

Use of laser ablation ICP-MS to determine trace element distributions in coals, with special reference to V, Ge and Al

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Abstract

Laser ablation ICP-MS has been used to produce element profiles from polished coal samples. The elements analysed (V, Ge, Ni, Cu, Zn, Sr and Ba) were those known to have an organic association, with the addition of Al and Fe as controls on the clay and pyrite abundances. The element profiles were compared with the petrography and a statistical analysis was also carried out. Sporinite was found to have low trace element concentrations, inertinite higher concentrations of detrital elements and vitrinite higher concentrations of V, Ge and Al. The relationships between these elements are explored and all are thought to be present in the organic matter and not as minerals. It is thought that these elements became concentrated during diagenesis, with the possibility that some of the Al could be residual. The Cu/Ni ratio in the pyrite is relatively constant, suggesting constant ionic proportions during diagenesis, and possibly a seawater source.

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1. Introduction

The utilisation of coals releases trace elements into the environment and concentrations are increased above the natural background levels, raising the possibility of an impact on ecosystems. It is not only absolute concentrations in coals that are important but also the distribution of trace elements within the coal. The mode of occurrence, and association with other elements, are important factors in influencing the fate of elements during combustion. In addition, if the association of trace elements with specific minerals and macerals is known, there is the possibility of reducing concentrations by selected mining and coal-cleaning. Information

on the distribution of trace elements within the coal also enables predictions to be made for other coals. In addition to the applied aspects, more precise information on the location of elements within the coal leads to a better understanding of geochemical processes during deposition and diagenesis.

One aim of the present study was to explore the potential of LA ICP-MS as an analytical tool for the in situ trace element analysis of minerals and macerals in coals. Laser ablation inductively coupled plasma-mass spectrometry (LA ICP-MS) offers the possibility of directly analysing individual, micron-sized coal components down to the ppm level using polished sections or blocks and, therefore, free from the need to separate components. The technique of LA ICP-MS is rapidly evolving and is now widely used in the fields of environmental and biological analysis. Lyons et al.

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(1990) used this approach in an examination of macerals in the UK Swallow Wood Coal, which comes from the same coalfield as one of the coals in the present study. Barium, Ca, Dy, Li, Mg, Sr and Y were present in higher concentrations in fusinite than in either vitrinite or cutinite. Vitrinite had more Ti, V, Cr and Ca than cutinite and both had more Cr, Sc, Ti and V than fusinite. The elements were believed to have a mineral-matter (inorganic) origin with the possible exception of Al, K, Fe, Ga and Sr in the vitrinite and cutinite. Only some of these elements have been analysed in the present work, because not all are believed to have a significant organic association. Querol and Chenery (1995) used LA ICP-MS to obtain trace element analyses of individual grains in polished blocks of coal. In addition to sulphide minerals, the macerals vitrinite, liptinite and fusinite were also analysed. Booth et al. (1999) used LA ICP-MS in a scanning mode to obtain average analyses for elements in coal samples to augment conventional analytical methods. The elements analysed, including Hg, Cd and Sb, were those for which detection limits were not sufficiently low using conventional XRF. The limits of detection achieved with the LA ICP-MS were in the $\mu\text{g/kg}$ range (ppb). The scanning mode of the LA ICP-MS was also adopted for the analysis of fly ash particles (Spears, 2004). The data were statistically analysed to overcome a problem associated with the small mean grain size of the particles (8 μm). Although the laser has a minimum beam diameter of 10 μm , a larger beam diameter was adopted to ensure that the sensitivity of key elements was not adversely affected.

Direct analysis of in situ minerals and macerals is also possible using electron beam methods, but many of the trace elements of interest fall below detection limits. In an electron microprobe investigation of the trace element composition of pyrite and marcasite in some UK coals (White et al., 1989) the minimum detection limit of 100 ppm was too high and analyses were completed using the synchrotron XRF at Brookhaven, New York. In another study of pyrite and marcasite in coal using the electron microprobe, Ruppert et al. (2005) recorded a detection limit of 0.05 wt.% for As, which was acceptable because As concentrations were relatively high. The detection limits for the synchrotron are in sub-ppm range, but instruments such as this, and ion microprobes, are not readily available, whereas laser ablation ICP-MS is increasingly becoming more common.

Indirect methods are usually used to determine the distribution of trace elements in coals and either make use of the natural variation in a suite of coals or involve fractionating the coals using chemical or physical

methods. A number of methods are described in Davidson (2000) for the analysis of single coals. Using the latter approach the composition of the organic matter in one of the present coals was determined (Spears and Booth, 2002; Spears, 2002). The calculated trace element distributions are shown in Table 1, together with the analysis of the whole coal. Statistically analysing the trace element data from a suite of coals is a long-established method to obtain element associations. This was done for a representative of UK coals by Spears and Zheng (1999) and most recently for other coals and lignites by Chatziapostolou et al. (2006), Kalkreuth et al. (2006) and Song et al. (2007). There is considerable current interest in trace elements in coals as these, and other recent papers demonstrate (for example Brownfield et al., 2005; Wagner and Hlatshwayo, 2005; Dai et al., 2006; Parzentny and Lewinska-Preis, 2006; Yang, 2006; Hower et al., 2007). These are important papers that focus more on a comprehensive range of trace elements and comparisons with other coals, including global averages, than is the case in the present work. The aims of this work, are on the one hand, to demonstrate the usefulness of LA ICP-MS as an

Table 1

To show the calculated percentage distribution of trace elements between organic matter, the clay fraction and pyrite in the Eggborough coal

	Organic (%)	Clay (%)	Pyrite (%)	Bulk pf (ppm)
V	68	32	0	90
Cr	37	63	0	47
Ni	51	28	21	36
Cu	49	16	36	47
Zn	31	37	31	33
Ga	35	65	0	8
Ge	93	7	0	5
As	9	2	89	27
Se	46	6	48	1.3
Br	100	0	0	41
Rb	0	100	0	28
Sr	40	60	0	45
Y	33	67	0	10
Zr	18	82	0	38
Nb	23	77	0	2.9
Mo	27	5	68	3.2
Sn		100		1
Sb	36	29	35	1.3
Ba	13	87	0	121
La	1	99	0	10
Ce	16	84	0	20
Sm	0	100	0	9.2
Pb	32	19	48	19
Th	0	100	0	3.5

The calculation method was outlined in Spears et al. (1999a) and extended in Spears (2002). The calculated values are from the latter publication as is the bulk composition in the final column.

analytical tool, and also to analyse a well-documented coal to investigate the association of key trace elements with specific macerals. In addition to confirming and extending the previous work on one coal, samples rich in specific macerals were also examined to provide additional information on the composition of the macerals.

