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The geochemistry of environmentally important trace elements in UK coals, with special reference to the Parkgate coal in the Yorkshire – Nottinghamshire Coalfield, UK

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Abstract

The Parkgate coal of Langsettian age in the Yorkshire-Nottinghamshire coalfield is typical of many coals in the UK in that it has a high sulphur (S) content. Detailed information on the distribution of the forms of S, both laterally and vertically through the seam, was known from previous investigations. In the present work, 38 interval samples from five measured sections of the coal were comprehensively analysed for major, minor and trace elements and the significance of relationships established using both raw and centered logtransformed data. The major elements are used to quantify the variations in the inorganic and organic coal components and determine the trace element associations. Pyrite contains nearly all of the Hg, As, Se, Tl and Pb and is also the major source of the Mo, Ni, Cd and Sb. The clays contain the following elements in decreasing order of association: Rb, Cs, Li, Ga, U, Cr, V, Sc, Y, Bi, Cu, Nb, Sn, Te and Th. Nearly all of the Rb is present in the clay fraction, whereas for elements such as V, Cu and U, a significant amount is thought to be present in the organic matter, based on the K vs trace element regression equations. Only Ge, and possibly Be, would appear to have a dominant organic source. The trace element concentrations are

calculated for pyrite, the clay fraction and organic matter. For pyrite it is noted that concentrations agree with published data from the Yorkshire-Nottinghamshire coalfield and also that Tl concentrations (median of 0.33 ppm) in the pyrite are greater than either Hg or Cd. Unlike these elements, Tl has attracted less attention and possibly more information is needed on its anthropogenic distribution and impacts on man and the environment. A seawater source is thought to be responsible for the high concentrations of S, Cl and the non-detrital trace elements in the Parkgate coal. Indicative of the seawater control is the Th/U ratio, which expresses the detrital to non-detrital element contributions. Using other elements, similar ratios can be calculated, which in combination offer greater interpretative value.

1. Introduction

Coal production in the UK has declined from a peak of 264 million tonnes in 1913 to only 17.0 million tonnes in 2007. However, coal remains about a third of the nations energy mix. Coal consumption was 62.7 million tonnes in 2007, most of which (84%) was used for electricity generation (Hetherington et al., 2008). The emissions from coal-fired power stations are of critical environmental importance. Sulphur (S) emissions were the main focus of attention some 20-30 years ago in the UK, but this has now expanded to include trace elements and Hg in particular. There is also a growing realisation that CO_2 emissions from coal utilization are a factor in climate change with the major thrust of research in this area towards CO_2 capture and storage (CCS) technology.

The Parkgate coal in the Yorkshire –Nottinghamshire coalfield (Figure 1) is of Pennsylvanian/Langsettian age (Westphalian A). It is a high-sulphur bituminous coal (Spears et al., 1999b), and is typical of many coals in the coalfield, which is one reason why production has declined. In common with many other coals from around the world, the coals were deposited on low-lying coastal areas (paralic). Over several

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decades the routine analysis of seam sections by the former British Coal Company led to a considerable database that was eventually computerised. This enabled the sulphur distributions to be studied in greater detail than had previously been possible (Cavender, 1995; Cavender and Spears, 1995, 1997). The results of the Parkgate study were also incorporated into a reappraisal of all the UK data on sulphur (Spears et al., 1999b). Cavender (1995) made supplementary analyses of the Parkgate coal to augment the database, but whole rock major and trace element analyses were not included. The opportunity to comprehensively analyse a suite of Parkgate coals arose from the need to include UK coals in the World Coal Quality Inventory Database being compiled by the USGS (Tewalt et al., 2005). Although there is a UK Coal Sample Bank, which has been analysed for trace elements (Spears and Zheng, 1999), the coals come from all the coalfields in the UK, most of which are no longer mined, and therefore the need for new samples more representative of current production. The seam section bench samples were provided by UK Coal Mining Ltd. and were comprehensively analysed by the USGS for major-, minor-, and trace-elements. This paper is based on 38 samples from five sections of the Parkgate seam covering the area studied by Cavender (1995) in the Yorkshire-Nottinghamshire coalfield.

The aims of the current paper include, 1) to upgrade published analyses on these coals with analyses that are more comprehensive in terms of the number of elements analysed and the detection levels achieved, 2) to determine the geochemical associations of this expanded trace element suite by reference to the major elements and the known mineralogy, 3) to quantify as far as possible the trace element concentrations in specific components, and finally (4) to determine the conditions under which the environmentally sensitive trace elements are concentrated in the coals based on the geochemical associations.

