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Selenium in the Mist Mountain Formation of Southeast British Columbia

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KEYWORDS: Selenium, coal, Mist Mountain Formation.

INTRODUCTION

This study documents the distribution of Selenium (Se) in the Jurassic-Cretaceous Mist Mountain Formation of southeastern British Columbia and in various materials segregated by the five coal mines in the area. This study is preliminary and will be followed up by more detailed and focused studies.

The Mist Mountain Formation, which is part of the Kootenay Group (Table 1), outcrops extensively in the east Kootenays and varies in thickness from 25 to 665 metres (Gibsons, 1985). Typically 8% to 12% of the thickness of the formation is coal and in places this is distributed in over 30 seams. The rest of the formation is composed of non-marine siltstones, mudstones and sandstones. The formation is underlain by the Morrissey Formation, which is a sandstone unit that forms the footwall to most of the mining activity. This formation is underlain in turn by the Fernie Formation composed predominantly of marine shales. The Mist Mountain Formation is overlain by the Elk Formation, a non-marine sandy formation containing thin sapropelic coal seams.

TABLE 1
JURASSIC-CRETACEOUS STRATIGRAPHY OF THE KOOTENAY GROUP

LOWER CRETACEOUS	CADOMIN FORMATION		
JURASSIC AND CRETACEOUS	KOOTENAY GROUP	ELK FORMATION	
		MIST MOUNTAIN FORMATION coal seams	
		MORRISSEY FORMATION	MOOSE MOUNTAIN MEMBER
			WEARY RIDGE MEMBER
JURASSIC	FERNIE FORMATION	PASSAGE BEDS	

The Mist Mountain Formation outcrops in three distinct coalfields (Figure 1).

The Elk valley coalfield in the north hosts three coal mines, the Crowsnest coalfield hosts two and there are exploration properties but no mines in the southern-most Flathead coalfield. The formation is thinner in the Flathead coalfield and thicker in the other two coalfields, though there do not appear to be any consistent regional trends in thickness in the coalfields. The volume of the formation outcropping in each basin varies and is most in the Elk Valley and least in the Flathead coalfield. The Kootenay Formation, which is equivalent to the Mist Mountain Formation, outcrops to the east in Alberta where it is much thinner, though it still contains some coal seams.

Coal mining started in the east Kootenays in 1898 and over 460 million tonnes have been extracted up to 1999. Since 1970 about 400 million tonnes of coal have been mined from surface pits representing removal of over 2.5 billion cubic metres of rock.

This paper provides preliminary lithologic sections of the Mist Mountain from a number of areas illustrating the major lithologies including coal seams and indicating their Se content. In addition, samples of materials disturbed by mining were analyzed. These include coarse refuse, tailings material and material from settling ponds adjacent to waste rock dumps. The partitioning of Se in coal seams and rocks associated with the coal seams is investigated. The relationship of Se to sulphur (S) in these rocks gives some indications of how Se is bound and how easily it might be released into the environment.

BACKGROUND

Selenium is an unusual trace element in that there is a very narrow band of tolerance in all animals. There is, therefore, a heightened interest in Se levels in the environment and how these levels are effected by human ac-

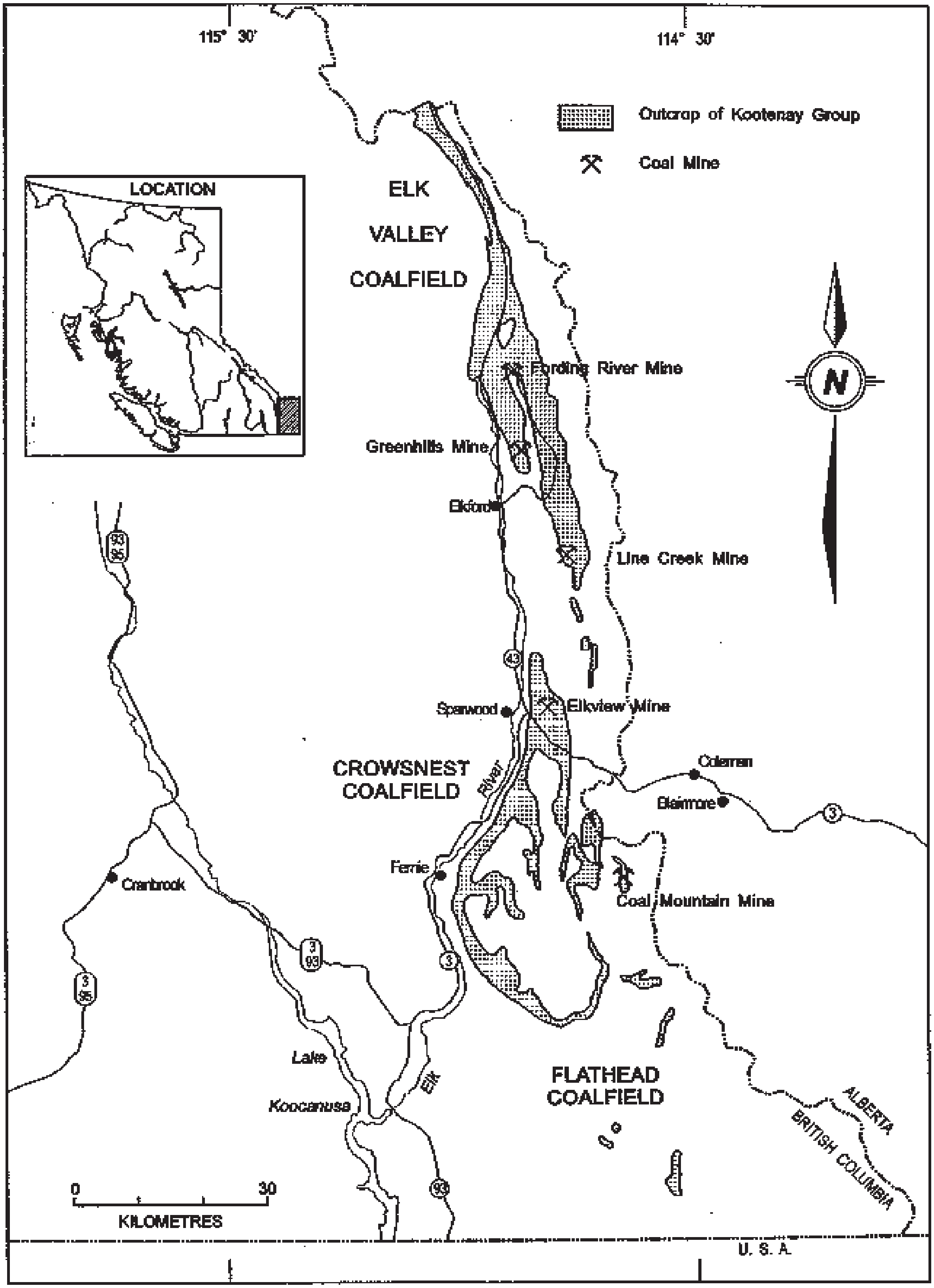


Figure 1. Elk Valley, Crowsnest and Flathead coalfields of southeast British Columbia.

tivity. It is considered to be a trace element of potential environmental concern (Harvey *et al.,* 1983) and a hazardous air pollutant (HAP) (Demir *et al.,* 1998). Cases of natural Se poisoning have been reported in China, but generally more problems result from Se deficiency in diets. In many areas soil is deficient in Se and available Se in vegetation is less than 0.05 ppm. Some countries such as New Zealand add Se to agricultural fertilizers to counter health problems in livestock resulting from Se deficiency in soil and vegetation. Salt licks often contain added Se for the same reason. If diets provide, on average, less than about 0.1 ppm, then Se deficiency problems occur that include impaired immunity, hepatic necrosis and cardiac functional changes (Keshan decease). If concentrations in soils are above about 4 ppm, then Se toxicity problems may occur. In farm animals these involve deformities, fertility problems and loss of muscle coordination referred to as the blind staggers. Chronic poisoning occurs in animals if they consistently ingest foods with average Se concentrations between 5 to 20 ppm daily.

In humans, it is recommended that the Se intake be between 100 and 250 mcg/day (therapeutic dose 350 - 400 mcg/day). This amount will usually be found in a normal diet, but not necessarily in what is sometimes referred to as the SAD diet (standard American diet). Foods especially rich in Se include meats, fish, whole grains, brewers yeast and mushrooms. Excess Se in humans may cause dental problems and very high levels reported in Hubei province in China caused hair loss, skin lesions and nerve damage (Zheng *et al.,* 1999).

Selenium is chemically similar to sulphur. It occurs in the ionic states, selenide (-2), elemental (0), selenite (+4), and selenate (+6). Selenium in Se bearing sulphides oxidizes readily to selenite and selenate. The latter is the most soluble and toxic form. In oxidizing conditions, selenate is usually reduced to selenite, which is easily removed from solution combined with $Fe(OH)_3$. In non oxidizing conditions Se is reduced to the elemental form, which is insoluble and generally non toxic.

World consumption of Se is probably in the range of 1000 to 2000 tonnes per year (1450 tonnes in 1989, Herring, 1990) . USA consumption in the 1990's has been between 500 and 600 tonnes. Uses for Se include, glass making (35%), agriculture and metallurgy (30%) chemical and pigments (20%) and electronics (15%). At present most of the Se is extracted as a by-product when smelting copper ore. In the future, the biggest resource of Se could well be world coal deposits. Se may be extracted from fly ash after coal combustion in power plants.

Average crustal abundance of Se is 0.05 - 0.1 ppm (Taylor 1964 and Turekian, and Wedephol, 1961), which is lower than its average concentration in the whole earth (6.1 ppm) because Se was easily volatilized from crustal rocks during crust formation. The value is usually calculated by dividing the Sulphur crustal average by a S/Se ratio. Selenium is concentrated in coal (average abundance about 2.15 ppm) and also in rocks rich in phosphate (Table 2).

In general Se concentrations in sedimentary rocks vary from less than 0.1 ppm in limestones and sandstones to an average of about 0.6 ppm in shales, which have a wide range of contents (<0.1-100 ppm) (Herring, 1990) (Table 2). Contents in marine or black shales tend to be higher than in other rock types and shales enriched in organic carbon (TOC) have higher concentrations because the micro organisms, responsible for the carbon, concentrate Se (Saiki *et al.,* 1993). Selenium is adsorbed onto clay minerals in shales as selenite under conditions of high pH and salinity. In sea water the S/Se ratio is very high (1.4×10^7) compared to about 2.5 to 3.5×10^3 in coal, because of adsorption of Se onto clays and the solubility of SO_4 in sea water. During diagenesis Se in clays may be incorporated into sulphides (pyrite) or remain as a trace element attached to the clay minerals.

Selenium is released as selenate (SeO_4^{-2}) during weathering when Se bearing sulphides oxidize or when clays are weathered. Once released, in alkaline environments, Se remains soluble as $CaSeO_4$ and is available to be taken up by plants. In humid conditions where soils are more acid it is either removed or converted to the less soluble selenite form.

Generally soils contain about 0.4 ppm Se. If the concentration is below 0.1 ppm they are considered to be deficient in Se and above 5 ppm enriched in Se. Soils in large areas of northeastern US and western parts of Washington and Oregon are considered to be Se deficient (Lag

TABLE 2
AVERAGE SE CONTENTS OF COMMON ROCK TYPES

	reference	Se range ppm	Se average	AREA
crustal average	G	0.05 - 0.1		
whole earth	G		6.1	
coal	D	<0.1ppm -5%	2.15	
sandstones	A	<0.1 - 1.7	0.1	
shale	A	<0.1 - 12	0.53	
cherts	A	<0.1 - 0.3	0.11	
limestones	A	<0.1 - 7.4	0.22	
sandstones	B	<0.1 - 1.5	0.22	Continental USA
siltstones	B	<0.1 - 0.79	0.21	
mudstones	D	0.4-0.6		
soil	F	0.14 - 4.32	0.45	Continental USA
Sandstones	D	0.05-0.08		
granites	D	0.01-0.05		
granodiorite	C	0.02 - 0.05		
mafic rocks	D	0.01-0.05		
ultramafic	D	0.02-0.05		
crude oil	D	0.01-1.4		
phosphate ore	E	0.7-7.0		

A	Connor and Shacklette, (1975)
B	Ebans and Shacklette (1982)
C	Kabata-Pendias and Pendias (1984)
D	Coleman *et al.* (1999)
E	Robbins and Carter, (1970)
F	Shacklette *et al.* (1974) and Shacklette and Boerngen (1984)
G	Herring (1990)
H	Taylor (1964), Turekian, and Wedephol, (1961)

and Agic, 1990), probably because of acid soil conditions. In dryer regions to the east (northwestern part of the great plains) Se contents are higher, possibly reflecting concentrations in the bedrock (Shacklette, 1974) or alkali soil conditions. Se can concentrate in the soil and in vegetation growing on the soil in semi-arid regions with impeded drainage. Crop plants in these areas may have toxic concentrations of Se (Gough *et al.,* 1979). Volcanic soils may have high Se contents depending on climate conditions.

Plants generally tolerate Se in amounts above the crustal average, though it is not clear what physiological role Se plays in plant growth. When available, in a soluble (oxidized) form, Se is readily absorbed by the plants, consequently the concentration in many plants reflects the concentration of the soluble component of total Se in the soil and is not particularly characteristic of the species. This means that Se concentrations in plants can vary year to year based on changes in climate, that effect soil conditions and solubility of Se (Erdman *et al*., 1990). Generally plant Se concentrations are less than that in soils except for mushrooms and other fungi, which are approximately 100 times better at extracting Se from soils than green plants and have contents that range from 0.1 to 16 ppm (Kabata-Pendias and Pendias, 1984). Some plants known as Se accumulators specifically concentrate Se and are toxic to animals; these plants often have a garlicky smell. When they decompose they release Se into the soil in a soluble form available to other species. Se concentrations in plants can range from 0 to 3% dry wt (Table 3).

Concentrations in cereals range 0 to 500 ppb and a general range for healthy leaves is 0.01 to 2 ppm. In plants, Se is concentrated in the growing points, seeds and roots. Concentrations in mature woody plants are probably less than those found in fast growing grasses. Generally Se concentrations in plants are less than concentrations in coal seams.

SELENIUM IN COAL

Selenium is enriched in coal compared to crustal average (0.05 to 0.1 ppm). Averages from different areas are hard to determine because of limited data and range of values; however Table 4 provides approximate numeric average data for a number of areas.

TABLE 3
AVERAGE SE CONTENTS IN SOME PLANTS

	Se concentrations in ppm		
	range ppm	mean	reference
corn	0.01 - 0.5	0.055	A
soybean	0.04 - 1.25	0.11	A
cedar	0.01 - 0.04	0.023	A
oak	<0.01 - 0.04	0.026	A
pine	0.02 - 0.2	0.062	A
wheat	0.15 - 2.2	0.57	B
sage brush	0.01 - 7	0.16	B
grasses	0.013 -0.35	0.074	C

A= Connor *et al*. (1975)
B= Shacklette and Boerngen (1982)
C= Kabata-Pendias and Pendias (1984)

A more complete table can be found in Swaine (1990). The number of analyses available from each area varies, and some data may be reported for clean coal. As discussed later, because Se tends to concentrate in the ash in coal, concentrations in clean coal are substantially lower than those in raw coal. The average concentration in world coals (raw basis) is about 2.15 ppm.