2. Methods

Coal samples were prepared as polished thin sections and the petrography was recorded across marked transects. These transects were then ablated and the counts for the chosen elements recorded. The distance scanned was of the order of 10 mm at a scan speed of 30 $\mu\text{m/s}$ with a beam diameter of 20 μm . The laser used was a New Wave UP266 Macro and the ICP-MS an Argilent HP 4500. The operating conditions used for the ICP-MS and the laser are given in Table 2. The diameter of the laser beam (20 μm) is greater than some of the coal components, especially the minerals such as pyrite. A smaller beam diameter was not used because this would have led to a reduced volume of sample ablated and a significant reduction in element sensitivity. A limited number of elements can be analysed at one time and the elements selected were those for which an organic source is thought to be important, based on the values in Table 1. The elements analysed were V, Ge, Ni, Cu, Zn, Sr and Ba. Aluminium and Fe were also included to provide a control on the clay and pyrite contents in the coal. The concentrations of these trace elements in the organic matter are shown in Table 3. Pyrite is the major location for As, Se, Mo, Sb and Pb and these elements were not therefore analysed. Minerals contribute to the Sr and Ba concentrations, but an organic source was also suspected and both elements were included in the scans. Conversion of the count rates for the selected elements into concentrations

Table 2
Laser ablation ICP-MS operating conditions

ICP-MS	
RF power	1150 W
Plasma gas	16.0 L/min
Carrier gas	1.24 L/min
Transient mode integration	0.1 s
Laser	
Power	0.037 mJ (12.24 J/cm ²)
Beam diameter	20 μm
Scan speed	30 mm/s
Frequency	10 Hz

Table 3

Selected major and trace element analyses for the four coals analysed in this work (samples A–D)

Sample	A	A _{ORG}	B	C	D
Al (%)	2.4		0.59	0.46	0.61
Fe (%)	1.6		0.01	0.05	0.14
V (ppm)	90	60	48	17	27
Ge (ppm)	5	4.6	2.1	4.3	0.8
Ni (ppm)	36	18			
Cu (ppm)	47	22	16	27	11
Zn (ppm)	33	10	26	22	21
Sr (ppm)	45	18			
Ba (ppm)	120	16			

Aluminium and Fe expressed as percentages, the trace elements as ppm. Sample A is the Eggborough coal (UK), sample B and C the inertinite- and vitrinite-rich representatives of the Grooteegeluk coal (SA) and sample D the Inesperada coal (ES). The calculated organic composition for sample A in ppm is given in column A_{ORG} and is based on values in Table 1.

was achieved using whole coal analyses (Table 3). To overcome a potential problem that the area scanned by the laser was not representative of the whole coal several samples of one coal were prepared and scanned. There is also the possibility that the components of the coal and especially the macerals will ablate significantly differently. However, in previous work (Booth et al., 1999) good calibrations were obtained with comparable coals to those used in the present study, indicating differential ablation was not a problem.

3. Coal samples

One of the coals chosen for study was one for which information on composition and element distributions was already available (Tables 1 and 3, sample A). This bituminous Pennsylvanian coal from the Yorkshire Coalfield was collected at the Eggborough Power Station. Three separate samples of this coal were prepared as polished thin sections and ablated. The samples were all banded on a scale less than the size of the transects, i.e. there was a significant petrographic variation (Fig. 1). Three other samples, rich in specific macerals were also chosen. Two samples were taken at the Grooteegeluk coal mine close to Ellisras (South Africa). Detailed information on the variation of trace elements within the Permian Grooteegeluk Fm. is to be found in Faure et al. (1996). Both samples were handpicked from the seam, one being rich in inertinite (sample B) and the other in vitrinite (sample C). The thin sections were prepared from small blocks of coal, which were afterwards ground, ashed and analysed (Table 3). Due to the generally small size of liptinite, and its typical occurrence as a dispersed component, a durain

sample was sought in which liptinite was enriched in specific areas, thus enabling a relatively pure component to be analysed. The durain sample (sample D) was taken at Inesperada mine near Oviedo (Northern Spain). The occurrence of durain layers is common in this high-volatile bituminous Pennsylvanian coal. As for the Grootegeluk samples, the same piece of coal from which the thin section was prepared was ashed and analysed. These are the only trace element analytical data available from this coal (Table 3). These coals were chosen to target the macerals and also to extend the study into other geographical areas.

4. Results

The petrographic variation across one of the Eggborough samples is illustrated in Fig. 1, with specific areas shown in greater detail. The element count profiles for the same transect, expressed on a log

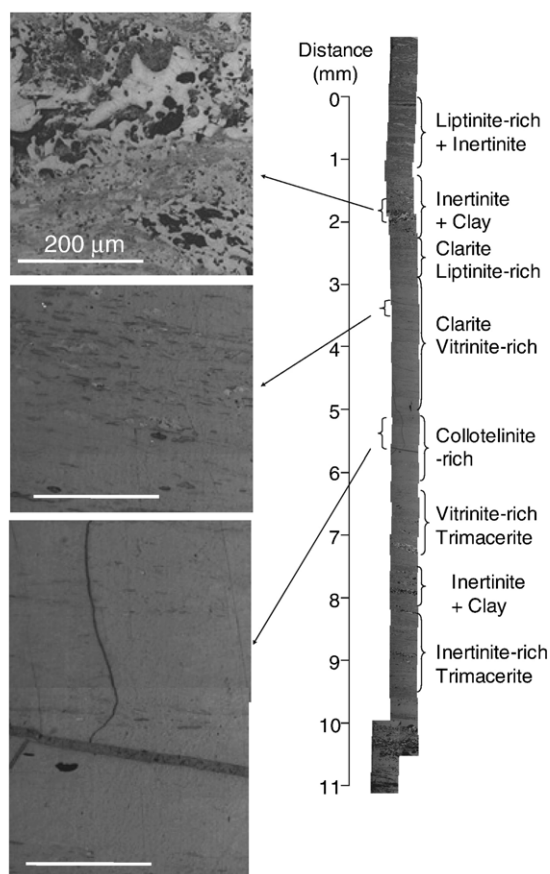


Fig. 1. Example of Eggborough transect showing the resolution at which the images from the coal transects were collected prior to laser ablation. Images were taken with dry objectives to avoid any possible contamination with immersion oil.