2. The Parkgate Seam in Nottinghamshire

The individual beds or benches within the seam (referred to as plies in the U.K.) have been mapped in detail and correlated over large distances.   The seam thickness of the Parkgate coal in the 225 km^2 area studied by Cavender (1995) averages about 160 cm.. Although the sulphur distributions in individual plies show consistent lateral trends over the area, there is little relationship between vertically adjacent plies. Analyses (Cavender, 1995) to determine the forms of sulphur show that the organic sulphur is relatively constant (1.09 ± 0.36%, n=75) and pyritic sulphur is responsible for most of the variation (1.17 ± 1.79%, n=75). In the work of Cavender (1995), the mineralogy of the Parkgate coal was determined by x-ray diffraction (XRD) using smear mounts prepared from low-temperature ashed coal. The main minerals present are kaolinite, illite, mixed-layer clays, quartz, pyrite and gypsum. The latter is an artifact of the ashing procedure and probably results from reaction between organic sulphur and traces of carbonate or calcium in the coal. Through the seam there is some variation in the clay proportions. Kaolinite dominates towards the base, with illite and the associated mixed-layer clay more common higher in the seam.

3. Samples and Analytical Methods

Five underground seam sections of the Parkgate coal were sampled at 30cm intervals (Table 1) for uniform lithotypes, usually bright coal, and more frequently if the coal type differed. Four of the sections are from Thoresby and Welbeck Collieries (Figure 1) and lie within the area studied by Cavender (1995). The fifth section is from Maltby Colliery, which is approximately 18 km to the north-northeast of the original study area. A typical log for one of the Thoresby sections is shown on Figure 2. The coal at the base is also known as the 2nd Piper (samples A and B) and this is

split from the overlying 1st Piper by a carbonaceous mudstone (sample C). Within the 1st Piper (samples D through I), another semi-persistent mudstone is also present (sample G). Indentifying numbers and locations of the 38 samples are given in Table 1.

The U.S. Geological Survey Geochemistry lab in Denver, Colorado analyzed the 38 Parkgate coal samples discussed in this paper in a single analytical run in June, 2005. The analytical methods used are generally those of ASTM (2007), but may vary slightly. Most USGS analytical methods remain the same as described in Bullock et al. (2002) and the main methods include inductively coupled plasma-atomic emission spectrometry (ICP-AES) for major and minor elements (Al, Ba, Be, Ca, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, S, Sc, Si, Sr, Th, Tl, V, and Y) and inductively coupled plasma-mass spectrometry (ICP-MS) for trace elements (Ag, As, Au, B, Bi, Cd, Cs, Ga, Ge, Mo, Nb, Pb, Rb, Sb, Sn, Te, Tl, U, Zn, and Zr) on multi-acid-digested coal ash samples (ASTM D-6349 and D-6357). Two separate ash samples are prepared, one created at 750 degrees Celsius (ASTM D-3174) for major and minor element analysis and one at 525 degrees Celsius for trace elements (USGS method). Sample (remnant) moisture is also determined (ASTM D-3173). Mercury (ASTM D-6414 method A) and Se (USGS in-house acid-digestion method) were analyzed independently by cold vapor-atomic absorption spectrometry (CV-AAS). Total sulphur is analysed using a LECO SC432 instrument (ASTM D-4239). Chlorine analyses were changed in March, 2005 to direct combustion using a TOX 100 Cl analyzer (ASTM D-6721). Descriptions of USGS standard analytical procedures may be found on-line at http://energy.cr.usgs.gov/gg/geochemlab/methodology.htm (accessed August, 2008).

Statistical analysis of the analyses (whole coal, residual moisture basis) has been performed using Excel. One of the problems associated with the interpretation of chemical analyses is that the data are constrained and spurious correlations may well result, particularly negative associations. Essentially if a major component increases one or more of the other components must decrease because of the constant sum. Chayes (1971) highlighted the problem in what was then referred to as closed and open data. Subsequently Aitcheson (1986, 1999) readdressed the problem, stressed the impossibility of interpreting correlations of raw compositional components and advocated centered logratio transformed (clr) data to overcome the problems. In a recent paper addressing the interpretation of major and trace element analyses of the Upper Freeport Coal (USA), Drew et al. (2008) provide a clear illustration of the use and advantages of the centered logratio transform. This transform is used in the present paper for correlation matrices and determining significance limits. Bivariate plots (Figures 3 and 4) based on raw data are also used to estimate compositions of components not plotted, but which are indirectly related to those plotted through the closure effect. Regression equations on raw data were used to calculate intercept values. Differences observed between correlation coefficients using raw and centered logratio data were relatively minor.

