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HYDRATED SULFATES IN THE SYDNEY COALFIELD, CAPE BRETON, NOVA SCOTIA*

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ABSTRACT

Hydrated sulfates associated with decomposition of pyrite and copper-iron sulfides occur in coal in contact with the atmosphere. Melanterite, rozenite, epsomite, pickeringite, halotrichite, aluminocopiapite and sideronatrite were identified from coal seams and mines in the Sydney coalfield. This is apparently the first reported occurrence of sideronatrite and alumino-copiapite in North America, and for the remaining minerals with the possible exception of melanterite, first occurrences from Cape Breton. Crystallization of melanterite, and possibly of other hydrated sulfates, contributed substantially to the mechanical instability of coal faces in old underground workings by erosion of supporting pillars. In addition, alunite, jarosite, natrojarosite and barite (?) were tentatively identified from the Evans coal mine situated in a Carboniferous basin somewhat older than the Sydney basin. These sulfates are associated with the decomposition of copper-iron sulfides and possibly pyrite. All minerals were identified by X-ray powder diffraction.

SOMMAIRE

On trouve des sulfates hydratés résultant de la décomposition de pyrite et de sulfures de Cu-Fe dans le charbon exposé à l'air. Mélantérite, rozénite, epsomite, pickeringite, halotrichite, aluminocopiapite et sidéronatrite ont été identifiées (par clichés de poudre) dans les couches de charbon des mines du bassin houiller de Sydney. C'est la première découverte de sidéronatrite et d'alumino-copiapite en Amérique du Nord; quant aux autres minéraux, sauf peut-être la mélantérite, c'est la première fois qu'on les trouve au cap Breton. La formation de la mélantérite, et peut-être aussi celle des autres sulfates hydratés, a grandement contribué à l'instabilité des fronts de taille, par érosion des piliers de soutènement, dans les anciens chantiers souterrains. De plus, alunite, jarosite, natrojarosite et barite(?) ont été identifiées provisoirement dans la mine Evans, située dans un bassin houiller carbonifère plus ancien que celui de Sydney. Ces sulfates sont des produits de la décomposition de sulfures de Cu-Fe et peut-être aussi de pyrite.

(Traduit par la Rédaction)

PYRITE IN COAL

An investigation of occurrences and patterns of distribution of hydrated sulfate minerals constitutes the first phase of a proposed environmental study program. The overall purpose of the investigation is to identify and define water pollutants associated with oxidation of pyrite in exposed coal seams, producing mines, and in coal piles stored in the open air. Pyrite is a ubiquitous mineral in the coal seams of the Sydney coalfield.

The Sydney coalfield, situated on 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. Bell (1938) divided the Sydney coalfield into three distinguishable zones using assemblages of fossil flora, *i.e.*, fern-like and fern-type fossils. All coal mines in this basin exploit coal measures that belong to the youngest zone, which may be equated with the Upper Pennsylvanian. The Lingan mine and the 1-A mine in #26 Colliery exploit the Harbour seam, and the Prince mine at Point Aconi, the Stubbart seam (Fig. 1). However, sampling has not been restricted to these seams.

Fine-grained pyrite in the coal measures of the Sydney coalfield originated in peats of Pennsylvanian age; however, structural studies indicate that coalification of the peat took place much later. Pyrite mineralization in coal is pos-

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*Contribution from the Nova Scotia Museum, Halifax, N.S.

