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Résumé de l'article

On a preleve des donnees sur 30 netaux et le soufre dans une suite d'ecbantillons de charbon global provenant de chenaux du bassln houiller de Sydney, en Nouvelle-Ecosse, afin d'en etudier la variation stratigraphlque, 1'abondance et l'orlgine. Leur traitement suggere la presence de patrons de distribution [tendances] sous la forme de pics de concentration qui se trouvent a la base ou au soomet des echantillons de chenal. On observe des tendances complexes ou cycliques dans les echantillons de charbon provenant deB couches plus epaisses [200 cm]. L'origin\* de ces tendances est reliee au depot de la pyrite alnsi qu's l'histolre du remplissage des tourbieres d'ou^ provient le charbon. A defaut d'avoir une tendance regionale, cea donnees condulsent a suggerer une dependence vis-a-vis l'age de certains nineraux chalcophiles qui se trouvent dans les lits plus jeunes de la region de Point Anconi.

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# GEOCHEMICAL TRENDS IN WHOLE-SEAM COAL CHANNEL SAMPLES FROM THE SYDNEY COALFIELD (UPPER CARBONIFEROUS), NOVA SCOTIA, CANADA

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From a series of whole-coal channel samples of the Sydney Coalfield of Nova Scotia, data on 30 metals and sulfur were obtained in order to study their stratigraphic variation, abundance, and origin. The data suggest the presence of distribution patterns (trends) that can be described in terms of concentration peaks occurring at the bottom or top of the channel samples. Complex or cyclical trends are observed in coal samples from the thicker 200 cm seams. These trends are genetically linked with deposition of pyrite and the depositional history of the peat swamps to form coal. Regional trends are not found in the data but there is a suggestion that some chalcophile metals are age-dependent and occur in the younger seams in the Point Aconi area.

On a prélevé des données sur 30 métaux et le soufre dans une suite d'échantillons de charbon global provenant de chenaux du bassin houiller de Sydney, en Nouvelle-Ecosse, afin d'en étudier la variation stratigraphique, l'abondance et l'origine. Leur traitement suggère la présence de patrons de distribution [tendances] sous la forme de pics de concentration qui se trouvent à la base ou au sommet des échantillons de chenal. On observe des tendances complexes ou cycliques dans les échantillons de charbon provenant des couches plus épaisses [200 cm]. L'origine de ces tendances est reliée au dépôt de la pyrite ainsi qu'à l'histoire du remplissage des tourbières d'ou provient le charbon. A défaut d'avoir une tendance régionale, ces données conduisent à suggèrer une dépendance vis-à-vis l'âge de certains minéraux chalcophiles qui se trouvent dans les lits plus jeunes de la région de Point Anconi.

[Traduit par le journal]

#### INTRODUCTION

The Sydney Coalfield contains a sequence of mineable coal seams that were deposited in a floodplain environment (Figs. 1 and 2; Hacquebard, 1983 and references therein). Coals are geochemically very interesting as they are known to contain almost all of the chemical elements (Goldschmidt, 1935), and many elements (about 19) in the volatile "A" bituminous coal samples from Sydney show a greater abundance than that found in the average composition of the continental crust (cf. Taylor, 1964). Despite our general knowledge about the geochemical make-up of coals, little is known about the stratigraphical variations and distributions of the geochemical variables, including ash and sulfur, in the coals from the Sydney Coalfield. Birk and Zodrow (in preparation) correlate certain aspects of coal geochemistry with mineral assem-Bulk geochemistry, as done on the coals blages. for this study, does not directly address the question of coal mineralogy (cf. Given et al., 1981, for norm calculations). A knowledge of geochemistry is of considerable industrial, environmental, and geological interest as it relates to the composition of coal dust, coal-ash washability, ash and sulfur contents (Walsh et al., 1969), and environment of coal deposition.

In the present paper, the emphasis is placed on examining the geochemical variables to address: 1. questions of stratigraphic variability and distribution between and within the coal channel samples; and 2. the origins of the variations. Conclusions lead to advances in statistical mean calculations and an understanding of pyrite as a contributor to the variation.

#### MATERIALS AND NOMENCLATURE

The Unnamed Seam, situated 8 m above the Lloyd Cove (-Bonar) Seam and documented by Zodrow (1985), was sampled in Brogan's open coal pit at sample site '26' (see Zodrow, 1983, Fig. 1). The Point Aconi Seam was sampled at localities 27, 28 and 29, the Lloyd Cove Seam in Brogan's pit and the Stubbart Seam underground in the Prince Mine. The Harbour Seam was laterally sampled:

(a) from the open pit mine of the NovaCo company, located on the anticline found west of the Prince Mine, representing the erosional western margin of the Sydney Basin (Harbour Seam sample 'W', Table 2; Fig. 2); and

(b) from the Lingan and #26 underground mines, representing the central portion of the coalfield (Harbour Seam sample 'CC', Table 2; Fig. 2). The Backpit Seam was sampled at site 3, the Phalen underground in #26 Mine, and the Shoemaker and the McAulay Seams at sites 5 and 4, respectively.