4. Results

4.1. Major element geochemistry

The major elements are considered first because they can be directly related to the minerals present. A summary of the analyses is given in Table 2 and this shows that Si, Al, Fe and sulphur are the main elements present. A product moment correlation coefficient matrix based on centered log transformed data was calculated for all the

analyses. One closely related group of elements is composed of Si, Al, K, Ti and Mg. Correlations between all these elements are highly significant, and this is illustrated for Si and Al on Figure 3, which plots the raw data and shows the correlation factors for the logcentered data. The slope of the regression equation (0.71) is less than the Al/Si ratio of kaolinite (0.96). This is consistent with the XRD results which show a mixed clay assemblage and quartz. The intercept of the regression equation is very close to zero, suggesting that Si and Al are closely associated even at low concentrations in the coal. The lack of scatter about the regression equation and the near zero intercept are important as they indicate a clay fraction of relatively constant proportions diluted to varying degrees by the organic matter. The clay assemblage is thought to be dominantly detrital in origin (see for example Spears, 2006) and the total amount present a balance between the detrital rate of supply and the rate of preservation of the organic matter.

The plot of K vs Al (Figure 3) also shows the variation in abundance of the silicate minerals. The K is attributed to detrital illite and associated mixed-layer clays. The Al is also present in kaolinite, most of which is thought to be detrital, although some could be diagenetic. The regression equation shows a small positive intercept on the Al axis, suggesting that some Al is not detrital. The location for this non-detrital Al is thought to be the diagenetic kaolinite. This is borne out by XRD work (Cavender, 1995) showing that kaolinite is proportionally more abundant when the ash content of the coal is low. As the clay content increases, it is thought that the diagenetic kaolinite is progressively diluted by the detrital clays, which could simply be due to an increase in the rate of detrital input. Cavender (1995) also noted that there was proportionally more kaolinite towards the base of the seam. Hower et al. (2007) used the K_2O/Al_2O_3 ratio as a measure of the proportions of illite to total clay.

The K_2O/Al_2O_3 ratio examined vertically through the Parkgate seam is similar in all five sections, with low values towards the base and higher values towards the top of the seam. Although the ratio changes progressively with time, with possible climatic/ source rock implications, we argue above that this is related to the total clay content and the relative increase in importance of diagenetic kaolinite when the total clay content is low. The interpretation of the chemistry is consistent with the XRD results. There is also the possibility that organic Al contributes to the observed trend. Organic Al has been detected in coals similar to the Parkgate coal using laser ablation ICP-MS (Spears et al., 2007). However, the amount is thought to be relatively minor, amounting to no more than 0.05% Al, which would have little influence on the K-Al regression equation.

Titanium and Mg also have highly significant correlations with Al, Si and K, demonstrating the same mineralogical controls. Magnesium is present in illite and mixed-layer clays whereas Ti also occurs as discrete TiO_2 minerals.

Two major elements showing a very close relationship are Fe and total sulphur (Figure 3). The correlation coefficient (0.92) is highly significant. Iron and sulphur increase together reflecting the abundance of pyrite, but the regression equation (Figure 3) has a positive intercept on the total sulphur axis of about 0.91% as a result of the presence of organic sulphur. Cavender and Spears (1997) obtained a similar graph in a plot of pyritic sulphur (S_{pyr}) against total S% and, in addition, noted a lack of apparent relationship between the contents of S_{pyr} and organic sulphur (S_{org}). Although Fe is also present in the clay minerals, mainly illite in these samples, the dominant control on the Fe variation is the abundance of pyrite. The validity of these conclusions may be demonstrated for the present data by calculating the mean S_{pyr} content from the average Fe content (Table 2) and comparing this with the pyritic

sulphur content calculated as the difference between the total sulphur (Table 2) and the inferred organic sulphur from Figure 3. The values obtained are respectively 1.21% S $_{pyr}$ and 1.22% S $_{pyr}$.

Sodium is also present in the clay minerals, but again there is a more important control on the distribution. There are positive correlations between Na, moisture content and Cl. In these coals, Cl is not a trace element and its abundance is comparable with the conventional major elements. It has been argued that Na and Cl are predominantly present in brines within the coal (Spears, 2005) and the results in this work are entirely consistent with such a conclusion. Further evidence that most of the Na is not present in the clay minerals is provided by the lack of correlation between Na and clay-related elements. Also the fact that Na content is greater than K in the coal (Table 2) does not agree with the predicted composition based on the known clay mineralogy. Sodium and Cl therefore provide evidence of another potential host for trace elements in the coal in addition to the silicates and pyrite considered above.