basis, are shown in Fig. 2. For some elements, including Ge and, to a lesser extent, Zn, the count rate is marginally higher than the background, but for other elements, such as Fe, there are more striking changes across the transect. There are major increases in Fe over restricted areas (Fig. 2) and these are due mainly to pyrite grains. There is also a minor increase above background level in the 100–250 s range of the profile. Most of the pyrite grains are micron sized, smaller than the diameter of the laser beam, and hence the sharp peaks. The Ni and Cu profiles have some features in common with that of Fe, but there are differences. These arise, so it is thought, because Fe is present in both pyrite and clay minerals, whereas most of the Cu and Ni are present in the pyrite. To take the element comparisons further, a statistical approach has been adopted using correlation matrices and element plots. The correlations between Fe, Cu and Ni counts in all the Eggborough data (1200 analysis points) are all significant, but the correlation between Cu and Ni is much better ($r = 0.90$). This is consistent with Fe having more than one source and Cu and Ni concentrated in pyrite. The correlation between Cu and Ni is influenced by a few high values, but if these are excluded the correlation coefficient remains highly significant ($r = 0.73$) and with an unchanged linear regression equation. What this demonstrates is that the Cu/Ni ratio in pyrite is relatively constant at the micro-scale within the coal. Sulphides with higher concentrations of either Cu or Ni were not detected. It can also be suggested that not only is the Cu/Ni ratio constant, but also that the pyrite has a relatively constant composition. The discussion so far for Ni and Cu has concentrated on the role of minerals. Not considered is the organic contribution. The Ni concentration is marginally higher at about 12 ppm over the central part of the scan in Fig. 2. The higher concentration occurs where the V shows a marked increase. This value is less than the calculated concentration of Ni (Table 3) of 18 ppm but is of a comparable order considering possible errors. The general concentration level of Cu in the organic matter is about 10 ppm without any specific increases. Although this is below the calculated composition (Table 3), the important point is that the presence of Cu in the organic matter is confirmed. Although the concentration levels for both Cu and Ni are low in the organic matter, the overall contribution of the organic matter to the whole coal is significant.

Fig. 2 shows that the Zn counts are generally low, but there are some peaks that cannot be readily matched with the behaviour of other elements. This is reflected in the lack of correlations involving Zn for this transect. In

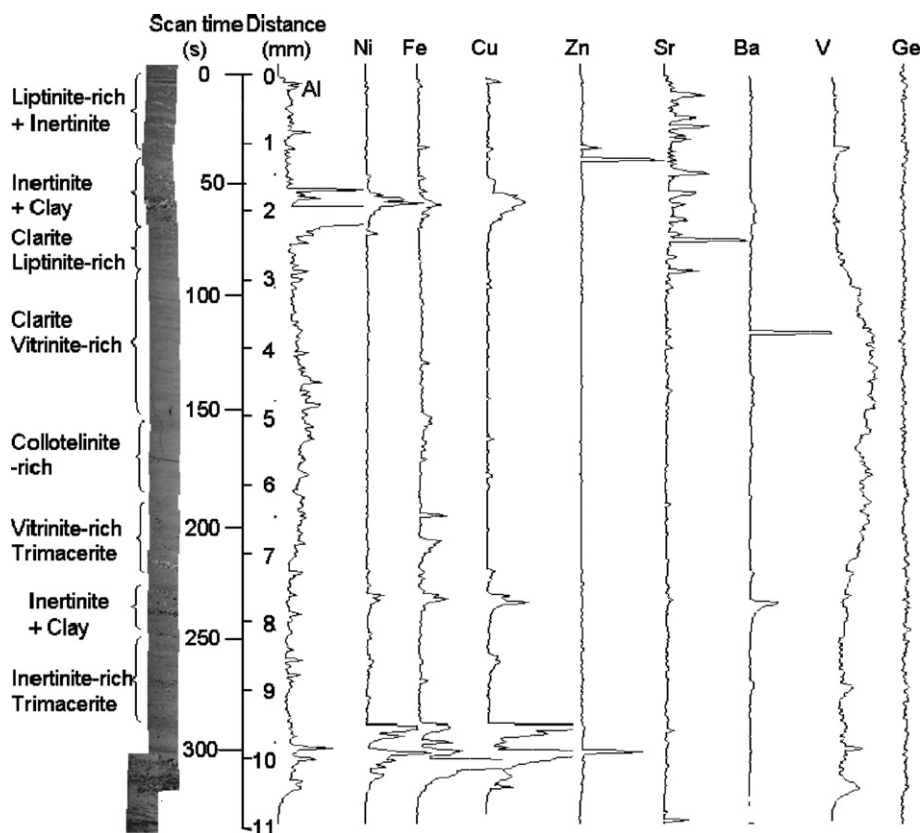


Fig. 2. Element counts, using LA ICP-MS, across a transect of the Eggborough coal.

other transects of this coal Zn correlates with Fe, Ni and Cu showing some sulphide association and also with Ba, which might be a minor amount of a phosphate mineral. It is valid to deal only with one transect, or indeed part of a transect, in addition to the analysis of all the data, because in specific areas individual components may be concentrated.

Vanadium is an element not exhibiting sharp peaks attributable to a specific mineral, but rather a broad peak in Fig. 2 from 100 to 250 s. Petrographically this corresponds to a vitrinite-rich area in which clean collotelinite bands are present at 150–180 s (see Fig. 1 for enlargement of the areas under discussion). Although sporinite is also present it is not thought to account for the higher V concentrations because where it is concentrated elsewhere in the coal V concentrations do not increase. In the other sections of this coal, V concentrations are again higher in the vitrinite-rich areas. The average V concentration in these areas is about 60 ppm, which agrees with the value shown in Table 3. Aluminium and Fe, to a lesser extent, also increase from 100 to 250 s (Fig. 2) in a similar manner to V. The increases are gradual and are not consistent with

an Al rich mineral, unless sub-micron-sized clay minerals are evenly distributed at low density, which is considered unlikely. This suggests some organic association for Al and possibly also for Fe. This is an important observation and is discussed more fully later.

In the Eggborough coal the concentration of Ge is 5.0 ppm, of which over 90% is thought to be in the organic matter (Table 1). In the laser scan shown in Fig. 2, the Ge counts do increase towards the end of the scan, but the increases are small and do not correspond with either any petrographic character or the V profile. The lack of agreement is borne out by the statistical analysis in which Ge does not correlate with V. The distribution of Ge is similar in another of the Eggborough sections, but in the third section the Ge count profile is similar to those of V. In this section Ge does correlate with V at the 95% confidence level. It would appear that Ge is concentrated in only some of the vitrinite-rich areas. The explanation for this could be that Ge has greater mobility in the diagenetic environment than V.

