

# Colliery and surface hazards through coal-pyrite oxidation (Pennsylvanian Sydney Coalfield, Nova Scotia, Canada)

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## Abstract

Pennsylvanian Sydney Coalfield, Nova Scotia, Canada, is submarine as coal mining took place beneath the North Atlantic Ocean. All collieries were shut down in 2001. The coal was on average sulfurous, pyrite-rich, (ca. 5% total sulfur), which on exposure to the atmosphere oxidized rapidly to form definite sequences of secondary hydrated-sulfate minerals. Thus, the collieries were veritable laboratories for studying in situ hydrated-sulfate paragenesis in roof rocks–coal–floor rocks.

Based on these studies, and on direct observations over several years, a conceptual model of roof-rock instability is proposed. This model explains rock falls in tunnels (slopes) during once-operating coal mines (short-term hazard), as well as surface subsidence in land areas undermined long ago by room-and-pillar methods in the Sydney Coalfield (long-term hazard). The model invites testing in other Pennsylvanian coalfields that have similar geochemical conditions and employ similar mining methods.

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**Keywords:** Pennsylvanian coal; Pyrite; Oxidation; Roof instability

## 1. Introduction

Sydney Coalfield, Cape Breton Island, Nova Scotia, Canada (Fig. 1), represents the on-shore portion of submarine Sydney Sub-Basin of the large Euramerican Carboniferous Maritimes Basin (Forgeson et al., 1986; Calder, 1998). Economical coal seams occur stratigraphically in the uppermost Westphalian D–basal Cantabrian age portion of the Coalfield (Cleal et al., 2003). The rank is mostly high

volatile A bituminous coal (Hacquebard and Cameron, 1989). The main mineralogic constituent within the microlithotypes is fine-grained pyrite that also occurs in the roofs and floors (seat earth) of coals, mostly associated with megafloral fossils (Zodrow, 1983). On exposure to the atmospheric condition, pyrite oxidizes rapidly forming hydrated-sulfate minerals in a definite discrete-phase sequence (paragenesis). The process can be regarded as “natural desulfurization” of the coal, and at the same time as “natural trace-metal concentrator and sulfuric acid producer”. Distinguished are pyritic-oxidation conditions that (a) occur on surface from

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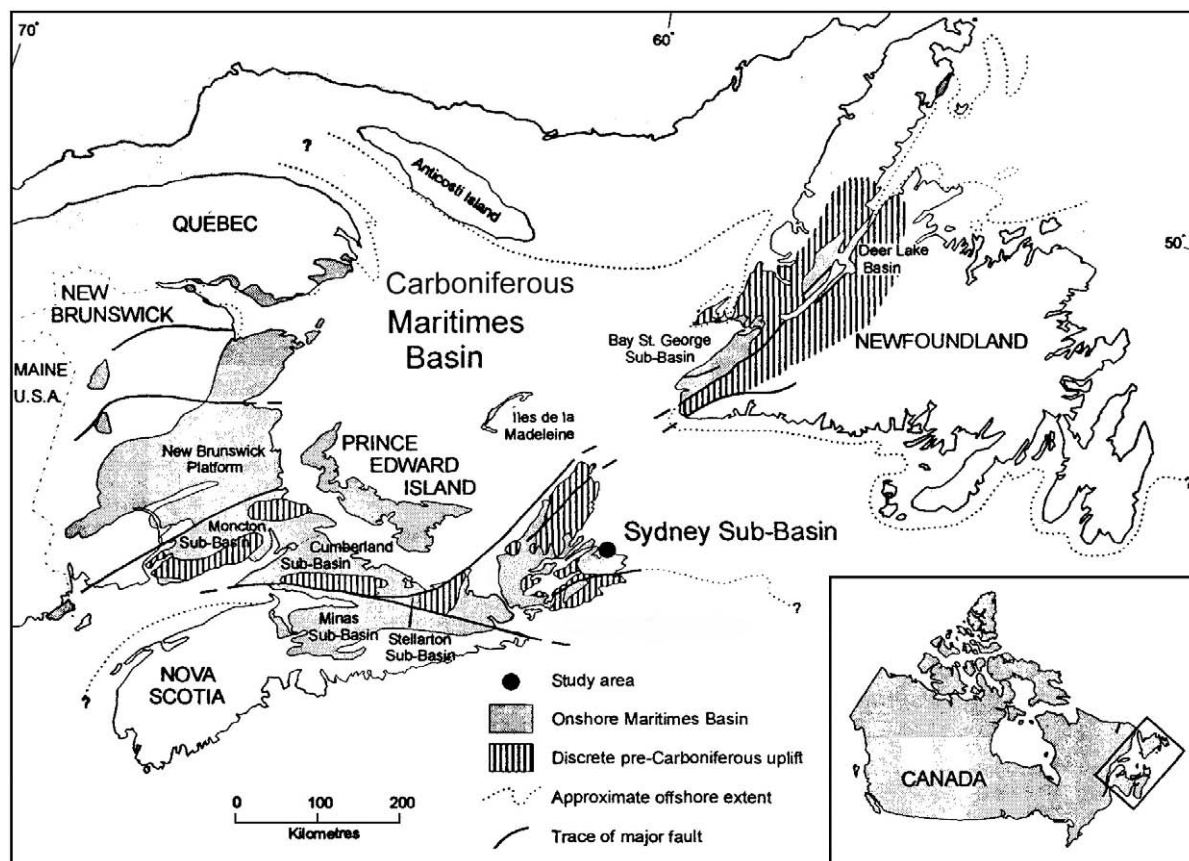


