Prince mine

Melanterite in the Stubbart coal seam at the Prince mine near the mouth of #4 Slope had disappeared, as observed on Feb. 1978. Instead, the coal seam in this area was covered to a remarkable degree with a light yellow, moist bloom of aluminocopiapite, (Fe,Mg)-$(Fe^{3+},Al^{3+})_4(SO_4)_6(OH)_2 \cdot 20H_2O$ (203*a*-moist and 202*a*-7days, Table 6). From XRD data, exposure of these moist samples to the air for an arbitrary number of days (7) produced rhomboclase, $HFe(SO_4)_2 \cdot 4H_2O$ (203*a*-7days). However, further work will be necessary as the diffractometer traces were of low absolute intensity. On the other hand, the chemical analyses presented in Table 6 do not negate the XRD interpretation. Recently, Buurman (1975) obtained rhomboclase, among other hydrated sulfates, from pyrite by *in vitro* weathering. Van Tassel (1974) and Mereiter (1974) discussed the structure and X-ray powder data of rhomboclase.

It is difficult to verify whether aluminocopiapite formed directly from melanterite. Melanterite apparently may give rise to at least two independent series of alteration products. The first series is characterized by a loss of coordinated water molecules, a low-energy phenomenon, to yield the tetrahydrate, rozenite, whose stability field and relationships with melanterite are given by Ehlers & Stiles (1965). A second alteration product is the pentahydrate, siderotil (not observed in the Sydney coalfield) whose formation may depend on the presence of small amounts of copper (Jambor & Traill 1963). The second series, a high-energy phenomenon, is based on hyperoxidation of iron, formation of the hydroxyl (base) or hydrogen ion (acid), substitutions involving Al, and changes in the number of coordinated water molecules. Bol'shakov & Ptushko (1971) consider the possibility that rhomboclase, siderotil and szomolnokite ($FeSO_4 \cdot H_2O$) are initial alteration products of melanterite.

PICKERINGITE AND HALOTRICHITE

The hydrated sulfates discussed so far occur as oxidation products of pyrite in the coal seams. Epsomite (Table 4) and halotrichite (Table 5) occur in the roof sandstones stratigraphically above the Phalen seam in #26 Colliery, 1–B mine.

Halotrichite 214^a (Table 5) occur as silky, fibrous crystals, 1 to 1.5 cm long, with a distinct greenish tint towards the base of attachment to the roof rocks. Halotrichite 247^b occurs nearby as small spherical amber masses which, on drying, form distinct fibres as long as 4 mm. The white fibres probably are a dehydration product. XRD data indicate that halotrichite and rozenite (356) coexist in contiguous masses.

PARAGENESIS

The ferrous precursor (pyrite?) and the source of Na must be considered in the paragenesis of sideronatrite in #26 Colliery. Different conditions must lead to the formation of melanterite rather than sideronatrite as both coexist on the same coal seam but not at the same specific location. Plasma spectroscopy of sample 245 (coal with sideronatrite) show that Fe is the main constituent (4.58%), followed by Ca from calcite(?) in the joint planes (0.80%), Na (0.59%), As (0.18%) plus 21 additional heavy cations including U. Randall & Jones (1966) suggested pyrite as the source of Fe for sideronatrite. One possible source for Na is thenardite, which occurs within the coal seam at sample site #1, the discovery site of sideronatrite. The only change observed in sideronatrite in ambient conditions was dehydration to metasideronatrite. No secondary

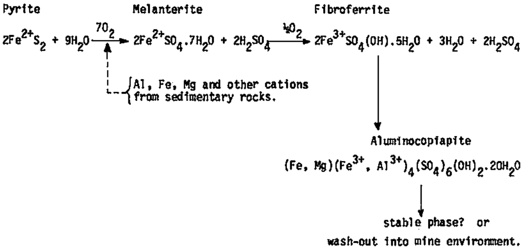


FIG. 4. Formation of hydrated sulfates from pyrite in #26 Colliery, 1–B mine. Broken lines indicate introduction of Al, Fe, Mg, *etc.* into the system. The step from fibroferrite to aluminocopiapite also requires an open chemical system.

minerals after sideronatrite have been observed in #26 Colliery over the last two years. Alteration of melanterite to fibroferrite in #26 Colliery, 1–B mine, is assumed to have taken place without the formation of an intermediate compound.

