

MACERAL AFFINITY OF PHOSPHORUS IN COALS FROM THE ELK VALLEY COALFIELD, BRITISH COLUMBIA.

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INTRODUCTION

British Columbia exports about 25 million tonnes per year of metallurgical coal from two coalfields, which follow the Rocky Mountains along the eastern edge of the Province. In the north there are two mines in the Peace River coalfield and in the south, five mines in the east Kootenay coalfields (Figure 1). The east Kootenay coalfields are divided into the Elk Valley, Crowsnest and Flathead fields (Figure 2). Three mines are situated in the Elk Valley coalfield, the most important coal-producing area in British Columbia, and they account for about 15.7 million tonnes of export coal. All the economic seams in the Kootenay coalfields are contained in the Mist Mountain Formation of late Jurassic to early Cretaceous age.

Phosphorus in steel reduces its flexibility and is generally considered to be an undesirable element in coal. Most steel mills blend coals to achieve a phosphorus concentration in coal of less than 0.04%.

Data collected during this study are not located with respect to any particular mine and the seams sampled are identified by sequential letters from A near the base of the section through the Mist Mountain Formation to near the top. The lettering system does not correspond exactly with the seam numbering in any particular mine, but does retain the relative stratigraphic positions of all the data discussed in this paper.

PREVIOUS WORK

The comprehensive paper by Gluskoter *et al.* (1977) used washability analysis to assign elements a coal (organic) or ash affinity. He found that phosphorus sometimes had an inorganic affinity, but in a majority of the cases followed the coal. Finkleman (1980) reviewed the existing literature and used XRD and SEM techniques to identify the modes of occurrence of many elements, including phosphorus in coal. Powell (1987) suggested that ionic potential can be used to separate elements into organic or inorganic affinities and that based on this, P^{3+} should have an organic affinity and P^{5+} an inorganic affinity.

Studies of phosphorus in British Columbia coals include Van Den Bussche and Grieve (1990), which provided information on average phosphorus

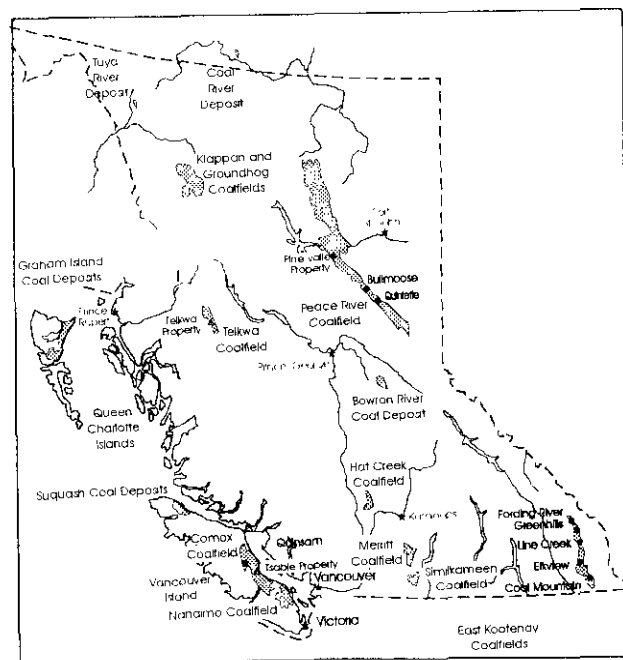


Figure 1 Location map of coalfields and coal deposits in British Columbia.

concentrations in the Gates, Gething and Mist Mountain formations; Grieve and Holuszko (1991), which provided phosphorus and trace element data and Grieve (1992), which compiled all previous data. Ryan and Grieve (1995) discussed the origin of phosphorus in coal and analyzed incremental samples through a number of seams in the Mist Mountain Formation.

A number of papers describe the distribution of elements, including phosphorus in seam sections. These include Karner *et al.* (1986) who studied the distribution of elements in a North Dakota lignite of Paleocene age and described phosphorus as having an uncertain or inorganic association. Other papers include Harris *et al.* (1981) who studied coals in eastern Tennessee and Hills (1990) who studied the Hat Creek deposit in British Columbia.

The distribution of phosphorus in Australian coals has been studied by Ward *et al.* (1996). They found a bimodal distribution of phosphorus in coals from Queensland. A bimodal distribution is not evident in coals from the Elk Valley coalfield.

ORGANIC OR INORGANIC AFFINITY OF PHOSPHORUS

There is considerable literature on major oxides, minor and trace elements in coal. Unfortunately a lot of phosphorus data is reported as P_2O_5 in ash without providing the concentration of ash in the sample, making it impossible to calculate the concentration of phosphorus in the total sample. Also it is often not clear if the samples were of raw or washed coal. In short, there is deceptively little useful published phosphorus data.

There have been a number of studies of the occurrence of phosphorous in coal but there is no direct evidence of a true organic bonding (Burchill *et al.*, 1990), though classic washability studies such as those of Gluskoter *et al.* (1977) indicate in part a coal affinity. In the classic sense organic affinity means that the element is part of the organic molecules that make up coal. In practice, elements that are difficult to remove by conventional washing methods and tend to remain with the coal are described as having an organic affinity. These elements may occur in very small mineral grains dispersed in the coal in a way not related to the amount of ash in the coal. Consequently the term organic affinity may be somewhat misleading and a better way of describing the occurrence of elements may be to simply to refer to them as elements that follow the coal, or the ash, during washing. Those following the coal will be difficult to remove and may be a problem for the purchaser. Those removed by washing may provide problems for the producer when disposing of the tails and coarse reject material.

PHOSPHORUS CONCENTRATIONS IN VEGETATION AND COAL

The main phosphorus minerals in coal are a calcium phosphate (apatite) and the two crandallite group minerals gorceixite (barium aluminum phosphate) and goyazite (strontium aluminum phosphate). It is not always possible to differentiate between goyazite and gorceixite and they are sometimes jointly referred to as crandallite.

The average phosphorus content of world coals is estimated by Bertine and Goldberg (1971) to be about 0.05% (500 ppm). Concentrations vary around the world and through time and there is a tendency for Permian coals from India and Australia, and Cretaceous coals from Western Canada, to have higher phosphorus concentrations than Carboniferous coals from Europe and USA (Ryan and Grieve, 1995 and Ward *et al.*, 1996). These authors suggest that most of the phosphorus in coal originates from the parent vegetation.

The tendency for Cretaceous and Permian coals to have higher phosphorus contents may be because of higher concentrations in the parent vegetation, either because of different species, or because of colder climates, in which vegetation requires more phosphorus to grow. There is a distinct shift to cooler climates and more polar latitudes from the Carboniferous to Permian and younger times

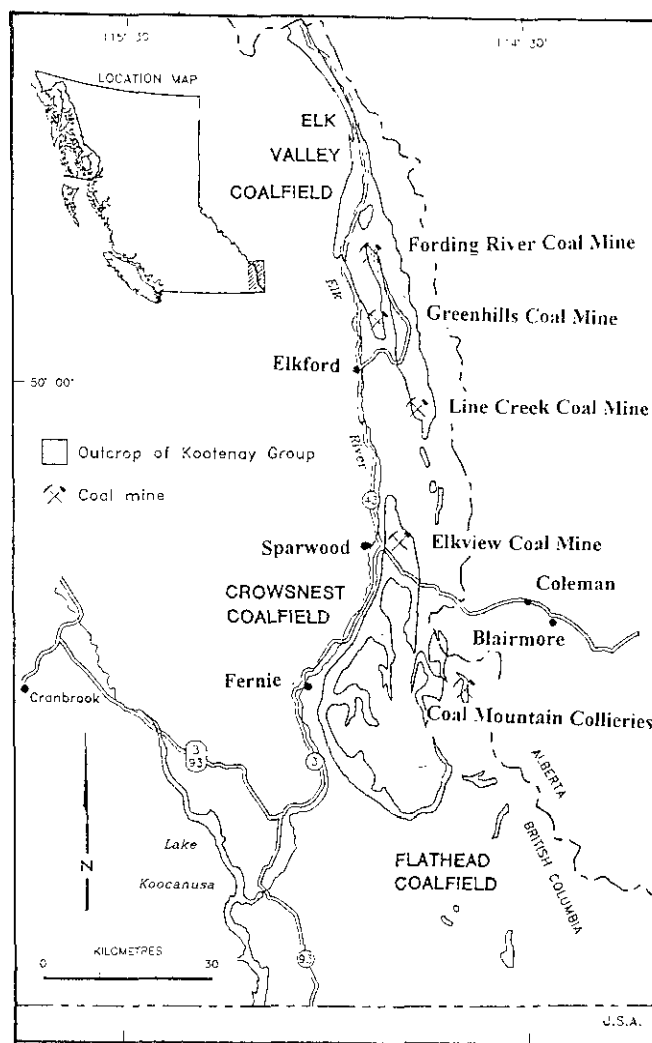


Figure 2: Coalfields and coal mines in southeastern British Columbia.

(Diessel, 1992, page 26). Alternatively the coal-forming swamp environment and maceral composition of these coals may have been less favourable for the removal of phosphorus.

Cretaceous coals could also contain phosphorous from bones, shells or guano, which generally contain more than 10% P_2O_5 and would probably dissolve in an acid swamp environment allowing the phosphorus to be redistributed. Flying reptiles, which appeared in the Jurassic, are known to have populated the western shoreline of the Fernie sea, which covered much of Alberta and parts of British Columbia in the Cretaceous. It has been suggested that high-phosphorus coal seams higher in the Mist Mountain Formation were derived from more woody vegetation than seams low in the section, which are low in phosphorus. The flying reptiles were not strong fliers and would have needed tall trees to perch on and glide from. Pterosaurs, which are known to have had a wing span of up to 23 metres, could have contributed a reasonable amount of phosphorus to the coastal swamp. Based on assuming, values for body weight, amount of guano produced, population density, vegetation accumulation rate and compaction factor, they could have contributed a minor amount of phosphorus to the coal.

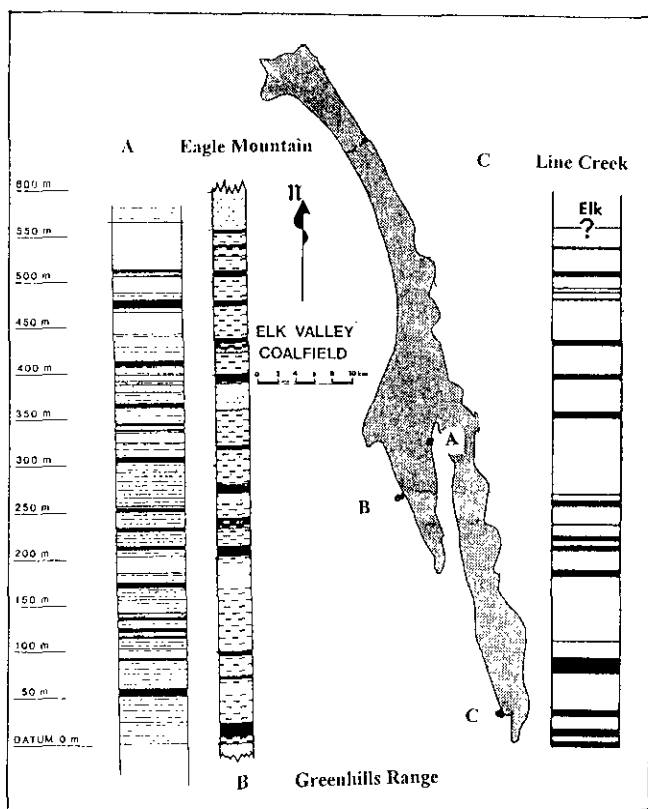


Figure 3: Mist Mountain seam sections for the Elk valley coalfield from Grieve (1993), Taplin (1976), Britch (1981) and Line Creek.

A comparison of phosphorus data for vegetation and coal indicates that concentrations in vegetation are much higher than those observed in coal. The phosphorus content of dried modern plants is estimated to be about 10 times higher than the concentration in coal (Francis, 1961). Phosphorus occurs in vegetation in low levels and is an essential nutrient. Salisbury and Ross (1969) indicate that 0.2% is the amount required in higher plants. Plants absorb phosphorus as the orthophosphate anion (H_2PO_4^- or $\text{H}_2\text{PO}_4^{--}$) or as inorganic phosphorus compounds, possibly finely dispersed varieties of apatite. The carbon content of dry conifers is about 49.6% (Ledig and Botkin, 1974) and for hard-woods varies from 50% to 53% on a dry basis (Shah *et al.*, 1992).

