

## SOME ASPECTS OF BASIC GEOCHEMISTRY IN COAL SCIENCE

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### ABSTRACT

Several instances of the use of basic geochemistry in coal science are given, using Australian bituminous coals as examples. The mode of occurrence of manganese is related to associations with siderite and calcite, the reason being cation replacement. High concentrations of boron, arsenic, phosphorus and other elements in deposits found in some boilers were due to the presence of boron phosphate and boron arsenate, two compounds that have not been found in nature. The proportions of soil/rock and flyash particles in atmospheric particulates deposited near a power station have been estimated by using the marked differences in germanium concentrations.

### INTRODUCTION

In his pioneering geochemical research, V.M. Goldschmidt studied trace elements in coal. Several elements were discovered and determined in coal by Goldschmidt and coworkers in Gottingen during the 1930s (1). The basic principles enunciated by Goldschmidt are applicable to coal geochemistry. Much of the early trace-element studies depended on the development of sensitive analytical methods, mainly in optical emission spectroscopy. Some examples of the applications of Goldschmidt's work will be outlined based on experimental work on Australian coal carried out at the CSIRO, North Ryde.

### MANGANESE IN BITUMINOUS COAL

As with other trace elements in coal, manganese can be found associated with the organic and with the inorganic matter. In most bituminous coals manganese occurs predominantly in the mineral matter fraction. In Australian bituminous coals from the Sydney Basin, New South Wales and from the Bowen Basin, Queensland, it was found that there was a marked concentration of manganese in siderite and in calcite (Table 1). On the basis of ionic radii (1)  $Mn^{2+}$  is expected to be able to substitute for some of the  $Fe^{2+}$  in siderite. Although the difference in ionic radius between  $Mn^{2+}$  and  $Ca^{2+}$  is greater than that for  $Mn^{2+}$  and  $Fe^{2+}$ , substitution can still occur in calcite. These results were used initially to propose that manganese occurs in Australian bituminous coals mainly in siderite and calcite components of the mineral matter. Direct evidence for the replacement of some  $Ca^{2+}$  ions by  $Mn^{2+}$  ions in calcite from a Pittsburgh coal was found by an electron paramagnetic resonance method (2). There is indirect evidence for the close association of manganese and 'carbonate' iron (that is, total iron less pyritic iron) from data for 56 samples of coal from the Lithgow seam, New South Wales (Figure 1, correlation coefficient  $r = 0.89$ ). Samples of coal containing dolomite had relatively low concentrations of manganese, namely 10-150 ppm Mn (3).

### TRACE ELEMENTS IN PHOSPHATIC BOILER DEPOSITS

When bituminous coal is fired in boilers using spreader stokers or chain grates, deposits were found in some parts of the boiler system. These deposits often had very high concentrations of phosphorus and many trace elements, including arsenic, boron, germanium, lead and zinc (Table 2). Indeed, bismuth, indium and thallium were found in some boiler deposits before they had been detected in Australian coals (4). Results in Table 2 show some of the concentrations in deposits from the burning of Australian bituminous coals which are relatively low in trace elements. The highest concentrations were found in specific locations in the boiler system, for example in the vertical riser tubes of the spreader stoker-fired boiler. The deposit on the superheater tubes of the chain grate stoker-fired boiler was in two distinct layers, namely a 2 mm thick inner layer with an outer layer superimposed on it. The high elemental concentrations were confined to the inner layer. On the basis of laboratory work by Schulze (5) who prepared boron phosphate ( $BPO_4$ ) and boron arsenate ( $BAsO_4$ ) and determined their crystal structures, Goldschmidt (1) stated that these two compounds are isostructural with  $\beta$ -cristobalite. Since these compounds have never been found in nature they were sought in the two deposits highest in arsenic, boron and phosphorus, and boron phosphate was identified. Later a further study established that  $BAsO_4$  was present in solid solution in  $BPO_4$  (6).

A possible mechanism for the formation of  $BPO_4$  involves a reaction between calcium phosphate and silica to give phosphorus pentoxide, which could then react with boron trioxide formed from the decomposition of organically-combined boron in coal, to give boron phosphate (4). A similar mechanism has been proposed for the formation of boron arsenate (6). It is interesting to note that there are some high concentrations of germanium in the boiler deposits, probably the highest found in coal-derived material. Such deposits have not been used for the production of germanium, but other coal-derived materials have been processed in several countries to yield small quantities of germanium for the manufacture of semi-conductors.