Some organic association for both Sr and Ba is demonstrated in the scans by the background counts

where peaks are absent. Both elements do show strong peaks in the scans, suggesting a mineralogical control, but the nature of that control is unclear. Strontium and Ba correlate in one of the scans, but in another they are largely independent with Sr showing a relationship with Al and Fe and Ba with Zn. No dependence on maceral type was noted.

The Grootegeluk coal is a high-volatile bituminous coal, typically vitrinite-rich, although locally it can have a high inertinite concentration. The Grootegeluk Fm. mudstones are dominated by kaolinite and quartz with minor amounts of apatite, smectite, illite and microcline (Faure et al., 1996). The two sections analysed contain both vitrinite and inertinite with one maceral group predominating over the other one in each section. The laser scans of most elements reflect this bipartite division and therefore only the one with higher inertinite concentration is shown (Fig. 3). In the inertinite-rich section, consisting of semifusinite, macrinite and funginite, there are higher count rates for Al and Fe to a lesser degree. These counts are equivalent to approximately 6.5% Al and 0.13% Fe, which is indicative of kaolinite rather than another clay mineral.

The maceral association is one associated with reworking and the kaolinite is probably detrital in origin, which is consistent with the mudstone mineralogy (Faure et al., 1996). Zinc and Cu also increase in the inertinite-rich section but the concentrations are low and the increases minor. A notable feature of the scan is that the counts for V, Ge, Ni, Sr and Ba are all high in the vitrinite-rich section and statistically the relationships between all elements are significant. Collotelinite is the main component of the vitrinite and the high V and Ge concentrations in this maceral are in agreement with the results from the Eggborough coal, but, in addition, Ni, Ba and Sr are also present in higher concentrations. The highly significant positive relationship between Ge and V for both samples is shown in Fig. 4. Higher Ge and V concentrations are recorded for the vitrinite-rich sample compared with the inertinite-rich sample. There is an overlap between the two samples because neither sample consists only of one maceral.

The Ni counts are marginally higher in the vitrinite-rich section of one sample, but not in the other where the Ni shows a rather uniform distribution. Strontium and Ba show a uniform increase corresponding to that of Ge

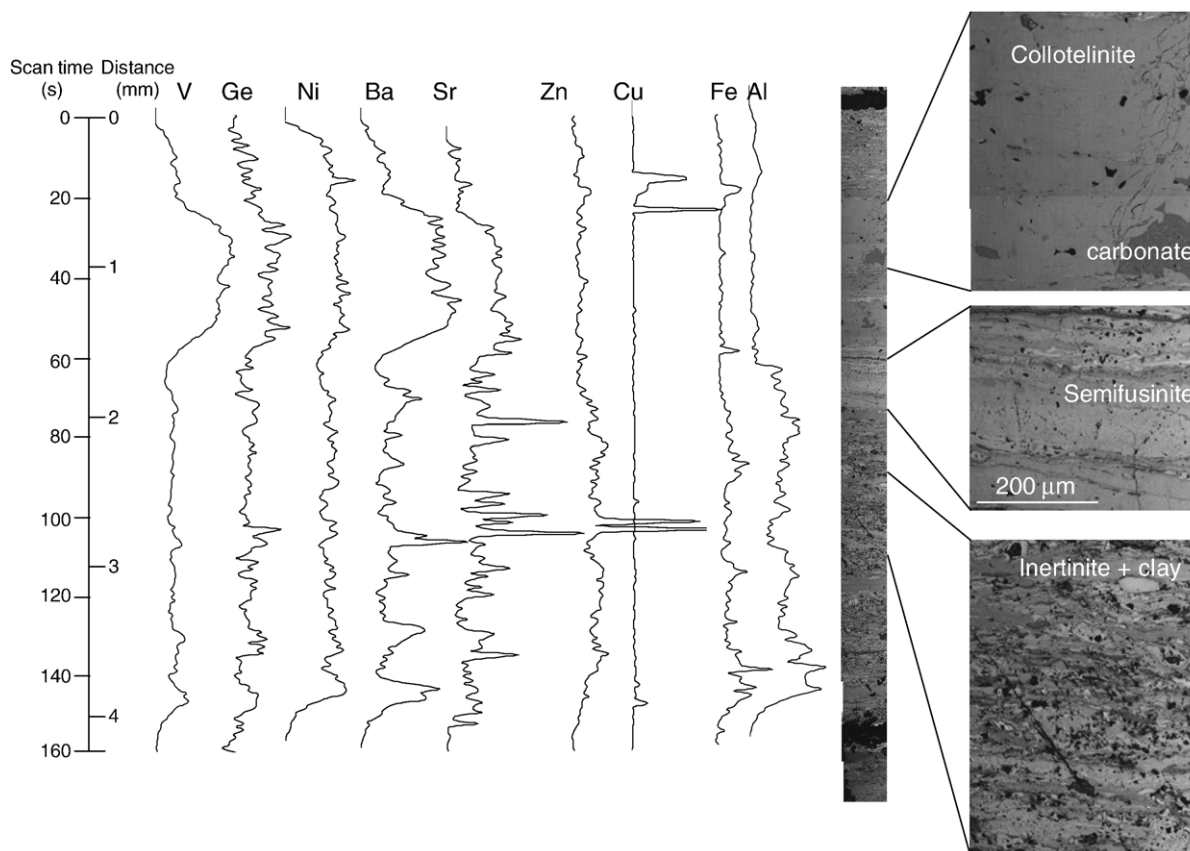


Fig. 3. Element counts, using LA ICP-MS, across a transect of the Grootegeluk coal.

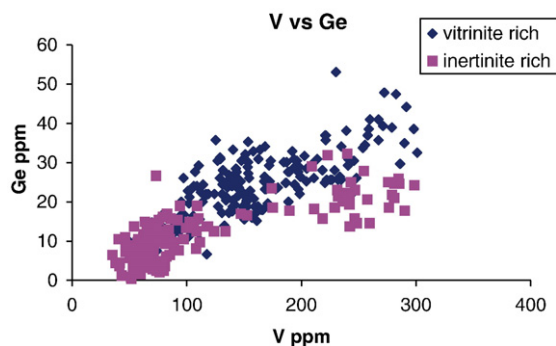


Fig. 4. The V (ppm) in the inertinite and vitrinite-rich samples of the Grooteegeluk coal plotted against the Ge (ppm).

and V and an organic association is indicated. However, in the other sample, Ba and Sr count rates show a sharp increase over a small part of the scan, which could be due to a Ba–Sr rich mineral, such as a carbonate or a phosphate mineral. Large carbonate grains have been identified in the collotelinite in both sections and are seen as darker areas in the images of Fig. 3. In support of a phosphate mineral, Faure et al. (1996) note that in the

Grooteegeluk Fm., the variations of Sr, Ba, and P_2O_5 are all similar in the coal-bearing part of the sequence. Although Fe increases in the inertinite, the counts are low and the absence of high intensity-short duration peaks indicates the absence of specific Fe-bearing minerals, such as pyrite. In general, the scans show a lack of influence from minerals other than the Al attributed to kaolinite and a possible phosphate/carbonate mineral. Kaolinite is a minor host for trace minerals and, therefore, its presence is not reflected in the total trace element counts in the scans.