In total, 10 successive coal seams were channel sampled (Fig. 2) by extracting a column of coal 8-14 cm wide and 5-12 cm deep from the entire thickness of the seams, with care being taken to avoid clastic sediment contamination. Each whole-seam sample was subdivided into 15 cm lengths, disregarding microlithotype distribution (cf. Hawley, 1955), to obtain a sample population of 137. Bottom samples are generally less than 15 cm long. The entire sample amount of coal (up to 1,200 g)

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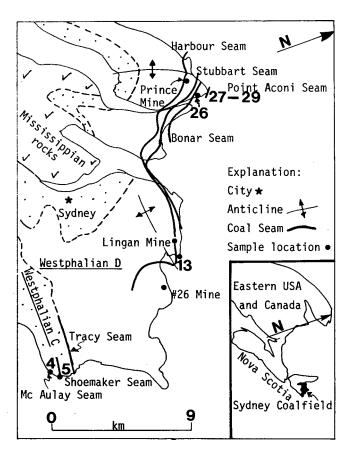


Fig. 1. Sample location map, Sydney Coalfield. [See Fig. 2 for further stratigraphic detail and the presence of lower Stephanian (i.e., Cantabrian) strata in the Point Aconi area.]

was dry-ground to pass through a (-200) standard Tyler mesh screen (<75 micrometres), and a sample portion ashed for 12 hours at a temperature not exceeding 450°C. For each of the 137 samples, 31 elements plus the ash content were determined by analytical procedures indicated in Table 1. Those marked '&' in the table have their concentration levels near or below the detection limit and so are not further considered in the paper. Efficient and reliable analytical procedures required that both whole-coal and coal ash be analyzed. Variables for which whole coal was used to determine their concentration levels are Au, Hg, As, Cr, Sb, Sc, Th, U, V, and S. For the remaining variables, the levels of element concentration in the ash were recalculated to whole-coal equivalent.

Enrichment/depletion patterns are relative to the <u>whole-coal sample</u>, and ash values are listed for information (Figs. 3, 4 and 7). No threshold ratios vis-à-vis the clarke value are used when referring to the patterns which can be recognized in the data in terms of varying concentration levels. These are relative to where the prominent peaks occur in the channel samples.

The Shoemaker Seam, the small seam above the Harbour Seam, and the Unnamed Seam (Fig. 2), which are each 35 cm thick or less, are defined as thin seams (Table 2).

# ZODROW

#### COAL GEOCHEMISTRY

To help understand the interpretation of the coal-chemical results, the nature of coal needs to be considered. Coal consists mainly of complex These can be classified into a organic compounds. series of macerals (- microlithotypes) and represent the organic equivalent of minerals. In addition, coal contains detrital, plant-derived and authigenic minerals (McCabe, 1984 and references therein). The authigenic minerals include those that are introduced in a peat swamp during or after its deposition, or in coal during or after the coalification process, i.e., syn- or epigenetic mineral formation (Mackowsky, 1968). The properties of coal are therefore the result of its depositional and diagenetic histories, and the composition of ash reflects the combined contributions from the organic compounds and the minerals, presenting a problem in correlation between organic complexes and minerals.

Coal mineralogy in the Sydney coals is dominated bγ iron disulfide minerals (pyrite, minor marcasite), clay minerals (illite, kaolinite and chlorite), followed by at least another 20 minerals which include quartz and its variety chalcedony. Scanning electron microscopy (SEM) investigation, coupled with spectral analysis, shows that the clays are ubiquitous and occur intimately associated with the macerals and that in samples taken from the top of the seam sampled by Beaton (1986), anhedral pyrite and illite often occur together as cellular fillings in fusain (Bogan This suggests fill-in as a model for fusinite). pyrite origin and questions if the pyrite is detrital in origin. Additional investigations by chemical, SEM and X-ray microprobe methods reveal an association between pyrite and the elements Cu, Ni, Se, Hg, As, Sb and Pb as expected. Based on work by Birk and Zodrow (in preparation), the major minerals (iron disulfide and the clays) are polygenetic in nature, as shown by microstructures of bedding, cell fillings, and replacement.