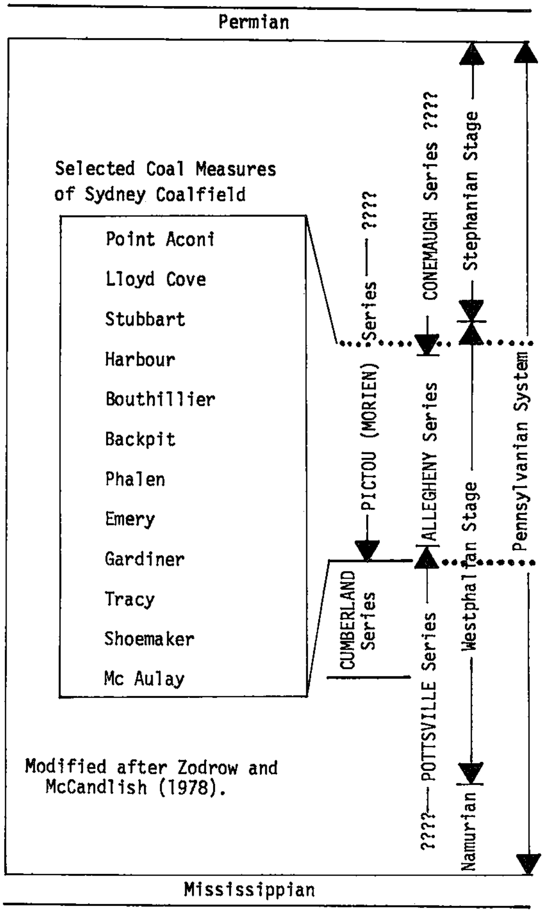

FIG. 1. Coal measures of Sydney coalfield in approximate correlation to the Pennsylvanian series of Nova Scotia (Cumberland to Morien), Pennsylvania (Pottsville to Conemaugh), and Europe (Namurian to Stephanian).

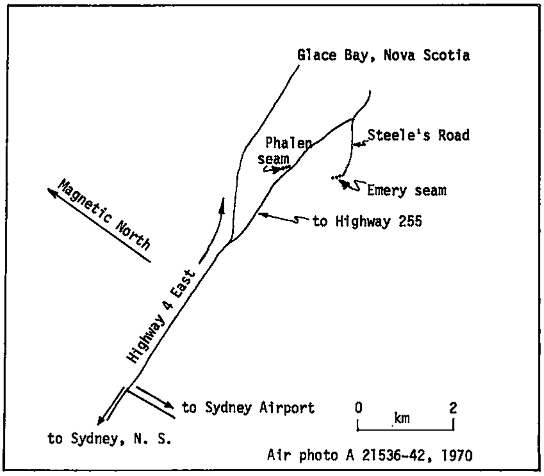

FIG. 2. Location map for the Phalen and Emery seams near Glace Bay, Cape Breton, N.S.

sibly derived from ester sulfates, hydrocarbon sulfates that originate from biogenic sources (Casagrande & Siefert 1977). Concentrations of ester sulfates are much greater in marine than in fresh-water peat.

Selected pyrite samples were examined by optical methods and by X-ray powder diffraction analysis (XRD). Preliminary results show traces only of marcasite in sample 977GF-58 (accession and catalogue number of the Nova Scotia Museum) from the McAulay seam. In samples 977GF-176, F-177, and F-178 from the Phalen seam (Fig. 2), polished sections (Fig. 3) show that pyrite is present in the coal a) as nodules with apparently unstable cores, and b) between veins of nodules as elongate crystals aligned perpendicular to the veins. In the second case the original marcasite has apparently been transformed to pyrite.

The Stubbart seam exploited in the Prince mine contains two conspicuous fine-grained pyrite bands; these may be traced over a wide area in the mine. They are irregular in thickness (pyrite specimen 977GF-622 is approximately 4 cm thick), locally nodular and discontinuous. Specimens of hydrated sulfates collected underground in the Prince mine occur in these two bands. In addition pyrite may occur in radiating rosette-type structures less than 6 cm across (977GF-243), and in isolated nodules of 3 to 5 cm (977GF-205). As a replacement of plant tissue, pyrite plays only a minor role, but in specimen 977GF-244 it replaces a stigmarian structure (root system of either *Lepidodendron* or *Sigillaria* species). Locally replacement of foliage of arborescent plants of the type *Lycopodites meekii* Lesquereux (977GF-97b) or *Lepidodendron dawsoni* Bell also occurs.

In the Phalen seam at the 1-B mine of #26 Colliery in Glace Bay, pyrite is disseminated in the coal, and hence hydrated sulfate minerals are distributed throughout this seam. In outcrops of the seam (Fig. 2) pyrite may be concentrated in bands or nodules; specimen 977GF-177 furnishes an example of nodular pyrite. The presence of pyrite in coal seams, however, is not a guarantee that hydrated sulfates have formed; certain pyrite specimens show no evidence of sulfate formation.

ANALYTICAL TECHNIQUES

XRD techniques were used in all identifica-

FIG. 3. Infrared reflection image of elongate crystals of pyrite perpendicular to the veins (x8); 977GF-177 Negative.

tions of sulfates; these were supplemented by qualitative chemical analyses and optical examination in specific cases. Melanterite and rozenite (977GF-653-2) were identified by comparison with Powder Diffraction File (PDF) 1-225 and 16-699, respectively; pickeringite (977GF-682-1) was compared to PDF 12-299. These minerals were exposed to Ni-filtered Cu*K*α radiation in a 57.3 mm Debye-Scherrer camera. Sideronatrite (977GF-653-1) and epsomite (977GF-653-3) were exposed to Fe-filtered Co*K*α radiation in the same camera, except that a 114.6 mm film of sideronatrite was also made. Epsomite was identified by comparison to a standard film, whereas sideronatrite was identified by comparison with PDF 17-156, and with a standard pattern at the Geological Survey of Canada (pers. comm. L. J. Cabri 1977).