Fig. 1. Carboniferous Maritimes Basin, and location of Sydney Coalfield in the Sydney Sub-Basin, Nova Scotia, Canada.

(b) those which take place in collieries, underground. Under (a), before rain, snow, or storm-tide wash-outs, coast-exposed coal seams are covered by spectacular “sulfur blooms” (Zodrow and McCandlish, 1978b), Fig. 2. These are composed mostly of stable copiapite (Zodrow, 1980), intermixed with white rozenite (e.g. melanterite) minerals, to impart varietal-yellow colors (“peaches and cream”) to the seam surfaces. See Appendix A for chemical composition of the sulfates mentioned in the text. Regeneration of hydrated sulfates on the washed-clean coal beds takes place with changing weather conditions without causing much coal erosion. Mined coal stored in open air at open-pit mines also showed such colors, accompanied however by spontaneous combustion, if the coal was left undisturbed. This was repeatedly observed by the author in summers of the 1980’s. Spontaneous combustion is triggered by pyrite oxidation that is

exothermic, coupled with certain thermophile-bacteria activity that aid pyritic oxidation (Brierley and Brierley, 2002).



Fig. 2. Oxidizing coal and “sulfur bloom” (white areas) showing oxidation cracks that reduce coal competency. Cantabrian coal, Sydney Coalfield, Nova Scotia.  $\times 2$ .

Under (b), these “catastrophic” events do not exist, but regeneration in collieries is triggered by changing seasonal ambient weather conditions, as air pumped into collieries for ventilation. However, in collieries mined-out decades ago, where air conditions are allowed to stagnate, remarkably narrow ranges of relative humidity and temperature existed. For example, in #26 Colliery, 1-B Mine relative humidity ranged from 81% to 90%, and temperature from 15.1 to 15.9 °C (Zodrow and McCandlish, 1978a,b). Here, paragenesis took its natural course in time and was sampled by the author at each succeeding stage (1977–1982).

This paper focuses on mine-roof instability, and post-coal-mining subsidence in which pyritic oxidation played a basic role. Direct observations by the author from 1977 to 2003 underscore the claim. Mentioned are certain environmental problems resulting from acid-mine effluent.

## 2. Sample depository

Over 300 samples of secondary-sulfate minerals were collected by the author mainly from the Prince Mine and #26 Colliery 1-B Mine, Sydney Coalfield. They are properly accessioned and documented, and preliminarily grouped into 36 species by means of powder X-ray diffraction analysis, combined with wet chemistry. Samples were previously donated to U.S. Steel Corporation; The University of Michigan; Smithsonian Institution; Museum of Natural History, Ottawa; École Nationale Supérieure des Mines Musée Nationale, Paris; and to Professor M. Barrás, Zaragoza, Spain. The entire collection is curated (since 2003) at Queen’s University, Kingston, Ontario, Canada, where it is studied as part of a PhD thesis investigating crysctochemistry and origin (in litt. R.W. Dalrymple, April 2004).