Grasses probably have a higher phosphorous/carbon ratio than trees (Marschner, 1986) and this implies possible phosphorous contents in coal averaging over 0.5% (5000 ppm). The phosphorus contents for a number of small plants range from 0.1% to 0.645% (daf basis) and for wheat range from 0.3% to 0.5% (Wedepohl, 1970). Generally there is more phosphorus in deciduous trees than pines, and within a single species the phosphorus is not uniformly distributed. Because it is an essential plant nutrient, it is usually found in those parts of the plant that grow most rapidly. For example, it is concentrated in bark and leaves of a number of different species (Kramer and Kozlowski, 1979).

The phosphorus to carbon ratio of woody vegetation is about 0.004 for woody vegetation. Medium-volatile bituminous coals have over 85% carbon on a dry ash-free basis, so that if all the phosphorus stays in the coal and the same phosphorous/carbon ratio is maintained, then 0.2%

phosphorus in vegetation would be equivalent to about 0.36% phosphorous in coal (daf basis) compared to a world average of about 0.05%. Either there is a process at work that removes variable amounts of phosphorus from the dead vegetation (Ward *et al.*, 1996 and Ryan and Grieve, 1995), or there may be a process of recycling the phosphorus upwards from rotting vegetation to overlying growing vegetation. In this case the amount of phosphorus required to account for all the vegetation that made a coal seam may be much less than expected.

Based on data in this study, it appears that phosphorus distribution in coal is controlled by petrographic composition. Different macerals have the potential to retain or attract phosphorus minerals. In this context it is useful to divide the vitrinite macerals into structured vitrinite (tellinite and telocollinite) and unstructured vitrinite (detrovitrinite and desmocollinite). Inertinite is divided into structured inertinite (semifusinite and fusinite) and unstructured inertinite (macrinite, micrinite and inertodetrinite). In a rough way these divisions separate maceral groups that may retain organic phosphorus (structured vitrinite) or have the phytal porosity available for secondary deposition of phosphorus minerals (structured inertinite) from those that probably lost phosphorus (unstructured vitrinite and inertinite).

REGIONAL GEOLOGY AND STRATIGRAPHY OF THE ELK VALLEY COALFIELD

The Elk Valley coalfield is composed of a north-trending synclorium of Jura-Cretaceous rocks situated in the Front Ranges of the Rocky Mountains and over thrust by older rocks from the west. On the local scale the geology varies from broad open synclines to tight folds complicated by many thrusts, that often repeat the coal section. The Mist Mountain Formation, which ranges in thickness from 425 to 700 metres in the Elk Valley coalfield, is the main coal bearing formation (Grieve, 1993). Coal makes up approximately 10 volume % of the formation, which contains over 29 seams in the Greenhills syncline, 15 seams in the Eagle Mountain block east of the Erichson fault and a thinner section of seams in the south (Figure 3). Donald and Bustin (1987) divided the Mist Mountain Formation at Eagle Mountain into three informal units. The lowest unit contains 2 seams, which formed behind beach and dune ridge deposits, and is dominated by sandstones. Unit 2 is 200 metres thick and includes coal seams and sediments, which were deposited in a fluvial-flood plain environment. Sedimentation was dominated by three major river systems that frequently flooded coal-forming swamps causing partings in the seams. Unit 3 formed in a flood plain environment, which did not contain major rivers in the area studied.

Table 1
FULL SEAM ANALYTICAL DATA

seam	Sple No	ADM	VM	Ash	FC	P%	Ba	Sr	SG	Yld	ADM	VM	Ash	FC	P%	S%	FSI
A	9	0.32	24.6	7.8	67.4	0.04	40	24	1.5	92.7	1.19	26.2	4.3	68.4	0.020	0.26	8.0
A	201	0.51	23.4	14.2	61.9	0.03			1.5	86.3	1.42	25.8	6.3	66.4	0.018		
average A		0.42	24.0	11.0	64.6	0.03	40	24	1.5	89.5	1.31	26.0	5.3	67.4	0.019	0.26	8.0
G	1	0.68	21.8	22.7	54.9	0.08	110	138	1.5	74.7	0.36	24.8	7.8	67.0	0.100	0.38	5.0
G	5	0.79	22.7	17.6	58.9	0.14	130	64	1.5	78.0	0.93	24.3	9.0	65.7	0.118	0.41	6.0
G	18	0.57	24.3	10.4	64.8	0.16			1.5	88.4	0.25	24.8	8.0	67.0	0.165	0.41	6.0
G	202	0.58	22.6	17.7	59.2	0.19			1.5	73.7	1.25	25.7	8.5	64.6	0.106		
G	203	0.53	23.3	17.0	59.2	0.12			1.5	81.5	0.67	25.4	7.9	66.1	0.110		
G	205	0.00	23.3	15.9	60.7	0.19			1.5	84.2	0.47	25.5	8.1	65.9	0.176		
G	101	0.34	18.3	31.8	49.5	0.12	420	130	1.5	50.5	0.68	21.9	8.6	68.8	0.056	0.61	5.5
G	102	0.35	18.0	33.0	48.7	0.15	260	68	1.5	50.5	1.07	21.5	11.6	65.9	0.030	0.54	7.0
G	103	0.37	19.4	27.2	53.0	0.10	200	74	1.5	64.4	1.71	22.2	7.6	68.5	0.073	0.39	4.0
G	113	0.33	18.4	33.0	48.2	0.12	360	60	1.5	52.2	1.18	21.7	9.8	67.3	0.078	0.55	7.5
average G		0.45	21.2	22.6	55.7	0.14	247	89	1.5	69.8	0.86	23.8	8.7	66.7	0.101	0.47	5.9
I	105	0.60	19.9	17.8	61.7	0.06	60	40	1.5	79.2	0.31	24.3	6.7	68.7	0.021	0.48	3.5
I	204	0.00	17.0	46.9	36.1	0.08			1.5	43.6	0.69	27.8	8.6	62.9	0.040		
I	206	0.00	23.5	23.2	53.4	0.03			1.5	65.9	0.32	26.0	9.7	64.0	0.041		
I	209	0.00	20.9	25.1	54.0	0.04			1.5	67.1	0.43	24.9	8.9	65.8	0.040		
average I		0.15	20.3	28.3	51.3	0.05	60	40	1.5	64.0	0.44	25.7	8.5	65.3	0.036	0.48	3.5
J	4	0.67	23.0	20.6	55.8	0.04	190	130	1.5	70.5	0.51	25.8	6.7	67.0	0.101	0.42	6.5
J	10	0.43	22.5	17.2	59.9	0.14			1.5	75.5	0.59	23.3	7.9	68.2	0.098	0.37	7.0
J	11	0.55	22.2	13.3	63.9	0.18	140	86	1.5	83.0	0.61	25.6	5.5	68.3	0.103	0.65	4.0
J	12	0.55	23.2	24.8	51.5	0.11	150	118	1.5	63.5	0.55	28.7	5.7	65.0	0.106	0.77	5.5
J	13	0.63	22.7	16.4	60.3	0.07			1.5	81.5	0.44	26.0	6.4	67.2	0.046	0.33	8.5
J	6	0.72	22.8	18.8	57.7	0.08			1.5	77.4	0.52	25.3	7.3	66.9	0.046	0.37	5.0
J	207	0.00	22.9	12.4	64.7	0.02			1.5	87.5	0.60	24.9	6.7	67.8	0.010		
J	210	0.00	23.0	15.3	61.7	0.04			1.5	83.8	0.46	25.4	7.4	66.8	0.046		
average J		0.44	22.8	17.4	59.4	0.08	160	111	1.5	77.8	0.54	25.6	6.7	67.1	0.070	0.49	6.1
K	2	0.85	23.8	25.5	49.9	0.06			1.5	68.2	0.81	29.5	6.6	63.1	0.089	0.73	8.5
K	14	0.57	25.4	14.2	59.8	0.08			1.5	83.4	0.33	28.2	7.2	64.2	0.078	0.78	5.0
K	19	0.60	25.5	13.9	59.9	0.05	180	78	1.5	80.9	0.52	29.0	6.3	64.2	0.046	0.70	8.0
K	208	0.00	23.7	24.2	52.1	0.12			1.5	73.4	0.50	28.2	6.9	64.5	0.126		
K	106	0.61	19.6	28.6	51.2	0.08			1.5	63.5	0.27	26.9	7.7	65.1	0.188	0.85	8.0
K	107	0.55	19.3	31.1	49.1	0.11	220	130	1.5	65.1	0.36	26.6	7.6	65.5	0.063	0.71	8.0
K	108	0.64	25.8	7.9	65.6	0.11			1.5	92.7	0.32	28.2	5.3	66.2	0.077	0.74	8.5
K	110	0.56	22.0	24.3	53.1	0.06			1.5	69.2	0.37	27.5	11.3	60.8	0.037	0.68	8.0
K	111	0.56	23.3	22.1	54.1	0.08			1.5	75.6	0.38	28.2	9.0	62.4	0.082	0.80	7.5
average K		0.55	23.2	21.3	55.0	0.08	200	104	1.5	74.7	0.43	28.0	7.6	64.0	0.087	0.75	7.7
L	109	0.70	24.2	18.4	56.6	0.11	170	60	1.5	77.0	0.37	27.7	7.2	64.7	0.075	0.99	7.5
L	112	0.52	18.8	27.7	53.0	0.08			1.5	59.4	0.39	22.7	7.5	69.4	0.044	0.38	3.5
average L		0.61	21.5	23.1	54.8	0.09	170	60	1.5	68.2	0.38	25.2	7.4	67.1	0.060	0.69	5.5
M	15	0.62	24.1	12.7	62.6	0.04	150	42	1.5	85.6	0.29	27.7	7.8	64.3	0.046	0.64	8.0
M	20	0.61	23.6	14.3	61.6	0.13			1.5	82.3	0.41	27.6	7.1	64.9	0.049	0.64	7.5
M	24	0.68	17.7	45.6	36.0	0.14			1.5	41.5	0.77	29.1	8.7	61.4	0.083	0.83	8.0
average M		0.64	21.8	24.2	53.4	0.10	150	42	1.5	69.8	0.49	28.1	7.8	63.5	0.059	0.70	7.8
N	104	0.76	27.2	15.2	56.8	0.15	260	118	1.5	84.4	0.36	30.8	5.7	63.1	0.089	0.72	8.0
P	3	0.86	28.4	10.1	60.6	0.03	140	82	1.5	88.4	0.36	29.7	4.8	65.1	0.107	0.53	8.5
P	16	0.58	26.9	8.4	64.1	0.12			1.5	93.9	0.40	28.0	6.8	64.9	0.098	0.74	7.0
P	23	0.60	23.8	16.2	59.4	0.16	300	350	1.5	79.1	0.39	25.1	9.1	65.5	0.157	0.70	2.5
average P		0.68	26.3	11.6	61.4	0.10	220	216	1.5	87.2	0.38	27.6	6.9	65.2	0.121	0.66	6.0
V	21	0.76	25.4	22.8	51.0	0.07	150	150	1.5	65.8	0.46	32.0	8.4	59.2	0.057	0.85	7.5
Y	22	0.80	27.6	18.4	53.2	0.07	190	146	1.5	77.9	0.70	32.7	8.0	58.5	0.045	0.83	8.0
Y	7	0.87	27.7	22.6	48.8	0.03	110	56	1.5	68.4	0.63	32.2	5.9	31.3	0.028	0.72	7.5
average Y		0.84	27.7	20.5	51.0	0.05	150	101	1.5	73.1	0.67	32.5	6.9	44.9	0.037	0.78	7.8
AB	8	0.74	27.4	26.6	45.2	0.01	280	300	1.5	61.2	0.42	33.1	7.4	59.2	0.079	0.77	8.0
AC	25	0.91	31.1	8.2	59.8	0.20			1.5	92.6	0.55	34.2	3.7	61.6	0.109	0.56	7.0
AE	26	3.52	25.8	12.1	58.6	0.12	220	150	1.5	76.3	1.05	31.8	7.1	60.1	0.062	0.64	0.5
AE	27	3.11	27.1	9.5	60.3	0.03			1.5	85.7	0.80	33.1	5.0	61.1	0.012	0.58	1.0
average AE		3.32	26.4	10.8	59.4	0.08	220	150	1.5	81.0	0.93	32.4	6.0	60.6	0.037	0.61	0.8

SAMPLE COLLECTION AND ANALYSIS

Data for this study were collected from a number of mines to provide a wide distribution of samples from seams so that lateral distribution patterns of phosphorus in a number of seams could be documented. Generally full-seam samples were collected, though for some seams an additional sample representing about 1 metre of hangingwall coal was also collected. Coal samples were analyzed for ash, volatile matter, fixed carbon and phosphorus on a raw basis and washed samples (1.5 specific gravity) were analyzed for sulphur and FSI. Some raw samples were analyzed for barium and strontium. For some seams, 5 centimetres of the hangingwall rock was sampled and analyzed for phosphorus. Analytical data for two mines is reported in Table 1.