There is a small amount of Ca present in the coals (Table 2). There is not a significant correlation between Ca and the clay-associated elements and the most likely locations for Ca are the interstitial fluids and carbonates. In the XRD scans of low temperature plasma ashed samples (Cavender, 1995) carbonates were not present, but gypsum was ubiquitous. This is an artifact usually associated with the reaction of carbonate with the S $_{org}$, but Ca dissolved in the interstitial fluids would react in a similar manner. However, as few trace elements are associated with Ca in these samples, the exact location of Ca is not of critical importance.

4.2. Trace element geochemistry

The very similar distributions of Si, Al, and K noted above means that any trace element showing a positive relationship with one also has a similar relationship with the others. Furthermore, such relationships reflect a dominantly detrital origin based on this origin for the Si, Al and the K. Trace elements correlating with K at more than the 99% significance level, in order of the value of the correlation coefficient (r), are Rb(0.99), Cs(0.99), Li(0.87), Ga(0.85), U(0.85), Cr(0.84), V(0.84), Ag(0.83), Sc(0.80), Y(0.78), Bi(0.78), Cu(0.77), Nb(0.76), Sn(0.75), Te(0.74), and Th(0.73). There are a number of samples in which Ag (22 samples) and Th (7 samples) were not detected. This does impose constraints on the interpretation of any statistical analysis, particularly for Ag. The plot of K vs Rb is shown on Figure 3. The lack of scatter about the regression equation and the near zero intercept are to be noted. The proportion of the variability in the Rb values explained by a straight line fitted by least squares (r^2) is over 99%, demonstrating the close geochemical similarity of K and Rb. For the other elements listed above, the r^2 values are progressively lower indicating more of the variability is unexplained by the regression equation. For example, in the case of V, although the dominant control on the concentration levels is the detrital input, nevertheless 30% of the V variability is unaccounted for.

In the previous section we noted that Fe and total sulphur correlate because of the variation in the abundance of pyrite. Trace elements that correlate with total sulphur and the values of those correlation coefficients, are Hg(0.82), Ni(0.82), Mo(0.81), Tl(0.78), Cd(0.78), Pb(0.76), As(0.75), Se(0.74), and Sb(0.67). Because the total sulphur includes on average about 1% S_{org} there is the possibility that some of the variation is due to organic matter and is not solely due to pyrite. However, the majority of the trace elements thought to be associated with pyrite plot in a similar manner to Fe against sulphur having a positive intercept on the sulphur axis. Because

of a potential variation in S_{org}, a more direct comparison is between the trace

elements and the Fe concentration. Showing highly significant correlations with Fe

are Hg(0.95), Tl(0.87), Pb(0.85), As(0.85), Se(0.84), Mo(0.80), Cd(0.78), Ni(0.77)

and Sb(0.73). The same nine elements are involved as for the correlations with S, but

the values of the correlation coefficient are in general higher with Fe than with S,

particularly for Tl, Pb, As and Se. On the basis that Fe is a more direct measure of the

variation in the pyrite content than total S, the improved correlations provide further

evidence for the important role of pyrite as a source of key trace elements. It is also

clear that as the content of pyrite increases in the coal the concentrations of the pyrite-

associated elements also increase. Possible implications of this will be discussed later.

Some trace elements will be contained within the organic matter. Those elements

that have a dominant organic association are negatively correlated with the ash

content. The Parkgate samples show that only Ge is in this category and the

relationship is below the 95% significance level. This approach was used by

Goldschmidt (1954) and others to demonstrate the organic association of Ge in coal.

Using a direct method (Spears et al., 2007), Ge and V have been shown to be

concentrated in vitrinite. In the present Parkgate samples, elements correlating with

Ge should also be organic associated. One possibility is Be (r = 0.69), but

correlations are generally lacking, showing that the organic matter has low

concentrations of trace elements compared with the mineral matter. Instead of looking

for negative relationships with the ash and ash-associated elements, information about

the organic contribution may also be obtained from positive relationships. The

positive relationships with K reflect the dominant detrital control, based on the detrital

(clay) origin of the K, but the contribution of other (minor) components may be

determined. The relevant information for the correlations involving K is shown on