Coleman *et al.* (1993) looked at the distribution of Se in U.S. coals and provided arithmetic and geometric averages for data from various regions of the U.S. The arithmetic averages are included in Table 4 because they are consistent with data from other countries. Coleman *et al.* (1993) obtained a geometric average for all coals in the U.S. of 1.7 ppm. Selenium concentrations are higher in coals from the eastern part of the continent irrespective of coal rank or age. Average Se concentration in the Rocky Mountain region, which is the southern extension of the Kootenay coal fields in southeast British Columbia, is 1.6 ppm compared to a combined average of data from previous publications and this study of 1.6 ppm for the Mist Mountain coals. In China the average Se concentration is 6.2 ppm (Ren *et al.,* 1999) and some coals are reported to have concentrations as high as 8.4% (Yang *et al.,* 1982). Older Carboniferous, Permian and Triassic coals in China have concentrations over 4 ppm and younger coals concentrations less than 2 ppm.

The detailed mineralogical associations and chemical forms of Se in coal are discussed subsequently using data collected in this study. Existing literature permits a general discussion of the association of Se with coal, mineral matter and pyrite. Generally authors attempt to outline an organic or non-organic affinity and look for correlations of Se with coal, ash, total, pyritic or organic sulphur. This does not necessarily reveal the source of the Se. Gluskoter *et al.* (1977) found that Se in coals from Illinois has an partial non-organic affinity and that there was no correlation of Se with organic sulphur. Consequently, Se may have a positive correlation with ash and to a lesser extent pyrite, which often tends to be associated with ash. Based on all the data in their paper, Se correlates with ash (r^2=0.4), uranium (r^2=0.38) and pyrite (r^2=0.29). A detailed look at four bench samples studied in their paper indicates that Se often concentrates in the upper part of seams and that this does not necessarily correlate with high ash concentrations (Figure 2).

Except for one bench, in which data are biased by a single sample containing a high pyrite concentration, Se tends not to correlate with pyritic or organic sulphur in the incremental bench samples. As with all the data in the paper, bench sample Se values correlate positively with ash and uranium. In fact the best overall correlation is with uranium despite the fact that uranium in contrast to Se has a clear organic affinity in coal seams.

The Se *versus* U correlation may result because both Se and U are removed from solution in the acid anaerobic conditions in coal swamps. The correlation does not appear to exist for marine influenced coals such as some Illi-

TABLE 4
AVERAGE SE CONTENTS FOR WORLD COALS

area	number of analyses	comments	value**	rank *	age	reference
Canada						
SE BC published+this study	208	raw	1.60	MV	Jura-Cretaceous	
BC Intermontane	59	raw	1.00	L, SB	Tertiary	Goodarzi and Van der Flier-Keller (1990)
BC Nanaimo coalfield	10	raw	0.60	HV	Cretaceous	Van der Flier-Keller and Dumais (1988)
BC	22	raw	0.91	HV	Cretaceous	Van der Flier-Keller and Dumais (1988)
Northeast BC	8	raw	1.5	MV	Cretaceous	Grieve and Goodarzi (1994)
Saskatchewan lignites			2.3,4.1	L	Tertiary	Beaton and Goodarzi (1989)
Nova Scotia	23	raw	1.90	MV	Pennsylvanian	Pilgrim and Zodrow (1990)
	452		0.8			Raask, (1985)
USA						
national average	86	raw	3.30		Variable	Pillar *et al.* (1969)
national average	101	raw	2.10	B		Raask (1985)
national average	799	raw	4.10	SB B		Raask (1985)
Eastern	4711	raw	4.20	HV to A	Pennsylvanian	Coleman *et al*. (1993)
Gulf	214	raw	5.60	L	Tertiary	Coleman *et al*. (1993)
Interior	705	raw	3.10	HV MV	Pennsylvanian	Coleman *et al*. (1993)
Northern Great Plains	1154	raw	0.99	SB	Cretaceous	Coleman *et al*. (1993)
Rocky Mountain	1615	raw	1.60	MV,HV	Jura Cretaceous	Coleman *et al*. (1993)
Alaska	258	raw	1.10	SB	Tertiary/Cretaceous	Coleman *et al*. (1993)
Pacific Coast	38	raw	1.90	L SB	Tertiary	Coleman *et al*. (1993)
Eastern Kentucky	22		4.29	MV	Pennsylvanian	Eble and Hower (1997)
Powder River			0.94	SB		Oman *et al*. (1988)
North Dakota	17		0.79	L	Tertiary	International Coal Reports, 1998 No. 463
Illinois			3.00	HV		International Coal Reports, 1998 No. 463
Appalachian			3.70	MV,HV		International Coal Reports, 1998 No. 463
England	24	raw	1.75	V	Carboniferous	Spears and Zheng (1999)
	23		2.70		Carboniferous	Raask, (1985)
	?		2.80	B	Carboniferous	Raask, (1985)
Indonesia	2	clean	0.17	HV	Tertiary	ACARP (1993)
Australia	?	raw	0.90	B	Permian	Swaine (1990)
Australia Bowen Basin	40	clean	0.44	B	Triassic-Jurassic	Riley and Dale (2000)
South Africa	6	clean	0.76	MV	Permian	ACARP (1993)
China	118	raw	6.22	V	variable	Ren *et al.* (1999)

rank* L=lignite SB=sub bituminous B=bituminous HV=high volatile bituminous
MV=medium-volatile bituminous LV=low-volatile bituminous LV=low-volatile bituminous A=Anthracite ** =Arithmetic mean V=variable

nois coals (Harvey *et al*., 1983) and coals from Nova Scotia (Pilgrim and Zodrow, 1990). These coals may have formed in more oxidizing environments in which U remained soluble. Boron concentrations are considered to indicate degree of salinity and therefore degree of marine influence. In the Coal Mountain mine data from Goodarzi (1987) both U and Se correlate negatively with B possibly indicating a preference for deposition in a non marine acid anaerobic environments.

They indicate an ash and pyrite association for Se with the pyrite connection being strongest. Finkelman (1994) considered Se to have a mixed association in coal with a significant organic component. Coleman *et al*. (1993) state that Se is associated with the organic fraction probably substituting for organic sulphur, though they did not always find a good correlation of Se with organic sulphur. Many other workers have found at least a partial association of Se with syngenetic pyrite (Clarke and Sloss, 1992). White *et al.,* (1989) found average concentrations of 97 and 64 ppm Se in pyrite and marcasite from UK coals. Higher concentrations have been found in pyrite and marcasite of higher temperature origin (up to 3% and 80 ppm respectively) (Wedepohl, 1978). Goodarzi and Swaine (1993) report finding trace amounts of clausthalite (PbSe) and ferroselite ($FeSe_2$) in coals. Harvey *et al*. (1983) found a mixed association of Se in coals from the Illinois basin. Data from their study can be used to estimate concentrations of Se in coal ash and pyrite. Sample Se concentrations were predicted using Se concentrations for the ash, coal and pyrite components of samples. The best fit (r^2=0.66) of predicted *versus* actual concentrations was obtained by assuming Se concentrations of 1 ppm in coal, 8 ppm in ash and 26 ppm in pyrite (Figure 3).

Obviously this solution is not unique but the analysis is consistent with lower concentrations in coal, moderate in ash and higher in pyrite, though not as high as found by White *et al*. (1989).

Few papers discuss the source of the Se in coal. Gluskoter *et al.* (1977) note the enrichment of Se in coal compared to average crustal abundance and attributed at least some of the Se to the original vegetation. However the amount of Se in coal often appears to be more than can be attributed to the vegetation from which the coal was derived. Most plant species average less than 1 ppm (Table 3) and even after increasing the Se concentration in coal, because of the loss of volatile matter during coalification, concentrations in coal still appear to be too high to be explained solely by concentrations in plants. It is also probable, that depending on conditions in the coal swamp, overlying vegetation may extract Se from the underlying rotting vegetation causing an upward migration of Se and consequently new vegetation may not be responsible for bringing additional Se into the coal swamp.

Some of the Se found in coal must be transported into the coal swamp either in solution or with detritus. In the Powder River coals, Se correlates positively with ash (r^2=0.62) and to a lesser extent with organic sulphur (r^2=0.4 in the south and 0.81 in the north) and pyritic sulphur (r^2=0.3) (Oman *et al*., 1988). The correlations with both organic sulphur and ash could imply that Se originated from Se rich Cretaceous formations to the south of the basin and was introduced into the coal swamp with detritus and in solution.

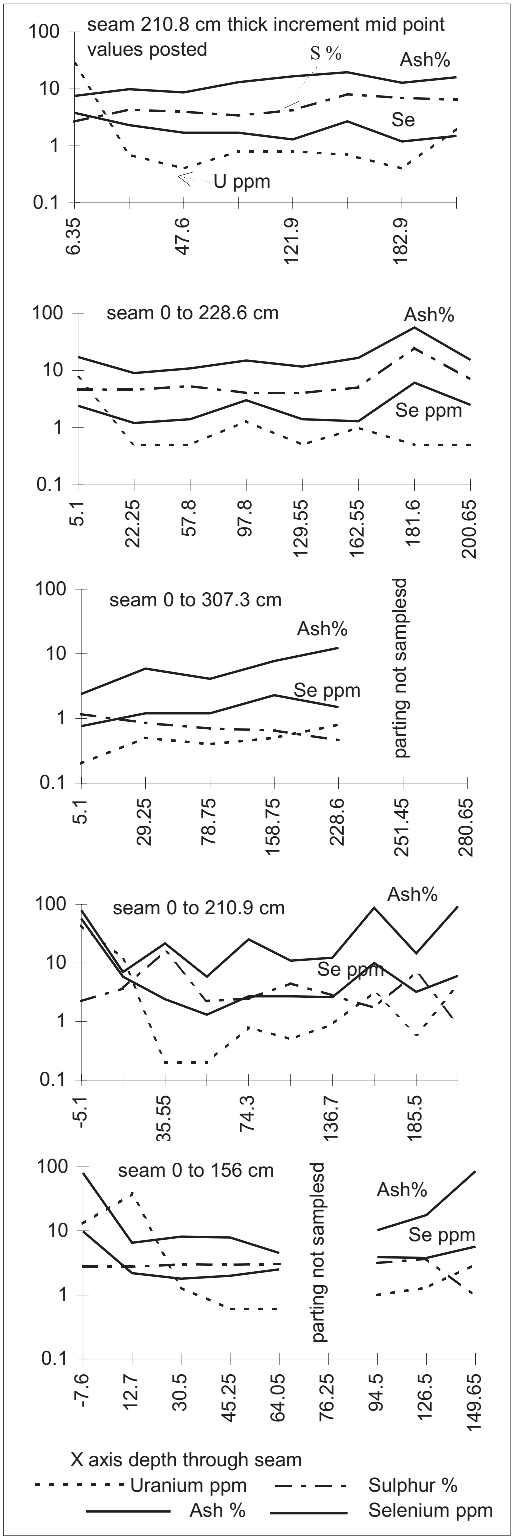


Figure 2. Se, U, S and ash in bench sample data from Gluskoter *et al*. (1977).

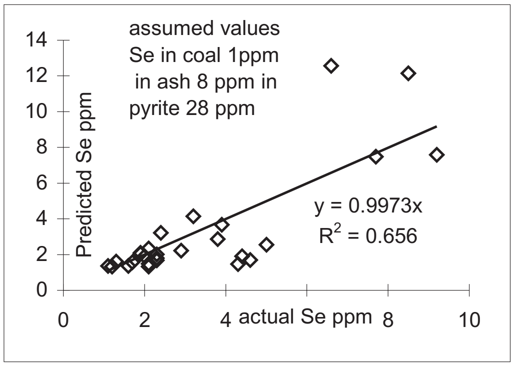


Figure 3. Predicted *versus* actual Se concentrations (analytical data from Harvey *et at*., 1983).

ANALYTICAL TECHNIQUES

Sample preparation for Se is important because it is very volatile and even with low temperature ashing of coal samples at less than 200°C, 10% to 30% of the Se may lost (Finkelman *et al*., 1990). Samples can be dissolved using wet chemical means in sealed containers or at low temperatures. Concentrations can be analyzed using atomic adsorption (AA) with hydride generation or a graphite furnace and using inductively coupled plasma mass spectroscopy (ICP-MS). Alternatively, samples can be analyzed using instrumental neutron activation analysis (INAA), which does not require any sample preparation other than crushing and pulverizing. INAA does take longer than techniques using AA or ICP-MS and Se analyses are effected by interference from tantalum, which can raise the detection limit. All these techniques have detection limits of 0.2 to 0.8 ppm. In this study INAA was used for determining Se concentrations, mainly because of concerns about Se volatility and chemical interferences.

The precision and accuracy of the data were checked by repeatedly analyzing one rock and one coal standard, by analyzing duplicates of samples and by obtaining duplicate analyses of some samples in a second laboratory also using INAA. The results of the various data checks (Table 5) indicate that in the range of 1 to 5 ppm, precision and accuracy are moderate, and there does not appear to be any systematic bias to the data.

Four analyses of the coal standard Lower Bakerstown CLB-1 provide an average result of 2.4 ppm compared to 2 ppm reported by the USGS. The value of 2 ppm is referred to as an information value based on analyses from less than 3 laboratories and the methods of analyses are not reported. Four analyses of a combined rock plus sulphide standard provide an average of 3.4 ppm compared to an average of 2.5 ppm obtained by wet chemical means. The latter value is low because of partial extraction of Se and loss of Se during acid digestion and heating. In general the analyses of standards and of duplicates indicate that the 1 sigma SD of the samples is probably less than 20%. There is no indication that the data is significantly biased and that the INAA is providing values that are too high or too low.

Some rock samples were analyzed for various metals including Se using ICP-MS. This technique uses an aqua regia digestion (samples heated to about 90°C) and provides ppm concentrations of a number of metals including Se. The acid digestion may only partially extract Se from silicates or organic material or may volatilize some, but in a cross plot with INAA results (Figure 4) there does not seem to be a bias.

In fact this analytical technique which is more sensitive for Se analyses than INAA provided a slightly higher averaged Se value of 3.4 compared to 2.7 for INAA. The ICP-MS technique was not used for coal samples because Se may not be completely extracted from organic samples using aqua regia.