The sulfur component in the coal occurs as three types (Beaton, 1986): organic, sulfatic, and pyritic, whose sum-total weight percent constitutes total sulfur as recorded in Table 2. Of these, the organic sulfur is the least understood (Spiro et al., 1984). In a high-sulfur coal (S is larger than 1.5%), about 80% of the total sulfur is pyrite-derived, the remaining 20% is split between the other two types in varying proportions (Beaton, 1986, Table 1). In contrast, in a low-sulfur coal pyrite is largely absent and the total sulfur content therein is determined by the organic type (Newman, 1935, p. 542). The inference therefore is that the correlation between sulfur and iron reflects the presence of pyrite (Fig. 7) only in the high sulfur coal. An example of a low-sulfur coal environment is represented by the Harbour-Seam sample 'CC' in Table 2.

The organic and the pyritic sulfur types are dependent on the distribution of the microlithotypes that comprise the coal, except that in a high-sulfur coal some portion of the pyritic component is epigenetic (Beaton, 1986). This epigenetic portion is derived from sulfate-rich solutions recycled from the Mississippian evaporite deposits

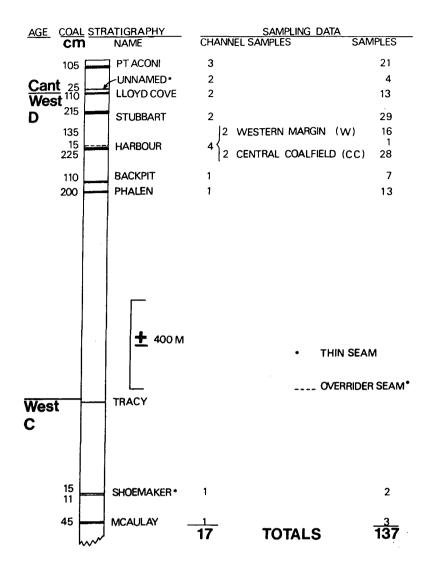


Fig. 2. Coal stratigraphy, Sydney Coalfield, Nova Scotia (Bell, 1938, Fig. 1), showing channel sample data. 'Cant' refers to Cantabrian and 'West' to Westphalian Stages of the Upper Carboniferous System. 'CC' and 'W' are explained further in the text.

(Bell, 1938; Haites, 1951; Gibling *et al.*, 1986) that surround the Sydney Coalfield as the Windsor Group (see Keppie, 1979). The non-marine origin for the sulfur is supported by paleontology (Dawson, 1878; Bell, 1938; Copeland, 1957; Vasey and Zodrow, 1983; Vasey, 1984), and by boron geochemistry (Vasey and Zodrow, 1983).

#### RESULTS AND DISCUSSION

Geochemical results are stratigraphically summarized (youngest to oldest seam-sample representation) in Table 2 to show mean-value concentrations for a) individual seam samples, b) thin- and thickseam samples, and c) laterally separate samples for the Harbour Seam.

On a between channel-sample basis, the data reveal great variability, no perceptible regional trend, and a suggestion of age dependency for the elements Pb, Zn, Fe, Ni and Cu, as their mean values are comparatively higher in the younger seam samples. The suggestion is supported by field observation of the combined presence of epigenetic galena, pyrite and chalcopyrite as cleat fillings in the roof portions of only the younger seams in the Point Aconi area.

Most thin-seam elemental concentrations are, on average, higher than those in the thick-seam samples, correlating with high sulfur and ash averages in the thin seams. The evidence is, however, equivocal for Au, except for the Harbour 'CC' and McAulay values. The differences in concentrations are probably related to facies differences as explained by Keiser et al. (1982) and by Cheek and Donaldson (1969). The expected positive correlation between gold content and seam thickness, known from the ability of plants to concentrate gold (Krejci-Graf, 1983, p. 541), is not evident from the data presented. The higher gold value in the McAulay Seam could likely be epigenetically related to the known Carboniferous unconformity, in the vicinity of which many other mineralization events occurred on Cape Breton Island. As yet, the larger Se value remains to be explained. Ca and Mn abundances in the McAulay Seam reflect the presence of a calcium manganese mineral whose identity is as yet undetermined.

More than one-half of the number of elements

lement	XRF <sup>1</sup>	DCP <sup>2</sup>	NA <sup>3</sup>		FAA <sup>4</sup>	Amount analyzed	Lower Detection	
	On Ash	(wt %,	ppm)	On Coal (ppb, ppm)		(g)	Limit (ppm, wt %,ppb)	
Au Hg Pd & Pt &					ppb ) ppb ) ppb ) ppb )	20-25	2 10 2 10	
Al Ca Fe K Mg Na Si Ti	wt % wt % wt % wt % wt % wt % wt %					) 1.3	0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01	
Ba Ga & Ge Nb & Rb Sr Y &	ppm ppm ppm ppm ppm ppm ppm					) 1-2	10 10 10 2 10 10	
Ag Be & Cd & Cu Mn Mo Ni Pb Zn B <sup>5</sup> Cs & Se		ррт ррт ррт ррт ррт ррт ррт ррт ррт	ppm ppm ppm			0.1-0.5	0.5 10 0.2 1 0.5 2 1 1 2 0.5 0.5 0.5 1	
As Cr Sb Sc Sm & Th U V W S				ррт ррт ррт ррт ррт ррт ррт ррт ррт	Leco	) 3-6 0.7-1.6 ) 3-6 1-2	0.5 2 0.1 0.1 0.1 0.1 0.01 0.8 1	