#### GERMANIUM AS AN INDICATOR OF FLYASH IN ATMOSPHERIC PARTICULATES

Power stations emit trace elements to the atmosphere, mostly associated with fine flyash particles. There is an on-going interest in the composition of atmospheric particulates, especially in the concentrations of trace elements of environmental significance. Samples of material deposited in areas near power stations, say up to about 20 km away, contain predominantly soil/rock and flyash particles in proportions that are not easily measured. A study of the trace-element contents of flyash from an Australian power station showed that there was a distinct enrichment of some elements in the fine particles (less than about 3  $\mu\text{m}$  diameter) which predominate in the stack emissions. Comparisons of the compositions of flyash with those for rocks and soils, using available geochemical data show that germanium has the highest ratio for flyash to soil/rock material (Table 3). The mean values for germanium in fine flyash and soils in the area around the Australian power station were 75 and 1.5 ppm respectively. Applying this to samples of deposition enabled the proportions of flyash to be calculated from results for 12 three-monthly samples (Table 4). As expected the proportions of flyash decreased with distance from the power station. The variations in the ranges of values at any location are caused by changes in meteorological conditions, especially wind direction. It is surprising to find some very low proportions, for example 4 and 7%, in samples collected near the power station, but this was in keeping with seasonal changes in wind direction. Another geochemical interpretation of these results was carried out by comparing them with the amounts of trace elements released by rock weathering (7).

#### CONCLUSIONS

The examples discussed here indicate how basic geochemistry, mostly emanating from Goldschmidt's work, can be used to elucidate some aspects of the trace-element geochemistry of coal and coal usage.

#### REFERENCES

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**Table 1. Manganese in carbonate minerals found in Australian bituminous coals**

Mineral and location	Mn (ppm)
Siderite, Tongarra seam, Sydney Basin	3000
Siderite, Benley seam, Queensland	10000
Calcite, Wallarah seam, Sydney Basin	10000
Calcite, Blackwater, Queensland	19000
Calcite from fissure in seam, Queensland	2240

**Table 2. Contents of trace elements in boiler deposits; based on (4)**

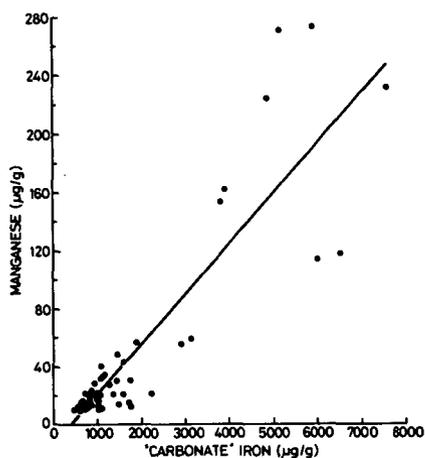
Type of boiler and coal	Content of trace element (as%)					
	As	B	Ge	P	Pb	Zn
<b>Spreader stoker:</b>						
superheater tubes	0.08	0.05	0.1	11.0	1.0	1.0
vertical riser tubes	0.8	3.0	0.1	15.0	0.3	0.6
economiser outlet dust	0.1	0.15	0.01	1.5	0.04	0.2
coal (ppm)	1	6	8	400	10	50
<b>Chain grate stoker:</b>						
superheater tubes						
inner layer	1.0	5.0	1.0	25	1.0	1.0
outer layer	0.0001	0.015	0.002	1.2	0.004	<0.03
coal (ppm)	1	15	9	580	10	50

**Table 3. Contents of germanium**

Earth's crust	1.5 ppm Ge	Soil	
Sandstone	0.8	- range	1-2.5 ppm Ge
Limestone	0.2	- mean	1.5
Shale	1.6	Fine flyash	
		- range	50-100
		- mean	75

**Table 4. Flyash in deposition at different locations**

<b>Distance of location from power station (km)</b>	<b>Flyash range (%)</b>	<b>Flyash mean (%)</b>
1.8	7-80	40
1.5	4-33	11
3.9	0.5-10	5
5.3	<1-5	2.5
27.4	0.1-2.5	0.7



**Figure 1. Plot of concentrations of manganese against 'carbonate' iron**