TABLE 5
ANALYSES OF STANDARDS AND DUPLICATE ANALYSES, INSTRUMENTAL NEUTRON ACTIVATION ANALYSES

Sulphide rich rock standard

sample 1	3.9	Se ppm		
2	3.7	Se ppm		
3	2.4	Se ppm		
4	3.6	Se ppm		
5	3.0	Se ppm		
Average	3.3	SD =	0.6	SD%=18.49

USGS coal standard Coal, lower Bakerstown CLB-1
medium-volatile bituminous coal
information value for Se given as 2ppm
i.e. less than 3 independent labs providing data

analysis 1	1.6	ppm		
2	2.9	ppm		
3	2.7	ppm		
4	2.2	ppm		
Average	2.4	SD	0.6	SD% 24.69

REPEAT ANALYSES AT LAB 1

	Se ppm		diff	% diff	composition
sample 1	1.6	1.5	-0.1	-6.5	coal
2	5.3	5.2	-0.1	-1.9	coal
3	2.0	2.1	0.1	4.9	coal
4	2.6	3.8	1.2	37.5	sed
5	4.3	4.8	0.5	11.0	footwall
6	7.0	6.5	-0.5	-7.4	coal

DUPLICATE ANALASES LAB 1 AND LAB 2

LABS	1	2	diff	% diff	composition
	Se ppm				
Sample 1	3.2	3.6	-0.4	-11.8	coal
2	2	2	0	0.0	coal
3	1.3	1.1	0.2	16.7	coal
4	2.5	2.6	-0.1	-3.9	mdst
5	2.2	2.8	-0.6	-24.0	mdst
6	3.6	3.3	0.3	8.7	rock stnd

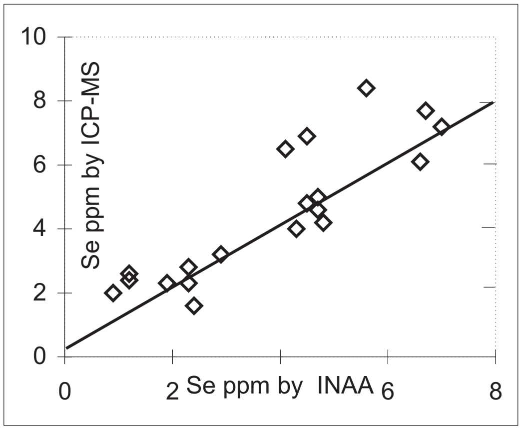


Figure 4. Cross plot of Se concentrations determined by INAA and ICP-MS.

In this study ash analyses were made on as-received samples. The small difference between as-received and air-dried results was not considered significant considering the cost saving and that the data are used only to outline the relationship between Se and ash. The ash analyses for samples that were analyzed for ash and oxides were made using a high temperature ashing technique that does not conform to the standard ASTM method but produces acceptable results (Figure 5).

EXISTING SELENIUM DATA FOR COALS IN BRITISH COLUMBIA

There is not a lot of data on Se in BC coals. Data for northeast BC (8 analyses) provides an average of 1.5 ppm for coal seams in the Jurassic-Cretaceous Gates Formation. Coal seams in the Cretaceous Telkwa deposit near Smithers in central BC have average Se contents of about 0.4 - 0.8 ppm with a lot of analyses below detection limit, which ranges from 0.2 to 0.8 ppm. Coal seams from the Upper Cretaceous Nanaimo and Comox coal basins average 0.6 ppm (10 analyses) and 0.91 ppm (22 analyses) respectively (Van der Keller and Dumais, 1998). The Tertiary Bowron Basin in the central part of the province has a higher average content of about 2.1 ppm and the Hat Creek Tertiary deposit a lower average of 1.1 ppm (Goodarzi and Van der Keller, 1988).

The Se content of coal seams in the Mist Mountain Formation has been studied by Goodarzi (1987, 1988 and 1993) who collected samples from the Fording River and Coal Mountain mines. Coal samples from a number of mines were analyzed by Grieve (personal communication, 1999). These data provide an average Se content in raw coals from the Mist Mountain Formation of 1.36 ppm. The average is biased by analyses of seams low in the section, which appear to have lower Se concentrations than seams higher in the section.

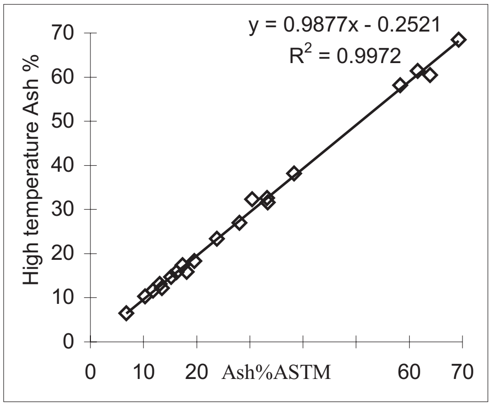


Figure 5. Cross plot of ash determined by ASTM and high temperature ashing methods.

EXISTING SELENIUM DATA FOR KOOTENAY GROUP ROCKS

Data on Se concentrations in rocks of the Kootenay group are not available. Analyses of water and sediments in areas adjacent to the coal mines were reported by McDonald and Strosher (1998) in a study of the potential effects of coal mining on Se concentrations in the Elk River basin. They documented a trend of increasing Se content over time in the Elk River measured at its mouth approximately 65 kilometres down river from the mines. They also documented increased concentrations of Se in tributary creeks draining areas of mining activity compared to concentrations in the Elk and Fording rivers up stream from the mines. Selenium contents of sediments range up to about 3 ppm except for the Michel Creek area where concentrations are lower. On average concentrations in sediments are higher in creeks draining mine areas (about 2 ppm) than in creeks above mining areas (less than 1ppm).

DATA

In this study approximately 375 samples were collected and over 400 Se analyses obtained. Samples were collected from the five coal mines in the east Kootenays identified by the letters A to E in this paper. Attempts were made to sample the complete exposed Mist Mountain section at each mine, however, because of mining activity this was not possible at all mines. At some mines, sections were sampled in more than one pit. Interburden rock was divided into simple rock units and sampled by collecting chips at approximately 1 to 3 metres intervals along high walls. Individual samples varied from 1 to 5 kilograms of rock or coal chips. Coal seams were sampled by channel sampling or by collecting chips. Hanging wall (HW) and foot wall (FW) material, adjacent to some seams, was sampled separately as were rock splits (partings) within some coal seams. All samples were analyzed for total Se. Some samples were also analyzed for total As using INAA; for major oxides using XRF and for metals using ICP-MS.

Coal samples were analyzed for ash and some for sulphur forms. Three coal seams were subjected to washability analysis. Incremental samples were collected across two seams to investigate the stratigraphic distribution of Se within seams.

Samples of wash plant reject material (coarse refuse > 0.15 mm and tails < 0.15 mm) were collected at each mine. At some mines the refuse material was screened into a number of size fractions. At one mine a sample of breaker reject was collected. More samples of this material were not collected because of the coarseness of the material and difficulty in getting a representative sample. At one wash plant samples of fine coal before and after the dryer were collected.

Rock and coal samples were crushed, split and then 100 to 200 grams pulverized to provide samples for INAA, XRF oxide and ICP-MS analyses. Splits of crushed material of samples containing coal were kept to be used for coal quality analyses. Some of these samples were floated in heavy liquids to provide separate coal and mudstone rich fractions, which were subjected to further analysis.

Before surface water from the mines is released into rivers, it is diverted through settling ponds, that collect fine sediment derived from waste dumps and other areas of the mine. Twenty nine sediment samples were collected from a number of settling ponds at each mine. Sediment samples were dried and minus 100 mesh material screened off and sent for oxide and Se analyses. Some sediment samples were also sent for total organic carbon (TOC) analysis.

SELENIUM STRATIGRAPHY IN THE MIST MOUNTAIN FORMATION

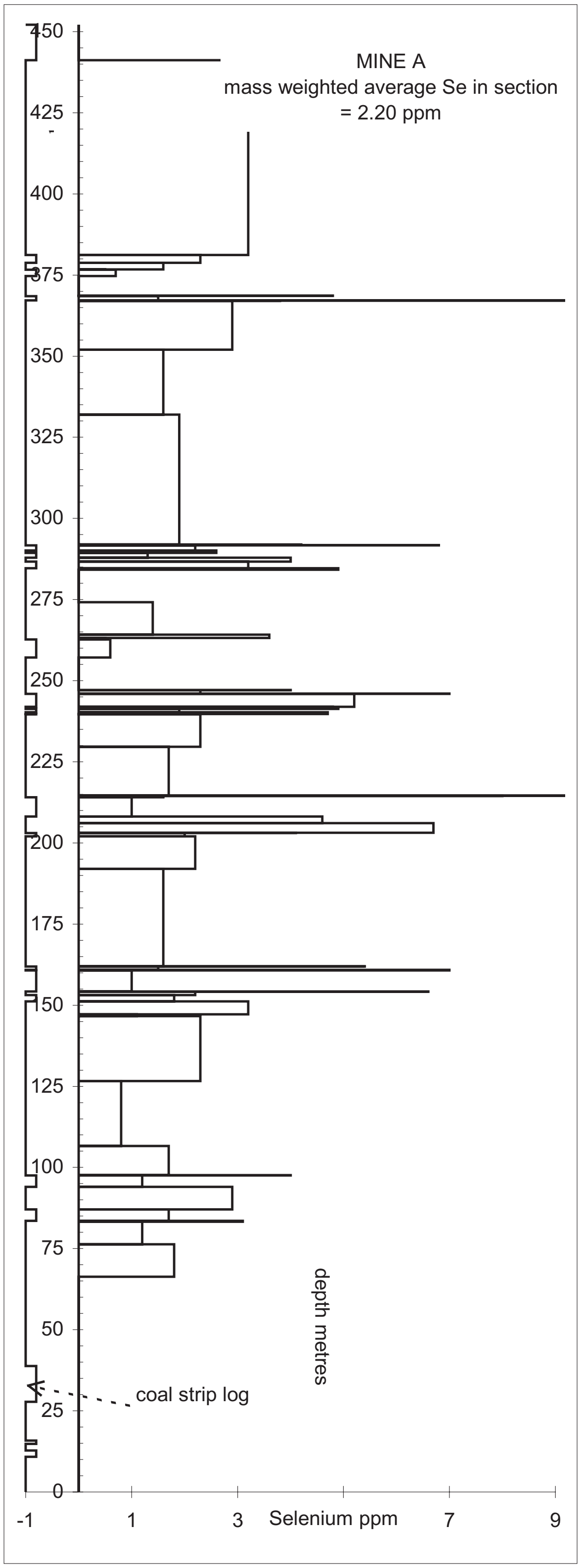
Based on sampling at the five mines 7 partial stratigraphic sections through the Mist Mountain Formation were established (Figures 6 to 10).

Sections were broken down into interburden rock and coal seams, which were generally sampled as single units, except in a few cases where partings 0.1 to 0.5 metre thick were sampled separately. Tonstein bands were identified in some seams and sampled separately. These are generally 0.01 to 0.05 metre thick brown kaolinite rich bands of volcanic origin. Interburden rock was subdivided into five units based on mudstone component (Table 6) ranging from carbonaceous mudstone to sandstone or siltstone.

Attempts were made to integrate units such that the minimum unit thickness was more than about 2 metres. Hanging wall (HW) and foot wall (FW) samples were collected for some seams, where there was an obvious gradation from coal seam to interburden lithology. These samples usually represented from 0.1 to 0.5 metre of mixed rock and coal and were not collected for all seams. A few samples were collected from the Fernie Formation, which underlies the Mist Mountain Formation and is exposed at some mines.

The Se concentrations and number of samples from each lithology are identified in Table 6 as composite averages and as averages for each mine. In each case two values are reported, the higher calculated assuming that values below detection limit are equivalent to the detection limit and the second calculated assuming that any value less than the detection limit is zero. The averages are weighted based on the thickness represented by each sample. Because coal and rock averages are calculated separately the thickness weighted averages are very close to mass weighted averages.

Individual lithologies are not identified on the sections (Figures 6 to 10) except for strip logs identifying location and thickness of coal seams. For all mines the lowest seam identified in the sections is the lowest seam mined and either rests on the Moose Mountain Member or is a few metres above it. Sections illustrate the approxi-



Figures 6 to 10. Stratigraphic sections at the 5 mines (A, B, C, D, and E) illustrating variation of Se content with depth. Locations of coal seams are indicated. Data below detection limit (0.2 to 0.8 ppm) are plotted as detection limit.