Table 1. Analytical methods and units of measurements

 $^{1}$ X-ray fluorescence. <sup>2</sup>Direct reading emission spectrometry with direct current argon plasma. <sup>3</sup>Neutron activation. <sup>4</sup>Hg by flameless atomic absorption; Hg, Pd and Pt by fire assay collection with DCP of Doré bead. <sup>5</sup>In two seams; not reported here. & concentration levels near or below detection limit.

studied are on average more highly concentrated at the margin of the basin (Harbour-Seam sample 'W') than in the portion of the central coalfield (Harbour-Seam sample 'CC'), including Be and Ge. The distribution pattern is consistent with the assumption that both elements concentrated near their sources (Zubovic, 1966; Stadnichenko *et al.*, 1953; Minchev and Eskenasy, 1966) and that the mineral content of the coal is detrital-dependent.

Within-sample variability for most of the elements can be described in terms of relative enrichment/depletion patterns vis-à-vis coal thickness as follows:

- either a) bottom and top are both enriched (Fig. 3a), or b) both bottom and top are depleted (Fig. 3b);
- either a) bottom is depleted and top is enriched (Fig. 3c), or b) top is depleted and bottom is enriched (Fig. 3d);
- 3) repetition of 1) or 2) in the sample.

The most common patterns conform with 1) and 2), but are variable for a given element from one seam sample to another.

Elements for which no pattern is discernible include Au (Stubbart sample), Mg (Harbour sample 'W'), Rb (Pt. Aconi sample), Sb (Phalen sample) and