Samples 977GF-691 and 977GF-704 from the Evans Mine at St. Rose, Cape Breton, were exposed to Ni-filtered Cu*K*α radiation (pers. comm. M. Zentilli 1977); samples 977GF-682-2 and 977GF-682-1-1 were exposed to Co*K*α radiation with an Fe-filter (pers. comm. J. K. Sutherland 1977).

HYDRATED SULFATES AT 1-B MINE, GLACE BAY

Co-existing in the Phalen seam (Fig. 4) are melanterite, sideronatrite, and epsomite. Melanterite, $FeSO_4 \cdot 7H_2O$, is the name given to the species wherever Fe > Cu. Melanterite occurs throughout the coal face and crystallized perpendicular to it as falcate fibres up to 3 cm long, and within the coal as oval-shaped, fibrous masses generally less than 5 cm long. Crystal growth of melanterite and other hydrated sulfates is directly responsible for fragmentation of coal faces, which leads to progressive mechanical erosion of supporting pillars. Indeed, the stress necessary for the mechanical erosion of coal is supplied by the oxidation of pyrite and

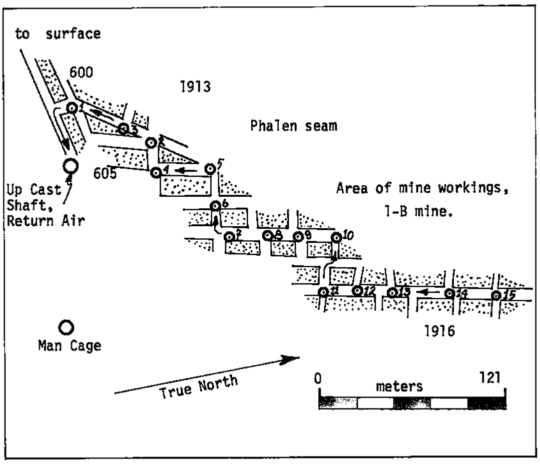

FIG. 4. Part plan of the 1-B mine, #26 Colliery, Glace Bay, N.S. showing numbered sample locations. Elevations (in feet) below sea level. Arrows indicate return air flow (to the surface). Roof-support pillars from mining activity (1913 to 1916) are shown as stippled areas.

attendant volume increases that occur to produce hydrated sulfates. Crosscuts driven sixty years ago now have a V-shaped appearance due to accumulation of melanterite-bearing coal detritus. Roofs consist of shales or shaly sandstone in which the fossil plant content is high; in addition, the growth of sideronatrite, epsomite and other unidentified non-metallic minerals may lead to weakening, then roof collapse. The fossil plants most detrimental in this context are large sigillarian trees, now compressed, and their abundant reed-like foliage. The carbon remains of this fossil material created planes of weakness in the sandstone; similar comments apply to selected roof zones in the Prince mine, where the most detrimental fossil to roof stability is *Calamites carinatus* Sternberg (977GF-245), herbaceous reed-like plants several meters long. However, as these old mine workings show, the size of the fallen slabs is largely dependent on enlargement of rooms by erosion of pillars.

Table 1 summarizes values of relative humidity and temperature of return air (ventilation) at which melanterite is found in the 1-B mine; no inference can be made from this tabulation concerning the lower limits of melanterite stability. The temperature and humidity of the air returning to the surface are constant and independent of surface atmospheric conditions; air pressure in the mine is directly under the influence of surface air pressure.

Experiments in our laboratory indicate that melanterite is stable in an atmosphere having a relative humidity as low as 60% at 25-28°C. The tetrahydrate rozenite, $FeSO_4 \cdot 4H_2O$, was obtained from melanterite specimens by dehydration in atmospheric conditions. However, it is not entirely clear whether the tetrahydrate can be formed without passing first through the heptahydrate stage, melanterite. Determination of optic signs of melanterite from various sample sites (Fig. 4) shows that the angle $2V$ lies close to ± 90°; this compares to 80° in Mason & Berry (1968), and 85°27′ for synthetic melanterite in Na light (Palache *et al.* 1951). Variability in the optic sign implies variability in the composition of melanterite. This conjecture may be supported by difference in color of specimens roughly equal in thickness, from greenish-blue to straw-yellow to white; impurities, of course, may also cause color changes. Variation in the composition of melanterite may reflect sample location; this aspect has not been investigated.