## 3. Coal pyrite in Sydney Coalfield

Geochemical trends of entire coal seams show top and bottom enrichment in total sulfur (Zodrow, 1986, 1988), in agreement with epigenetic modes of deposition that are related to sources of sulfur from underlying gypsum deposits (see later). Estimates that

circumscribe the range of *total-coal-sulfur* content, based on whole-coal channel samples from 10 successive coal seams, Sydney Coalfield, are from < 0.5% to > 22%, average  $4.78\% \pm 4.31\%$  (Zodrow, 1991). Total-coal sulfur is defined by:

$$\begin{aligned} \text{total sulfur} &= \text{organic sulfur} + \text{sulfate sulfur} \\ &+ \text{pyritic sulfur}, \end{aligned} \quad (1)$$

where native sulfur as yet has not been identified. Organic sulfur, probably plant-related and inconsistently associated with the microlithotype vitrite (Beaton, 1986; Birk et al., 1986; Casagrande, 1987), is difficult to determine by ASTM standards. Assuming three sources for (1), organic sulfur is calculated by difference. As a generalization for Sydney Coalfield, a total-sulfur level of < 2% in the coals is considered to be of organic origin, following Casagrande (1987), although this has not been verified microscopically, but has been used statistically (Zodrow, 1991). On atmospheric exposure, coals with such small amounts of total sulfur show little or no weathering effects (oxidation), and remain intact over time, whereas those with higher-sulfur [pyrite] content weather and disintegrate rapidly as measured in weeks. A general estimate is that ca. 90% of total-coal sulfur in the Sydney Coalfield is pyritic in origin (Beaton, 1986). As a rule of thumb, surfacial oxidation patterns on coal not only trace pyrite deposition, but also indicate variable pyritic content by variation in density pattern (Fig. 3).

Sulfate sulfur is derived from the crystalline gypsum-anhydrate complex deposited in coal cleats and coal-bedding planes.

Pyrite is known from two modes of epigenetic deposition in the coal. One is manifested as cleat pyrite (Birk, 1990; Birk et al., 1986; Casagrande, 1987) that occurs as submillimetre-thick “sheets” in coal joints, cross-cutting coal-bedding planes, and the second conformable to bedding planes. The latter is very fine-grained pyrite, however, deposited as discontinuous stringers, submillimetre to over 10 mm thick (Fig. 4), lens-like, or as lenticular deposits (“dogs” in coal miner’s parlance). The author collected “dogs” that weighed more than 5 kg each. Some of these showed pyritized plant remains that are, however, acellurally preserved as thin-section work demonstrated. This type of pyrite deposition is also

epigenetic because coalification is demonstratively postdeformational (Hacquebard and Cameron, 1989; Ryan et al., 1991). Marcasite is a relatively small sulfide component that occurs within the pyrite phase (Beaton, 1986).

In the basal Cantabrian Lloyd Cove Seam, however, galena rather than pyrite is persistently deposited in coal cleats, with pyrite still deposited in the bedding planes. Lead-isotopic values can be used for modeling evolution of crustal lead (Nov. 1992, Krueger Enterprises, Inc., Geochron Laboratories, Cambridge, MA, USA). Middle Westphalian D coals show cleats that are filled with calcite in which minor pyrite dissemination occurs.

Commonly, coals with higher-sulfur content are considered influenced by open-marine incursion that supplied sulfate ions for the precipitation of pyrite (see Casagrande, 1987). Sydney's coals, however, are exceptionally different in this respect from other higher-sulfur coals of Pennsylvanian age because sulfate ions for higher sulfur content (= higher pyrite content) originated from recycled Mississippian gypsum-anhydrite deposits that underlie the Pennsylvanian Sydney Sub-Basin. This conclusion is based on stable sulfur-isotopic studies of pyrite and gypsum from the Sydney Coalfield (Gibling et al., 1989), and confirms earlier views by Sydney Sub-Basin coal-



Fig. 3. Coal on which pyritic deposition is outlined by oxidation to hydrated-sulfate minerals (white). Cantabrian coal, Sydney Coalfield, Nova Scotia.  $\times 2$ .