	Pt Aconi	Lloyd Cove	Stubbart	Harbour		Backpit	Phalen	Mc Aulay	THICK SEAMS	THIN SEAMS #
				CC #	W #				+	
Ag	0.56 <u>+</u> 0.51	0.74 <u>+</u> 0.84	0.05 <u>+</u> 0.05	0.02 <u>+</u> 0.01	0.69 <u>+</u> 0.80	0.07 <u>+</u> 0.01	0.05 <u>+</u> 0.03	0.50 <u>+</u> 0.01	0.29 <u>+</u> 0.52	0.83 <u>+</u> 0.81
A1	0.55 <u>+</u> 0.45	0.22 <u>+</u> 0.30	0.85 <u>+</u> 0.82	0.28 <u>+</u> 0.12	0.88 <u>+</u> 1.52	0.67 <u>+</u> 0.96	0.68 <u>+</u> 0.44	0.31 <u>+</u> 0.06	0.58 <u>+</u> 0.76	3.19 <u>+</u> 1.73
As	222.3 <u>+</u> 180.2	99.9 <u>+</u> 51.9	139.6 <u>+</u> 104.4	8.7 <u>+</u> 13.2	83.1 <u>+</u> 53.4	62.0 <u>+</u> 64.1	28.9 <u>+</u> 26.9	125.0 <u>+</u> 26.1	98.2 <u>+</u> 116.3	254.6 <u>+</u> 111.5
ash	10.8 <u>+</u> 8.9	6.0 <u>+</u> 2.9	11.0 <u>+</u> 7.1	3.4 <u>+</u> 2.2	11.9 <u>+</u> 10.8	10.6 <u>+</u> 7.3	6.3 <u>+</u> 2.8	13.9 <u>+</u> 3.2	8.6 <u>+</u> 7.2	30.7 <u>+</u> 9.8
Au	4 <u>+</u> 6	13 <u>+</u> 30	2 <u>+</u> 5	35 <u>+</u> 77	3 <u>+</u> 4	7 <u>+</u> 5	12+10	86 <u>+</u> 125	11 <u>+</u> 36	10 <u>+</u> 12
Ba	33.9 <u>+</u> 33.8	26.3+40.2	39.6 <u>+</u> 34.2	17.5 <u>+</u> 8.9	53.6 <u>+</u> 95.6	38.0+51.0	18.1 <u>+</u> 10.7	23.3 <u>+</u> 5.8	31.7 <u>+</u> 44.0	194.1 <u>+</u> 85.1
Be	6.7 <u>+</u> 4.4	4.5 <u>+</u> 3.9	1.7 <u>+</u> 1.8	0.4 <u>+</u> 0.4	6.1 <u>+</u> 5.9	1.2 <u>+</u> 0.7	0.4 <u>+</u> 0.1	14.7 <u>+</u> 2.3	3.2 <u>+</u> 4.3	12.2 <u>+</u> 5.4
Ca	0.09 <u>+</u> 0.04	0.04 <u>+</u> 0.01	0.08 <u>+</u> 0.08	0.07 <u>+</u> 0.04	0.09 <u>+</u> 0.10	0.51 <u>+</u> 0.26	0.41 <u>+</u> 0.26	0.82+0.14	0.15 <u>+</u> 0.20	0.15 <u>+</u> 0.05
Со	2.9 <u>+</u> 5.6	1.8 <u>+</u> 2.6	6.4 <u>+</u> 14.0	1.6 <u>+</u> 0.8	7.4 <u>+</u> 8.8	1.9 <u>+</u> 2.0	1.8 <u>+</u> 0.9	3.3 <u>+</u> 3.2	3.7 <u>+</u> 7.9	28.5 <u>+</u> 7.9
Cr	7 <u>+</u> 8	5 <u>+</u> 5	9 <u>+</u> 7	3 <u>+</u> 2	14 <u>+</u> 20	8 <u>+</u> 8	7 <u>+</u> 4	5 <u>+</u> 1	7 <u>+</u> 9	37 <u>+</u> 17
Cu	30.2 <u>+</u> 24.2	14.0+ 5.9	16.2 <u>+</u> 16.7	5.6 <u>+</u> 1.8	28.3+22.3	11.4 <u>+</u> 5.3	8.4 <u>+</u> 2.4	18.7 <u>+</u> 2.9	16.5 <u>+</u> 17.2	67.8 <u>+</u> 23.3
Fe	5.16 <u>+</u> 4.96	3.16 <u>+</u> 1.33	4.10+2.99	1.08 <u>+</u> 1.12	4.38 <u>+</u> 2.48	3.30 <u>+</u> 1.82	0.74+0.43	5.73 <u>+</u> 1.46	3.22 <u>+</u> 3.13	7.15+3.92
Ge	8.7 <u>+</u> 9.4	7.3+ 8.0	8.5 <u>+</u> 13.6	1.8 <u>+</u> 3.3	8.8 <u>+</u> 9.2	9.6 <u>+</u> 14.3	1.1 <u>+</u> 0.8	5.3 <u>+</u> 2.3	6.3 <u>+</u> 9.6	13.8 <u>+</u> 11.9
Нg	130+70	126+64	153 <u>+</u> 96	297+148	49+45	70 <u>+</u> 34	77 <u>+</u> 36	133 <u>+</u> 42	129 <u>+</u> 109	271 <u>+</u> 120
к	0.041+0.074	0.020+0.027	0.086+0.108	0.024+0.023	0.120+0.248	0.160+0.296	0.075+0.058	0.030+0.017	0.065+0.129	0.539+0.380
Mg	0.031+0.025	0.018+0.012	0.026+0.020	0.031+0.026	0.041+0.054	0.037+0.058	0.027+0.014	0.040+0.010	0.030+0.030	0.164+0.088
Mn	41.8 <u>+</u> 18.9	23.0+15.6	40.3+36.2	232.2 <u>+</u> 366.9	34.1 <u>+</u> 30.9	69.2+40.5	49.5+27.3	1223.3+332.6	104.5+238.5	118.4+44.9
No. of channel samples:									TOT	ALS
	3	2	2	2	2	1	1	l	14	3
sam	ples: 21	13	29	28	16	7	13	3	130	7

Table 2. Stratigraphic variation of sample mean<u>+</u>std

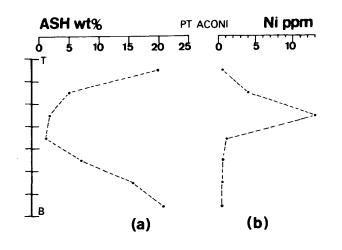
# Refer to Fig. 2.