The profile through the durain (Inesperada Mine, Spain), shown in Fig. 5, indicates a maceral composition consisting of nearly pure sporinite at the top with local abundance of macrinite and a significant enrichment of vitrinite (collodetrinite) towards the base. The laser scans for a number of elements in this sample are similar. Aluminium, V, Ni, Zn and Sr all correlate with each other at a significant level. Concentrations rise, most noticeably for Al and V, towards the end of the scan where the proportion of collodetrinite is much higher compared with sporinite. Aluminium and V show a strong positive correlation, demonstrating a relationship also observed

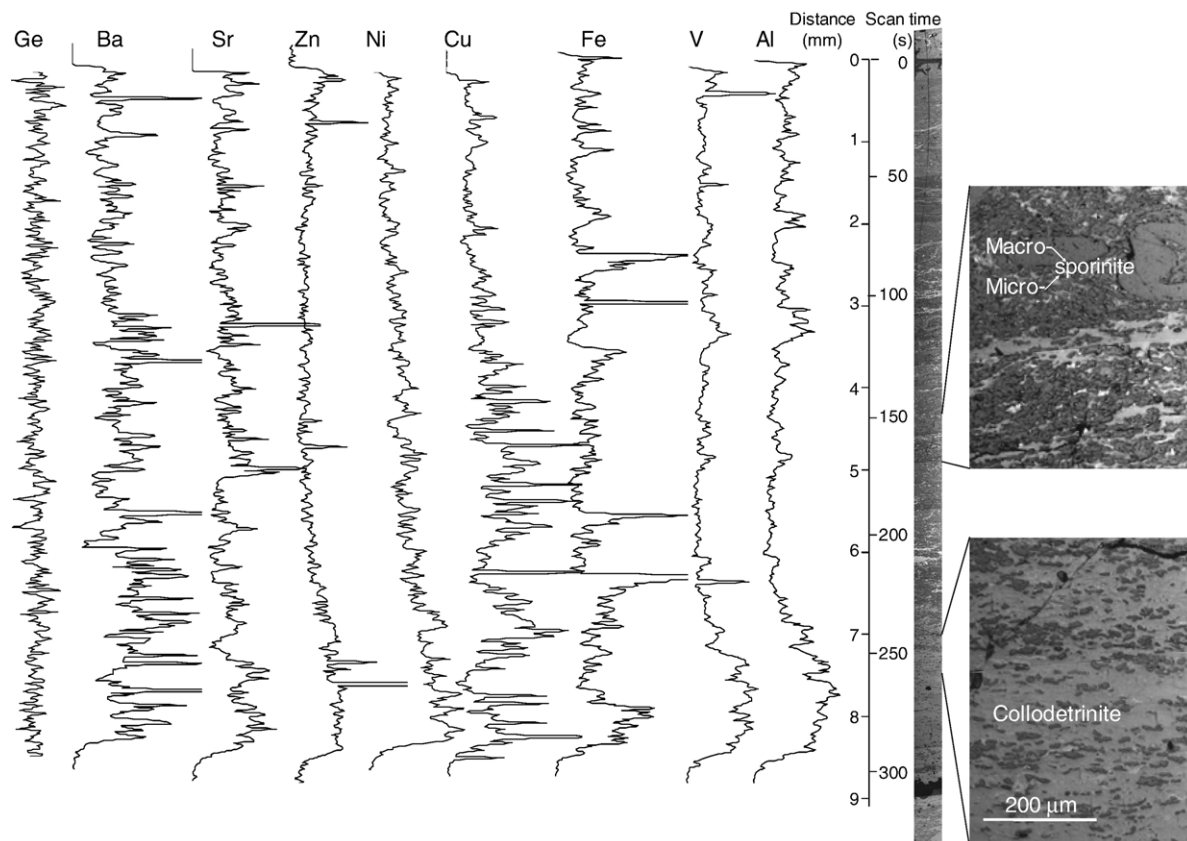


Fig. 5. Element counts, using LA ICP-MS, across a transect of the Inesperada durain.

in the Eggborough coal scans. Nickel and Zn increase their concentration towards the bottom of the section. The Fe counts do show some peaks and these could be Fe-bearing, micron-sized minerals, possibly siderite rather than pyrite because the Fe peaks do not match with those of other elements such as Ni and Cu. A relationship between V and Ge has been noted in some of the previous scans. No such relationship is apparent here and the Ge count rate is very close to background level across the whole of the scan. This is similar to one of the scans for the Eggborough coal in that there is a positive V–Al relationship but not one with Ge. A noticeable feature of the petrography is the concentration of sporinite, particularly at the top of Fig. 5. In this area the elements all show uniformly low concentrations and remain so when specific macrosporinite and microsporinite grains were ablated. In all the scans there is little evidence of significant trace element concentrations in macerals other than the collodetrinite.

5. Discussion

The laser ablation ICP-MS analyses show that sporinite is particularly lean in trace elements, which is consistent with the origin of this maceral as well-preserved exines of resistant material. The natural protection of the spores restricts reaction between the organic matter and ions present in the interstitial waters. Inertinite, on the other hand, contains higher concentrations of some elements, but essentially those that are they are thought to have a detrital origin. Inertinite is typically associated with higher contents of clastic material that may be present as infilling intermaceral spaces and cells. The dry periods in which inertinite is preferentially formed favour the input of detrital minerals. In this work we have focussed on elements with an organic association, with the exception of Al and Fe, which we have used as a measure of the clay minerals and minerals such as pyrite. The inertinite contains higher concentrations of these detrital elements as would be predicted (ICCP, 2001). Of the trace elements analysed in this work Zn and Cu show minor increases in concentration in the South African sample. In the Eggborough coal elements that would be expected to show higher concentrations in the inertinite compared with other macerals are those that are clay-associated (Table 3). Most of the elements analysed by Lyons et al. (1990) were thought to be present in the mineral matter.