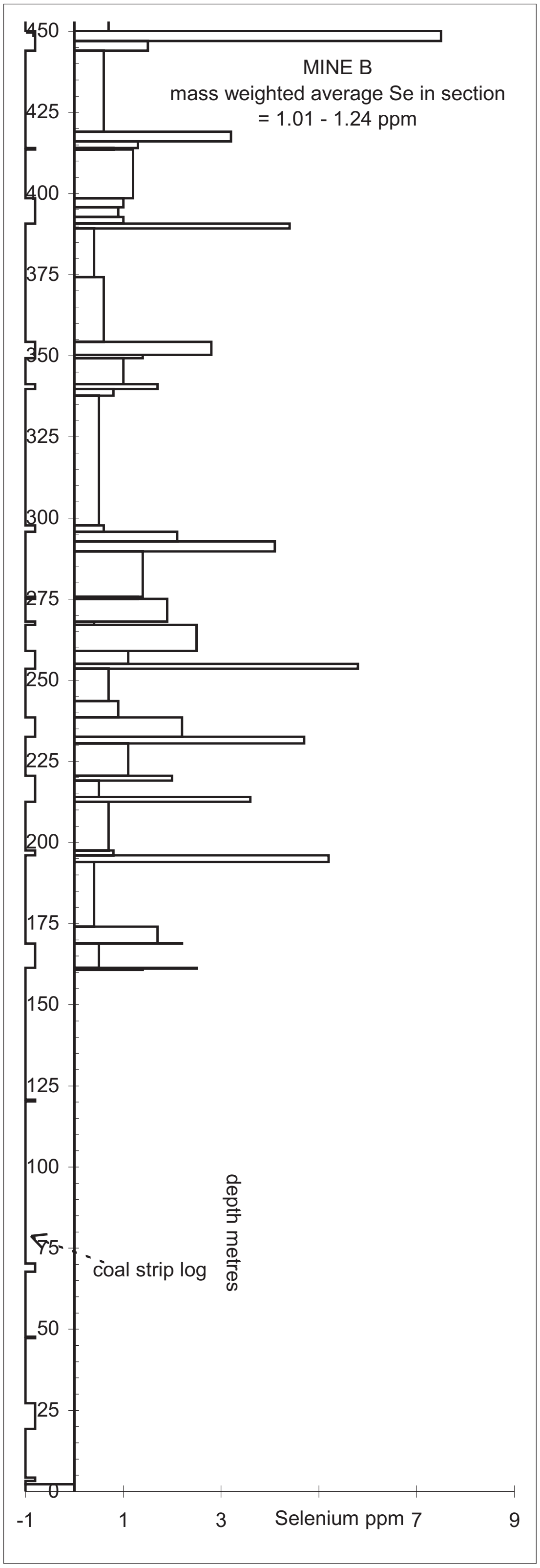


Figure 7

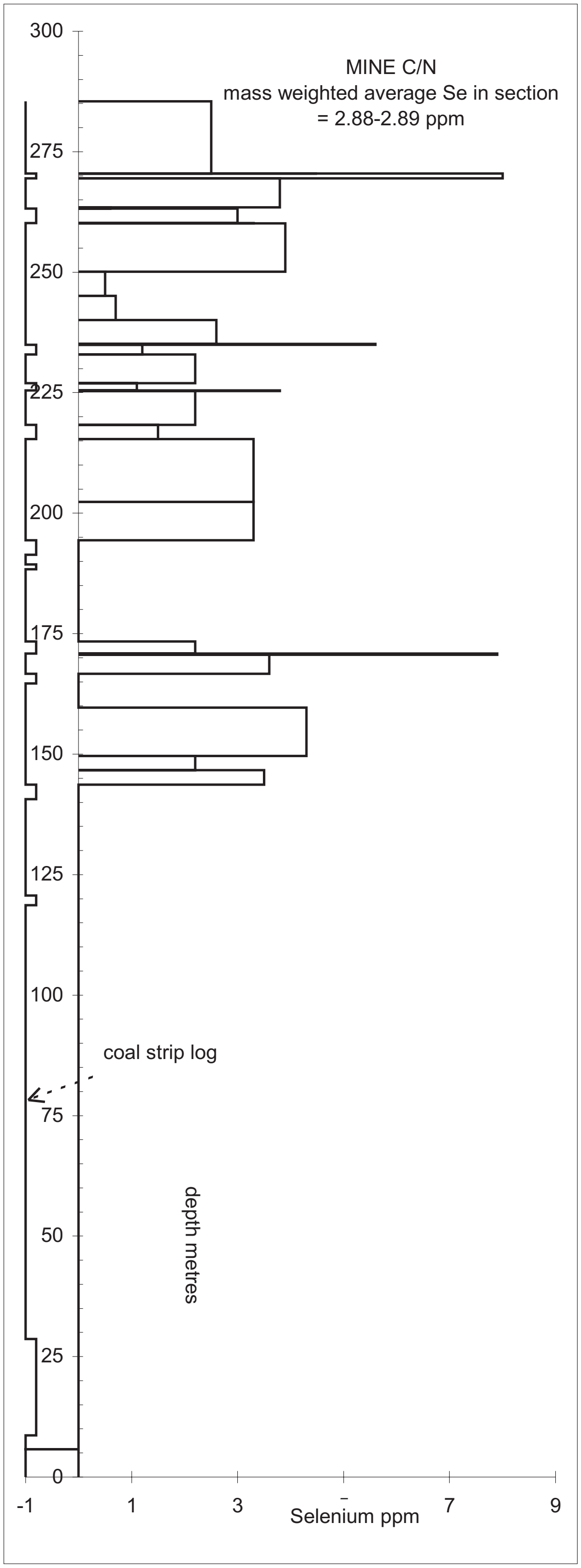


Figure 8a

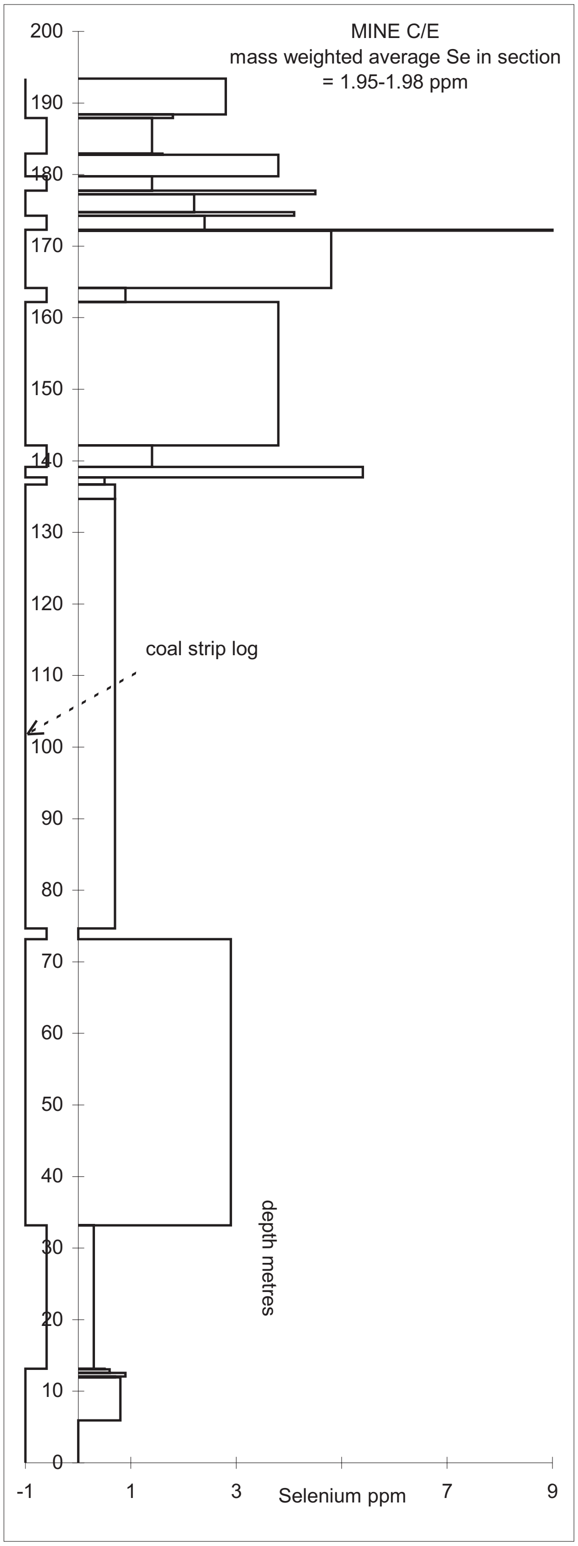


Figure 8b

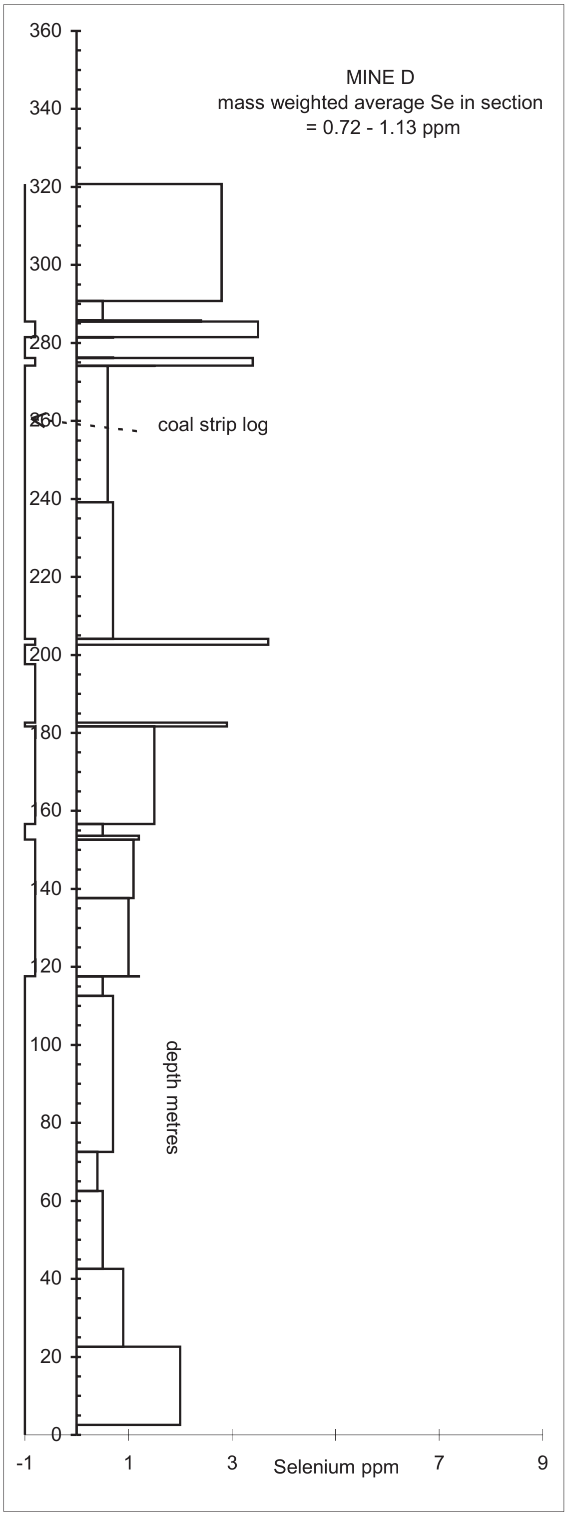


Figure 9

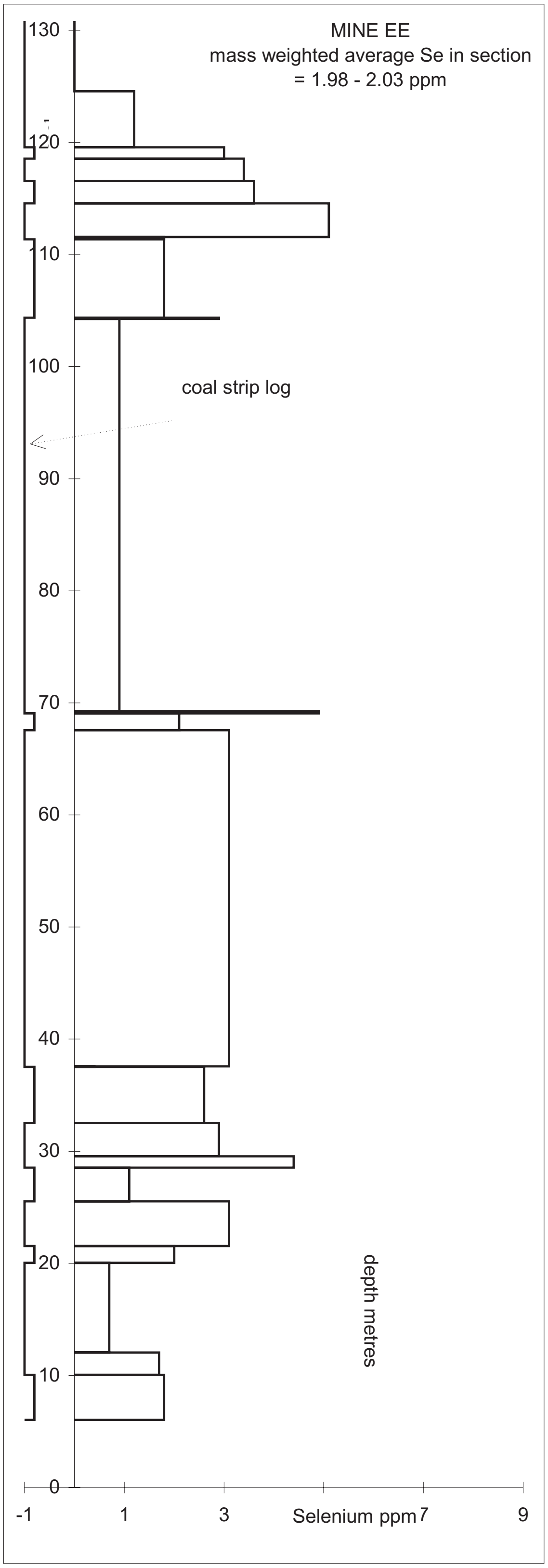


Figure 10a

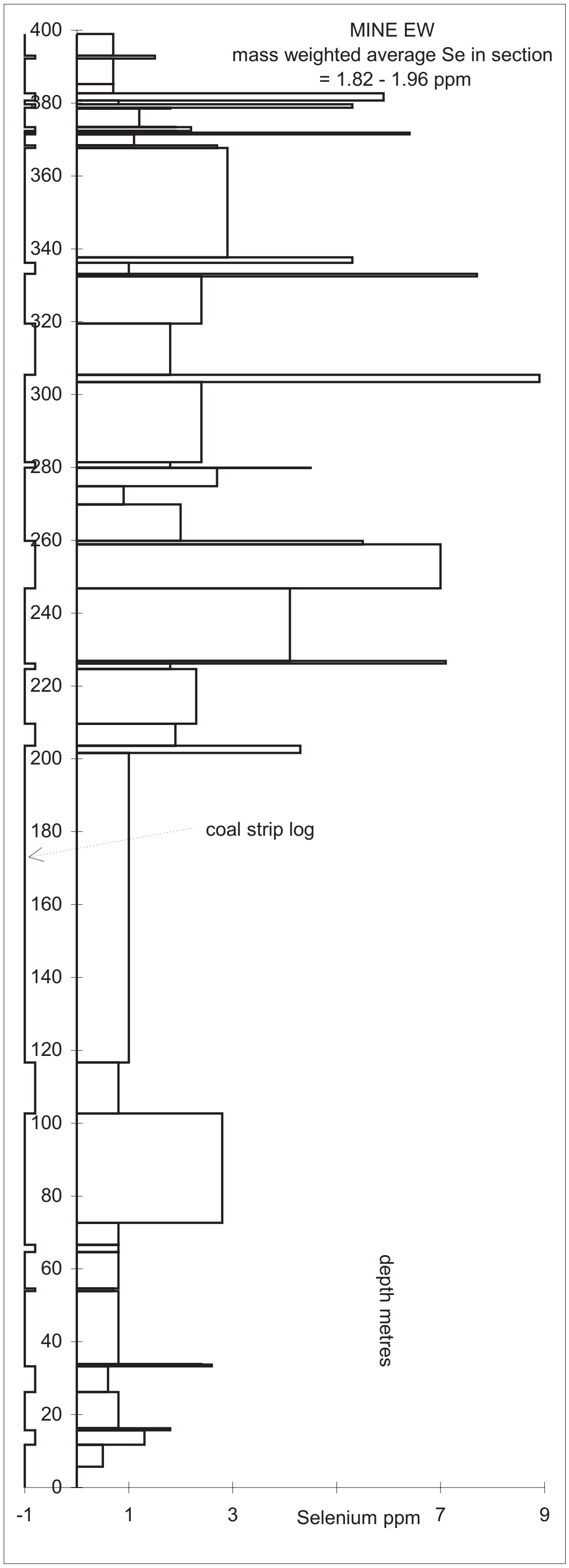


Figure 10b

TABLE 6
THICKNESS WEIGHTED AVERAGE SELENIUM CONCENTRATIONS BY MINE AND BY LITHOLOGY

	ALL MINES					MINE A			MINE B			MINE C			MINE D			MINE E		
	samples	Se high	Se low	samples	As	samples	Se high	Se low	samples	Se high	Se low	samples	Se high	Se low	samples	Se high	Se low	samples	Se high	Se low
coal seams	107	1.9	1.9	55	2.4	24	1.7	1.7	28	2.0	2.0	17	1.5	1.4	7	1.5	1.5	31	2.4	2.4
HW rock	21	4.2	4.2	8	3.7	10	4.2	4.2	1	2.2	2.2	4	2.8	2.8	2	1.8	1.6	4	5.6	5.6
FW rock	21	4.2	4.1	8	5.3	3	4.7	4.7	4	4.2	4.2	8	1.3	1.3	3	1.0	0.5	3	6.8	6.8
partings in coal seams	23	3.2	3.2	5	10.0	7	4.8	4.8	0			3	7.2	7.2	2	2.1	2.1	11	2.5	2.5
tonstein	3	1.8	1.8	0		1	1.6	1.6	0			0			0			2	2.1	2.1
mdst with coal stringers	20	3.2	3.2	2	2.7	3	3.1	3.1	7	2.9	2.9	3	3.9	3.9	0			7	3.1	3.1
mdst	24	2.8	1.9	4	4.6	7	2.5	2.5	4	1.5	0.9	9	2.3	2.3	0			4	1.2	1.2
silty mdst	26	2.0	1.9	2	9.3	4	1.8	1.8	8	1.1	0.9	8	2.9	2.9	0			6	2.4	2.4
muddy siltstone	33	2.0	1.9	4	7.4	4	3.0	3.0	7	0.9	0.9	14	2.1	2.1	4	1.2	0.8	4	2.5	2.5
siltstone/sandstone	27	1.1	0.9	4	12.9	5	1.5	1.5	5	0.6	0.0	7	1.8	1.8	2	0.5	0.0	8	0.9	0.7
refuse coarse and tails	23	2.8	2.8	7	3.6	7	3.2	3.2	4	2.7	2.7	4	1.6	1.6	4	1.8	1.8	4	2.9	2.9
breaker	1	2.1	2.1	1	4.7	0			0			1	2.1	2.1	0			0		
Fernie shale/siltstone passage beds	9	1.1	0.9	4	5.7	2	0.8	0.0	0			2	2.4	2.4	5	0.9	0.2	0		
sediments - 100 mesh fraction	29	3.1	3.0	13	5.4	8	2.4	2.4	6	5.7	5.7	5	2.1	2.1	3	0.9	0.5	7	3.3	3.3
pyrite	3	10.2	10.2	3	670	3	10.2	10.2	0			0			0			0		
clean coal	4	1.1	1.1																	
sample count	374			120		88			74			85			32			91		

note averages are weighted by unit thickness except for refuse, Fernie shale, sediments, pyrite and clean coal.
HW=hangingwall FW=footwall mdst=mudstone
Se high average calculated assuming data below detection limit=detection limit.
Se low average calculated assuming data below detection limit=0

mate thickness of rock and coal units and their Se contents. A Se content of zero indicates that the zone was not analyzed. In cases where Se concentrations were below the detection limit, the value plotted is the detection limit and consequently the sections tend to slightly over emphasize some Se concentrations. However the mass weighted average Se concentrations reported in Figures 6 to 10 are calculated in two ways similar to the data in Table 6. This provides a maximum and minimum estimate of the average Se concentration in the sections and in most cases there is not a lot of difference between the two values.