Some samples were prepared for petrographic and SEM work. Samples were crushed to pass a 20 mesh screen, mixed 50/50 with a binder and compacted under pressure and a temperature of 140°C. Petrographic analyses involved counting 300 grains using oil immersion. This number is only sufficient to estimate petrographic distributions. Where ever possible geophysical logs were collected for holes close to the sample sites.

A MODEL FOR PHOSPHORUS MOBILITY IN COAL-FORMING ENVIRONMENTS

Phosphorus may be removed from vegetation during humification as $\text{H}_2\text{PO}_4^{2-}$. If it remains in solution it may leave the peat as the interstitial water is expelled during compaction. If it remains in the peat it may recrystallize as aluminium or iron phosphates in low pH environments or as apatite in moderate pH environments, assuming that the required cations are available. It is possible to match these environments in general terms to those that form different macerals.

In dry environments, that favour the formation of inertinite and destruction of woody tissue, the phosphorus may remain largely insoluble, finely dispersed in inertinite or authogenic mineral matter. Phosphorus has low volatility and remains in coal during carbonization or ashing in an oxidizing environment (Mahony *et al.*, 1981) and consequently it probably also remains in inertinite formed by forest fires. In this case the phosphorus content of inert macerals may approach that of the original vegetation if it is not subsequently leached out. If the vegetation is completely destroyed by fire then the phosphorus will be dispersed as fine particles, that may or may not settle back into the swamp.

In wet acid environments phosphorus will be leached out of the vegetation during humification as H_2PO_4^- and in more strongly acid environments as H_2PO_4^- . At pH values of 4 to 5 crandallite group minerals are stable but apatite is soluble. As phosphorus is leached out of the vegetation it combines with aluminum in part extracted from the vegetation and strontium, barium and calcium, either derived from the vegetation or from the interstitial water. Because of the insolubility of crandallite minerals they will

tend to form close to source. Other minerals that will form using the Al^{+3} , Fe^{+2} , Ca^{+2} , Ba^{+2} and Sr^{+2} in solution with the available orthophosphoric acid are wavellite $\text{Al}_3(\text{OH})_3(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$ and vivianite $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$. Vivianite has been reported in recent sediments (Coleman, 1966) in association with pyrite. It has not been identified in British Columbia coals, but is reported in other coals (Mahony *et al.*, 1981). At higher pH values aluminum and iron are not soluble, the solubility of orthophosphoric acid is less, and the phosphorus probably crystallizes as apatite ($\text{Ca}_5(\text{PO}_4)_3$) using available calcium.

The environment that is ideal for the formation of the maximum amount of vitrinite and minimum amount of inertinite is one of moderate pH and saturation below the water table. Within this environment higher pH values are characterized by high contents of structured vitrinite (tellinite or telocollinite) with finely dispersed phosphorous and low contents of inherent mineral matter and unstructured vitrinite. If the pH is somewhat lower, then unstructured vitrinite (gelovitrinite and detrovitrinite, or vitrinite B) will predominate. The phosphorus will be dissolved from the gellified humic material and either, removed from the peat, or redeposited as apatite in available porosity in semifusinite or fusinite when pH values increase. It is reasonable therefore to expect higher phosphorus concentrations in structured vitrinite than in unstructured vitrinite, which has been completely gellified. Phosphorus contents will be higher in inertinite-rich seams if they contain a high proportion of porous semifusinite and fusinite, which are generally generated by burning or charring woody material.

Environments which are generally wet with moderate pH, but have dry periods when inertinite macerals form, will experience some mobilization of phosphorus. If the inertinite has a high percentage of semifusinite derived from woody plants, then some of the phosphorus may be redeposited as apatite in semifusinite lumen. If at a later time there is introduction of less acid water, then apatite may crystallize on fractures in the coal and the surrounding rocks. If it crystallizes in coal on cleats it will be preferentially concentrated in the structured vitrinite because this maceral usually develops the best micro-cleats.

Liptinite material probably contained high concentrations of phosphorus prior to peatification. Concentrations could be in the percent range, in which case 1% liptinite could account for 0.01% phosphorus in the peat. In medium-volatile coals the liptinite is largely destroyed but variations in phosphorus content related to variations in original liptinite content may remain and produce unpredictable variations in concentration.

Phosphorus is most easily removed from highly acid peat swamps, in which there is not a lot of Ca, Al and Fe available to form insoluble compounds with the orthophosphate. As the interstitial water is removed during compaction the phosphorus is carried into the surrounding rocks. There are a number of studies indicating that hangingwall and footwall rock is sometimes enriched in phosphorus (Dixon *et al.*, 1964).

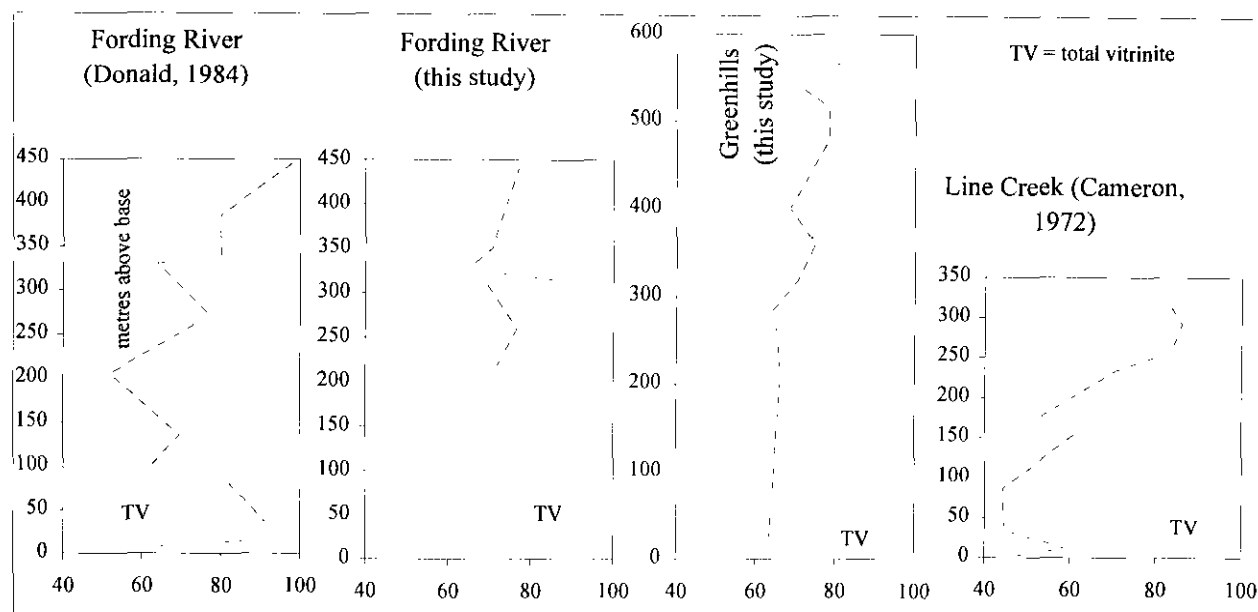


Figure 4: Total vitrinite *versus* distance from base of Mist Mountain Formation for a number of sections in the Elk Valley coalfield. TV = total vitrinite.

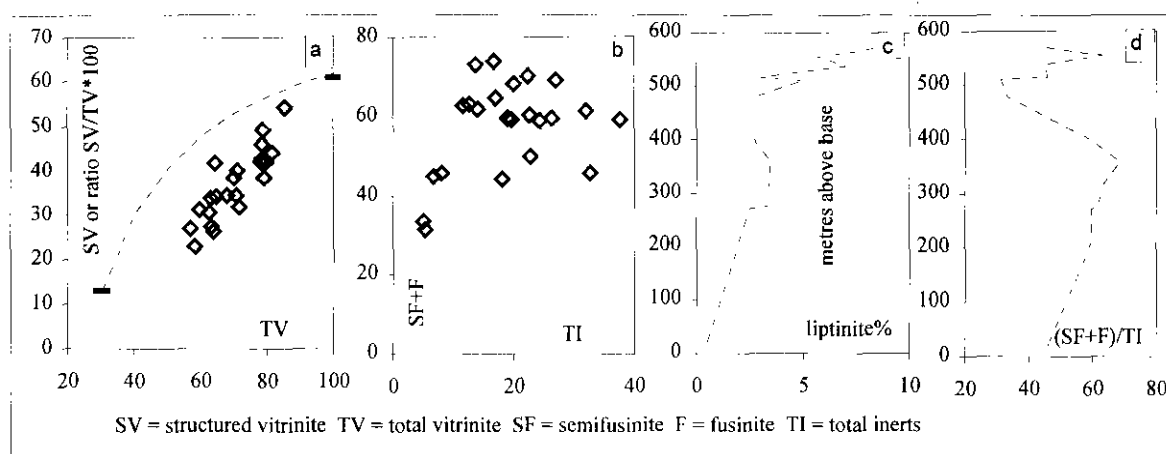


Figure 5: Maceral *versus* maceral and maceral *versus* depth relationships: (a) structured vitrinite *versus* total vitrinite and ratio of structured vitrinite/ total vitrinite *versus* total vitrinite; (b) semifusinite+ fusinite *versus* total inerts; (c) structured inertinite (semifusinite+ fusinite) *versus* distance from base of Mist Mountain Formation; (d) liptinite *versus* distance from base of Mist Mountain Formation. SF = semifusinite. F = fusinite TV = total vitrinite. SV = structured vitrinite TI = total inerts.

It appears that the phosphorus distribution in coal is probably complex. Phosphorus mobilized out of gellified humic material (unstructured vitrinite) may precipitate as apatite in semifusinite porosity or crystallize as apatite on cleats, which are concentrated in structured vitrinite. Some structured vitrinite and possibly liptinites may retain near original contents of phosphorus. Semifusinite based on its porosity may contain high concentrations of remobilized phosphorus, whereas unstructured vitrinite may be largely flushed of phosphorus. Phosphorus in structured vitrinite and semifusinite will be very difficult to remove, whereas phosphorus on cleats may be more easy to remove.

If the phosphorus is removed from the peat (mainly the gellified humic material), then it may be recycled upwards from the dead vegetation into the overlying growing vegetation and therefore effectively migrate upwards through the swamp. In this case, because a small initial source of phosphorus is constantly reused by new vegetation the total phosphorus content of the seam may be

less than expected, based on the amount of vegetation represented by the seam. In this situation there need be no process of phosphorus removal at work to explain phosphorus contents of coal that are lower than those of vegetation. If the upper part of the seam is rich in semifusinite, then the phosphorus will be trapped in the hangingwall coal, otherwise it may move into the unconsolidated overlying sediments or be redispersed through decomposing vegetation by acid peat waters. In this case it will probably crystallize as crandallite between macerals in the lower pH environments deeper in the peat swamp. The phosphorus content of a seam will be controlled by the initial amount of phosphorus leached from the footwall rocks. There need be no additional source of phosphorus as the peat accumulates as long as the phosphorus is effectively recycled upwards into the growing vegetation. If the process is effective, then there should be an inverse correlation between thickness and phosphorus content of the seam and there should be a

tendency for the phosphorus contents to be higher in hangingwall coal. There is sometimes a weak tendency for higher phosphorus in hangingwall coal as seen in striplog data in Ward *et al.*, (1996), Ryan and Grieve, (1995) and Gluskoter *et al.* (1977). No inverse correlation of phosphorus content and seam thickness has been observed, but variations in rank and petrography may have masked the effect.

REGIONAL PETROGRAPHY

A total of 38 petrographic analyses were completed on full seam samples (Table 2) from two general areas in the Elk Valley coalfield. There is a general tendency for vitrinite to increase and inertinite to decrease up section (Cameron, 1972); Grieve, 1993; Donald, 1994) and is seen in the present study (Figure 4). Cameron and Donald suggest that this is related to a progressive change in vegetation type from grasses low in the section to trees higher in the section. Grieve suggests that it may be due to higher ground water levels in coal forming environments higher in the section. A swamp dominated by grasses, if burnt over by summer fires, would probably generate a higher proportion of fine inertinite (inertodetrinite) derived from charring and seams low in the section are characterized by high percentages of inertinite and inertodetrinite (Figure 5d).