One of the important findings from the present work is that where collotelinite and collodetrinite are most abundant the concentration of V is significantly higher, the same is probably true of Al, but this is difficult to

prove in one sample, and Ge is also higher but not in all samples. Both macerals originated from similar plant material composed of lignin and cellulose, although the primary structures were largely destroyed early in the peat stage with subsequent gelification. The macerals are reactive and would be expected to react with any Ge and V present in pore solution. There is good evidence from the literature (see, for example, Yudovich, 2003a) that these elements may have been available in the pore solutions during diagenesis and therefore an association with the more reactive macerals is to be expected.

The stable oxidation state of Ge is Ge(IV). Because of ionic charge and size Ge will tend to form complexes with hard bases such as OH^- , F^- and organic ligands, including acetate, oxalate, humic and fulvic acids (Wood and Samson, 2006). These ions would be present in the peat and complex formation with Ge would be predicted. Unlike Ge, V is present in more than one oxidation state in natural environments and, because redox-sensitive trace metals are less soluble under reducing conditions, V, along with Mo and U is used as a paleoredox indicator (Tribouillard et al., 2006). In oxic waters, V is present as V(V) in the form of oxyanions. As the Eh falls during diagenesis, V is reduced to V(IV), forming insoluble hydroxides and ionic species which may be removed from solution by the formation of organometallic ligands. Under more extreme reducing conditions, in the presence of free H_2S , the V is reduced to V(III). The existence of reduced sulphur species at one time within the peat is shown by the presence of pyrite in some of the coals examined.

Yudovich (2003b) demonstrated that, in coalfields around the World, Ge is often enriched at the margins of the coal seams. Possible origins are reviewed (Yudovich, 2003b) and the one favoured is of Ge input into buried peat caused by diagenetic flow of the soluble matter. The enrichment mechanism was thought to be similar to that for coal inclusions (reviewed in Yudovich, 2003a). Coal inclusions in sedimentary rocks are enriched in other elements, including V, (see Yudovich, 2003a) and a post-depositional origin for the enrichment is indicated. There is, therefore, good evidence of the mobility of Ge and V during diagenesis and of incorporation into the organic matter.

The role of Al is more enigmatic. There is unequivocal evidence for the positive relationship between Al and V. There is also little doubt that the V is organic associated and it follows from this that a case can be made for an organic origin for the Al. This is supported by the uniform element profiles in the LA ICP-MS scans. Where minerals are present there are sharp peaks

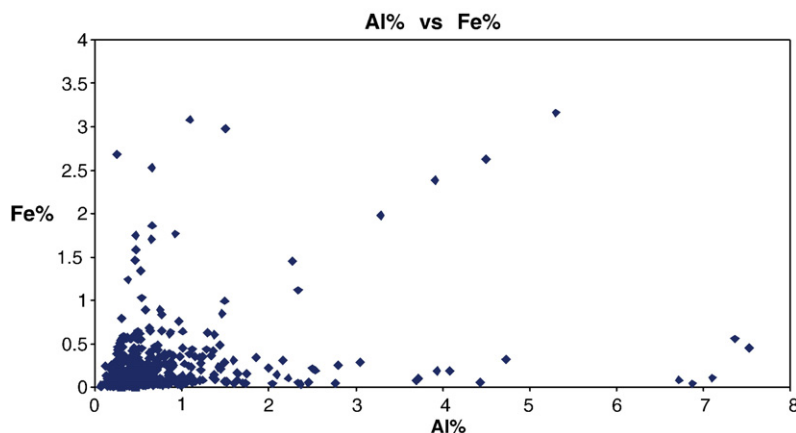


Fig. 6. The Al (%) in the Eggborough coal plotted against the Fe (%).

on the scans. It could be argued that the Al is present in sub-micron-sized mineral grains, but this would require an unlikely combination of uniform distribution and low density. Furthermore, the most likely mineral would be kaolinite, based on what is known of the minerals present in this coal (Spears and Martinez-Tarazona, 1993) and the surrounding mudrocks (Spears, 2006), and yet the Fe concentration is also higher in the vitrinite, which is not consistent with the presence of kaolinite. This may be illustrated with a plot of Al against Fe (Fig. 6) for all the Eggborough coal analyses (1200 analysis spots). A trend showing high Al and low Fe values is thought to be due to kaolinite grains and Fe is not associated. The reason why the Al concentrations are less than the structural formula value is that the grains are smaller than the beam diameter of the laser. Two other trends are apparent in Fig. 6, one with high Fe and low Al concentrations is attributed to pyrite and the

other, in which Al and Fe increase together, is thought to be due to detrital clay minerals. The majority of analyses in Fig. 6 have low Al and Fe values. In this grouping it is noteworthy that the Al consistently shows a small positive value and this is attributed to the organic matter. Within this group there are also similarities with Fig. 7 in that there is a minimum Al for any Fe value, suggesting that some Fe is also organically bound. Although the minerals may be much smaller than the diameter of the laser beam, the volume ablated is very small and mineralogical controls and trends can be identified that would not be apparent with larger sample volumes.

Non-mineral, inorganic elements in coals have recently been described by Ward et al. (2007), and Zhongsheng et al. (2007), based on the electron microprobe. In the latter publication values of up to 1.5% Ca, 0.5% Al and up to 0.7% Fe are reported for macerals from low rank coals. One line of evidence for

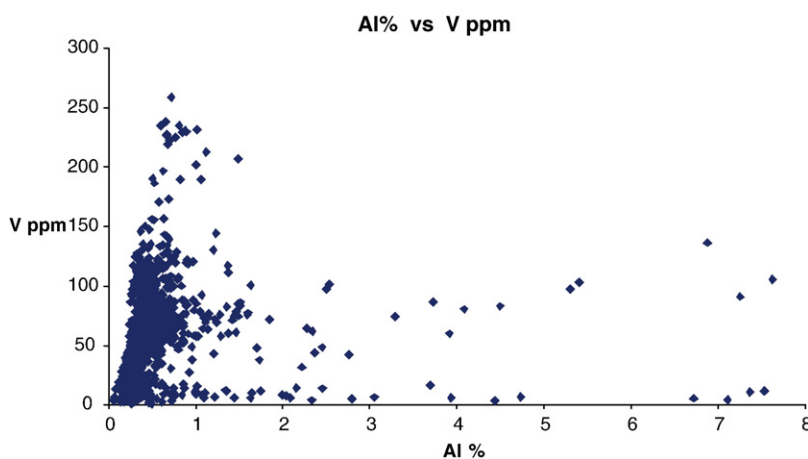


Fig. 7. The Al (%) in the Eggborough coal plotted against the V (ppm).

the organic location, also used in the present work, comes from the uniform distribution of elements and the overall consistency in the baseline levels, rather than the spike-like peaks expected from micron-sized mineral inclusions. Further evidence for an organic source in the macerals is provided by the similar distributions of Al, Fe and Ca with that of organic S (Zhongsheng et al., 2007). These authors also make an important point that in coal utilisation processes organically bound elements are not going to behave in the same way to the elements located in minerals. Ward et al. (2007) also note that Al occurs in vitrinites in bituminous coals, especially those that are S rich; an observation that is especially relevant to the present work.