The Se concentration of rocks and coal in the sections at two of the mines average about 1 ppm and at the other mines 2 ppm to 3 ppm. Based on the number of samples and the thickesses of the sections these averages should no be considered as definitive. The sections clearly illustrate that Se concentrates in rocks adjacent to coal seams (HW and FW) and in some partings in the coal seams, but not necessarily in tonstein bands. In interburden rocks the Se content increases as the mudstone content of the units increases (Table 6). A lot of the analyses for the sand rich units were below detection limits, which vary from 0.2 ppm to 0.8 ppm depending on interferences from other elements. The Se concentrations in coal seams are generally less than in the HW and FW rocks. There is also a weak tendency for the Se concentrations in rocks to increase up section; this is probably related to the increased amount of mudstone in the upper part of the Mist Mountain section. There does not appear to be any major stratigraphic control of Se concentrations in seams, though there is a tendency for concentrations to be higher in the mid part of the section (Figure 11).

The concentration of Se in the Fernie Formation shale, which underlies the Mist Mountain Formation, ranges from below detection to 2.6 ppm, averaging about 1ppm, and is therefore not high based on the marine origin and mudstone composition of the formation.

The average Se concentrations for the lithologic subdivisions of the Mist Mountain Formation are generally higher than those reported in the literature for similar lithologies (Table 2). This is probably because of the amount of dispersed organic material in the section. However there are no major units that stand out as consistently having very high Se concentrations. No Se analyses were made of the overlying Elk Formation, which contains thin sapropelic coal seams. These seams may have high Se concentrations because of their high algae content.

As discussed later, the Se content of seams is influenced by ash content and seam petrography and therefore lateral consistency of Se concentrations in individual seams will probably depend on these variables. The Se content of seams from one mine were analyzed during this study and by Goodarzi (1988) and there is a tendency

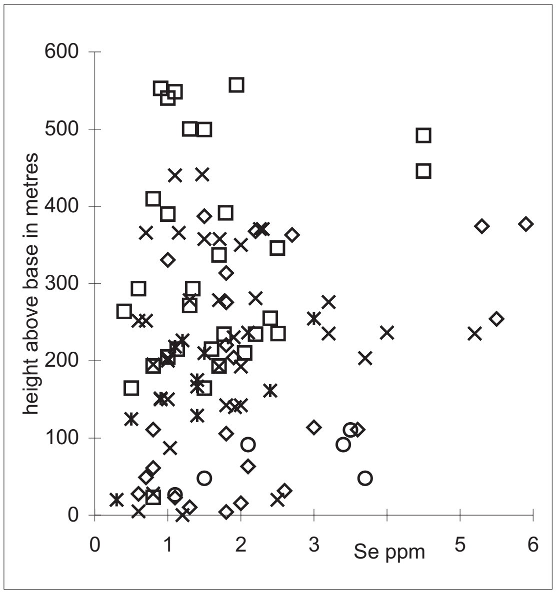


Figure 11. Se content in seams *versus* elevation above Moose Mountain Sandstone, data for all five mines; cross=mine A, square=mine B, star=mine C, circle=mine D, diamond = mine E.

for samples from the same seam to have similar Se concentrations (Figure 12).

The Se concentrates in HW and FW samples. However not all hanging wall and foot walls of seams were sampled so that these averages are not representative of the rock dilution that might be expected to be mined with the seams. In an attempt to get more representative averages, in cases where HW and FW material was not sampled, 0.5 metre of adjacent interburden was assigned to represent HW or FW and new averages calculated. Because Se tends to concentrate in rocks adjacent to seams, these second averages (contact rock Table 7) are probably lower than the averages that would have been obtained had all HW plus FW material been systematically sampled. The concentration of Se near seams is illustrated by 2 samples of FW material one representing 0.2 metres adjacent to the seam contained 2.5 ppm Se and another sample representing 0.4 metres also adjacent to the seam contained 1.4 ppm Se.

Sections totally representative of present mining operations were not sampled, however it is useful to calculate the average Se concentrations and the amount of Se in what is likely to be segregated as waste rock, run-of-mine coal and contact rock (Table 7).

Generally contact rock has the highest Se concentrations followed by raw coal and then interburden rock. Based on the 0.5 metre assignment to HW or FW (which is probably high) interburden rock accounts for over 80%, coal from 6% to 20% and contact rock 5% to 10% of the total Se in the section. The interburden material is transported to waste rock dumps. A lot of the contact material will after processing be segregated as coarse refuse and dumped somewhere on the mine site.

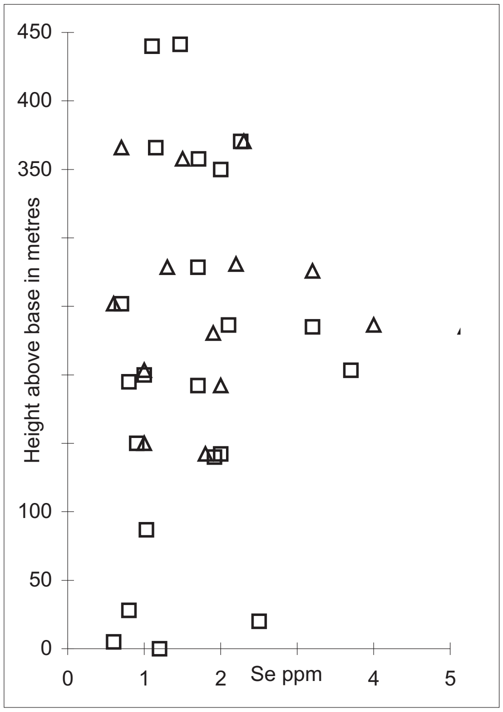


Figure 12. Comparison of Se contents for equivalent seams from this study and Goodarzi (1988); squares = Goodarzi (1988) data, triangles = this study.

Refuse material is composed of contact material plus fine ash liberated from the coal. It should therefore be possible to estimate the average Se content of refuse material. The Se concentration of the contact material will be between that calculated in Table 7 and that calculated for HW+FW material in Table 6. The fine ash, which probably has Se concentrations in the range of 3.8 to 4.9 ppm based on ash *versus* Se plots (Figure 13), is extracted from the raw coal and ends up mainly as the tailings component of the refuse material.

Therefore average refuse material should have Se concentrations higher than the values for contact material in Table 7. Actually most of the refuse material has averages noticeably lower. A possible explanation is that some Se is lost easily and quickly from the fine ash and contact material during mining, crushing and washing.

SELENIUM IN COALS FROM THE MIST MOUNTAIN FORMATION

Coal samples from the Mist Mountain Formation, analyzed in this study, have average Se concentrations of about 1.9 ppm, (Table 6), when this data is combined with existing data for Mist Mountain coals the combined numeric average is about 1.6 ppm. This compares to a world average of 2.15 ppm (Coleman *et al.,* 1993). There are no

TABLE 7
AVERAGE SE CONCENTRATIONS AND PERCENTAGES OF MAJOR ROCK TYPES SEGREGATED BY MINING

		Mine A		Mine B		Mine C		Mine D		Mine E		Average	
	unit	ppm Se	% of total Se	ppm Se	% of total Se	ppm Se	% of total Se	ppm Se	total	ppm Se	% of total Se	ppm Se	% of total Se
section 1	coal	1.7	6.3	2.0	20.8	0.7	13.2	1.5	25.9	2.1	10.1	1.9	13.6
	contact	3.5	6.7	2.0	9.2	2.9	5.0	1.2	2.0	3.2	4.7	2.8	5.3
	interburden	2.2	87.0	1.0	70.0	2.2	81.7	1.1	72.0	1.3	85.2	1.8	81.1
section 2	coal					2.4	6.9			2.5	12.2		
	contact					3.1	3.9			3.4	5.4		
	interburden					2.9	89.2			1.8	82.5		
	refuse	3.2		2.7		1.6		1.8		2.9		2.4	

note mine C has sections CN and CE and mine E has sections EE and EW

major variations in the average Se content of coals from the 5 mines. At two mines incremental samples were taken though seams (Figure 14).

At one mine, Se and ash concentrations increase in the HW and FW parts of the seam (mine E) and the major control on Se concentrations is ash and not organic S. In the other seam from mine A, Se concentrations are high in the 2 partings and variable through the rest of the seam.

In Mist Mountain coals, which have low concentrations of pyrite, most of the Se is associated with ash rather than pyrite or coal. In general the Se *versus* ash correlations are moderate to poor. However in a number of plots (Figure 13) the Se concentrations in zero ash coal vary from 0.3 to 1.9 ppm and at 85% ash (100% mineral matter) from 1.8 to 9.1 ppm. The projected Se content of ash free coals in this study is higher for coals higher in the section than lower in the section (1.9 ppm compared to 0.4 ppm, Figure 13). This is probably because seams higher in the section tend to contain more vitrinite, which is host for more organic S and therefore probably more Se. The projected Se concentrations of 85% ash (4.9 and 3.8 ppm, Figure 13) are similar to the HW and FW material averages of about 4 ppm (Table 6). In coal seams, which average about 2 ppm Se (Table 6) and 23% ash, It appears that about half the Se is contained in the coal and half is associated with the ash. The Se concentration is reduced to the range 1 to 1.5 ppm in washed coals with about 10% ash (Table 6, Figure 13).

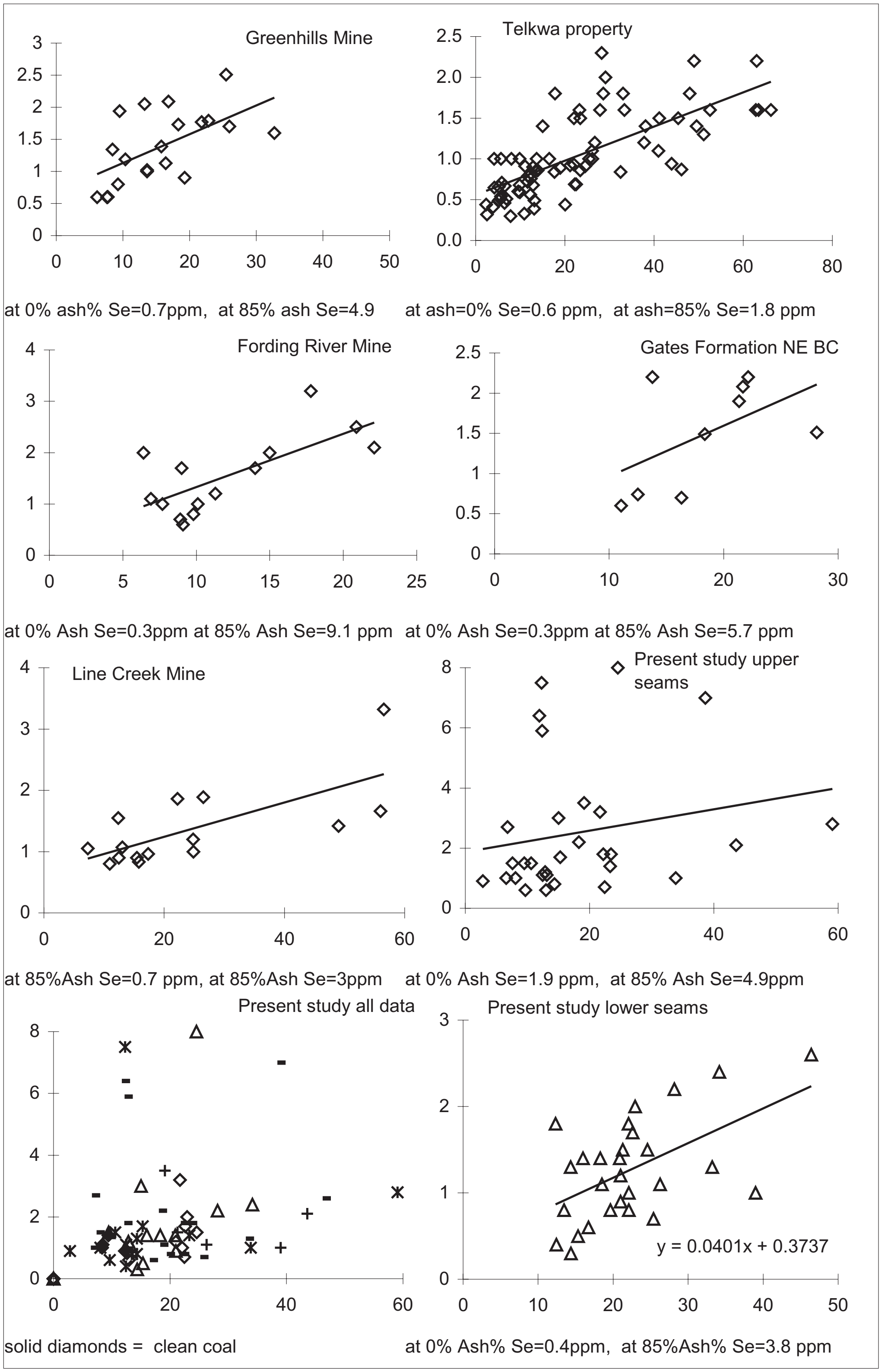
Selenium is similar to sulphur in terms of its chemical properties and one would expect an association of Se with pyrite or organic sulphur in the coal. In Mist Mountain coals the concentration of Se in pyrite appears to be low (about 10 ppm in massive pyrite, Table 6) and seams contain very little pyrite. Therefore Se in pyrite can not contribute much to the total Se concentration in samples. The concentration of Se in ash is higher than in ash-free coal, which makes it difficult to see if there is a relationship between Se and organic S in ash-free coal. To document a Se *versus* organic S relationship all the available samples for which Se, ash and organic S analyses were available were sorted based on ash content. Se *versus* organic S plots were then constructed for samples with limited ranges of ash contents (Figure 15).

In all cases Se correlates weakly with organic S though in higher ash ranges the Se/organic S ratio increases indicating introduction of Se but not organic S.