There are a number of other progressive changes in petrography up section that are important. The proportion of structured vitrinite to total vitrinite increases as the amount of total vitrinite increases (Figure 5a). This is also documented by Diessel (1992, page 99) for Carboniferous and Permian coals. There is an increase in the amount of liptinite up section (Figure 5c), which is largely related to rank. Few papers discuss the relationship between the petrographic composition of a seam and the lithology of the footwall and hangingwall rocks. Cameron (1972) did observe a correlation between the amount of sandstone in the hangingwall and the amount of inertodetrinite in the seam. If there is a relationship between interburden lithology and seam petrography, then this might provide a preliminary way of estimating phosphorus content and other coal-quality parameters that depend on petrography.

PETROGRAPHY AND PHOSPHORUS DATA

As a start to analyzing the data, raw phosphorus *versus* distance from base of Mist Mountain Formation. profiles are constructed for a number areas (Figure 6). There are general similarities and it appears that there are at least three intervals in the coal section (at about 200, 400 and 550 metres) where the phosphorus tends to be higher.

The model discussed above proposes that there should be a correlation between structured vitrinite plus structured inertinite and P contents. Correlation matrixes for phosphorus and maceral data from this study and that of Ward *et al.* (1996) indicate that for data sets with higher

Table 2
Preliminary petrography for samples from 2 areas Elk Valley coalfield

sample	seam	liptinite	tellinite	telocollinite	desmocollinite	detrovitrinite	total reactives	semifusinite	fusinite	macrinite	inertodetrinite	total inert	mineral matter	ash wt %
9	A	0	2	25	35	1	63	14	1	7	10	33	4	7
102	G	0	3	18	19	5	45	11	0	5	11	27	29	39
103	G	0	6	28	26	3	63	7	0	5	5	17	19	28
112	G	2	11	25	23	2	63	4	0	3	6	12	25	35
113	G	0	6	23	20	6	56	4	1	3	5	12	32	42
101	G1	0	15	27	21	8	71	4	0	2	7	12	17	25
5	G	3	8	28	30	1	70	10	1	6	5	23	7	12
10	G	3	5	34	21	2	64	17	1	6	2	27	9	14
18	G	1	11	29	31	0	71	13	2	4	3	22	7	11
1	G	2	10	20	26	2	60	14	1	2	8	24	16	24
105	I	1	16	31	29	1	77	7	0	3	6	16	7	11
4	J	2	7	25	33	0	68	11	1	3	5	20	12	19
6	J	2	6	26	33	2	71	10	1	3	4	19	10	16
12	J	2	6	19	25	5	57	14	0	3	6	23	20	29
13	J	3	7	24	29	1	65	15	0	4	7	26	9	14
11	J4	3	6	21	31	1	63	19	1	6	6	32	5	9
19	K	4	7	31	32	3	78	9	0	3	2	14	8	13
107	K	4	8	27	27	4	69	2	0	3	5	11	20	29
108	K	2	15	41	33	0	91	3	1	1	2	7	2	4
110	K1	1	8	30	30	10	79	2	0	1	3	6	15	23
106	K2	1	9	27	20	7	65	7	0	2	3	12	23	33
2	K	3	5	27	28	1	63	10	1	2	4	17	20	29
109	L	1	4	35	27	4	71	2	0	1	5	9	21	30
15	M	2	6	19	36	2	64	13	0	2	4	20	16	24
17	M	4	6	34	33	4	81	7	1	2	3	13	6	10
20	M	5	10	28	37	1	80	11	1	2	2	17	4	6
104	N1	4	9	24	36	4	77	6	1	1	3	11	12	19
3	P	3	8	28	39	1	79	9	1	3	1	14	7	12
16	P	3	6	14	34	1	58	22	0	7	9	38	4	7
21	V1	3	7	36	28	4	78	2	0	2	2	5	17	25
7	Y	5	16	21	31	6	79	2	0	2	1	5	16	24
22	Y4	3	8	32	29	6	78	3	0	1	3	8	14	21
8	AB	7	5	20	32	7	72	2	1	2	1	7	22	31
25	AC	6	8	40	30	1	85	7	0	3	2	12	3	5
27	AE	8	8	33	27	2	79	7	1	5	5	18	3	6

minor amounts of gelovitrinite added to detrovitrinite

minor amounts of micrinite added to inertodetrinite

phosphorus contents, phosphorus correlates with structured vitrinite (tellinite or telocollinite) and structured inertinite (semifusinite and fusinite) (Table 3). Phosphorus correlates with mineral matter in one data set (hole 15177), which is characterized by low phosphorus contents. Phosphorus does not correlate with liptinite or micrinite which is probably developed from liptinite. There are therefore two major variables, the amount of structured vitrinite and structured inertinite, that influence the concentration of phosphorus in a coal. A plot of structured vitrinite plus structured inertinite *versus* P% for data set 1 (Table 3) does in fact have a slightly better correlation coefficient (0.38) than values for telocollinite (0.33) or semifusinite (0.31) (Figure 7), though all these coefficients are marginally significant.

The data can also be displayed using triangular plots, in which the three corners of the triangle are inertinite, structured vitrinite and unstructured vitrinite plotted on an

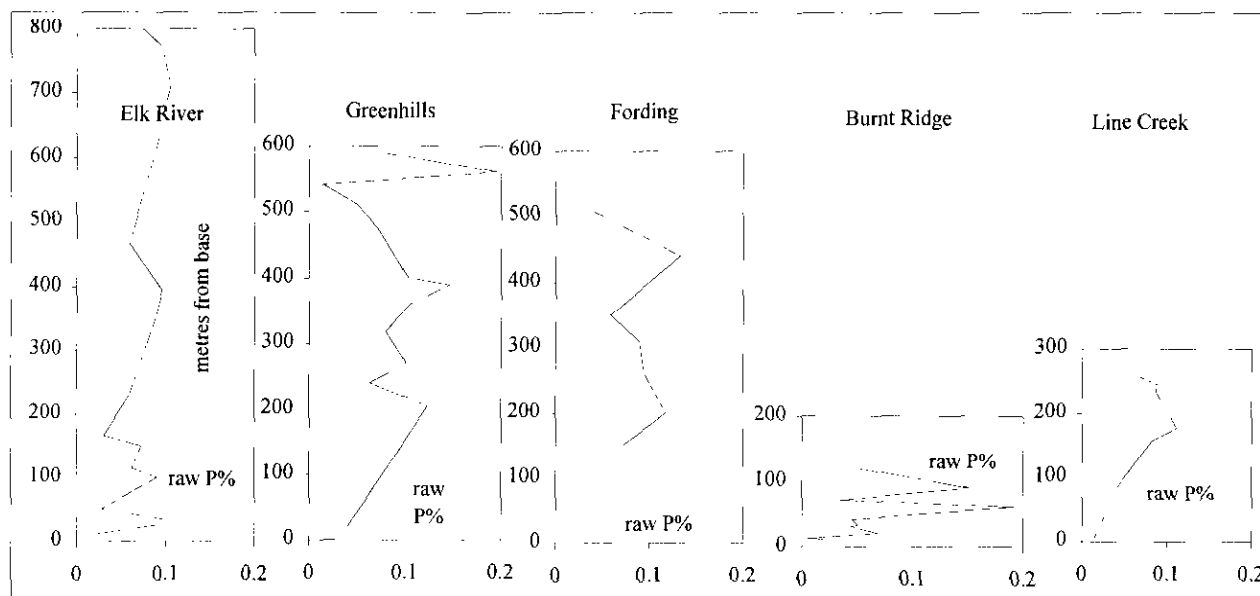


Figure 6: Phosphorus profiles for generalized stratigraphic sections of the Mist Mountain Formation, Elk Valley Coalfield.

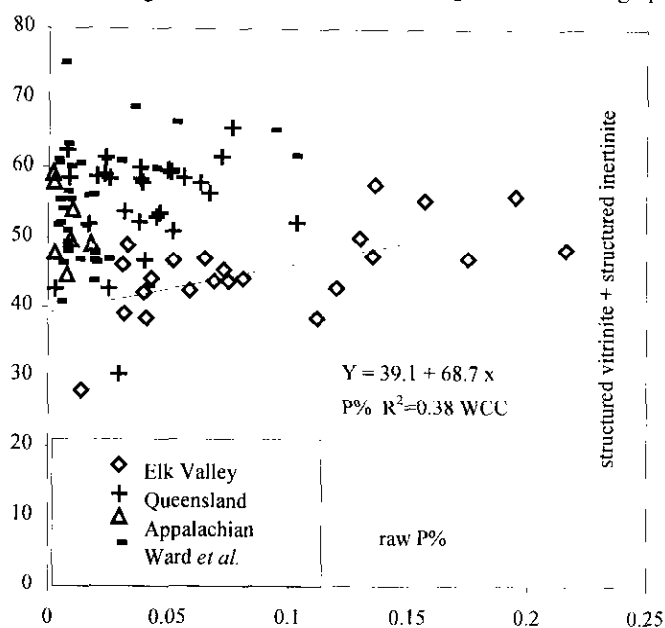


Figure 7: Raw phosphorus versus (structured vitrinite + structured inertinite) plot for coals from Elk Valley coalfield, Australia and eastern USA. Diamonds = Elk Valley data, Cross = Australian data from Ward *et al.* (1996), dash = data from Queensland Coal Board, Triangle = Appalachian data from Price *et al.* (1987).

ash free basis. Phosphorus contents are posted next to the plotted position of the data (Figures 8, 9 and 10). Though there is considerable scatter in the data there is a distinct tendency for phosphorus concentrations to decrease towards the unstructured vitrinite corner. The petrography of the 1.5 specific gravity wash samples is somewhat different from that of the raw petrographic samples, however by posting a phosphorus ease-of-washing number next to the data in a triangular plot it is possible to estimate the ease of extraction of phosphorus from the three maceral groups (Figures 8 and 9). This approach differentiates phosphorus disseminated in structured vitrinite from phosphorus on cleats in vitrinite, because the

later will be easier to wash out. Phosphorus is very difficult to remove from unstructured vitrinite and about equally difficult to remove from inertinite and structured vitrinite.

The petrographic data and phosphorus data add support to the model outlined above and provide an explanation for why, though apatite is present in the porosity in semifusinite and fusinite, the total phosphorus content often correlates with the reactive content of seams. Previously Ryan and Grieve (1995) and Ward *et al.*, (1966) explained this by assuming that inertinite in vitrinite-rich seams contained a higher proportion of phosphorus than inertinite in vitrinite-poor seam. Apatite contains about 17% phosphorus and therefore a semifusinite grain with 10% porosity could have a phosphorus content of 1.7% and if grains of this composition made up 10% of the seam then they would contribute 0.17% phosphorus to the sample. High phosphorus concentrations in vitrinite-rich samples can be explained if the remaining small percentage of inertinite has apatite filled porosities in the range of 5 to 20% and that in inertinite rich, phosphorus poor, samples the apatite-filled porosity is less than 1%. Obviously the explanation is feasible but it is difficult to derive a process that causes inertinite-poor samples to have a higher proportion of semifusinite and fusinite. In fact data from this study indicates either no correlation between structured inertinite and total inertinite or at low inertinite contents the proportion of structured inertinite decreases (Figure 5b). Other authors (Grieve, 1993) have found that the ratio of semifusinite+fusinite to total inertinite is constant for varying concentrations of inertinite.