Table 3. As noted earlier, there is a highly significant correlation between K and Rb with an intercept close to zero (Figure 3). The intercept value for all trace elements is given in Table 3, where it is also expressed as a percentage of the median value of all the samples in order to quantify the value of the intercept relative to the actual concentrations. The 95% confidence limits have been determined (Table 3), and if the lower limit does not include zero the intercept is judged to be statistically meaningful. Elements with either no significant intercept value, or where the intercept percentage is less than 50%, are Rb, Cs, Li, Ga, Cr, Sc, and Th. However, where the intercept percentage is greater than 50% a source other than the detrital fraction is indicated, which in all probability is the organic matter. Elements for which such a source is more important in these samples are V, Cu, U, Sn, Y and Bi. The intercept value measures the concentration of an element in the organic matter and on Table 3 are also shown similarly calculated trace element concentrations for the organic matter in the Eggborough coal (Spears, 2002). The organic matter could vary in composition between the two coals, but for the elements in common, there is good agreement for Cu, Nb and Y and reasonable agreement for V.

When the significant relationships between Fe and the trace elements are examined, Tl, Se, Pb, Hg and As all show intercept values not significantly different to zero, thus demonstrating the dominance of pyrite as a source for these elements. For the remaining elements, namely Mo, Ni, Cd and Sb, the intercept values are significantly different to zero and a small proportion of these elements is in a non-pyrite source. This could be attributed to the organic matter, but what is important is that pyrite is by far the dominant source in the coal and the concentrations in pyrite are much higher than in other sources.

The value of the correlation coefficient between Fe and Hg is high and therefore high correlations between the other pyrite associated trace elements and Hg would be anticipated. The scatter plots for four of the elements against Hg are shown on Figure 4. The value of the correlations between Hg and As (0.92), Tl (0.91), Se (0.86), Pb (0.82) and Cd (0.78) are very similar to those with Fe, which again highlights the dominance of pyrite as a host for these elements. It is noteworthy that the correlations also signify a pyrite with relatively constant trace element concentrations, the implications of which are considered in the next section.

5. Discussion

In the Parkgate coal pyrite is an important location for trace elements. This mineral contains nearly all the Hg, As, Se, Tl and Pb and most of the Mo, Ni, Cd and Sb. Sulphides in coal, and pyrite in particular, have long been recognised as an important location for many of the chalcophile trace elements (see for example Finkelman, 1982; Hower, 1997; Gayer et al., 1999). In general, coals high in sulphur typically contain more Hg, which is usually in pyrite (Yudovich and Ketris, 2005). Based on direct micro-analytical techniques, Diehl et al. (2004) noted that pyrite in coal from Alabama is the dominant host for Hg, Mo, Se, Cu and Tl and that concentrations of Hg, As, Mo, Sb, Tl and Pb in pyrite are one to three orders higher than in the surrounding coal. These results are very similar to the findings in the present work.

The importance of pyrite as a source of trace elements has environmental/industrial implications. Coal-cleaning to reduce the pyrite content will not only reduce S emissions, historically the primary aim in the UK, but will also significantly reduce the content of some of the key environmental trace elements. It is also important to note that these elements are volatile during coal combustion, which means special steps may be needed to retain one or more elements in the system and then to safely dispose of the residue. As most of the volatile elements are retained on the surfaces of the fly ash particles, they are potentially mobile in an

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aqueous weathering environment, which may lead to disposal safety issues. The weathering of

pyrite itself in discarded material is not without problems.

Based on the statistical relationships described earlier it is possible to calculate the trace

element concentrations in the pyrite. This has been done in the present work by substituting

the Fe content of pyrite in the Fe regression equations. The values on Table 4, column 1 are

shown in decreasing order of the correlation coefficient and therefore in increasing order of

error in extrapolating to the Fe content of pyrite. In particular the values for Zn and Co

should be treated with caution. Also obtained by a similar procedure to that adopted in the

current work, but using a physically fractionated coal, are the values in columns 2 (Harworth

coal, Spears et al., 1999a) and column 3 (Eggborough coal, Spears, 2002, Spears et al., 2007)

for coals from the same coalfield. Comparing the values in the three columns reveals that

there are similarities, but also some differences. Molybdenum and As are comparable,

whereas Se, Ni and Pb are all higher in the Parkgate coal, although the higher Ni may be

attributed to the influence of two samples with over 200 ppm Ni.

The concentration values in Table 4 show that Tl is several times higher than Hg, which in

turn is higher than Cd by a comparable amount. Unlike some of the other volatile elements,

notably Hg, Tl has received relatively little attention. In a review of Tl in the environment

Kazantis (2000) noted that sulphide-associated Tl is a major source of Tl release into the

environment. Thallium condenses on the surfaces of the fly ash particles in power plants and

concentrations are highest in the most difficult to capture very fine-grained fraction. We have

observed this surface association using laser ablation ICP-MS (Spears, 2004) and also for As,

U, Pb and Zn, but not for Hg, presumably through loss in the gaseous phase. Heim et al.