A number of washability experiments were performed to further investigate the relationship of Se to total, pyritic S, organic S and ash. The data (Figure 16) indicate a positive correlation of Se to ash in Mines A and D, with the pure ash (mineral matter) containing over 7 ppm and 2 ppm Se in ash from mines A and D. In mine C, Selenium concentrations do not increase systematically as ash increases, possibly because of changing maceral composition in the float fractions. Washability data confirms that Se concentrations are reduced in washed coal. Total S concentrations decrease as ash concentrations increase and the pyritic S component is small in all samples except for high ash samples from Mine C.

A maceral influence on Se contents in coal has been hinted at above. At present no data-bases of petrography and Se concentration on the same samples could be located. However average petrography does exist for seams from the various mines and when this is compared to the Se concentrations for the same numbered seams at each mine rough trends are apparent. Se concentrations tend to increase as the reactive maceral contents increase (Figure 17).

A probably explanation for this derives from the origin of inert macerals, which are formed by various degrees of charring of vegetation in the coal swamp (Lamberson *et al.,* 1996). This probably volatilizes some if not most of the Se from the vegetation before it forms inert coal macerals. Sulphur is less susceptible to volatilization and therefore inert macerals probably have lower Se/S ratios than reactive macerals. The Se and organic S are enriched in vitrinite macerals compared to the inert macerals (Demir and Harvey, 1991) and especially in the liptinite macerals, which are usually a minor constituent of coal. This explanation is supported by some washability data. It has been documented a number of



at 0% ash% Se=0.7ppm, at 85% ash Se=4.9

at ash=0% Se=0.6 ppm, at ash=85% Se=1.8 ppm

at 0% Ash Se=0.3ppm at 85% Ash Se=9.1 ppm

at 0% Ash Se=0.3ppm at 85% Ash Se=5.7 ppm

at 85%Ash Se=0.7 ppm, at 85%Ash Se=3ppm

at 0% Ash Se=1.9 ppm, at 85% Ash Se=4.9ppm

solid diamonds = clean coal

at 0% Ash% Se=0.4ppm, at 85%Ash% Se=3.8 ppm

Figure 13. Ash *versus* Se plots for coal samples from a number of mines and properties data from this study, unpublished Geological Survey reports, Grieve and Goodarzi (1994) and Goodarzi (1988).

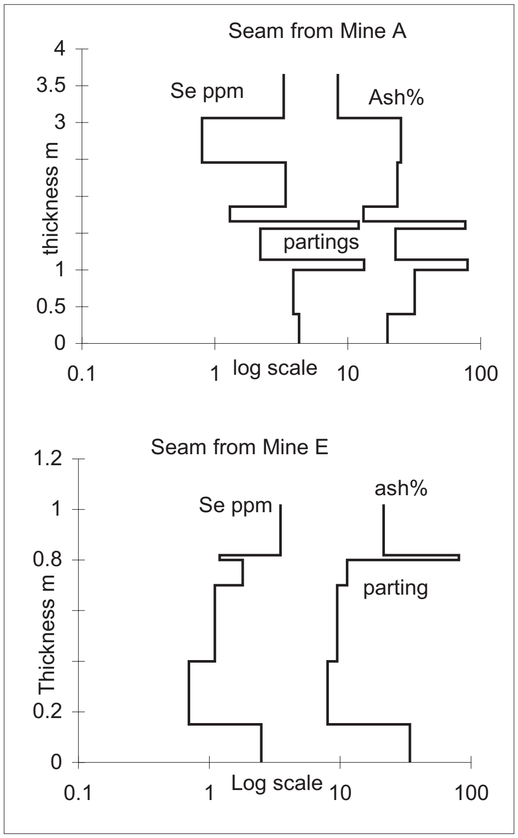


Figure 14. Se concentrations of incremental samples through 2 seams, Mines A and E.

times, that in float-sink data, reactive macerals (vitrinite) concentrate in the low SG fractions and inert macerals in the intermediate SG fractions (Ryan *et al.*, 1999). This means that Se contents should decrease in intermediate SG fractions and the organic Se/S ratio decrease. These trends are seen in some of the data from Harvey *et al.* (1983) (Figure 18).

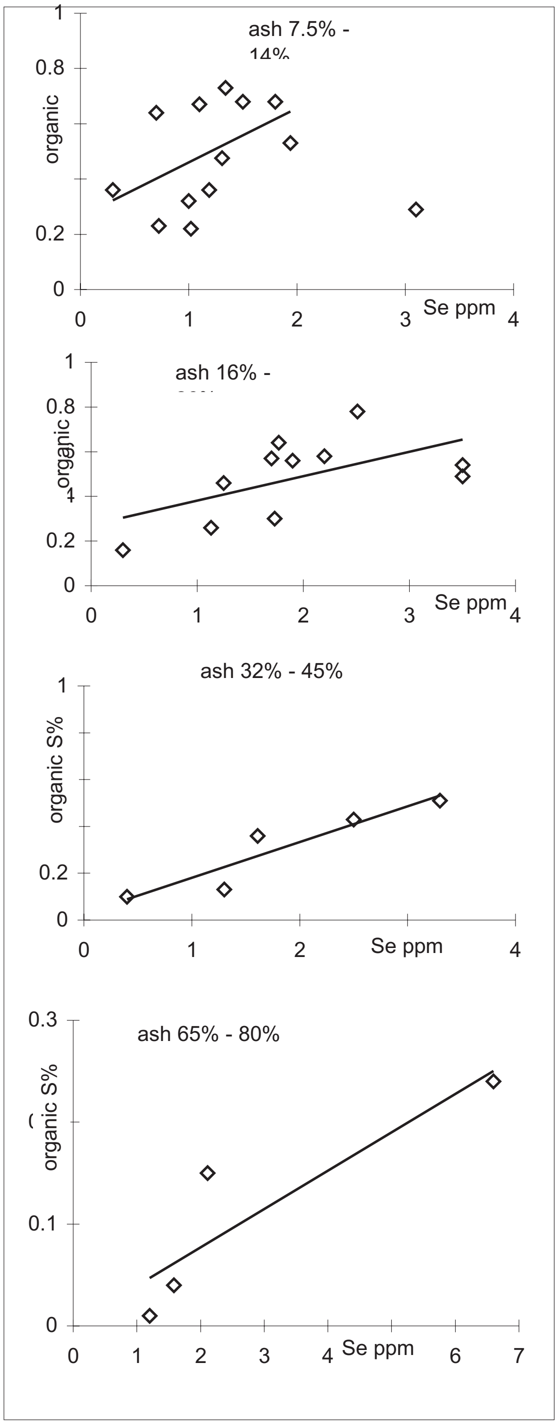


Figure 15. Se *versus* organic sulphur concentrations for all the data from this study, grouped in ash brackets.

Selenium in coal seams in the Mist Mountain Formation comes from three major sources. A component that comes from the original vegetation and components introduced into the coal swamp either in solution or with detritus. The component from vegetation will be decreased by an amount based on the amount of charring by forest fires as indicated by the amount inert macerals in the coal. There should therefore be maceral control on the amount of vegetation derived Se. The externally sourced Se, which is introduced in solution, once in the swamp may bond with the detritus (ash) or substitute for S, which, based on the Eh pH environment, may form authogenic pyrite or organic S in the coal. The pyrite forms in low pH Eh swamp environments if excess S is available and may be associated with the ash or coal. The Se substituting for organic S is probably incorporated mainly into the rotting vegetation as Se^{-2} after reaction of H_2Se with the vegetation (Finkelman *et al.,* 1990). This material will evolve during coalification into the reactive macerals. The Se introduced with the detritus may be fixed in one of four ways; as elemental Se, as selinides, adsorbed onto clays as Se^{+4} or be bonded to iron hydroxides. Balistrieri and Chao (1987) have demonstrated that selinite is adsorbed by goethite. All of these ash associa-

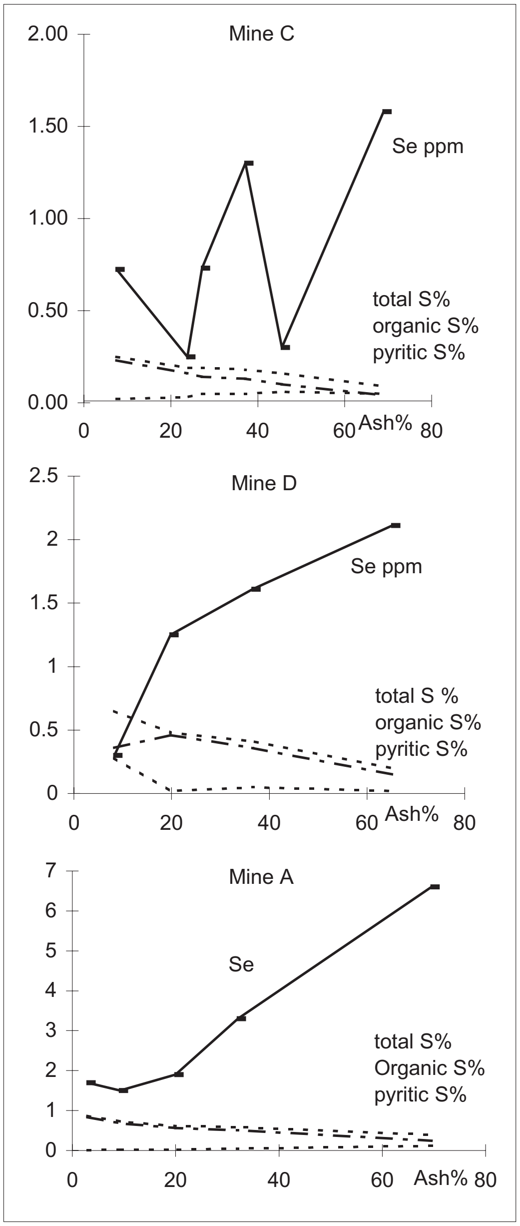


Figure 16. Se wash dta for coal samples from mines C, D and E.

tions with the exception of a pyrite association probably produce high Se/S ratios.

The Se that is introduced with the detritus probably remains fixed in the detritus. The fact that total Se tends to correlate with ash does not necessarily indicate that major source of Se is detritus because some Se introduced in solution may be added to the detritus. It appears that for Mist Mountain coals Se content will depend largely on ash content with an underlying maceral control, but correlations can not be expected to be good.

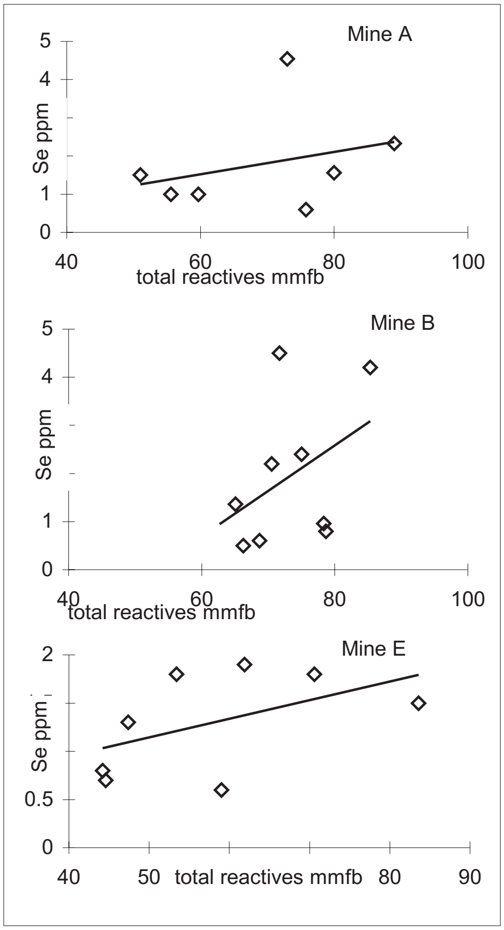


Figure 17. Average total reactives for seams from mines A, B and E *versus* Se content (mmfb, mineral matter free basis).

The Se that is volatilized by forest fires from the precursor of inert macerals is not lost to the system. Based on studies in power plants (Clarke and Sloss, 1992), Se is moderately to highly volatile during combustion but precipitates onto fine fly ash as the temperature falls. In a forest fire situation one can expect Se to condense onto fine ash particles that will be carried by the wind, eventually falling to earth possibly in rain drops. This Se may add to the Se already entering the coal swamp in solution or with fine detritus and consequently seams with high inert maceral contents may not always have lower Se contents, the Se may simply be redistributed with more occurring in the ash.

In order to investigate more closely the partitioning of Se between ash and coal in HW and FW samples, a number of samples were floated at 1.6 SG to produce low ash float and high ash sink samples (Table 8).

The Se and ash concentrations and yield were measured for the float and sink samples. The data confirm that Se is concentrated in the ash component of the HW and FW samples. In fact its concentration in coal ash and HW and FW material is greater than its concentration in

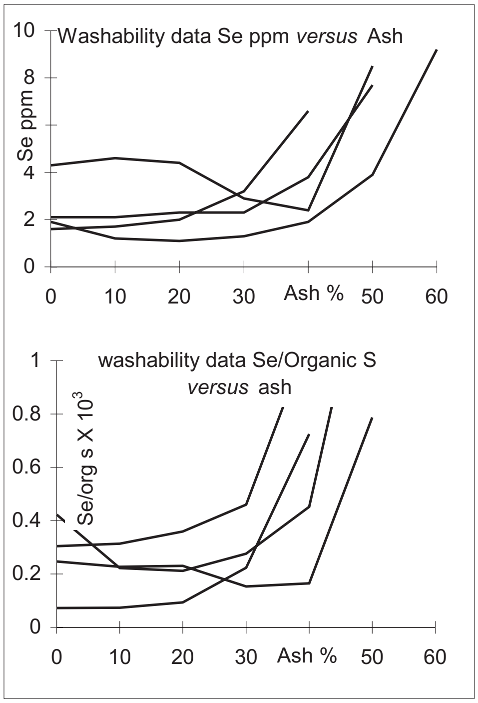


Figure 18. Se/organic S ratios *versus* ash for various SG splits, data from Harvey *et al*. (1983).

TABLE 8
FLOAT SINK DATA FOR HW AND FW SAMPLES

	raw		sink			float			
sample 99	ash %	Se M	wt > 1.6	ash %	Se M	wt<1.6	ash %	Se M	Se lost C
A-12	69.8	8.00	99.4	70.1	5.80	0.6	25.9		
A-15	55.6	4.60	66.5	75.7	3.40	33.5	15.5	2.50	1.50
B-34	56.7	4.40	70.2	72.0	3.60	29.8	20.8	2.20	1.22
B-23	22.6	4.10	22.2	59.5	2.30	77.8	12.1	3.10	1.18
B-16	72.7	5.80	84.3	83.1	3.70	15.7	16.6	2.90	2.23
B-12	64.2	4.70	79.7	74.4	4.00	20.3	24.1		
E-17	58.5	5.30	70.6	76.1	4.40	29.4	16.1		
E-45	78.4	7.10	95.2	80.6	6.20	4.8	34.2		

M = measured C = calculated

mudstone. It also appears that the chlorine based heavy liquid used to separate the samples has leached Se from the samples and this is discussed later.