Some samples were analyzed for barium and strontium concentrations (Table 1). A number of studies indicate that despite reported occurrences of apatite in coal, phosphorus often correlates with strontium (Gluskoter *et al.*, 1977), probably because of the presence of goyazite. Generally phosphorus concentrations in

Table 3
Correlation matrixes for Elk Valley and Australian data
from Ward *et al.* (1996). mic=micrinite

	p% raw	lipinitite	tellinitite	telocollinitite	desmoV	detroV	semi fusinitite	fusinitite	macrinite	inertedetrinite	min matter
	A	B	C	D	E	F	G	H	I	J	K
A	1.00	GREENHILLS									
B	-.05	1.00									
C	.01	.25	1.00								
D	.33	.29	.00	1.00							
E	-.16	-.08	.01	-.20	1.00						
F	-.19	.35	.20	-.10	-.23	1.00					
G	.31	-.53	-.33	-.43	-.07	-.56	1.00				
H	.15	-.15	-.03	.13	.05	-.42	.08	1.00			
I	.20	-.22	-.36	-.10	-.11	-.43	.63	.15	1.00		
J	-.07	-.39	-.43	-.57	-.06	-.27	.61	.01	.54	1.00	
K	-.45	-.07	.02	-.36	-.29	.57	-.34	-.20	-.59	-.09	1
A	1.00	FORDING									
B	.13	1.00									
C	-.20	.15	1.00								
D	-.13	.09	.44	1.00							
E	.08	.64	.30	.52	1.00						
F	-.16	-.30	-.30	-.36	-.36	1.00					
G	.20	-.34	-.18	-.59	-.34	-.11	1.00				
H	.58	.28	.12	.19	.41	-.24	-.13	1.00			
I	.03	-.39	-.33	-.58	-.54	-.17	.65	-.35	1.00		
J	.22	-.43	-.27	-.63	-.62	.03	.57	-.44	.70	1.00	
K	.02	-.35	-.71	-.69	-.80	.40	.22	-.22	.49	.51	1
A	1.00	Goonyella lower seam riverside hole 15177									
B	-.47	1.00									
C	-.10	-.04	1.00								
F	-.57	.45	.69	ND	ND	1.00					
G	-.01	.19	-.81	ND	ND	-.57	1.00				
H	-.40	.28	.76	ND	ND	.66	-.51	1.00			
I	-.21	.36	-.75	ND	ND	-.29	.79	-.52	1.00		
mic	-.57	.11	.03	ND	ND	.37	-.05	.32	.04		
J	.15	-.15	-.81	ND	ND	-.72	.71	-.76	.72	1.00	
K	.53	-.45	-.50	ND	ND	-.65	.02	-.54	-.08	.27	1
A	1.00	Goonyella lower seam riverside hole 15176									
B	-.07	1.00									
C	.79	.14	1.00								
F	.33	.32	.62	ND	ND	1.00					
G	-.80	-.20	-.93	ND	ND	-.64	1.00				
H	.47	.13	.58	ND	ND	.25	-.50	1.00			
I	-.44	.24	-.60	ND	ND	-.55	.65	-.30	1.00		
mic	-.26	.65	.05	ND	ND	.49	-.20	.02	-.02		
J	-.61	.04	-.80	ND	ND	-.56	.82	-.20	.86	1.00	
K	-.15	-.36	-.41	ND	ND	-.50	.20	-.54	-.17	-.11	1

plants are 20 to 40 times higher than concentrations of aluminum, barium and strontium and 10 to 20 times less than that of calcium (Mason, 1966, page 228). The proportions of these elements in Goyazite is Sr/P=1.4, Ba/P=2.2 and Al/P=1.3. Consequently there has to be an external source of barium, strontium and aluminum to crystallize goyazite or gorceixite using phosphorus from the vegetation. Average concentrations of strontium in vegetation and fresh water are <100 ppm and 1 ppm respectively, whereas the average content in samples from

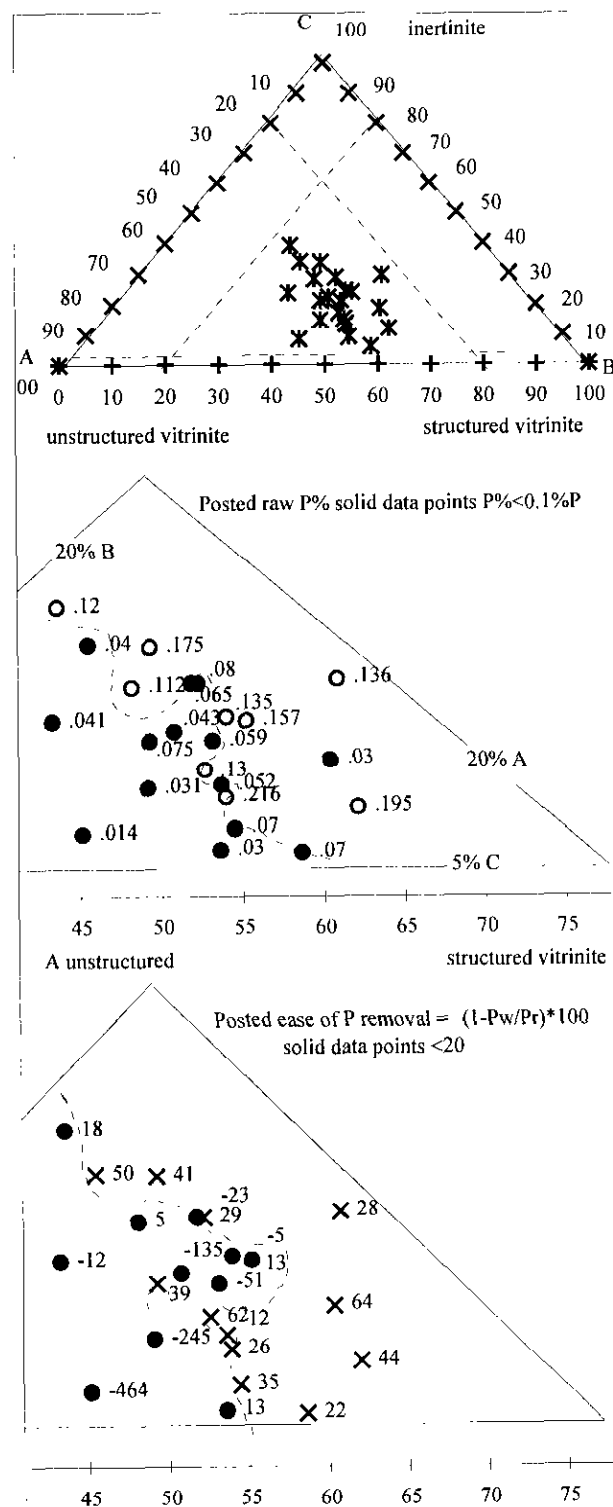


Figure 8: Triangular plots of maceral composition with posted phosphorus contents from Greenhills mine samples. Triangles B and C are the area enclosed by dashed lines in triangle A. Contour lines separate higher P concentrations from lower concentrations (plot B) and difficult to wash samples from easier to wash samples.

this study is 113 ppm. Correlation matrixes indicate that both strontium and barium correlate weakly with structured vitrinite and mineral matter but do not correlate with inertinite or unstructured vitrinite (Table 4). This supports an association of crandallite minerals with

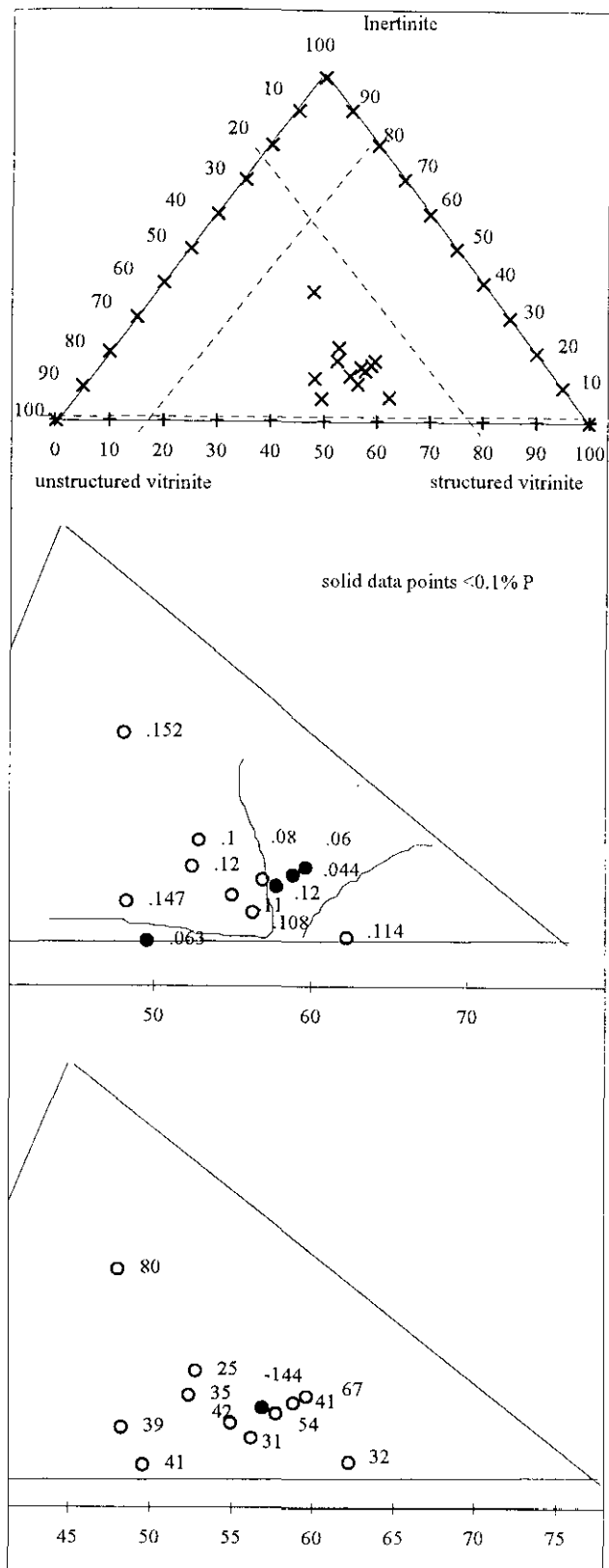


Figure 9: Triangular plots of maceral composition with posted phosphorus contents, Fording mine. Format similar to Figure 8.

Figure 10: On right. Triangular plots of maceral composition with posted phosphorus contents; data from Ward *et al.* (1996). Circle plots =Warkworth, Cross =Tahmoor, Star= Hole 15176, Diamond =hole 15177.

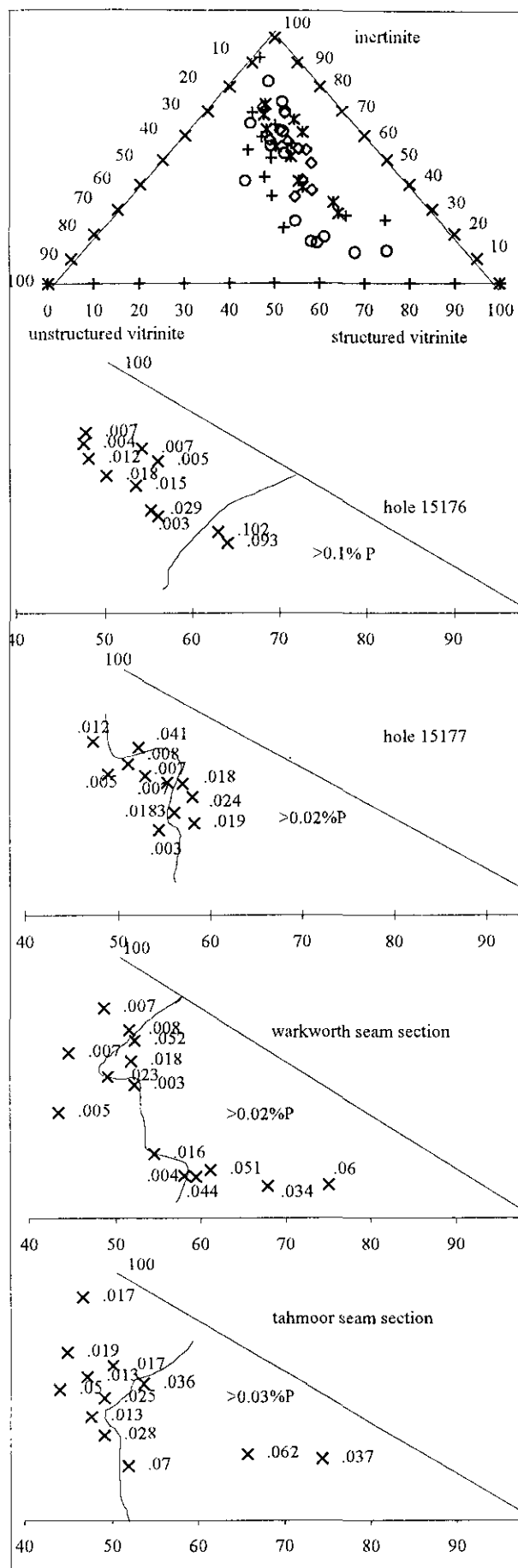


Table 4
Correlation matrix for Ba and Sr versus all petrography data

	Ba	lipinitic	telinitic	telocollinite	desmoV	detroV	semi fusinite	fusinite	macrinite	inertdetritite	min matter
	Ba	A	B	C	D	E	F	G	H	I	J
Ba	1.00										
A	.43	1.00									
B	.10	.25	1.00								
C	.21	.29	.00	1.00							
D	-.07	-.08	.01	-.20	1.00						
E	.00	.35	.20	-.10	-.23	1.00					
F	-.12	-.53	-.33	-.43	-.07	-.56	1.00				
G	-.30	-.15	-.03	.13	.05	-.42	.08	1.00			
H	-.49	-.22	-.36	-.10	-.11	-.43	.63	.15	1.00		
I	-.55	-.39	-.43	-.57	-.06	-.27	.61	.01	.54	1.00	
J	.27	-.07	.02	-.36	-.29	.57	-.34	-.20	-.59	-.09	1.00
Sr	1.00										
A	.08	1.00									
B	.12	.25	1.00								
C	.23	.29	.00	1.00							
D	-.60	-.08	.01	-.20	1.00						
E	.11	.35	.20	-.10	-.23	1.00					
F	-.13	-.53	-.33	-.43	-.07	-.56	1.00				
G	-.02	-.15	-.03	.13	.05	-.42	.08	1.00			
H	-.48	-.22	-.36	-.10	-.11	-.43	.63	.15	1.00		
I	-.08	-.39	-.43	-.57	-.06	-.27	.61	.01	.54	1.00	
J	.50	-.07	.02	-.36	-.29	.57	-.34	-.20	-.59	-.09	1.00

structured vitrinite and also in that phosphorus does not correlate with ash that the source for the barium and strontium is probably the extraneous ash.