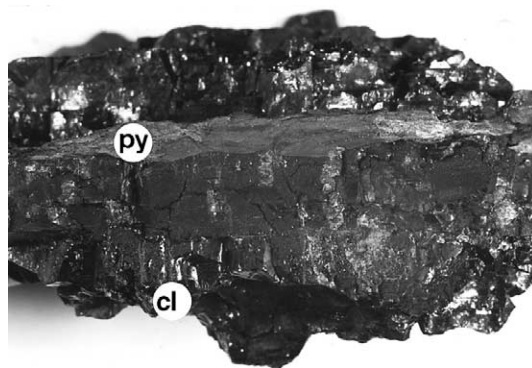


Fig. 4. Pyrite stringer "py" parallel to coal-bedding plane, and cleats "cl" filled with pyrite. Cantabrian coal, Sydney Coalfield, Nova Scotia.  $\times 2$ .

mine geologists from the 1950s (Haite, 1951; summary: Gibling et al., 1989). Low boron content in coals (maximally 50 ppm, Vasey and Zodrow, 1983; Zodrow, 1991), and absence of certain piscine species, confirm the absence of open marine influence. Agglutinated foraminifera, however, found in seat earth of many coals permits interpretation of brackish-estuarine influence in certain parts of the Sydney Coalfield (Thibaudeau, 1987; Wightman et al., 1994).

#### 4. Roof and floor rocks in collieries

Roof rocks in collieries basically consist of sequences of clastic sedimentary rocks.<sup>1</sup> These are notoriously variable in thickness and in extent (facies variations), as was already recognized by Brown (1845). Included are shale, silty shale (overbank deposits), sandstones (channel lag, crevasse-splays), and mud rocks (Zodrow, 1983). Conglomeritic roofs are not known.

In collieries, a general roof-rock sequence (upwards from the coal) consists of a 1–2-cm-thick clayey layer, a few mm-thick pyritic layer, some kennel coal, followed by rich-macro- and microfloral silty shale that is variably several metres thick (fining upwards). Abundant discontinuous sideritic bands or nodules decrease

<sup>1</sup> Coal roofs composed of limestone, or shell-rich calcareous rocks (bivalves, ostracods, fish spines and scales) are known from coastal exposures and open-pit mines but not from collieries in Sydney Coalfield, as part of cyclothems.



Table 1

Total sulfur in selected roof–coal–floor sequences, Sydney Coalfield, Nova Scotia, Canada

Coal seam, cm <sup>a</sup> thickness	Colliery	Weight per cent total sulfur		
		Roof rock <sup>b</sup> rock type	Coal seam <sup>c</sup>	Floor rock <sup>b</sup> rock type
Point Aconi 105	–	0.06–0.14 (2) fissile shale	7.5 ± 5.4 (21)	–
Stubbart 215	Prince Mine	0.24–1.26 (3) fissile shale	5.7 ± 3.5 (29)	1.4–1.80 (2) claystone
Phalen 200	#26 1-B Mine	0.28–3.95 (6) fissile shale	1.5 ± 0.5 (13)	–
Mc Aulay 45	–	0.29 (1) silty shale	7.6 ± 1.3 (3)	–

Number of samples are bracketed.

<sup>a</sup> At point of sampling.<sup>b</sup> Unpublished data by the author, 1977–1978.<sup>c</sup> Channel samples, 15-cm intervals (Zodrow, 1988, Fig. 2).

upwards in this sequence. Mudstone is not common in roofs. Sandstone channels cutting into coal, however, may replace the general sequence in certain collieries.

Floor rocks consist exclusively of clastic sedimentary rocks, and are comparatively more clayey, as judged from their propensity to form large muddy areas in collieries (MacLean and Merner, 1978). Generally, floor rocks are poor in macrofloral content, except for abundant in situ stigmarian systems, i.e., rooted soil representing lycophyte-growth positions. This demonstrates the autochthonous nature of the coal seams (Brown, 1845).

Systematic mineralogic data are not available, except a few total-sulfur analyses (Table 1) for selected clastic roof and floor rocks. Thin-section analysis, and pyrite typically deposited on coalified-plant material because of prevailing reducing conditions (Mraw et al., 1983; Garrels and Christ, 1965: geochemical-fence concept; Zentilli, 1991) confirm that total sulfur is largely of pyritic origin. Contribution of organic sulfur from organic debris (megaspores, spores, and cuticles) dispersed in these sedimentary rocks cannot be ruled out.