(2002) have observed toxicity of Tl of up to 100 times higher than Cd. Despite evidence that

Tl can have a harmful effect on the environment and man, less attention has been directed

towards Tl concentrations. It is clear that more information is needed on the anthropogenic distribution of Tl and its impact on the environment and man.

In addition to discussing where elements are located and the environmental implications it is also important to consider the origins of the elements and particularly the non detrital elements. The Parkgate coal is typical of many coals in the Yorkshire-Nottinghamshire coalfield in that it is high in sulphur, with S_{pyr} (1.17 ± 1.79%, n=75) greater than S_{org} (1.09 ± 0.36%, n=75) and responsible for most of the variation in the total sulphur. The sulphur is thought to be derived from seawater sulphate. In the Parkgate coal the spatial variation in the sulphur content in individual plies points to a depositional control (Cavender, 1995), which is consistent with the early diagenetic form of the pyrite and the quantitative insignificance of post-coalification pyrite in cleat and other fractures. A depositional control on the sulphur distribution can also be demonstrated from the inverse relationship between the sulphur content and distance from contemporaneous river channels in the Main Bright and Threequarters seams in the same coalfield. The channels are thought to have provided a means of access of more sulphate-rich seawater into the peat mire (Spears et al., 1999b). Unambiguous evidence for the role of seawater in introducing sulphur into the peat mire is provided by highly pyritic coals below some of the major marine bands in the sequence, such as the Amman Rider seam in South Wales (Gayer et al., 1999). Although the coal-bearing sequence is paralic and dominantly non-marine, it is possible that the marine influence is more pervasive than is generally thought. A reduction in vitrinite reflectance at the margins of many seams has been attributed to alkaline seawater percolation (Diessel, 1998). It is noteworthy that an increase in the activity of anaerobic bacteria, associated with the alkalinity, means that sulphate reduction is also quicker. The ingress of seawater not only introduces sulphate in the porewaters, but also enhances the rate of microbial action.

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The coals under study are also high in Cl**.** The Cl relationships in the present work indicate a source in the inherent moisture, which is entirely consistent with data for other coals in the coalfield, where it is thought Cl was concentrated as a conservative element during burial diagenesis (Spears, 2005) but probably starting from a high initial concentration due to seawater.

In the present work the correlations observed between Fe and some of the trace elements and the relationships between the trace elements demonstrate that the composition of the pyrite is relatively constant between samples. A similar observation was made for a suite of UK coals drawn from a much wider geographical area (Spears and Zheng, 1999), and constant Cu-Ni proportions were also noted in analyses of single micron-sized pyrite grains (Spears et al., 2007). Such relative constancy in the supply of trace elements is best explained if seawater was the reservoir. A seawater source for some trace elements in coals has been suggested by a number of authors, including Gayer et al. (1999) in the UK, but the coal they describe, the Amman Rider, has a major marine horizon in the roof measures.thus the link with seawater is not contentious.

Another line of investigation for the trace elements in coals is a comparison of element enrichments compared with seawater or, alternatively, contemporaneous marine shales. In work on Eggborough power station coal from the same coalfield as the Parkgate coal (Spears and Martinez-Tarazona, 1993), it was noted that some trace elements are enriched in coal and marine shales compared to a non-marine mudrock, thus supporting a seawater source. Because the mudrock chosen had a similar detrital mineralogy to that of the coal, therefore the ratio of a detrital element in the coal (expressed on an ash basis) to that in the mudrock is expected to be close to unity. For an element with a significant non-detrital fraction in the coal, the ratio is higher. This ratio (Spears and Martinez-Tarazona, 1993) was then compared with a similar ratio for a marine shale using the same mudrock. An improved calculation has

been made for the Parkgate samples using a shale ratio based on a non-marine shale from the same borehole as the marine shale (analyses from Spears and Amin, 1981) rather than a Coal Measures mudrock. Plotting those two ratios against each other shows a highly significant (r > 0.99) linear relationship, as does a recalculation of the Eggborough data. Lead, Cu, Ni, V, Sr and Zn to a lesser extent, all increase in similar proportions in both coal and marine shale, which strongly supports a seawater source. The comparison did not include key elements such as Hg, As, Se, Tl and Cd, because comprehensive data is currently lacking for the mudrocks.