Table 2. Continued Stratigraphic variation of sample mean<u>+</u>std

	Pt Aconi	Lloyd Cove	Stubbart	Harbou	r	Backpit	Phalen	Mc Aulay	THICK SEAMS	THIN SEAMS#	
Мо	7.6+6.8	4.1+1.7	9.2+7.5	2.2+1.0	4.7+3.4	11.9 <u>+</u> 4.7	2.5 <u>+</u> 1.4	14.7 <u>+</u> 1.6	6.0 <u>+</u> 5.8	15.5 <u>+</u> 14.3	
Na	0.020 <u>+</u> 0.015	0.010+0.008	0.036+0.018	0.014+0.005	0.021+0.034	0.007+0.011	0.040+0.012	0.027 <u>+</u> 0.005	0.023 <u>+</u> 0.020	0.069 <u>+</u> 0.036	
Ni	11.4 <u>+</u> 22.2	12.1 <u>+</u> 15.0	15.2 <u>+</u> 31.8	3.0 <u>+</u> 2.0	16.7 <u>+</u> 15.4	4.8+ 4.9	3.1 <u>+</u> 1.8	7.2 <u>+</u> 8.0	9.9 <u>+</u> 19.4	57.6 <u>+</u> 17.1	
Pb	42.5 <u>+</u> 72.6	29.9 <u>+</u> 33.4	56.9 <u>+</u> 48.2	2.7 <u>+</u> 1.8	94.0+72.5	2.4+ 2.5	3.6 <u>+</u> 1.8	55.7 <u>+</u> 15.6	36.5 <u>+</u> 54.6	157.4 <u>+</u> 296.3	
Rb	13.5 <u>+</u> 9.4	8.2 <u>+</u> 9.8	4.7 <u>+</u> 5.9	3.0+ 4.4	13.1 <u>+</u> 13.8	7.9 <u>+</u> 13.8	6.1 <u>+</u> 6.2	20.0 <u>+</u> 0.0	7.8 <u>+</u> 9.4	29.8 <u>+</u> 20.4	
S	7.5 <u>+</u> 5.4	4.7 <u>+</u> 1.6	5.7 <u>+</u> 3.5	0.84+ 0.5	5.6+ 2.6	4.0 <u>+</u> 1.9	1.5 <u>+</u> 0.5	7.6 <u>+</u> 1.3	4.3 <u>+</u> 3.8	12.9 <u>+</u> 5.8	
Sb	3.1+3.1	2.7 <u>+</u> 2.9	0.8+1.5	3.1+2.0	0.2+0.4	1.1 <u>+</u> 1.5	0.2 <u>+</u> 0.1	3.7 <u>+</u> 1.2	1.5 <u>+</u> 2.3	7.1 <u>+</u> 3.2	
Sc	0.9 <u>+</u> 1.1	1.0 <u>+</u> 1.2	1.7 <u>+</u> 1.5	2.6+3.9	0.5 <u>+</u> 0.3	1.2 <u>+</u> 1.5	1.2+0.7	0.5 <u>+</u> 0.3	1.2 <u>+</u> 1.8	6.6 <u>+</u> 3.2	
Se	7.7 <u>+</u> 6.2	5.3 <u>+</u> 6.1	0.3 <u>+</u> 0.5	0.0 <u>+</u> 0.0	6.7 <u>+</u> 6.9	0.3 <u>+</u> 0.2	0.2 <u>+</u> 0.1	16.6 <u>+</u> 5.8	3.1 <u>+</u> 5.5	7.5 <u>+</u> 4.3	
Si	0.76 <u>+</u> 0.70	0.30 <u>+</u> 0.36	1.17 <u>+</u> 1.21	0.42 <u>+</u> 0.23	0.95 <u>+</u> 1.90	1.31 <u>+</u> 1.71	1.10 <u>+</u> 0.72	0.59 <u>+</u> 0.34	0.82 <u>+</u> 1.07	4.73 <u>+</u> 2.39	
Sr	19.9 <u>+</u> 24.1	31.0 <u>+</u> 70.0	22.3 <u>+</u> 45.6	6.8 <u>+</u> 3.6	32.4 <u>+</u> 58.8	21.1 <u>+</u> 10.9	45.6 <u>+</u> 8.5	23.3 <u>+</u> 5.8	23.0 <u>+</u> 39.3	145.1 <u>+</u> 122.5	
Th	0.7 <u>+</u> 0.67	0.5 <u>+</u> 0.88	1.3 <u>+</u> 1.33	2.2+4.28	0.4+0.23	1.0 <u>+</u> 1.26	1.0 <u>+</u> 0.64	0.5 <u>+</u> 0.15	1.0 <u>+</u> 1.76	5.5 <u>+</u> 3.55	
Ti	0.018 <u>+</u> 0.017	0.010+0.008	0.040+0.042	0.017 <u>+</u> 0.010	0.050+0.098	0.025+0.024	0.038+0.026	0.010+0.000	0.028+0.043	0.108 <u>+</u> 0.050	
U	0.40 <u>+</u> 0.59	0.29 <u>+</u> 0.46	0.44 <u>+</u> 0.42	0.70 <u>+</u> 1.07	0.12+0.07	0.30+0.31	0.29 <u>+</u> 0.18	0.28+0.21	0.36+0.53	3.34 <u>+</u> 2.46	
V	11.2 <u>+</u> 20.5	9.4 <u>+</u> 17.5	15.8 <u>+</u> 15.1	21.5+27.1	4.0+ 2.5	10.0 <u>+</u> 13.0	8.3+ 5.9	7.9 <u>+</u> 4.7	11.3 <u>+</u> 16.5	71.6 <u>+</u> 34.4	
Zn	203.3+403.9	71.3 <u>+</u> 105.7	14.9 <u>+</u> 9.0	3.5 <u>+</u> 2.8	104.0 <u>+</u> 184.1	8.4 <u>+</u> 3.1	4.0 <u>+</u> 0.7	25.7 <u>+</u> 11.1	58.3 <u>+</u> 188.5	440.2 <u>+</u> 336 <sup>.</sup> .3	
I	No. of channel samples:									TOTALS:	
	3	2	2	2	2	'n	1	1	14	3	
samp	oles: 21	13	29	28	16	7	13	3	130	7	