The strontium and barium data do not correlate well with raw phosphorus because of the presence of apatite. There is however a better correlation of Sr+Ba with wash phosphorus indicating that some apatite is being removed, but crandallite minerals are remaining. Assuming that all the strontium and barium occurs in crandallite minerals and that the average ratio of Ba+Sr to phosphorus in these minerals is about 2, it is then possible to estimate the total amount of phosphorus present in crandallite minerals rather than apatite. It appears that the crandallite minerals account for up to 0.02% phosphorus and therefore account for less than half the phosphorus present in most samples.

SCANNING ELECTRON MICROSCOPE WORK

A number of samples were studied using back scattered electron imaging technique on a Philips XL30 scanning electron microscope (SEM). Pellets analyzed by the SEM were made with a binder doped with one part in five of calcium fluoride. This increased the average atomic number of the binder and provided a better back scattered definition of the coal grains. The effect was to outline grains of the transoptic binder and produce a

groundmass mosaic pattern, which made it easier to locate coal fragments. The polished surfaces of pellets were photographed using a close-up lens. The colour print film negatives were then mounted as slides and the negative image enlarged using a projection and colour photocopy

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Using back scattered electron images, minerals with higher average atomic number appear bright where as the coal fragments remain dark. It is easy to adjust the brightness for the coarser grains to differentiate between quartz, kaolinite, carbonates and phosphorus minerals. The EDS provided X-ray spectra of individual minerals allowing positive identification.

Back scattered electron scans of the mounts identified phosphorus minerals within maceral fragments, often in semifusinite, and occasionally as isolated grains. No phosphorus minerals were observed filling microfractures. The most conspicuous phosphorus mineral identified was apatite (Photo 2), which filled lumen in semifusinite, often in association with kaolinite. Kaolinite is probably the most common cell-filling material, sometimes completely and other times partially filling cells (Photos 3 and 4). Occasionally rounded grains of gorceixite were identified. It was noticeable that whereas the apatite filled cell lumen the gorceixite formed rounded grains and was much rarer and did not obviously fill cells (Photo 2).

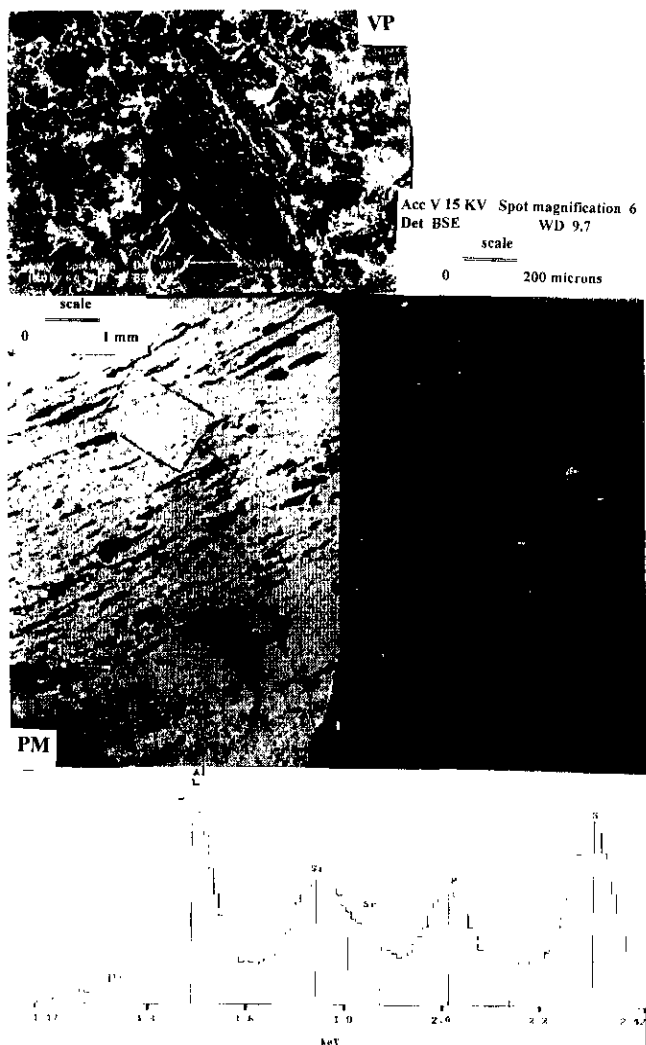


Photo 1: Grain of tellinite filled with liptinite; photomicrographs (PM) of grain before and after SEM EDS analysis showing square burn area on photomicrograph. Also videoprint (VP) of grain in SEM. Frame area analyzed was tellinite with minor liptinite. Scan revealed presence of aluminum, silica, phosphorus and possibly Strontium. The 0.1 millimetre scale bar applies to all photomicrographs and scale bar and operating conditions are also provided for the SEM videoprint.

An EDS X-ray scan in spot mode was used to identify elements in the mineral grains. Phosphorus minerals were differentiated by the relative proportions of calcium, barium, strontium and aluminum accompanying the phosphorus. Detection of calcium and phosphorus and absence of aluminum was assumed to confirm the presence of apatite whereas the presence of phosphorus and aluminum and absence of a large calcium peak was assumed to confirm the presence of the crandallite group minerals (Figure 11). Vivianite, $(\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O})$ was not identified. In a number of cases it appeared that siderite was associated with crandallite minerals and they might be derived from the alteration of vivianite. It is not always possible to distinguish between gorcexite (barium rich) and goyazite (strontium rich). Generally the crandallite minerals contained both elements and it is difficult to estimate relative proportions of strontium because its peak is masked by the silica peak.

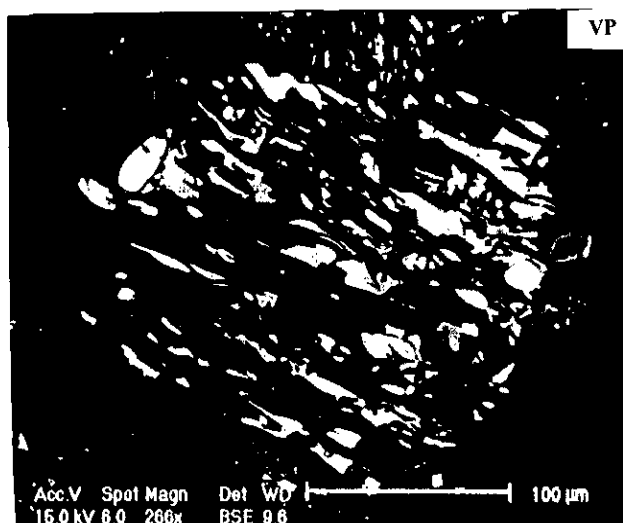


Photo 2: Apatite in phytal porosity in semifusinite. Duller mineral half filling cell in centre is kaolinite and rounded grains on left and right edge of coal fragment are crandallite possibly gorcexite.

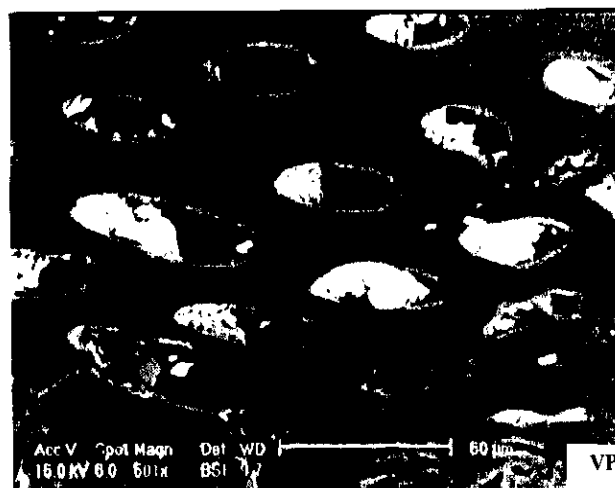


Photo 3 : Kaolinite partially filling cells in semifusinite; note the increase in brightness of cell walls.

Small areas of macerals, free from inclusions, were analyzed in EDS mode using a spot scan, in which an area of less than 5 microns is x-rayed in an attempt to measure dispersed phosphorus levels in different macerals. Spot EDS scans of different macerals failed to detect any phosphorus while at the same time detecting moderate sulphur peaks (Figure 12). The organic sulphur content of these coals averages about 0.6%, and therefore the phosphorus peak should be in the range of 1/50 to 1/10 the size of the sulphur peak based on phosphorus concentrations of 0.012% to 0.06%. Peaks of this size were within detection range based on the size of the sulphur peak. Consequently it appears that phosphorus in all macerals is no longer uniformly distributed and has either been removed, or has concentrated into distinct phosphorus minerals within the macerals.

Some fragments of tellinite and telocollinite contained very small, micron-sized, inclusions of minerals,

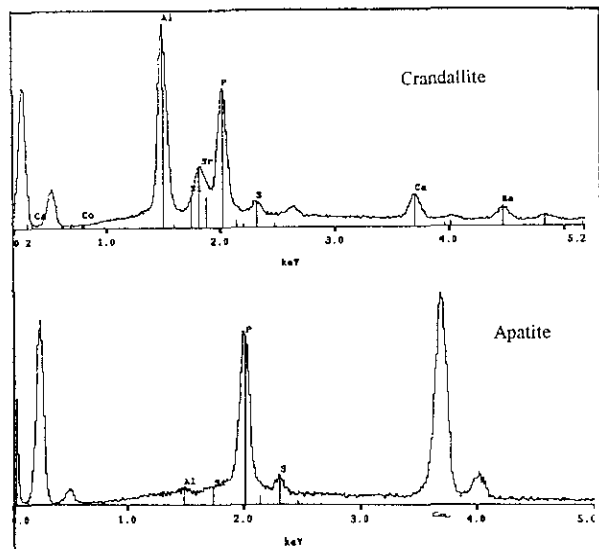


Figure 11: X-ray scans of apatite and crandallite group minerals (goyazite and gorceixite) from samples in this study.

sometimes outlining internal maceral structure. Spot scans of these grains identified them as crandallite minerals, kaolinite or apatite. The grains were so fine that it was easy to miss the fact that they were of varying composition. The occurrence of very small grains of goyazite dispersed in structured vitrinite is important because it explains the correlation of strontium and phosphorus seen in the work of Gluskoter *et al.* (1977) and the correlation of phosphorus with structured vitrinite seen in some of the data in Ward *et al.* (1996) and in this study (Figures 8, 9 and 10). The preferential presence of crandallite group minerals finely dispersed in structured vitrinite also explains why strontium and barium tend to correlate with these macerals (Table 4). The small grains appear to have crystallized out of the enclosing maceral. It is likely that the strontium and aluminum were derived from an external source because the macerals are deficient in these elements compared to phosphorus.