In order to explore more fully the relationships between Al and V, all the Eggborough analyses are shown plotted in Fig. 7. High Al concentrations are due to clay minerals, and possibly there are two trends, one due to kaolinite (diagenetic) with low V values, and the other to a mixed clay assemblage (detrital) with marginally higher V values. Most of the analyses fall into a third group showing the highest V and lowest Al values. This is the organic associated V and the high values are attributed to vitrinite. In this group it is noteworthy that the V is not independent of the Al because there is a high gradient trend showing a positive relationship between the two elements. This trend is particularly good evidence for the presence of non-mineral organic Al. For any V value there is a minimum Al value. There is some scatter towards higher Al values that we attribute to clay particles.

Vanadium and Ge are known to be mobile during diagenesis. Aluminium, on the other hand, is relatively immobile. One possibility for the organic association of Al, V and Ge could therefore be that Al originates in the plant material and is retained to a significant degree, whereas Ge and V, similarly sourced, are more mobile and may be lost by leaching or retained by the reactivity of the macerals. Such an explanation envisages redistribution of V and Ge within the peat during coalification. In some samples, Ge does not follow V, which could be due to greater mobility. However, the presence of diagenetic kaolinite infilling cell structures is clear evidence of the mobility of Al within the coal. In soils the decomposition of organic matter leads to the formation of oxygen containing functional groups with a high affinity for Al and complex formation (Stevenson and Vance, 1989; Wong et al., 2000). From this evidence some mobility of Al during diagenesis in the coal can be assumed and the observed higher concentrations of Al, V and Ge in the vitrinite may be a function of the reactivity of the maceral during coalification and its ability to capture all three elements from solution.

Finally, in the Eggborough coal there is a consistent relationship between Cu and Ni in the pyrite that probably reflects fixed ionic proportions in the pore waters. If this is the explanation it means that ionic proportions remain relatively constant even over micro distances within the coal. In earlier work on this coal (Spears and Martinez-Tarazona, 1993), it was noted that some trace elements in the coal are enriched to a comparable degree compared with non-marine shales, as are marine shales. From this, it was suggested, marine waters could also be the source of these trace elements in the coal. In other work, coal samples from all the UK coalfields show correlations between the Fe present in pyrite in the coal and the concentrations of As, Mo, Sb, Tl and Se (Spears and Zheng, 1999). In addition to demonstrating the importance of pyrite as a host for these elements, it also demonstrates that the pyrite has a relatively uniform composition, which again can be attributed to a common source, such as seawater. Finally, the distribution of pyritic S in UK coals provides further evidence for a pervasive marine influence (Spears et al., 1999b). It could therefore be that the Cu and Ni proportions in the pyrite in the present work are a reflection of a seawater input. It should be noted that elements such as As, which are mainly present in the pyrite, were not targeted in the current work because the focus was on those elements with a significant organic association.

In the Introduction we noted that a long-established method of establishing trace element affinities was to statistically analyse the data from a suite of coals. We are essentially doing the same with the LA ICP-MS, but on a micro-scale. It could be argued that because the beam diameter is larger than the minerals the method is not ideal. Unfortunately, there is no ideal method, and using the laser as we have may well represent the best that can be achieved for many elements.

6. Conclusions

- Laser ablation ICP-MS is an extremely useful method for the in situ determination of trace element distributions in coals. The elements analysed were V, Ge, Ni, Cu, Zn, Sr and Ba, all of which were known to have a significant organic association from previous work, and Al and Fe as controls on mineral abundances.
- Using the laser in the scanning mode reveals the non-uniform nature of the coal with sharp peaks associated with minerals such as pyrite, whereas the count rates for the macerals are more uniform.
- In addition to a visual comparison of petrography and element profiles in the scans, a statistical analysis of

the data has proved invaluable. Using this approach it is possible to obtain concentration levels for individual components, even though the grain size is significantly less than the diameter of the laser beam.

- Sporinite contains low trace element concentrations; inertinite has higher concentrations of detrital-associated elements, and vitrinite (collotelinite and collodetrinite) higher concentrations of V, Ge and Al.
- It is proposed that V, Ge and Al were concentrated during diagenesis, possibly entirely from redistribution within the coal seam. It is possible, and for Al in particular, that some proportion of that present was residual from the parent material.
- The presence of non-mineral organic Al has implications in coal utilisation in that its behaviour will not be the same as that of mineral Al.
- Although the study did not focus on those elements for which pyrite is known to be a significant source in the coal, nevertheless Cu and Ni are present in pyrite and the ratio between the two elements is relatively constant, which implies constant proportions in the pore waters during diagenesis and, speculatively, a seawater source.