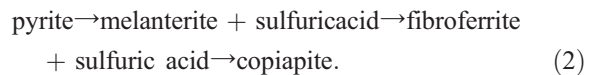
## 5. Hydrated-sulfate paragenesis

### 5.1. Paragenesis

Literature on hydrated-sulfate minerals is comprehensively treated by Palache et al. (1957), based mainly as alteration products of pyrite in sulfide-metal mines. However, earlier observations by McCaughey (1917) established a paragenetic link between melanterite and copiapite, based on coal from Ohio, USA,

and Palache et al. (1957, p. 503) mentioned similar observation for coal pyrite. Based on systematic studies and repeated observations, Zodrow and McCandlish (1978a,b), Zodrow et al. (1979), and Zodrow (1980) determined for the first time the complete phase sequence of hydrated-sulfate minerals, after coal-pyrite oxidation. In this sequence, copiapite is the stable end phase, confirmed on theoretical grounds by Jamieson et al. (2003).

Of specific interest are mineralization and mineralogic phases in the paragenetic sequence that were observed in coal debris, but also in clastic roof rocks in #26 Colliery, 1-B mine (Zodrow et al., 1979), noting the two-stage sulfuric acid production (Fig. 5):



This process produced copious amounts of the secondary minerals to be able to routinely collect 150 to 300 g of each phase from one coal-pillar, attesting the chemical vitality of this process (see later).

Pyrite oxidation without intermediate hydrated-sulfate phases was also observed, this includes:



As a consequence, these minerals are almost free of contaminating intermediate phases, and close to being 100% mineralogically pure, confirmed by the absence of extraneous lines in their powder X-ray films.

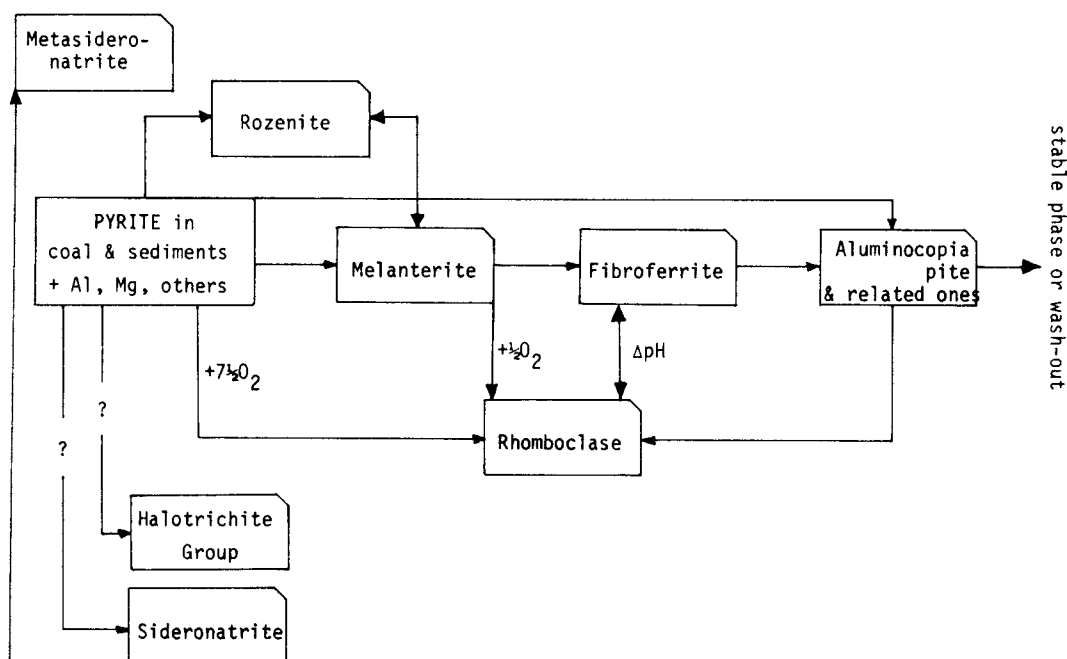


Fig. 5. Paragenetic scheme for some hydrated-sulfate minerals in the Sydney Coalfield, Nova Scotia, Canada (Zodrow et al., 1979).