As mentioned, semifusinite contains easily identifiable apatite in cell lumen. Other macerals such as tellinite, telocollinite and desmocollinite contain finely dispersed mineral matter. In an attempt to get integrated phosphorus concentrations of these macerals, EDS scans of 20 x 20 micron frames were made with a count time of 300 seconds real time, which is equivalent to about 200 seconds live time (dead time varied from 30% to 33%). A scan of a mass of liptinite (Photo 5) did not detect phosphorus and apparently this maceral does not contain high levels of dispersed phosphorus. Other macerals do contain measurable amounts of phosphorus within 20 x 20 micron frames that include fine inclusions. The EDS scans on 20 x 20 micron frames indicate that the phosphorus content of structured vitrinite grains (Photo 6a, 6b) is very variable depending on how many dispersed crandallite grains were in the EDS frames. However the average phosphorus counts were about 1/3 that of sulphur counts. The average counts for unstructured vitrinite were about 1/6 that of sulphur. The numerical average wash sulphur

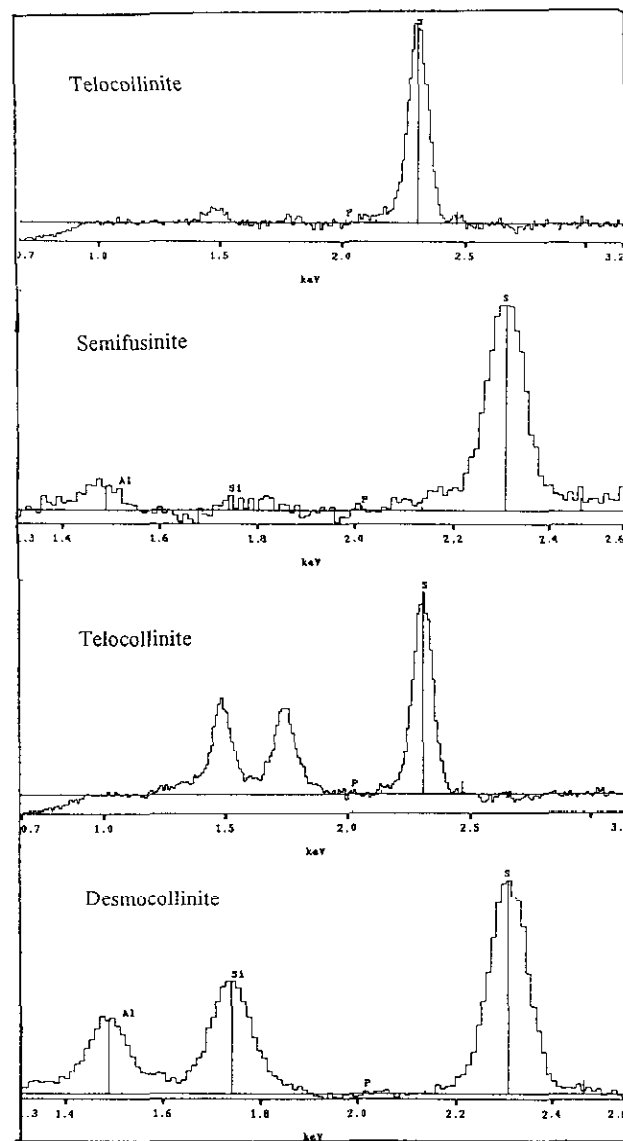


Figure 12: EDS spot scans of inclusion-free areas of macerals.

for the data in Table 1 is 0.62%. If the sulphur and phosphorus K α peaks have roughly the same relationship to concentration, then this implies a background distribution of phosphorus of very roughly of up to 0.3% in tellinite. This agrees with the data in Ward *et al.* (1996), which indicates about 0.25% phosphorus in 100% telovitrinite. This concentration is not excessive in terms of what would be expected in the original vegetation and therefore adds weight to the argument that the phosphorus is in the process of being "sweated out" of the maceral and not being added to it. In unstructured vitrinite the SEM data indicates up to 0.1% phosphorus, which appears to be associated with the finely dispersed mineral matter as indicated by strong aluminum and silica peaks (Photo 7)

It is not possible to quantify the amount of phosphorus occurring in semifusinite and structured vitrinite and compare the total to the phosphorus content of the sample; however the SEM work indicates that much of the phosphorus is as apatite in semifusinite or as crandallite minerals in structured vitrinite. The data indicates that very little phosphorus remains uniformly distributed in the

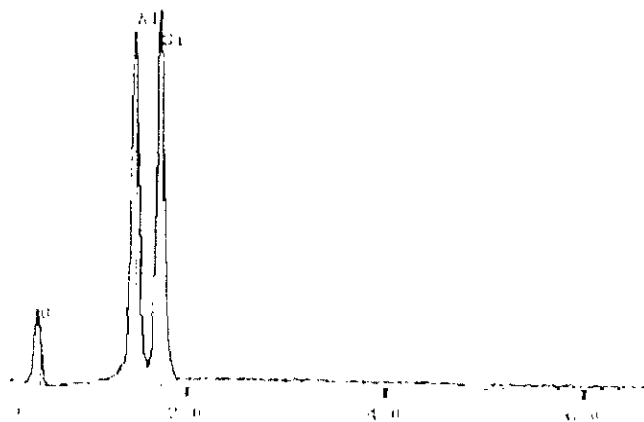


Photo 4: Grain of semifusinite with cells filled with kaolinite, SEM videoprint and spot scan of kaolinite.

macerals or scattered as detrital or cleat filling material. Ward *et al.* (1996) identified some phosphorus minerals occurring in late fractures but this does not appear to be a common occurrence in the Australian coals and has not been observed in this study. The amount of apatite in semifusinite grains varies based on the phytal porosity and on percentage filled by apatite. If semifusinite grain contained 5% apatite filled lumen then the grain as a whole would contain about 0.85% P. Porosities of 5% or higher

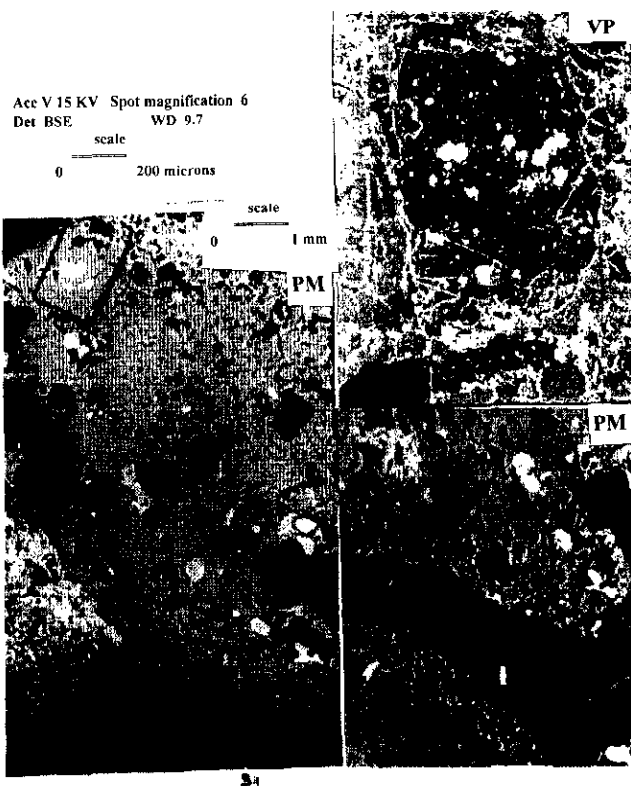


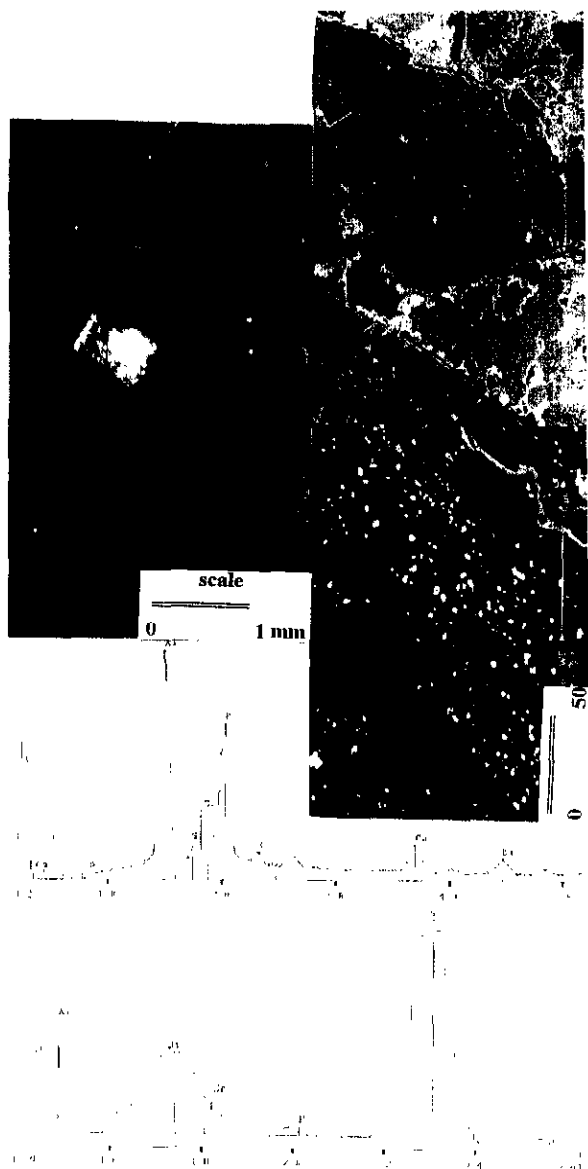
Photo 5: Desmocollinite with large area of liptinite. Photomicrograph, SEM videoprint and x ray spectra of a 20 x 20 micron area of liptinite. Some area of desmocollinite was scanned but no phosphorus was detected.

are not uncommon and consequently these grains contain more phosphorus than the original vegetation and clearly indicate addition of phosphorus to the maceral.

The SEM data confirms the association of phosphorus with structured inertinite and structured vitrinite as seen in Figures 8, 9 and 10 and eliminates the apparent contradiction of phosphorus appearing in semifusinite but the total concentration often correlating with percent reactivities as discussed Ryan and Grieve (1995) and Ward *et al.* (1996).

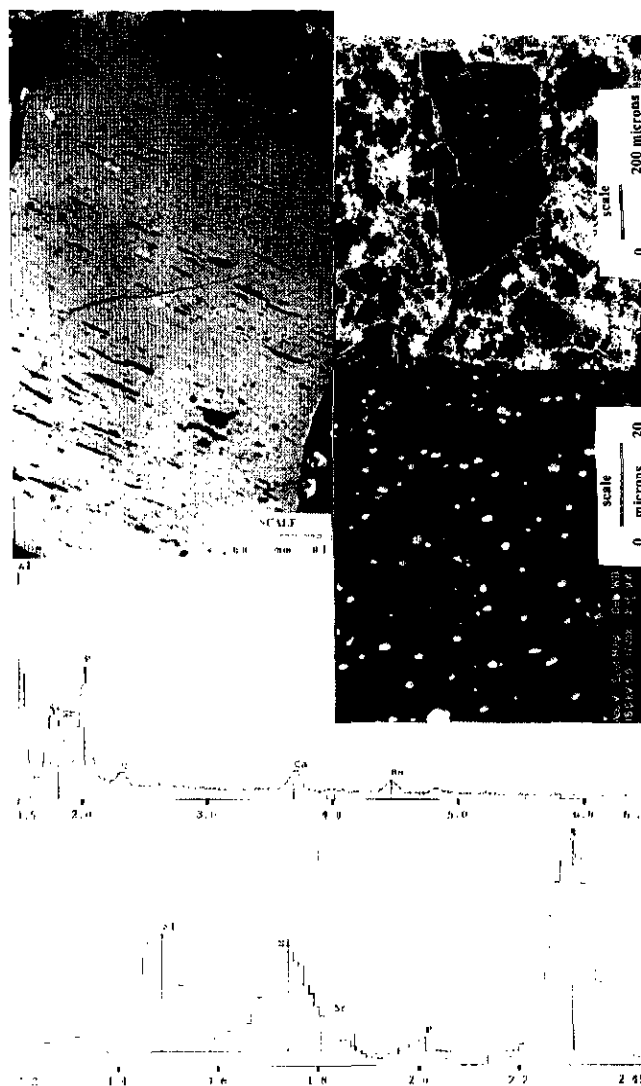
LATERAL VARIATIONS OF PHOSPHORUS WITHIN SINGLE SEAMS

Data (Figure 6) indicate that certain seams consistently have higher phosphorus concentrations. Based on Figure 7 this is explained by the average petrography in terms of the sum of structured vitrinite plus structured inertinite. However variations within a seam are



not explained by this relationship and appear to be dependent on variations in the smaller component of semifusinite. A small percentage of semifusinite mineralized with apatite has the potential to drastically increase the phosphorus-content of a seam. For example a 1% increase in semifusinite with a 20% apatite filled porosity can increase the phosphorus content of a sample by 0.035%. Much larger changes in the proportion of structured vitrinite would be required to produce the same change in phosphorus concentration.