SEDIMENT SAMPLES

TABLE 9
TOTAL ORGANIC CARBON (TOC) AND SE DATA FOR SEDIMENT SETTLING POND SAMPLES

SAMPLE	TOC %	Se ppm	As ppm
A99-86	2.3	1.1	5.4
A99-92	<.01	5.4	
A99-93	1.76	4.4	
B99-70	0.11	12.8	
B99-71	<.01	7.8	
B99-73	<.01	2.4	
C99-90	<.01	3.8	
C99-94	1.69	1.7	6.6
D99-31	<.01	1.6	7.9
E99-77	<.01	1.4	5.8
E99-78	<.01	3	7
E99-79	<.01	1.7	
E99-81	4.91	1	3.8
E99-82	0.92	2.4	

Twenty nine sediment samples were collected from settling ponds at the five mines. Samples of fine sediment were collected from as close to the inflow as possible. The quality of the samples varied considerably. At some sites samples were covered with algae and at others there was very little fine material. Samples were dried and the minus 100 mesh fraction recovered. Selenium and oxide analyses were performed on all sediment samples and total organic carbon (TOC) analyses on 14. The average Se content is 3 ppm but there is a wide spread of values and the average is influenced by 2 very high values. The Se concentrations of the sediment samples are in the range and a bit higher than that which would be expected based on the average values for mudstones and silty mudstones in the interburden (2-2.8 ppm). There is therefore no strong evidence that fine sediments washing out of the waste dumps are taking up or losing Se. McDonald and Strosher (1998) report finding no relationship between TOC and Se content in sediments. Despite a lot of the samples in this study having TOC values below detection limit (0.01%) there also appears to be no correlation of Se and TOC values (Table 9).

Selenium does not correlate with Fe_2O_3 so there is no evidence of Se being taken up by iron hydroxides in the sediments (Table 10).

There is however a weak correlation with Mn indicating the possible presence of a secondary Mn mineral that is taking up Se.

SOURCE OF AND PARTITIONING OF SELENIUM IN COAL SWAMPS

A discussion of how Se is fixed in coal swamps requires a basic understanding of the geochemistry of a swamp environment. Bass-Becking *et al*. (1960) outlined fields on an Eh *versus* pH diagram of naturally occurring environments, shallow marine rocks and for coal formation (Figure 19).

Herring (1990) used a similar diagram to outlined fields of stability for the various Se ions and this information is included in Figure 19. Within the field of naturally occurring Eh and pH conditions Se can occur as Se^{-2} , Se^0, Se^{+4} and Se^{+6}. Selenium in a coal swamp environment is more likely to be fixed as a selinide (Se^{-2}) or elemental Se (Se^0), where as in a shallow water marine or terrestrial environment Se is more likely to be fixed as selinite

TABLE 10
CORRELATION FACTORS FOR SE *VERSUS* OXIDES FOR VARIOUS ROCK TYPES

Samples	COAL 11	HW+FW 5	MUDSTONES 7	PARTINGS 4	REFUSE 6	SEDIMENTS 26
Ash%	**0.70**	0.36		-0.56	0.29	-0.08
SiO2	**0.66**	**0.54**	-0.06	-0.21	0.28	-0.17
TiO2	**0.70**	-0.10	0.00	-0.55	-0.49	0.04
Al2O3	**0.64**	-0.10	0.00	-0.55	-0.05	-0.01
Fe2O3	0.41	0.31	-0.33	0.21	**0.91**	-0.16
MnO	0.34	0.36	-0.56	0.02	0.43	**0.52**
MgO	**0.75**	0.06	-0.25	**0.77**	**0.76**	-0.30
CaO	**0.64**	0.07	-0.26	0.09	-0.52	0.20
Na2O	0.44	-0.37		**0.82**	-0.67	-0.17
K2O	**0.67**	-0.03	0.01	-0.60	**0.80**	0.08
P2O5	0.36	**0.61**	0.14	-0.10	**0.91**	0.10
Ba(4)	0.48	0.20	-0.02	-0.05	0.14	0.30

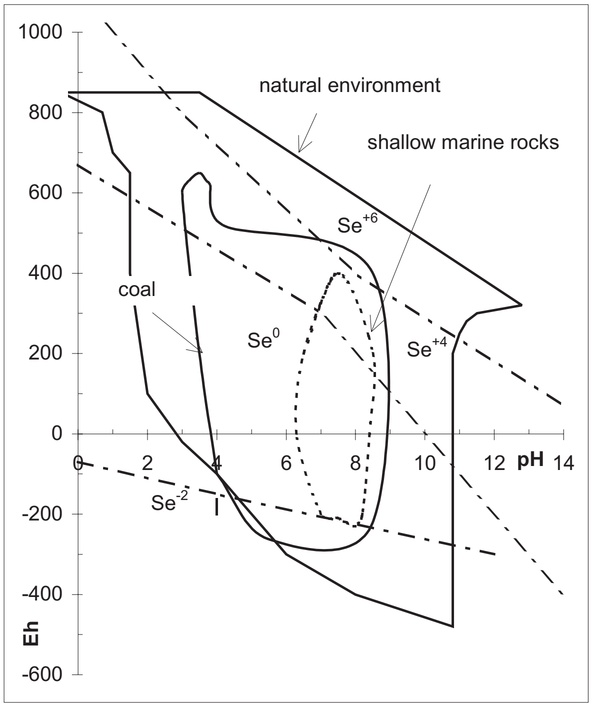


Figure 19. Viable Eh *versus* pH environments for coal, shallow marine rocks and selenium ions, data from Bass-Becking *et al*. (1960) and Herring (1990).

(Se^{+4}) or selenate (Se^{+6}). The shallow marine environment of Bass-Becking is probably similar to the shallow water terrestrial environment in which the interburden mudstones sampled in this study were deposited.

The partitioning of Se in coal seams in terms of source and present location has been discussed above. The concentration of Se in the fine detritus that enters the swamp, either water or air borne, is probably similar to the Se concentration of the mudstones i.e. in the 2 ppm range (Table 6). The Se concentration of the coal-ash and HW plus FW material is higher than that of mudstones averaging about 4 ppm with a wide range (Table 6 and Figure 13). The difference, 4 ppm minus 2 ppm times the ash content is probably a minimum estimate of the Se introduced into the coal swamp in solution in water. It is a minimum estimate because it does not take into account Se introduced in solution that is later fixed in the coal. For a coal seam with 25% ash and approximately 2 ppm Se, about half the Se is in the coal and half in the ash. Half of the Se in the ash was originally in solution and half was introduced with the detritus. The Se that was in solution and is now associated with the ash is more likely to form selinides or elemental Se in the seam, whereas the Se introduced with the detritus probably remains adsorbed onto the clays. Some of the Se introduced in solution will probably substitute for organic S in the reactive coal macerals to join the Se derived from the original vegetation. A small proportion of Se may be incorporated into pyrite.

Support for the suggestion that a substantial amount of the Se in coal seams was introduced in solution into the coal swamp comes from the correlation of Se with U seen in many East Kootenay coals (Figure 20).

The correlation probably indicates a common mode of introduction. Uranium like Se is soluble in alkaline high Eh environments and is probably introduced into the coal swamp in surface or ground water as complex alkali uranyl carbonates (Breger, 1974). It is insoluble once reduced in low pH-Eh coal swamp environments and will be extracted from water probably as uranyl-organic complexes (Swaine, 1990). Some Se is also introduced in this way being transported to the coal swamps in surface and ground waters with high pH and alkalinity that aid mobilization of Se. The Se *versus* U relationships vary between the different coal suites and for the mudstone and for HW+FW rock suites probably indicating a common mode of introduction but different host sites within the coal seams and rocks.

Selenium concentrations in surface water can range from below 1 ppb to 1 ppm depending on pH. Based on the low concentrations of Se in water and apparently moderately large proportion that it contributes to the 2 ppm Se in coal seams, a large volume of water is required to import the Se found in a coal seams. As an example, if the Se concentration of material in a coal swamp is to be increased by 1 ppm, by extracting Se from pore water with a concentration of 10 ppb, then there have to be 100 exchanges of pore water based on a 50% porosity. Obviously there has to be a continuous source of Se in ground and surface water. This implies moderate levels of Se in bed rocks in the region and a climate, which favours the ability of water to transport Se.

There is some evidence that a minor component of the Se in Mist Mountain coals may be contained in pyrite. Goodarzi (1987) studied samples of fresh and weathered coal. A plot of Se *versus* ash indicates that 3 of the 4

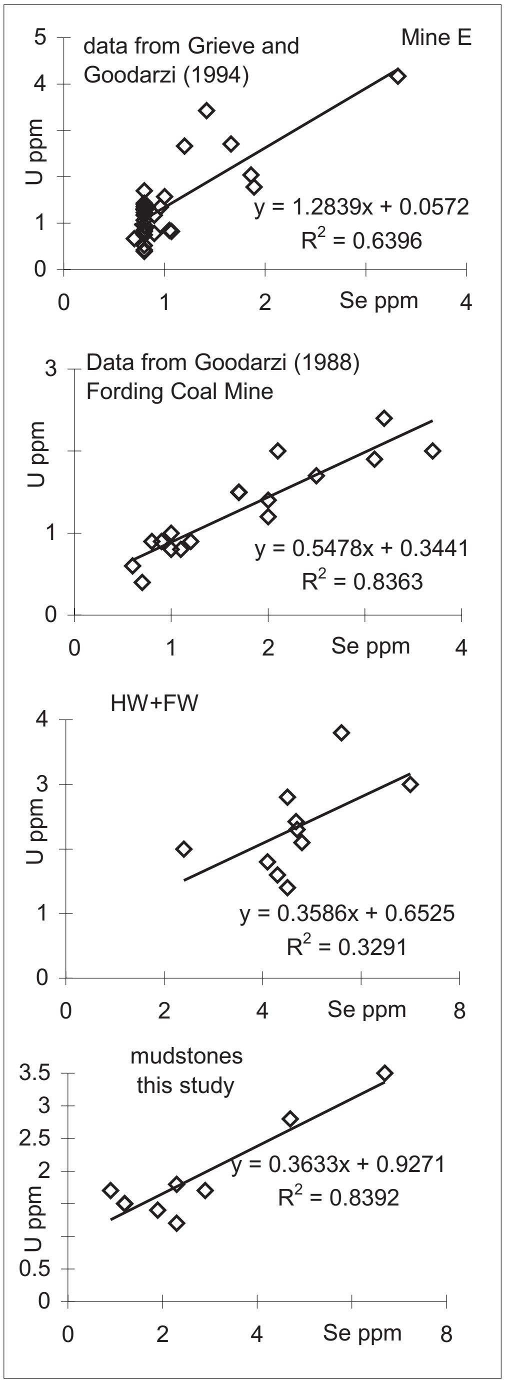


Figure 20. Se *versus* U concentrations in East Kootenay coals and rocks, data from this study, Grieve and Goodarzi (194) and Goodarzi (1988).

weathered samples may have lost Se and that the average amount of Se lost from all four samples is about 0.5 ppm. The Se/S ratio increases for the four weathered samples implying that S is more easily lost by weathering than the Se. This is consistent with the removal, from the weathered samples, of small quantities of pyrite, which have the lowest Se/S ratios of any phase in the sample (Table 6). Pyrite is susceptible to oxidation, which will release Se and S in soluble form. Mist Mountain coals generally contain low concentrations of pyrite and release of Se will depend on how easily it is removed from ash and coal.

DETAILED ASSOCIATION OF SELENIUM IN COAL AND ASSOCIATED SEDIMENTS

Four possible associations of Se in coal and associated sediments are considered these are:

- adsorption onto clay minerals in coal mineral matter and associated HW and FW mudstones. trace
- selinides such as clausthalite associated with the mineral matter.
- substitution for organic sulphur in reactive coal macerals.
- substitution for S in sulphides (mainly pyrite)

The Al_2O_3/SiO_2 ratio is a good indicator of clay content of a rock and therefore a correlation between Se contents with Al_2O_3/SiO_2 ratios may indicate that Se is adsorbed onto clays. Similarly a relationship between Se and trace metal contents may also indicate adsorption or an association with trace sulphides. These relationships can help in indicating how the Se is fixed in the various rock types, which include the coal and coal-ash fractions in coal seams; HW, FW and parting material and interburden lithologies.

Much of the Se in the coal fraction is probably substituting for organic S in the reactive macerals. As shown Se correlates with organic S and reactive coal macerals (Figures 15 and 17). The Se/S ratios for coal samples (Figure 21) are about 0.2 to 0.4 x 10^{-3} , which are much higher than the ratios for pyrite (about 0.02 x 10^{-3}) and probably characteristic of the ratio of Se/S in reactive macerals.

The coal probably formed in a low pH and Eh environment (Figure 19), which would also encourage the substitution of Se^{-2} for organic S in the coal fraction of the samples. Ren *et al.* (1999) suggest that high concentrations of chalcophile elements (including Se) are found in coals formed in low Eh environments favouring the growth of algae, which may contain high concentrations of S and Se.

In coal seams about half of the Se is associated with the ash. Total Se concentrations correlate with Cu, Zn and other metals but not Fe in the ash (Tables 9 and 10) indicating in part a common association of trace metals and Se, probably in the ash component of the samples. Coal samples generally have the high Al_2O_3/SiO_2 ratios, some samples approaching the ratio for kaolinite (0.847) (Figure 22) indicating that the included ash is almost exclusively clay.

There is a weak negative correlation of Se with the Al_2O_3/SiO_2 ratio, indicating that as more detritus with lower Al_2O_3/SiO_2 ratios is introduced the Se content increases. This combined with the trace metal association indicates that some of the Se associated with coal-ash may occur as trace selinides such as clausthalite (PbSe) or

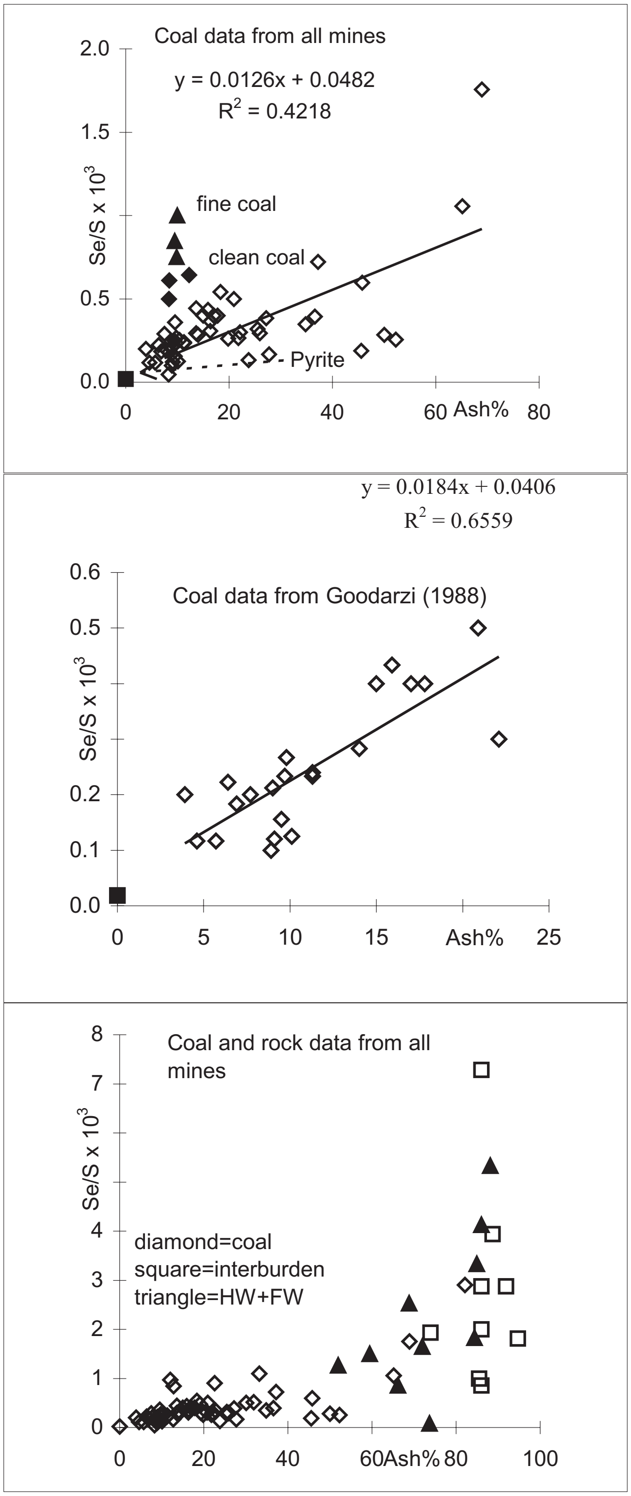


Figure 21. Se/S ratios *versus* ash contents for samples from this study.