The oxidation reactions

pyrite → pickeringite – halotrichite, (5)

and

pyrite → tamarugite, also iron tamarugite (6)

were best observed in roof rocks, and also represent rather pure phases.

Other hydrated sulfates, such as rhomboclase, are dependent on low pH levels for deposition, (index mineral for acidic environment), and have only been identified from acid-run offs underground (pH as low as 1.5). Of the above-mentioned sulfates, metavoltine is the rarest, and the various Al–Mg–Fe(III)–Fe(II) copiapite species the most common in coal, both underground and on costal exposures along the North Atlantic Ocean.

### 5.2. Bacterial role in sulfur-isotopic fractionation in hydrated sulfates?

A series of stable sulfur-isotope determinations were done on selected hydrated-sulfate minerals (Table 2). The results clearly show variable distribution of the heavier sulfur isotope ( $S_{34}$ ) in the

copiapites, relative to the standard Canyon Diablo troilite. Also, enrichment–depletion trends of the heavy S isotope in situ paragenetic melanterite–fibroferrite–magnesiocopiapite differ from in vitro paragenetic fibroferrite–aluminocopiapite. The spread of sulfur fractionation suggest that probably

Table 2

Stable sulfur isotope values, 0/00 relative to Canyon Diablo troilite, of hydrated-sulfate phases from, Sydney Coalfield, Nova Scotia, Canada

In situ paragenesis, #26 Colliery		
Melanterite	→	Fibroferrite → Magnesiocopiapite
+9.3		+1.3 +15.8
In vitro observation		
		Fibroferrite → Aluminocopiapite
		+1.3 –5.3

Chemically identified copiapites, confirmed by X-ray analyses (Zodrow, 1980)

Magnesiocopiapite +6.7, +7.3

Ferrocopiapite –2.7

Aluminocopiapite –13.7

Unpublished data by the author, 1982: analysis performed by McMaster University, Nuclear Research, Hamilton, Ontario, Canada.

Arrows indicate direction of paragenesis (Fig. 5).

*Thiobacillus ferrooxidans* (Brierley and Brierley, 2002), aided the chemical reaction of pyrite for hydrated-sulfate formation. Controlled studies demonstrated (summary: Brierley and Brierley, 2002) that *T. ferrooxidans* is capable of accelerating (by catalysis) chemical breakdown of pyrite 500,000 to 1,000,000-fold.

Since pyrite in the Sydney Coalfield commonly contains a variety of different sulfide inclusions (Birk, 1990; Zodrow and Goodarzi, 1993), isotopic diversity has to be delineated first before it is possible to map out isotopic signature of sulfophile bacteria (see also Gibling et al., 1989).

### 5.3. Pyrite-hydrated-sulfate reaction as a concentration process for certain metals

Analyses of samples of syngenetic and epigenetic-pyrite concentrates (+95% chemical purity) from nine successive coal seams of the Sydney Coalfield show the presence of over 20 chalcophile elements (Zodrow and Goodarzi, 1993). Of interest are Cu, Co, Ni, Mn, and Zn, as they are also reported (but not exclusively) from phases in hydrated-sulfate paragenesis (Table 3). Moreover, iron-bearing tamarugite with 5.3 ppm U, however, shows the highest recorded U content of any hydrated-sulfate minerals analyzed. For comparisons, sedimentary rocks across Sydney Coalfield show 5.0 ppm in seat earth, and up to 2.2 ppm in sandstones (Zodrow and Zentilli, 1979, Table 5.2). Consistent trends in Table 3 suggest that paragenesis acts as a concentration

process for the metals determined, and by the same token as an agent for metal-enrichment in acidic-mine effluent. The metals find their way into the terrestrial environment, and into certain coastal marine areas along the shores of Cape Breton Island where collieries were situated. Systematic quantitative data are not available for environmental evaluation.

## 6. Discussion

Roof instability primarily, and floor condition secondarily, were geologically based safety hazards in the once-operating collieries of Sydney Coalfield. Methane explosion was not, as collieries were not particularly gaseous. One gas explosion occurred in #26 Colliery in 1979 resulting into 12 fatalities (Giggey, 1979, p. 3).