It is suggested that the regional water table at the time of coal formation controls the general petrography of a seam, which in turn controls the average phosphorus content. Lateral changes in the phosphorus content of a seam are caused by variations in the amount of semifusinite. Variations in the amount of semifusinite are related to the availability of trees and the degree of charring by forest fires. Seams derived predominantly from grasses may have high inertinite contents but low semifusinite and fusinite contents and therefore will have



Photos 6a and 6b: Photomicrograph, SEM videoprint and x ray spectra of desmocolinite or tellinite grain with dispersed kaolinite and crandallite minerals. Upper x-ray scan is a spot scan and lower scan is a frame scan of the area outlined in the photomicrograph.

moderate or low phosphorus contents. For example the base seam in the Mist Mountain section (Ryan and Grieve, 1995), which is characterized by low phosphorus and high inertinite contents is composed predominantly of macrinite and inertodetrinite with low phytal porosity.

There is sufficient data for three seams to produce phosphorus content maps covering an area of approximately 120 square kilometres (Figure 13). There is some uncertainty concerning seam correlation but the data sets do come from seams occupying similar levels in the stratigraphy. For two of the seams the phosphorus contents are quite consistent but the third seam data is more variable.

There is a high phosphorus seam in the lower part of the section in most of the mines in southeast British Columbia that extends north to the Elk River property at the northern end of the Elk Valley coalfield (Grieve, 1992). It is not known if the seams represent the same stratigraphic horizon.

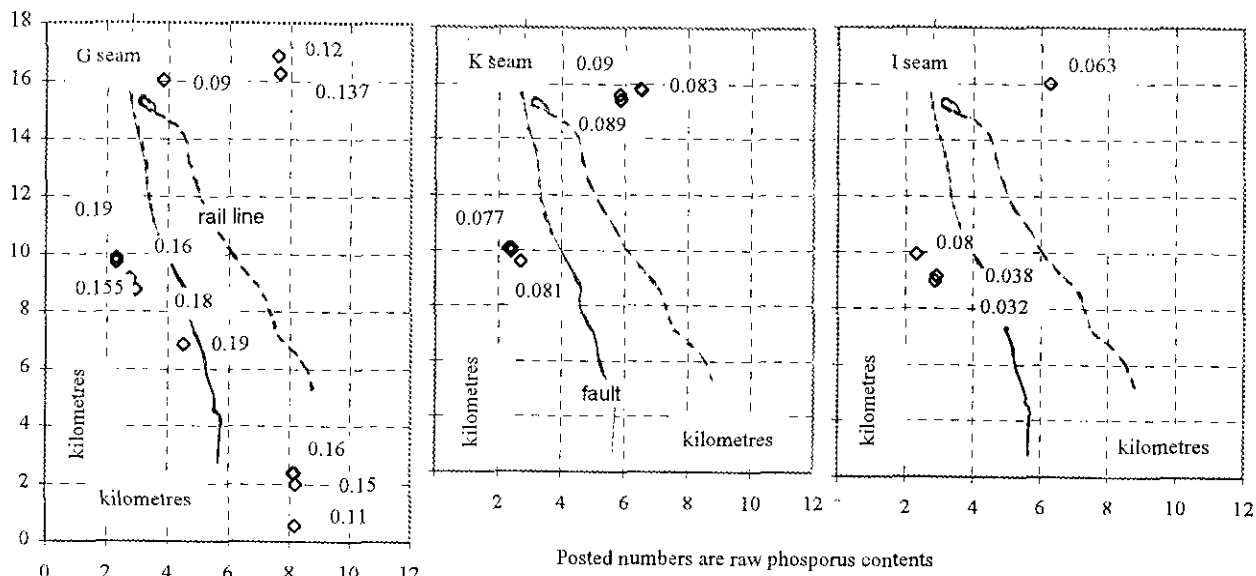


Figure 13: Maps indicating position and concentration of phosphorus in three seams.

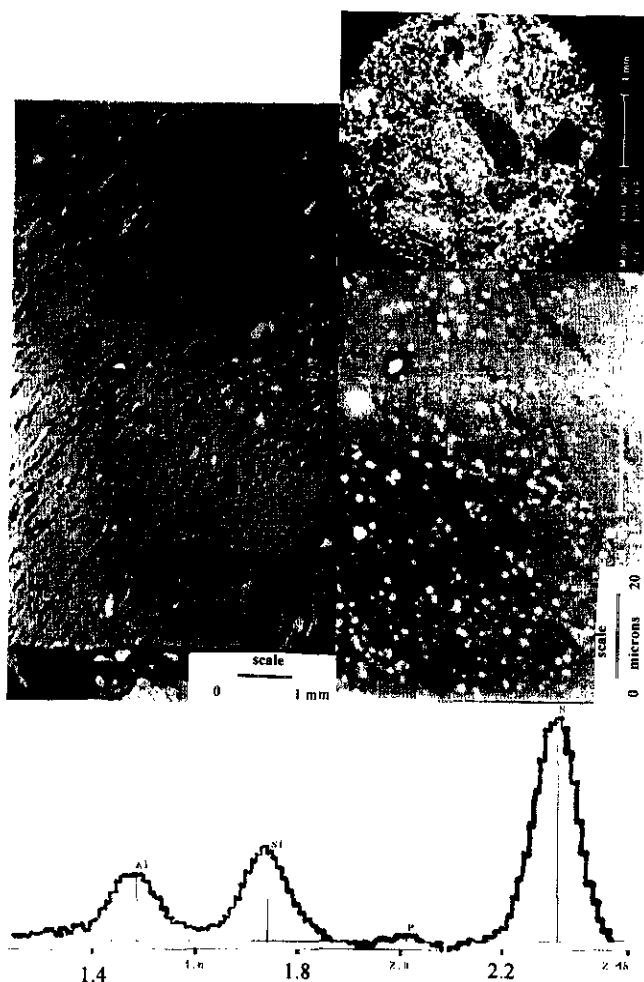


Photo 7: Photomicrograph, SEM videoprint and x ray spectra of desmocollinite with finely dispersed kaolinite and minor phosphorus.

RELATIONSHIP BETWEEN IN SEAM PHOSPHORUS CONTENT AND HANGINGWALL LITHOLOGY

Lateral variations in phosphorus content of seams are related to petrography. But it is little help in a mining environment to know that a petrographic analysis will provide some indication of changes in phosphorus content. What would be more helpful would be some flag in the regional lithology or structure that signals changes in both petrography and phosphorus content. The observation that the amount of inertodetrinite correlates with the amount of sandstone in the hangingwall (Cameron, 1972) may mean that seams with sandstone hangingwalls have less structured inertinite and therefore less phosphorus.

If there is a relationship between interburden lithology and seam petrography, then this might provide a preliminary way of estimating phosphorus content and other coal-quality parameters that depend on petrography. In an attempt to find useful field criteria for flagging seams with high phosphorus contents, a number of drill holes were examined where a gamma log and phosphorus concentration of the coal were available. Various features such as composition, sharpness of hangingwall and footwall and presence of overlying fining or coarsening upwards successions were noted. An unsuccessful attempt was made to correlate these geophysical log features with the phosphorus content of the enclosed seam. If the enclosing rock lithology is correlated with the phosphorus content of the coal seam, then the features defining the correlation appear to be too subtle to be identified on geophysical logs.

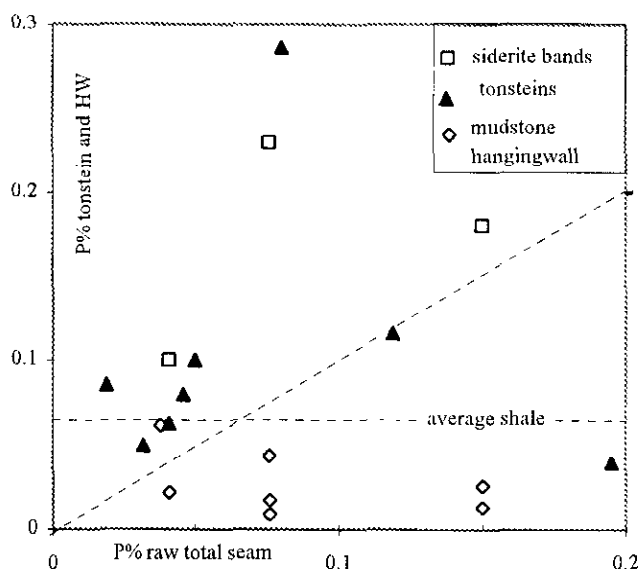


Figure 14: Plot of average seam phosphorus content *versus* hangingwall rock samples and in-seam tonsteins and siderite-rich bands.

A number of in-seam tonstein and siderite-rich bands and hangingwall rock samples were collected. The latter represented about 5 centimetres of contact rock. These samples provide some insight into the movement of phosphorus. In nearly all cases the hangingwall samples contain more phosphorus than the seams as whole (Figure 14) and in that the seam phosphorus content is less than believed to be in the original vegetation, this implies an outward movement of. Most of the hangingwall rock samples have higher phosphorus contents than the average for shale (0.065%). The phosphorus did not originate from, or find a home in, the tonstein bands, which generally have lower phosphorus contents than the seams. There is an association of siderite with phosphorus, which probably relates to temporary low pH environments in the swamp that cause the precipitation of siderite and apatite.

COMPARISON TO OTHER COALFIELDS

Phosphorus concentrations in coal from the Gates and Gething formations in the Peace River coalfield are generally lower than those in the Elk Valley coalfield (Grieve 1992). In fact there is a consistent decrease in average raw phosphorus content with age of the Jura-Cretaceous coal-bearing formations. The oldest Mist Mountain Formation has an average of 0.076% followed by the younger Gething Formation (0.063%) and the youngest Gates Formation (0.043%). This may correlate with the amount of structured inertinite in coals from the different formations. A preliminary examination of Gething Formation coals indicated that a lot of the inertinite is macrinite (Ryan, 1997). The amount of structured inertinite in a coal is related to the frequency of wildfires (Lamberson and Bustin, 1966) and is therefore related to climate; specifically the amount of precipitation and the oxygen content of the atmosphere, which has varied over geological time.

There is insufficient data to compare phosphorus concentrations in the Elk Valley with those in the Crowsnest coalfield to the south. The lowermost seam in the Crowsnest coalfield has low phosphorus concentrations but data on seams higher in the section is sparse.

Some data has been located for some Australian coals (Ward *et al.*, 1996 and Queensland Coal Board, 1995) and for Appalachian coals (Price and Gransden, 1987). The Elk valley coals are distinguished from the Australian coals by the presence of some high values (Figure 7). Appalachian coals have distinctly lower phosphorus concentrations. There is no obvious petrographic reason for the difference in concentrations; for example the Elk Valley coals do not have more semifusinite than the Australian coals. However there is some uncertainty in the petrographic data because of differences in the way the macerals were described and there is a mixing of raw and wash data. The difference in average phosphorus concentrations may be explained by global climate or vegetation changes over time.

CONCLUSIONS

It is proposed that much of the phosphorus in coal originates from the parent vegetation, in which there is ample to account for all that is found in coal. In fact vegetation contains on average 10 times as much phosphorus as coal and either phosphorus is lost from vegetation during coalification or growing vegetation scavenges phosphorus from underlying humus. Within the coal, macerals are divided into three groups based on their phosphorus content. The phosphorus content of structured inertinite is variable to high depending on how much apatite is introduced into the phytal porosity. The phosphorus content of structured vitrinite is moderate and probably close to that of the original vegetation. It is partially sweated out of the original vegetation and finely dispersed as crandallite minerals. Phosphorus has been largely removed from unstructured vitrinite and inertinite but some may remain associated with kaolinite.

Petrography and analytical data confirm that, in coal from the Elk Valley coalfield, the structured inertinite and vitrinite phosphorus association. Correlation data indicates that the barium and strontium tend to be associated with the finely dispersed phosphorus in structured vitrinite.

Scanning electron microscope work confirms that much of the visible phosphorus occurs as apatite or occasionally as gorceixite occupying lumen (cells or phytal porosity) in the semifusinite or fusinite. However there are also finely dispersed grains of apatite and goyazite in tellinite and telocollinite. This explains why regional studies reveal a positive correlation between phosphorus and reactive maceral contents of seams.

The phosphorus content of seams in the Elk Valley Mist Mountain Formation is related to the sum of structured vitrinite plus structured inertinite. However variations within a single seam are related to small changes

in the amount of semifusinite, which can have very high concentrations of phosphorus.

Because much of the phosphorus is present as phosphorus minerals enclosed by coal macerals it is difficult to liberate and remove during washing. Inert maceral fragments tend to accumulate in the intermediate size range in crushed coal and in the intermediate specific gravity splits. However it will be difficult for a wash plant to make use of these differentiation's. The best way of reducing the average content of phosphorus in the clean coal is by blending the ROM coal. This will require good advanced knowledge of phosphorus concentrations in the seams so that the information can be built into long range mine plans.

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