TABLE 1. AIR TEMPERATURE (°C) AND RELATIVE HUMIDITY (%) FROM HYGROMETRIC DATA ALONG THE TRAVEL ROAD IN 1-B MINE, GLACE BAY, N. S.

Sample Site	T°C	R.H.%
1	15.9	90
2	15.5	90
3	15.4	90
4	15.5	81
5	15.8	81
6	15.7	81
7	15.5	81
8	15.5	81
9	15.5	81
10	15.5	81
11	15.8	81
12	15.8	81
13	15.3	81
14	15.5	90
15	15.1	90

Sideronatrite, $Na_2Fe(SO_4)_2(OH) \cdot 3H_2O$, is bright lemon yellow and occurs as a fibrous crust on coal; it is stable in surface conditions. Because of their similar colors, sideronatrite and jarosite may be confused. Qualitative wet chemical analysis indicates the presence of phosphate, chromate, and possibly Ni, Al, and Mg in our sideronatrite samples (977GF-653-1). Under the polarizing microscope, parallel extinction can be easily observed due to the excellent cleavage on {100}. Since the discovery of this mineral in the Sydney coalfield, we suspect that many mineral specimens tagged as jarosite are actually sideronatrite. This applies especially to the roofs of various working areas of the Prince mine and the 1-B mine.

The only location of sideronatrite known to the authors is in the 1-B mine. At samples sites 1 and 7, Figure 4, sideronatrite "mushrooms" out of the coal face in patches parallel to the bedding planes. Flecks of a yellow mineral are visible throughout the coal faces along the travel road (escape drift to surface); the mineral is assumed to be sideronatrite. Yellow material also coats fossil plants, especially *Sigillaria,* that are preserved in the syringodendron condition (977GF-625, F-627).

Epsomite, $MgSO_4 \cdot 7H_2O$, is white and fibrous; the fibres attain 3-4 cm. Epsomite cannot be confused with rozenite because of their different modes of origin and crystal habits. Epsomite is highly localized in the roof of the Phalen seam and occurs with quartz; an inverse correlation is observed between the occurrence of epsomite and melanterite. Epsomite was not observed on coal faces. Therefore, we conclude that this seam did not carry sufficient quantities of magnesium to form the mineral. The 1-B mine provides the only occurrence of this mineral known so far. The collection sites include 5, 6 and 10 (Fig. 4), where tthe mineral was collected from slabs of sandstone caved in from the roof.

Hoffmann (1890) was the first to report melanterite and epsomite in Nova Scotia (Traill 1970); he found melanterite on shale of mined coal in Glace Bay, and epsomite in a gypsum quarry in Hants County.

HYDRATED SULFATES AT THE PRINCE MINE, POINT ACONI

Melanterite and rozenite are the hydrated sulfates that have been identified from this mine. Rozenite, $FeSO_4 \cdot 4H_2O$, is white and powdery, and readily soluble in water as is melanterite. Some optical and chemical data relating to rozenite are given by Jambor & Traill (1963). This mineral is stable over a large range of fluctuating atmospheric conditions. Our investigation into sulfate mineralization was confined to areas about 450 m from surface entrances of adits #4 and #5. In this area humidity and temperature conditions are dependent in part on atmospheric conditions at the surface. Relative humidity recorded on 28th September 1977 was between 90 and 98% and the fresh-air temperature between 12.1 and 16.8°C. As a result of variation of humidity and temperature in this area, melanterite growth is not spectacular, and is restricted to short fibres in small quantities; therefore, mechanical erosion of the coal faces is hardly noticeable.

Melanterite and rozenite are believed to coexist in these two adits; however, a phase equilibrium study would be necessary to check this preliminary hypothesis. Rozenite is also observed on surface outcrops of the Stubbart seam (977GF - 660). Rain water that percolated through coal storage piles has a low pH value of about 2.0; bacterial activity is believed to aid in the breakdown of pyrite.

Pyrite specimen 977GF-655-1 continues to grow melanterite crystals (+ rozenite?) in a hermetically sealed glass container stored in our laboratory. The relative humidity in the container is kept at about 90%. However, additional XRD data are needed to confirm that rozenite is growing directly on the pyrite without passing through the heptahydrate stage. A 28 by 15 cm pyrite specimen (977GF-622) collected from a coal storage pile and now stored in atmospheric conditions in the laboratory is developing fracture planes; we believe that these are due to the growth of a fine-grained whitish, unidentified material.