# Refer to Fig. 2.

ZODROW



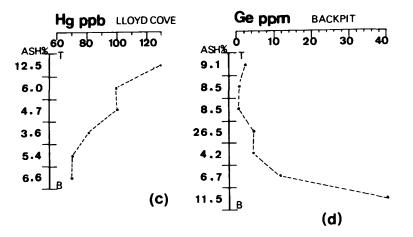


Fig. 3. Simple trend patterns in reference to the whole-coal channel samples that are indicated by the vertical black bars. 'T' refers to the top and 'B' to the bottom of the channel sample, in which 15 cm sample divisions are indicated by the horizontal cross bars (see also Figs. 3 and 6). The coal ash percent (ASH%) is listed for each 15 cm long sample to provide additional information.

Ti (Lloyd Cove sample). Pattern 3) is found where sample thickness is greater than 200 cm as in the Stubbart, Harbour 'CC' and Phalen seams. Usually, the geochemical variables show complex trends in these three sample sites (Fig. 4). As in the case for the simple trends, the repetitive pattern 3) for a given variable may not be duplicated in the data from one sample to another.

The observed trend patterns preclude the use of a normal population model. Frequency analysis shows positively skewed histograms (e.g., Fig. 5) that are L-shaped, many of them unimodal at this level of sample size. Probability density modeling to investigate the underlying population suggests a Pearsonian Type I model (Elderton and Johnson, 1969) to represent the data. The Type I model (Schuegraf and Zodrow, 1974) is based on the beta integral but has transformation potential to the log-normal model. Frequencies for U (Fig. 6), Th, Pb and Ti were fitted to the Type I Model with varying measures of success. The reader is cautioned about the difficulties, however, that exist with this sample size to decide on a model for data representation (Zodrow et al., 1987).

The geochemical variables Ca, Mn, Sb, Fe, Si, Pb and Zn show large ranges (difference between smallest and largest data points), disjoint frequencies, or multimodal histograms in their sample distributions. These statistical characteristics are indicative of the presence of several mineral phases for each variable, involving sulfide, carbonate and silicate groups.

Comparisons of skewness values among some of the presently studied variables and those from the U.S.A. (Gluskoter et al., 1977) and Australian (Slansky, 1985) coal samples show many similarities notable differences. One difference is and manifested by the smaller skewness values (i.e., 'better' symmetrical conditions) that are observed in histograms for coal ash in the other two coalfield samples, in comparison with the L-shaped frequency histogram of Sydney's coal ash (Fig. 5). It is suggested that the skewness differences reflect differing depositional environments, as is found in ash studies of modern-day peats (e.g., Bustin et al., 1985).

## PATTERNS; GENETIC CONSIDERATION

Simple trends, represented by 1a), reflect a situation of uninterrupted peat accumulation in a Increased interactions occurred between swamp. iron-organic complexes (clay colloids) and sulfaterich solutions to deposit increasing amounts of

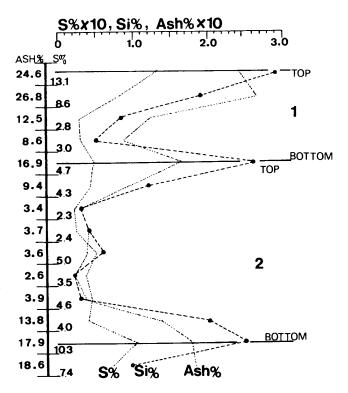


Fig. 4. Complex cyclical trend pattern in reference to the whole-coal channel sample from the Stubbart Seam. 'Topbottom 1 and 2' each represent simple 1a) trend pattern analogues. The coal ash percent (ASH%) and the sulfur content (S%) are listed for each 15 cm long sample to provide additional information.

pyrite at the initial and terminal stages of peat accumulation (Newman, 1935; Williams and Keith, 1963; Nicholls, 1968, p. 283). Peat accumulation continued in an environment progressively less affected by sedimentary influxes and in which poor drainage developed, resulting in lower ash and sulfur peat (until the terminal-stage conditions are imposed). Fig. 7 represents the geochemical signature, showing high sulfur and ash at the bottom and roof of the Pt. Aconi Seam, with progressive decreases of these concentration levels towards the middle portion of the seam.

Patterns represented by 1b) and 2a, b) are mostly associated with the chalcophile elements and basic to their genesis is the complex polygenetic history of pyrite deposition.