Included in Table 4, column 4, are results obtained by direct analysis of *in situ* sulphide grains in East Midlands coals from the same coalfield as the Parkgate coal using synchrotron radiation XRF (White et al., 1989). Grains less than 50 micrometers (μm) in size could not be analysed and samples were therefore limited to nodules and cleat infill. Pyrite was found to be the dominant sulphide, but marcasite, chalcopyrite, galena and sphalerite were also identified. The trace elements showed log-normal distributions and the overriding impression reached by White et al. (1989) was of extreme heterogeneity in the sulphide microchemistry, although a tendency was noted for concentrations to increase in the later stages of the cleat infill. The log normal distribution may be attributed in part to possible time dependant increases in concentration, but an important factor is the larger grain size in the cleat and the greater opportunity for element segregation within the cleat compared to the early diagenetic pyrite. In spite of the differences in the analytical methods and the nature of the samples, the mean values in column 4 are similar to other calculated values in Table 4, suggesting that the calculated concentrations are of the correct magnitude. In spite of the heterogeneity noted by White et al. (1989), the bulk cleat infill does not apparently differ significantly in composition to the early diagenetic pyrite, suggesting a diagenetic origin for both. In some US coals it has been noted that the trace element composition of pyrite varies significantly both between samples and also within sample grains (Hower et al., 1997, 2007; Ruppert et al., 2005;

Goldhaber et al., 2002; Diehl et al., 2004), which does not conflict with the conclusions of White et al. (1989).

Late stage diagenetic/epigenetic fluids are known to be responsible for high concentrations of trace elements in some coals (see for example Gayer et al., 1999; Goldhaber et al., 2002; Diehl et al., 2004; Dai et al., 2005, 2006, Yudovich and Ketris, 2005; Hower et al., 2007). In the Yorkshire–Nottinghamshire coalfield, multistage formation of the cleat and its infill were described by Fellows (1979). The observations were extended by Spears and Caswell (1986) to an adjacent coalfield (Cannock) in the same depositional basin. A similar sequence of sulphides, silicates and carbonates were identified as in the Illinois coals (Hatch et al., 1976). The sequence of minerals, and their compositions, can be matched with diagenetic sequences that occur in clastic rocks undergoing burial diagenesis (Spears and Caswell, 1986). Hatch et al. (1976) concluded that the cleat provided channels for fluid flow and the coal was either a source of reduced sulphur species or it provided a substrate for bacterial sulphate reduction. The maturation of the organic matter and mineral transformations, such as progressive illitisation of mixed-layer clay, could have generated the necessary ions in solution, including reduced sulphur species from the coal itself (Spears and Caswell, 1986). Diehl et al. (2004) linked cleat mineralization with the movement of hydrothermal solutions driven by Alleghanian age tectonic activity in the Black Warrior Basin, Alabama. The analyses of pyrite in the work of Diehl et al. (2004) are very detailed and include Hg, As, Mo, Se, Cu and Tl. High concentrations of these elements are noted in late stage pyrite, but it is noteworthy that in the pre-compaction cell infill pyrite, Hg, As and Se concentrations are directly comparable with the values determined in the present work (Table 4). Diehl et al. (2004) note that the mechanism for trapping Hg and associated trace elements in pyrite is presently not well characterized but likely involves addition of either Fe or sulphur to a hydrothermal solution passing through the coal. Goldhaber et al. (2002) argues

that the hydrothermal solution in Alabama was probably H_2S-bearing, because complexation with bisulfide ion (HS^-) is the dominant mechanism for transport of As and associated trace elements in such fluids. One possibility these authors considered for the formation of the As- and Hg-rich pyrite was the addition of Fe to the fluid, possibly from siderite, with additional reduced sulphur species coming from thermally unstable organic sulphur within the coal. In Spears and Caswell (1986) it was proposed that the Fe in the cleat pyrite came from a source external to the seam in contrast to the sulphur which was sourced from within the seam by the thermal maturation of S_{org}. The nature of the ions in solution was not considered by Spears and Caswell (1986) for the trace elements, but complexation with bisulphide is certainly a possibility, although Cl complexes could also be important as the interstitial fluid is thought to have been Cl rich. The Fe could come from reaction with siderite in the shales, but how reactive the common nodular siderite would be is a matter of conjecture. Alternative Fe sources include the progressive illitisation of mixed-layer clay and dissolution of oxyhydroxide material. Although elimination of the latter would be predicted during early diagenesis in the mudrocks, oxyhydroxide material may have survived for longer in the sandstones present in the sequence.