Rock falls, occasionally large-scale roof collapses occurred in the Prince Mine, presumed to be caused by change in strata (MacLean and Merner, 1978; Cape Breton Post, 1978). Also, rock falls occurred in other collieries, presumably triggered by secondary sedimentary structures such as joints in roof rocks, or sandstone intrusion (Forgeron et al., 1986). To stabilize shaley roof rocks, preventive measures taken included roof bolting that was used only if flat-lying sandstone strata formed the roof for secure anchorage, installments of steel tresses at cross-cut intersections, and steel arching on which mainly corrugated metal sheets were placed (MacLean and Merner, 1978). Also used effectively for stabilization were various methods of resin or low-density cement injections into coal pillars and roof rocks (personal communication, S. Forgeron, former chief geologist, coal operation, 1998).

The author noted that applying limestone dust to coal faces in collieries, intended to control coal-dust conditions (i.e., prevent as much as possible “black lung” disease, and reduce potential for coal-dust flash fire), effectively inhibited pyritic oxidation and paragenesis. This effect is explained through neutralizing acid production that usually occurs when pyrite oxidizes, which in turn prevented growth of acidophile bacteria (summary: Brierley and Brierley, 2002). In effect, this suggests a method for controlling mine-roof problems.

Table 3  
Enrichment of certain transition elements in hydrated-sulfate phases from in situ paragenetic stages in #26 Colliery 1-B Mine

Pyrite	→ Melanterite	→ Fibroferrite	→ Copiapite
Cu: 48	44	50	129
Co: 8	35	nd	nd
Ni: 37	46	63	307
Mn: 4	166	nd	400
Zn: 71	17	45	556
U: < 0.5	< 0.2–0.28	< 0.2–0.30	< 0.2–0.4

Sydney Coalfield, Nova Scotia, Canada. Values in ppm.

nd=not determined.

Data from Zodrow (1980), Zodrow et al. (1979), and unpublished data by the author based on delayed nuclear-activation method (1980–1982).

Arrows indicate direction of paragenesis (Fig. 5).



Fig. 6. Roof rock, #26 Colliery, 1-B Mine, spalling in silty shale by crystallizing tamarugite “t”. Westphalian D coal, Sydney Coalfield, Nova Scotia.  $\times 2$ .

Floor-mud conditions were controlled mainly by clay species (kaolinite and illite), and their proportion present in the rocks. When these clays were present in sufficient amounts, mud formed the mining floor and caused slippery conditions for coal miners and machinery (MacLean and Merner, 1978).

Recently (2002–2003), increasing incidences of subsidence over collieries mined-out many decades ago by the room-and-pillar methods caused damages to private dwellings and schools in certain areas of the Sydney Coalfield. The author hypothesizes that in general roof-rock instability in Sydney’s collieries is a phenomenon best explained on the molecular level, when hydrated sulfates formed and exerted crystallization pressure on confined sedimentary layers (Figs. 6 and 7), aided by corrosive effects of sulfuric acid (Fig. 5) on rocks. Two interrelated phenomena are distinguished, labeled short- and long-term roof hazards for convenience.

The short-term hazard is manifested by repeated rock falls that occurred in slopes or tunnels in some once-operating collieries, basically due to regenerative cycles of hydrated sulfate mineralization, after pyrite oxidation. The generality of this process is based on evidence from the former Prince Mine, dating between June 1977 and September 1978. In this time interval, two regenerative cycles were documented (Zodrow et al., 1979, Fig. 5) that are directly linked to changing seasonal atmospheric conditions that were transmitted underground via mine ventilation (Zodrow and McCandlish, 1978b). However, underpinning the process is that pyritic oxidation proceeded rapidly in a matter of weeks, confirmed time and again by the author (1977–2004). Involved, however, was not only pyritic oxidation in the clastic fraction of exposed roof rock that continued to operate in the contacts between different sedimentary layers (facies changes), but also that which occurred in pyrite



Fig. 7. Roof rock, #26 Colliery, 1-B Mine, showing spalling in silty shale by crystallizing tamarugite “t”. Westphalian D coal, Sydney Coalfield, Nova Scotia.  $\times 2$ .



preferentially deposited with coalified megaplant-plant remains. These are entombed parallel to the sedimentary bedding planes, and are identified as meter-long calamites stems, cordaites leaves up to 1 m long, lycophyte trunks that can be up to 3–5 m long, or large seed-fern foliage that is ubiquitous in roof rocks of coal seams of Pennsylvanian age (Bell, 1938). This generalized process constitutes the proposed model for explaining roof weakness, and rapidly developing rock falls, in advancing slopes in coal mines.