HYDRATED SULFATES, SULFATES, SULFIDES, AND CARBONATES AT OTHER LOCATIONS ON CAPE BRETON ISLAND

Rozenite occurs also in minor quantities in outcrops of the Phalen seam in Glace Bay (Fig. 2), where it is visibly associated with fine-grained pyrite (977GF - 177). Pickeringite, $MgAl_2(SO_4)_4 \cdot 22H_2O$ (977GF-682-1), aluminocopiapite, $MgAlFe(SO_4)OH \cdot H_2O$ (977GF-682), and halotrichite. $FeAl_2(SO_4)_4 \cdot 22H_2O$ (977GF-682-1-1) coexisted in surface outcrops of the Emery seam; heavy rains have since obliterated these water-soluble minerals.

The Evans coal mine, situated in an Upper Carboniferous basin near the town of Inverness, exploits the #5 coal seam. Typical fresh-water fauna, *Anthraconaia cf. modiolaris,* a pelecypod, and *Carbonita fabulina,* an ostracod (977GF-696, F-697, respectively) occur in the roof of this coal seam. The faunal association can be directly correlated with that of the Lower Coal Measures of Great Britain: Westphalian A, early B, *i.e.*, older than the strata of Sydney coalfield (Copeland 1977). Preliminary interpretation of XRD data suggested the presence of barite and alunite, $KAl_3(SO_4)(OH)_6$, in a discordant 2-5 mm vein cutting the upper contact between coal and overlying sediments (977GF-691); however, further analytical work is necessary on this specimen to confirm the presence of these minerals. Sample 977GF-704 and others originating from the top of the producing coal seam, #5, show evidence of gypsum and members of the jarosite-natrojarosite series in which Na substitutes for K: $(K,Na)Fe_3(SO_4)_2(OH)_6$.

The distribution and occurrence of hydrated sulfates and sulfides in the Evans coal mine are fundamentally different from those in the Sydney coalfield. In this mine all hydrated sulfates and sulfides are restricted to a 3-5 mm vein that contains bornite, chalcopyrite, pyrite and other unidentified minerals. The vein, concordant with the coal seam and directly on top of it, is a tracer horizon in the mine and may indeed be an indicator of the #5 seam. However, hydrated sulfates occur only in those places where the sulfide vein has been exposed to the atmosphere for a number of years, and thus never along working faces. Indeed, no sulfates have yet been collected from these faces; this is also true for Prince mine, Lingan mine, and 1-A mine of #26 Colliery in the Sydney coalfield. The #5 coal seam has prominently developed joint planes perpendicular to the seam and trending along its strike; the planes are occupied by thin sheets of calcite (977GF-699); a similar situation exists in the Sydney coalfield (977GF-719). Calcite (977GF-700) was also identified from a very small stalactitic-type of structure on a coal face. Rozenite is also suspected at this mine but not yet identified.

DISCUSSION

Apart from having world-famous fossils of the type *Lonchopteris eschweileriana* Andrae (977GF-463), the coal mines of the Sydney coalfield show renewable hydrated sulfate minerals in their natural environments. As many of these salts are readily soluble in water, the occurrence of some of them is dependent on hot, humid weather conditions. Simple experiments in the laboratory show that fine-grained pyrite started to "grow" sulfates within three days after collection at ambient temperatures of about 25-28°C. However, the chemical process in the Sydney specimens did not take place if copper sulfides were present in addition to pyrite (977-GF-308, F-382). We have collected only the obvious, but are convinced that many esoteric sulfates await discovery. The research needed for this investigation includes ore microscopy, to investigate the relationship between marcasite and pyrite, not only *vis-à-vis* oxidation to produce hydrated sulfates, but also in search of geochemical factors that played a temporal role in the coalification of the Pennsylvanian swamps. Thus elucidation of the origin of pyrite, and hence its distribution in the coal, would form a firm basis for environmental studies and the study of hydrated sulfates; geostatistical methods, such as oblique factor analysis (Zodrow 1976) are appropriate. Detailed optical and chemical data from collected samples may aid in fitting the empirical data to theoretically possible solid-solution series of the type alunite-jarosite-natrojarosite (Mason & Berry 1968) and to substitution schemes in sideronatrite and pickeringite as well.

Questions of environmental nature are also broached by this investigation: the role of bacteria in the formation of sulfuric acid in storage piles of coal, and spontaneous combustion *vis-à-vis* hydrated sulfate-mineral formation.

ACKNOWLEDGEMENTS

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Note added in proof: Fibroferrite, $Fe(OH)SO_4 \cdot 5H_2O$ has been identified in coal specimen 977GF-655-13, from the Stubbart seam at the Prince mine, Point Aconi.

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