In work on the Parkgate coal we have concluded that depositional processes control both the amount of pyrite and also its trace element composition. The presence of seawater is thought to be an important factor in facilitating the slow rate of transfer of ions into the sediment. Such a transfer is rate dependent, which would make the coal precursor an ideal substrate as the rate of accumulation is generally thought to be very slow. In addition, there is an abundance of organic matter to drive microbial reactions and create suitable conditions for element transfer. Alkaline conditions linked to the presence of seawater would also enhance microbial activity. In our Parkgate samples, the cleat minerals are thought to be syngenetic-diagenetic and not epigenetic in origin and are of minor importance. There is significant

epigenetic mineralization in areas adjacent to the coalfield, but this is thought to be

independent of fluid evolution in the coal basins (Cann and Banks, 2001).

6. Conclusions

(1) In the Yorkshire-Nottinghamshire coalfield Parkgate seam the main silicate

minerals present are kaolinite, illite, mixed-layer clays and quartz. Plots of Si-Al and

K-Al for the samples analysed in this work show only minor scatter about the

regression equations, indicating a clay fraction of relatively constant proportions

diluted to varying degrees by the organic matter. The clay fraction is thought to be

dominantly detrital with diagenetic kaolinite proportionally more important when the

total clay content is low, as for example towards the base of the seam. Changes in the

K_2O/Al_2O_3 ratio, measured vertically through the seam, are therefore seen as a

reflection of the total amount of clay rather than a time dependent change in clay

composition. The amount of total clay is a function of both the rate of supply and the

rate of organic preservation.

(2) The distributions of Si, Al, and K in the coal are very similar and are thought to

be controlled by the detrital input. Trace elements that are significantly correlated

with K, and thus detrital input, are Rb, Cs, Li, Ga, U, Cr, V, Ag, Sc, Y, Bi, Cu, Nb,

Sn, Te and Th. In the case of Rb there is very little scatter about the straight line

regression equation, which accounts for 99% of the variability. With decreasing value

of the correlation coefficient, the variability not attributable to the detrital input

increases.

(3) Iron and total sulphur are closely correlated, which is due to the occurrence of

pyrite. Although Fe is also present in the clay minerals, mainly illite in these samples,

the dominant control on the Fe variation in the samples is the amount of pyrite. A

number of trace elements increase in concentration with increases in the pyrite

content. Pyrite contains most of the Hg, As, Se, Tl and Pb and this mineral is also the major source of the Mo, Ni, Cd and Sb, with other sources in the coal making a minor contribution. The concentrations of these elements in the pyrite have been calculated, based on the regression equations. The As concentration is greater than 1000 ppm and it is noteworthy that highly toxic Tl (40 ppm) is more abundant than Hg (7.2 ppm) and Cd (0.9 ppm).

(4) Ge is thought to be mainly present in the organic matter and possibly Be is similarly located. From intercept values on the K regression equations contributions from sources other than the dominant clay minerals may be detected. Elements in this category, and probably present in the organic matter, include V, Cu and U and possibly Sn, Y and Bi.

(5) The Parkgate coal is typical of coals in the Yorkshire-Nottinghamshire coalfield in that it is high in both sulphur and Cl. This is attributed to a seawater influence, which probably controls many of the trace elements that are also enriched. The pyrite does appear to have a relatively constant trace element composition, both on the micro and macro scales. Such constancy in supply is consistent with a marine influence. A comparison of trace element enrichment factors in the coal with marine shales supports the seawater source.

(6) Finally, although cleat minerals *per se* have not been analysed in the current work, previous analyses are broadly in agreement with the present analyses. This is consistent with the view that the cleat minerals are also diagenetic, as also is the fact that although epigenetic mineralization is extensive in areas adjacent to the coalfield the hydrothermal solutions responsible appear to be unrelated to the interstitial fluids in the coalfield.

Acknowlegements

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Figure captions

Figure 1. Location of the Yorkshire-Nottinghamshire coalfield in the United
Kingdom. Collieries from which samples were collected are Maltby (M), Thoresby
(T) and Welbeck (W).

Figure 2. Parkgate seam section, Thoresby colliery.(Nat grid ref E461578 N374957).

Figure 3.Correlation plots of raw data (dry, whole-coal) with correlation coefficients
from centred logratio values for closely associated elements in the Parkgate coal.

Figure 4. Correlation plots for raw Hg versus As, Tl, Cd and Se in the Parkgate coal

samples and the correlation coefficients for the centred logratio value.