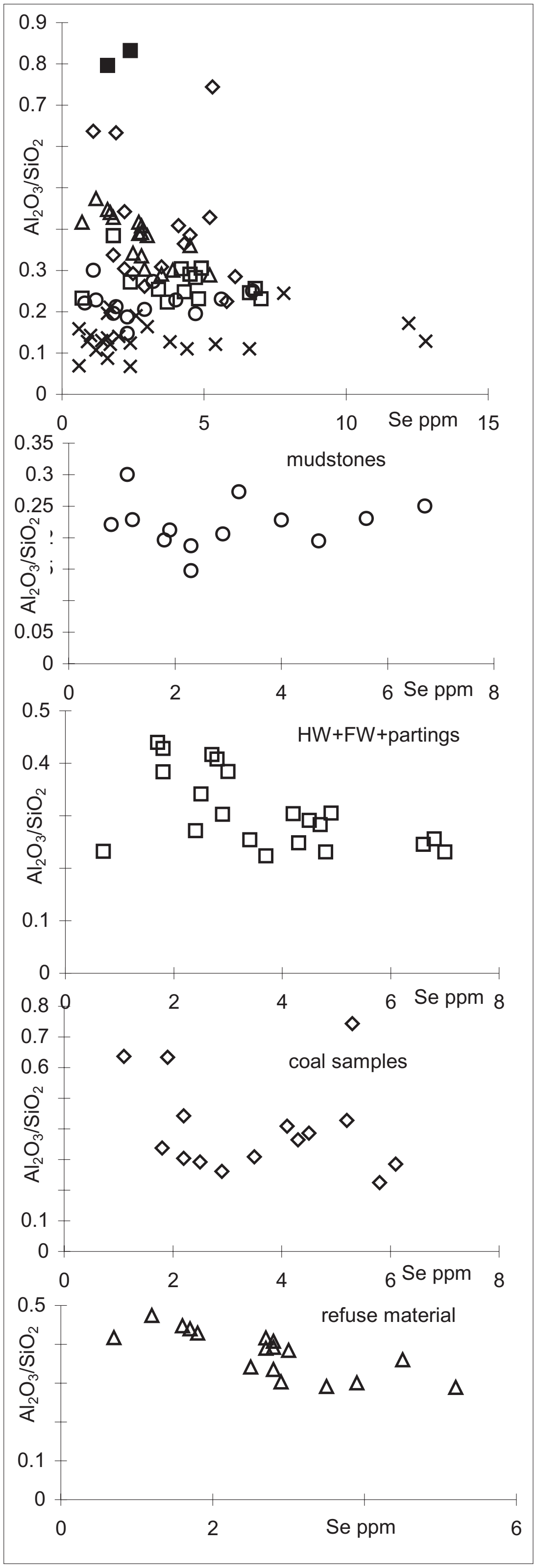


Figure 22. Plot of Al_2O_3/SiO_2 ratios *versus* Se contents of rocks; data from this study; cross = sediments, circle = mudstone, triangle = refuse, square = HW, FW & partings, diamond = coal, solid square = tonsteins.

ferrosilite ($FeSe_2$) or elemental selenium. Some Se is also probably adsorbed on clays because that was how it was introduced into the coal swamp. The lack of a good correlation between Al_2O_3/SiO_2 ratio and Se (Figure 22) indicates that in the coal ash, adsorption onto clays is not the major mode of occurrence. The Se/S ratio increases as the ash and Se contents increase indicating that Se is not associated with sulphides in the ash (Figure 21).

Mudrocks in the interburden probably formed in an environment characterized by higher Eh and pH values than the environment in which coal, coal-ash and HW+FW material were deposited (Figure 19). They were probably deposited in shallow marine or terrestrial environments in which Se would be stable as Se^{+4} or Se^{+6}. In these environments a higher proportion of the Se may be adsorbed onto clays such as montmorillonite or kaolinte and in fact based on limited number of mudstone samples, there is a tendency for the Se to increase as the Al_2O_3/SiO_2 ratio increases (Figure 22). Se in the mudstones has the strongest correlation with trace metals (Table 11), probably because these metals are also adsorbed onto clays.

It has been reported (Balistrieri and Chao, 1987; Hayes *et al.,* 1987) that selinite ions can be bonded directly onto goethite surfaces however in this study there is a negative correlation of Fe to Se in mudstones (Table 10). Based on limited data the average S contents of the mudstones is 0.08%.

The Se/S ratios for HW and FW material are generally higher than those for coal seams and they increase as ash contents increase (Figure 21) ruling out a sulphide association for the Se in this material. On a Al_2O_3/SiO_2 ratio *versus* Se plot (Figure 22) HW and FW material have lower Al_2O_3/SiO_2 ratios than coal ash and there is a negative correlation of Se with the Al_2O_3/SiO_2 ratio, indicating that not all the Se is associated with clay minerals.

TABLE 11
CORRELATION FACTORS FOR SE *VERSUS* TRACE METALS FOR VARIOUS ROCK TYPES

	HW+FW	mdst	Coal
No Samples	15	15	23
element	Se INAA	Se INAA	Se
Se ICP-MS	1	1	
Fe	0.43	-0.68	-0.03
Pb	0.58	0.93	
Cu	0.49	0.91	0.60
Zn	0.65	0.89	0.56
U	0.73	0.94	0.93
Co	0.40	0.60	0.37
Cr	-0.72	-0.65	0.70
Mn	-0.15	-0.76	-0.03
Ni	0.66	0.93	
Ag	0.48	0.93	
As	0.29	0.31	0.30
Au	-0.33	-0.38	
Hg	0.19	0.90	
Bi	0.55	0.79	
Mo	0.41	0.95	0.49

Coal data from Goodarzi (1988)

Also there is no correlation of $Fe_2O_3$with Se (Table 10) making an iron hydroxide association unlikely. It therefore appears that, in HW and FW material, a reasonable amount of the Se occurs in selinides or as elemental selenium The Se does correlate with a number of trace metals in HW and FW material (Table 11). The S content of the HW and FW material is 0.8% based on limited data.

Two tonsteins samples have high Al_2O_3/SiO_2 ratios but relatively low Se contents supporting the suggestion that adsorption of Se onto clays in the coal swamp environment is probably not the preferred mode of occurrence for Se in coal ash and HW and FW material.

The Se contents in sandstones and siltstones are generally low and often below detection limit. No trace metal or oxide data are available for these rocks. The higher As concentrations in these samples (Table 6) probably indicates the presence of trace amounts of arsenopyrite. There is a weak negative correlation of As to Se so it does not appear that arsenopyrite is the host for Se. The minus 100 mesh sediment samples have lower Al_2O_3/SiO_2 ratios than the mudstones and the ratios do not correlate with Se content (Figure 22).

In summary there is limited evidence to suggest that Se has four major modes of occurrence controlled by depositional environments. In the low pH-Eh environment of the coal swamp Se either substitutes for organic S in the reactive coal macerals or forms selinides or metallic Se associated with the coal ash. Some of the Se in this environment is introduced adsorbed on clays and probably remains adsorbed. The environment, in which HW, FW and parting material were deposited, may have been characterized by higher pH and Eh values than the environment in which coal was deposited, but there is still evidence that the Se occurs as selinides or metallic Se with probably some adsorbed onto the clays as Se^{+4}. Mudstones adjacent to coal seams probably formed in shallow water near shore or terrestrial environments characterized by neutral pH and high Eh values. In these rocks Se correlates with a number of trace metals (Table 11) and weakly with Al_2O_3/SiO_2 ratios and more of the Se may be adsorbed onto clays as Se^{+4} or Se^{+6} .

REMOVAL OF SELENIUM FROM COAL AND ASSOCIATED ROCKS

The ease with which Se may be removed from rocks during mining probably relates to the way it is bound in the rocks. Se substituting for organic S in coals is probably not easily removed. This Se accounts for about a third to half the Se in the coal and it is bound in the reactive macerals. An indication of this is the fact that the clean coal samples after crushing and washing do not indicate any loss of Se compared to the raw coal samples based on their ash content (Figure 13). The selinide and elemental Se components in the coal ash and HW plus FW material may be more easily removed. This might be indicated by the higher Se concentrations of HW and FW material compared to the concentrations for refuse material (Table 7). Also float sink data on HW and FW samples (Table 11) appear to indicate that the chlorine based heavy liquid used for the separation was removing Se from the high ash component. In every case the calculated Se content of the raw sample calculated using data from the float and sink samples is less than the measured Se content of the raw samples. In that the Se content of the float samples is similar to the average Se content of coals and the Se content of the sink samples is less than the average content of HW and FW samples, it appears that the Se is being removed from the ash component of the samples. In fact the amount of Se lost correlates with the ash content of the raw samples (Table 8) and at 30% ash is about 1 ppm increasing to about 2 ppm at 85% ash.

Se adsorbed onto clays in the mudstone units may be fairly immobile in the mine environment. Small grains of Se bearing sulphides in sandstones may oxidize easily if exposed, but the large fragment size of the rock after blasting will limit the number of grains exposed.

Se can be volatile if samples are heated. In coal wash plants, ash is removed using water based processes after which coal is partially dried. This can heat the fine coal to a high temperature for a short time. To see if Se is volatilized in the thermal dryer in the plant, fine coal samples before and after the dryer were analyzed for Se. The minus 100 mesh feed and dried coal both had Se concentrations in the range 1 to 1.4 ppm and there is no evidence of substantial amounts of Se being volatilized in the dryer (Figure 21).

Sometimes coal seams catch on fire probably ignited by lightning. The coal burns and bakes the surrounding rock producing clinker and rocks with various hues of orange and red. As an interesting aside samples of baked rock were analyzed for Se. The original material would probably have been HW or FW mudstone with Se concentrations in the 4 ppm range. The burnt rock had concentrations ranging from less than 0.4 ppm to 1 ppm indicating substantial volatilization of Se. The Se may be lost into the air or condense onto cooler rocks probably as a soluble compound.

ARSENIC IN COAL AND INTERBURDEN ROCKS

Arsenic was analyzed in a number of rock types. It is usually considered to be associated with sulphides in coal or rock. Its concentration is lowest in raw coal at 2.4 ppm. Swaine (1990) states that As ranges from 0.5 ppm to 80 ppm for most coals with averages of 1.5 ppm for Australian, 4 ppm for South African, 14 ppm for United States and 15 ppm for United Kingdom coals. The concentration increases in interburden rocks to a high of about 10 ppm in muddy siltstones and sandstones probably because of trace amounts of dispersed pyrite and arsenopyrite in the rocks. There is no trend of increasing As with increasing Se for any of the rock types (Figure 23).

CONCLUSIONS

Coals in the Mist Mountain Formation have world average levels of Se. Interburden rocks in the formation tend to have higher Se contents than rocks of similar lithology in other formations that do not contain coal. No lithologies were identified that consistently contained high concentrations of Se. Within the section, Se is concentrated in HW, FW and parting material associated with coal seams and the coal seams. Concentrations in interburden rocks are lower and depend on the mudstone content. In an average mining section, from 70% to 87% of the Se is in interburden rocks, 6% to 25% in coal and 4% to 7% in the material adjacent to the coal seams (contact material).

The low pH-Eh coal swamp environment is ideal for accumulating Se and much of the Se found in coal probably originates from outside the coal swamp and not from the original vegetation. This externally sourced Se enters the coal swamp in solution or adsorbed onto fine detritus. The coal swamp environment is a sink for Se. Se entering

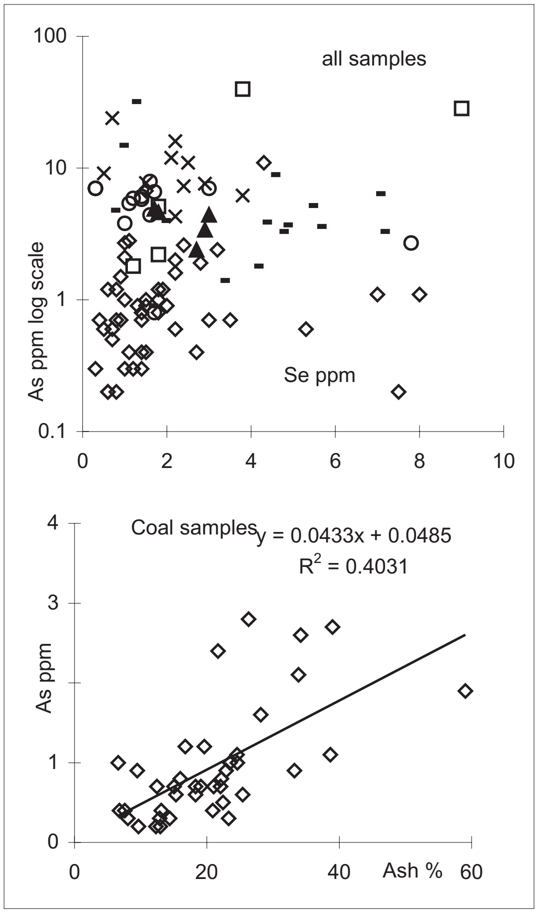


Figure 23. Plot of Se *versus* As for all rock types; data from this study; diamond=coal, dash= HW and FW, triangle = refuse, Square=partings, cross=interburden rocks, circle=sediment.

the coal swamp in solution substitutes for organic S in the reactive macerals in coal or forms selinides or metallic Se associated with the coal ash and HW and FW rock. About half of the Se in the coal is associated with the ash and about half of this may occur as selinides or as metallic Se. This Se may be easy to remove once the coal and associated rocks are brought to surface and crushed.

Compared to the coal swamp environment Se is not as concentrated in the higher Eh and pH environments associated with deposition of interburden mudstones. In these rocks the Se is probably adsorbed onto clay minerals as Se^{+4} and may be less easily removed than Se in coal, HW or FW rocks. Siltstones and sandstones have low Se concentrations and the Se is probably contained in small amounts of mudstone and pyrite. This Se could be easily released after oxidation of the sulphides, but the sulphide grains are contained in large blocks of rock which isolate them from the surface environment and consequently they either do not oxidize or they oxidize slowly.

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