References

- Booth, C.A., Spears, D.A., Krause, P., Cox, A.G., 1999. The determination of low-level trace elements in coals: the use of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). *Fuel* 78, 1665–1670.
- Brownfield, M.E., Affolter, R.H., Cathcart, J.D., Johnson, S.Y., Brownfield, I.K., Rice, C.A., 2005. Geologic setting and characterization of coals and the modes of occurrence of selected elements from the Franklin coal zone, Puget Group, John Henry no. 1 mine, King County, Washington, USA. *International Journal of Coal Geology* 63, 247–275.
- Chatziapostolou, A., Kalaitzidis, S., Papazisimou, S., Christanis, K., Vagias, D., 2006. Mode of occurrence of trace elements in the Pellana lignite (SE Peloponnese, Greece). *International Journal of Coal Geology* 65, 3–16.
- Dai, S., Ren, D., Chou, C., Li, S., Jiang, Y., 2006. Mineralogy and geochemistry of the no. 6 coal (Pennsylvanian) in the Junger coalfield, Ordos Basin, China. *International Journal of Coal Geology* 66, 253–270.
- Davidson, R.M., 2000. Modes of Occurrence of Trace Elements in Coal: Results from an International Collaborative Programme. IEA Coal Research, London, pp. 1–36.
- Faure, K., Willis, J.P., Dreyer, J.C., 1996. The Grooteegeluk Formation in the Waterberg Coalfield, South Africa: facies, palaeoenvironment and thermal history — evidence from organic and clastic matter. *International Journal of Coal Geology* 29, 147–186.
- Hower, J.C., Ruppert, L.F., Eble, C.F., 2007. Lateral variation in geochemistry, petrology, and palynology in the Elswick coal bed, Pike County, Kentucky. *International Journal of Coal Geology* 69, 165–178.
- International Committee for Coal and Organic Petrology (ICCP), 2001. The new inertinite classification (ICCP System 1994). *Fuel* 80, 459–471.
- Kalkreuth, W., Holz, M., Kern, M., Machado, G., Mexias, A., Silva, M.B., Willett, J., Finkelman, R., Burger, H., 2006. Petrology and chemistry of Permian coals from the Parana Basin: 1. Santa Terezinha, Leao-Butia and Candiota Coalfields, Rio Grande do Sul, Brazil. *International Journal of Coal Geology* 68, 79–116.
- Lyons, P.C., Morelli, J.J., Hercules, D.M., Lineman, D., Thompson-Rizer, C.L., Dulong, F.T., 1990. The laser microprobe mass analyser for determining partitioning of minor and trace elements among intimately associated macerals: an example from the Swallow Wood coal bed, Yorkshire, UK. *Fuel* 69, 771–775.
- Parzentny, H.R., Lewinska-Preis, L., 2006. The role of sulphide and carbonate minerals in the concentration of chalcophile elements in the bituminous coal seams of a paralic series (Upper Carboniferous) in the Upper Silesian Coal Basin (USCB), Poland. *Chemie der Erde* 66, 227–247.
- Querol, X., Chenery, S., 1995. The determination of trace element affinities in coal by laser ablation microprobe-inductively coupled plasma mass spectrometry. In: Whateley, M.K.G., Spears, D.A. (Eds.), *European Coal Geology*. Geological Society London Special Publication, 82, pp. 137–146.
- Ruppert, L.F., Hower, J.C., Eble, C.F., 2005. Arsenic-bearing pyrite and marcasite in the Fire Clay coal bed, Middle Pennsylvanian Breathitt Formation, eastern Kentucky. *International Journal of Coal Geology* 63, 27–35.
- Song, D., Qin, Y., Zhang, J., Wang, W., Zheng, C., 2007. Concentration and distribution of trace elements in some coals from Northern China. *International Journal of Coal Geology* 69, 179–191.
- Spears, D.A., 2002. Trace elements in some UK coals: quantitative distribution within the coal. CD ROM Publication of the Proceedings of the Eighteenth Annual International Pittsburgh Coal Conference, Newcastle, New South Wales, Australia.
- Spears, D.A., 2004. The use of laser ablation inductively coupled plasma-mass spectrometry (LA ICP-MS) for the analysis of fly ash. *Fuel* 83, 1765–1770.
- Spears, D.A., 2006. Clay mineralogy of onshore UK Carboniferous mudrocks. *Clay Minerals* 41, 395–416.
- Spears, D.A., Booth, C.A., 2002. The composition of size-fractionated pulverised coal and the trace element associations. *Fuel* 81, 683–690.
- Spears, D.A., Martinez-Tarazona, M.R., 1993. Geochemical and mineralogical characteristics of a power-station feed-coal, Eggborough, England. *International Journal of Coal Geology* 22, 1–20.
- Spears, D.A., Zheng, Y., 1999. Geochemistry and origin of elements in some UK coals. *International Journal of Coal Geology* 38, 161–179.
- Spears, D.A., Manzanares-Papayanopoulos, L.I., Booth, C.A., 1999a. The distribution and origin of trace elements in UK coal and the importance of pyrite. *Fuel* 78, 1671–1677.
- Spears, D.A., Rippon, J.H., Cavender, P.F., 1999b. Geological controls on the sulphur distribution in British Carboniferous coals: a review and reappraisal. *International Journal of Coal Geology* 40, 59–81.
- Stevenson, F.J., Vance, G.F., 1989. Naturally occurring aluminium–organic complexes. *The Environmental Chemistry of Aluminium*. CRC Press, Boca Raton, FL, pp. 117–145.
- Tribouillard, N., Algeo, T.J., Lyons, T., Riboulleau, A., 2006. Trace metals as paleoredox and paleoproductivity proxies: an update. *Chemical Geology* 232, 12–32.
- Ward, C.R., Zhongsheng, Li., Gurba, L., 2007. Variations in elemental composition of macerals with vitrinite reflectance and organic sulphur in the Greta Coal Measures, New South Wales, Australia. *International Journal of Coal Geology* 69, 205–219.

- Wagner, N.J., Hlatshwayo, B., 2005. The occurrence of potentially hazardous trace elements in five Highveld coals, South Africa. *International Journal of Coal Geology* 63, 228–246.
- White, R.N., Smith, J.V., Spears, D.A., Rivers, M.L., Sutton, S.R., 1989. Analysis of iron sulphides from U.K. coal by synchrotron radiation X-ray fluorescence. *Fuel* 68, 1480–1486.
- Wong, M.T.F., Gibbs, S., Nortcliff, S., Swift, R.S., 2000. Measurement of the acid neutralizing capacity of agroforestry tree prunings added to tropical soils. *Journal of Agricultural Science* 134, 269–276 (Cambridge).
- Wood, S.A., Samson, I.M., 2006. The aqueous geochemistry of gallium, germanium, indium and scandium. *Ore Geology Reviews* 28, 57–102.
- Yang, J., 2006. Concentrations and modes of occurrence of trace elements in the late Permian coals from the Puan Coalfield, Southwestern Guizhou, China. *Environmental Geochemistry and Health* 28, 567–576.
- Yudovich, Ya.E., 2003a. Coal inclusions in sedimentary rocks: a geochemical phenomenon. A review. *International Journal of Coal Geology* 56, 203–222.
- Yudovich, Ya.E., 2003b. Notes on the marginal enrichment of germanium in coal beds. *International Journal of Coal Geology* 56, 223–232.
- Zhongsheng, L., Ward, C.R., Gurba, L.W., 2007. Occurrence of non-mineral inorganic elements in low-rank coal macerals as shown by electron microprobe element mapping technique. *International Journal of Coal Geology* 70, 137–149.