Cyclical patterns can be broken down into simple patterns (Fig. 4). The interfaces defined at any high/low concentration peaks represent а temporal initial/terminal stage situation, showing the enrichment/depletion patterns analogous to the simple pattern of 1a) and the distribution of This situation marks punctuated sulfur and ash. peat accumulation caused by influx of clayey sediments when levees are breached. The flooding events can be localized and discontinuous or extensive to form thicker sedimentary deposits that split the seams. These seam splits are macromanifestations of punctuated peat accumulation in a developing coal swamp. An exception to the variability of patterns is found in the geochemical variables of the Backpit-Seam sample, where they show mostly la) trends. The nature of the roof rocks, lacustrine deposits in this case, may

influence coal geochemistry as observed by McCabe (1984, p. 17-18) and Haites (1950, p. 81).

### CONCLUSIONS

Marine-influenced coal deposition is reflected in high-sulfur coal whose sulfur content is variable both laterally and vertically. In contrast, lowsulfur coal shows comparatively less sulfur variability. An unresolved problem is presented by the high-sulfur content that is also very variable in the coals from the Sydney Coalfield, in the absence of marine incursions. The high variability also occurs in the ash and includes not only sulfur but all of the geochemical variables examined. This implies influxes of detrital minerals and authigenic mineral formation (which are reflected in the amount and composition of the coal ash; Nicholls, 1968, p. 283). Patterns can be simple or complex cyclical, but they could be refined through a study of shorter sample lengths than the 15 cm lengths employed. Additionally, compaction ratios in peat-coal (McCabe, 1984, p. 2) and epigenetic mineralization undoubtedly influenced the distribution of the elements to form the observed pattern. In this context, the hypothesis by Goldschmidt (1937) that physical rather than geochemical

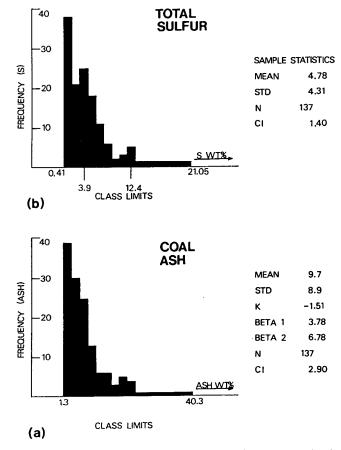


Fig. 5. Sample frequencies and statistics for sulfur and ash contents of the sample population. 'STD' is the standard deviation, 'K' the classification criterion for the Type I model, 'Beta 1 and Beta 2' skewness and kurtosis, respectively, 'N' the sample size, and 'CI' is the class interval. The linear correlation coefficient between sulfur and ash is 0.91.

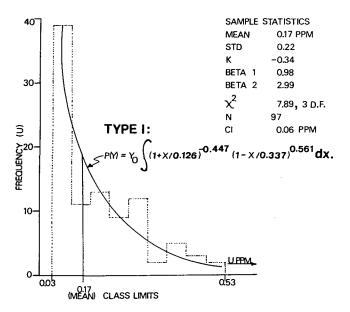


Fig. 6. Type I probability model (solid line) fitted to uranium frequencies (stippled bars). 'P' is the probability, ' $X^{2'}$ ' and 'D.F.' are the "goodness-of-fit" statistic and associate number of degrees of freedom.

Refer to Fig. 4 for explanation of other letters used.

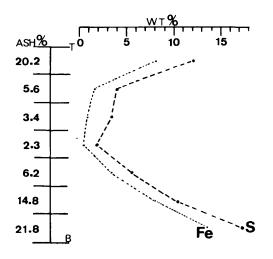


Fig. 7. Uninterrupted peat accumulation in the Pt. Aconi coal and its geochemical signature of sulfur and iron (pyrite correlative) in the setting of ash content (ASH%) variation. The simple la) patterns for S and Fe are in reference to the whole-coal sample.

phenomena are responsible for the patterns remains to be confirmed.

The results obtained by Hawley (1955), i.e., that microlithotypes correlate poorly with trace elements and it is difficult to correlate coal seams on that basis, are not surprising in view of the variability of geochemical trends in the coal. Hacquebard's suggestion (1986) for the use of petrological profiles for correlation is probably the best viable alternative. Clearly, grab or runof-the-mine samples (cf. Landheer et al., 1982; Sandeman, 1979) can only furnish biased mean values for coal. Of possible mineral exploration interest is the observation that in the younger seams, near the Permo-Carboniferous boundary, increased sulfide mineralization was found.

Recent discoveries of <u>Note added in proof</u>: foraminifera, fragments of conodonts and cephalopods by S. Thibaudeau of Dalhousie University, Halifax, Nova Scotia (personal communication, September 1987) constitute positive proof for the first time of marginal marine influences in the Sydney Coalfield.

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