Development of roof hazard in the long term was observed in #26 Colliery, 1-B Mine. This mine represented a unique opportunity to study the extent of coal erosion in cross cuts, coal pillars left as [permanent] roof support, and spalling effects in the roof of a coal seam (Phalen seam) mined out between 1913 to 1916 (Zodrow and McCandlish, 1978a, Fig. 4; Zodrow et al., 1979; unpublished research notes by the author). All of the cross cuts showed a V-shaped appearance caused by eroded walls, with the fragmentary coal accumulated as a talus slope. Moreover, erosion obliterated shape and size of pillars, surrounding them with fragmentary coal. In total, the depth of fragmentary-coal accumulation on the former mining floor was 60 to 90 cm. Constituent fragments were < 2 cm in size.

These erosional features are clearly explained by coal-pyrite oxidation. Confirming this causal relationship are observation of continued oxidation and reactions that resulted in increasing amounts of deposited paragenetic mineral phases (Fig. 5) on these coal fragments. It is noted that this occurred during one sustained regenerative cycle, i.e., in the study period 1977–1979.

Evidence from the 1-B Mine suggests the mechanism for roof collapse. Basic is that given sufficient time, pillars and cross cuts are weakened by oxidation and erosion, and that this process helped enlarging roof areas for less and less support. Under these condition, roof collapse is virtually inevitable, and eventually leads to surface subsidence in on-shore areas that were undermined by the roof and pillar method many decades ago. Although mining maps exist that identify these areas, prediction of future subsidence is impossible because of lack of monitoring advances in pillar erosion under such areas.

## 7. Conclusion

- (1) The pyritiferous Pennsylvanian coals in the Sydney Coalfield offered an unprecedented opportunity for studying complete secondary hydrated-sulfate paragenesis, which provides impetus for such studies to be carried out in presently mined coal deposits of the world.
- (2) “#26 Colliery 1-B Mine” is proposed as the conceptual geological model of surface subsidence as a long-term hazard in the Sydney Coalfield mined out by room and pillar methods. A submodel explains repeated rock falls during mining as short-term hazard caused by regenerative hydrated-sulfate cycles in roof rocks.
- (3) The model can be tested in coal-mining areas which operate under similar conditions: (a) coal-pyrite geochemistry, and (b) mining methods.

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## Appendix A. Empirical formulae of hydrated-sulfate minerals

Except where otherwise indicated, formulae are from Palache et al. (1957), assuming full hydration spheres, except for copiapite.

Copiapite (Zodrow, 1980)	$(\text{Na,Ca,Mg,Fe}^{+2}, \text{Al})(\text{Fe}^{+3}\text{Al})_4(\text{SO}_4)_6(\text{OH})_2 \cdot 16\text{--}20\text{H}_2\text{O}$
Fibroferrite	$\text{Fe}(\text{SO}_4)(\text{OH}) \cdot 5\text{H}_2\text{O}$
Halotrichite	$\text{Fe}^{+2}\text{Al}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$
Melanterite	$\text{Fe}(\text{SO}_4) \cdot 7\text{H}_2\text{O}$
Metavoltine	$(\text{K,Na,Fe}^{+2})_5\text{Fe}_3^{+3}(\text{SO}_4)_6(\text{OH})_2 \cdot 9\text{H}_2\text{O}$
Metasideronatrite	$\text{Na}_4\text{Fe}_2(\text{SO}_4)_4(\text{OH})_2 \cdot 3\text{H}_2\text{O}$
Pickeringite	$\text{MgAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$
Rhombochase	$\text{HFe}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$
Rozenite	$\text{Fe}(\text{SO}_4) \cdot 4\text{H}_2\text{O}$
Sideronatrite	$\text{Na}_2\text{Fe}(\text{SO}_4)_2(\text{OH}) \cdot 3\text{H}_2\text{O}$
Tamarugite, iron	$\text{NaAl}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$
tamarugite	trivalent iron substituting for Al?

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