The reactions that yield various hydrated sulfates on coal from autochthonous pyrite in coal are given in Figure 4 for #26 Colliery, 1–B mine. Oxidation of pyrite and some secondary minerals, and the presence of aluminum-rich sediments (for the formation of aluminocopiapite) are assumed. The formation of fibroferrite, and subsequently aluminocopiapite after melanterite, has been observed in stored melanterite samples collected from this mine in 1977. In the step from melanterite to fibroferrite (Fig. 4), iron is oxidized. Perhaps oxygen variations also play a role as the atmosphere in the sample area of #26 Colliery, 1–B mine, consists of return air ("used air" underground)

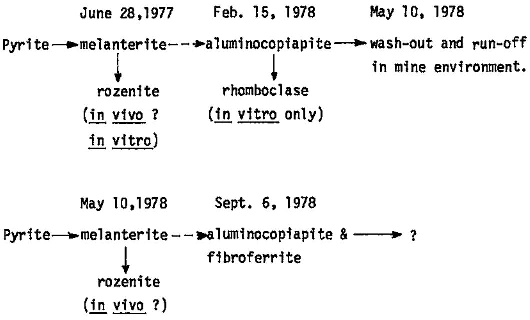


FIG. 5. Proposed alteration scheme for the formation of sulfates in the Prince mine. Dates of observations are shown above the mineral names. The broken arrow indicates that the formation of aluminocopiapite or fibroferrite and melanterite is conjectural.

with variable O_2. For the step from fibroferrite to aluminocopiapite, introduction of cations from the sediments intercalated with coal is assumed. Mg and Al are available from fibroferrite (Table 5) and further concentration of the introduced elements may have occurred during hydration alteration in the step from fibroferrite to aluminocopiapite.

A scheme for the observed alteration of pyrite in the Prince mine is shown in Figure 5. Aeration and the presence of Al in the sediments within the coal are assumed. Aside from the uncertainty that melanterite is the precursor of aluminocopiapite, the above scheme suggests a cyclical type of paragenesis (Zodrow & McCandlish 1978b). The observed terminal stage is a wash-out of the minerals into the mine

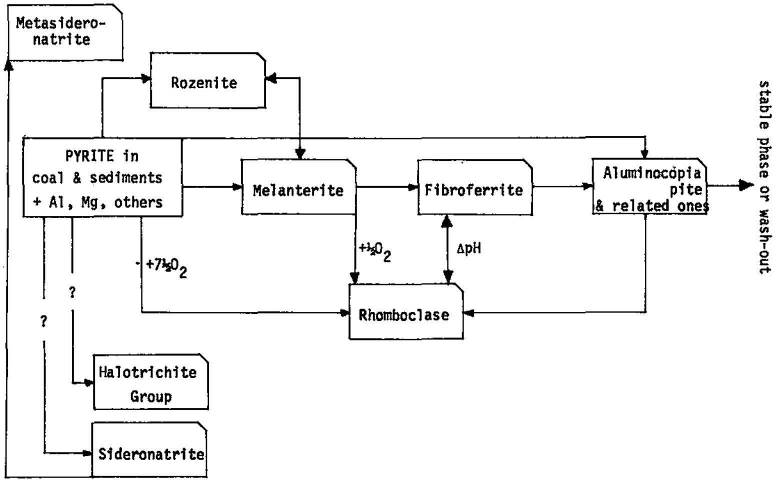


FIG. 6. General outline of paragenesis for some hydrated sulfate minerals in the Sydney coalfield, Nova Scotia.

environment. As the collection area in the Prince mine is near the portal and thus in direct contact with ambient conditions, cyclical paragenesis seems to be induced by seasonal climatic changes. In #26 Colliery, 1–B mine, cyclical paragenesis has not been observed over the past two years.

Figure 6 summarizes some alteration products of pyrite and their interrelationships in the Sydney coalfield. The pyrite–rozenite link is based on apparently direct crystallization of rozenite on a block of pyritic shale. The connections between pyrite and halotrichite, and pyrite and sideronatrite, although tenuous, are based on laboratory and field observations. The formation of rhomboclase from pyrite, melanterite, or fibroferrite, is theoretical and can be derived either by oxidation or acid reaction. Aluminocopiapite and related minerals are common in the Sydney coalfield and found under diverse atmospheric conditions, such as in mines, on mine dumps and on exposed coal seams. In some instances, both surface and underground, it appears that aluminocopiapite oozed out of coal seams and thus could have been formed directly from pyrite.

RECENTLY IDENTIFIED SULFATES

Iron-bearing tamarugite, $NaAl(SO_4)_2 \cdot 6H_2O$, was collected from coal and sedimentary rocks of the Phalen seam, #26 Colliery, 1–B mine; this mineral coexist with all of the other hydrated sulfates found in this mine. Gypsum, both from roof rocks and the coal face, was identified in samples from the Prince mine. Bloedite, $Na_2Mg(SO_4)_2 \cdot 4H_2O$, was identified in efflorescence on the floor of the Lingan mine dump. The position of these minerals in the scheme in Figure 6 is not known.

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Note added in proof: Siderite occurs in coal specimens from the Harbour seam at Lingan mine (977GF-308).