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The Role of Seawater on the Trace Element Geochemistry of Some UK Coals and a Tribute to Goldschmidt

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Abstract: The Pennsylvanian coals in the UK were deposited in a low-lying delta plain which was periodically inundated by the sea. This resulted in high S contents, mainly due to early diagenetic pyrite. Based on a statistical analysis of the geochemical data, pyrite is the major host for As, Se, Hg, Tl and Pb and an important host for Mo, Cd, Ni, Sb and Cu. All of these elements are enriched in the coals compared with non-marine mudrocks in the sequence, as is Ge and Be, although theirs is an organic association. The pattern of enrichment in the coals is similar to that in marine shales and coals overlain by marine shales, demonstrating the seawater influence. Goldschmidt was a pioneer in the geochemical study of coals and this paper will demonstrate that many of his ideas have stood the test of time.

Keywords: coal; trace elements; germanium; pyrite; vitrinite; enrichment; Goldschmidt

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1. Introduction

It has long been known that trace elements are enriched in coals. In the late 1920s and early 1930s Goldschmidt and his co-workers established that trace elements, such as Ge, As, Ag, Au and Bi, could be enriched in the ash residues resulting from coal combustion by a factor of about 1000 compared with averages for ordinary rocks at the earth's surface [1,2]. Goldschmidt, with his co-workers, had developed an optical spectrographic method of analysis giving improved element detection levels. Although this method has now been superseded it was capable of quantitative analyses for a significant number of elements, but it was time consuming. The first samples Goldschmidt [1] analysed included flue dust from the coal-fired heating system in the laboratory because it was in a suitable form for analysis. Goldschmidt would also be well aware of element fractionation during coal combustion due to differing element volatilities. High Ge concentrations were recorded in the flue dust and follow up analyses of coal samples showed Ge concentrations of over 1% in coal ashes, including samples from the UK. The coals described by Goldschmidt [1] came mainly from the Carboniferous Coalfields of western and central Europe. The coals were deposited in a low-lying, paralic environment, which was periodically inundated by seawater. The main aim of this paper is to establish what influence, if any, the ingress of seawater into the coal-swamp environment had on the trace element composition of the coals. Goldschmidt is known as the father of modern geochemistry, but possibly less well known are his contributions linked directly to coals and this paper will, in part, attempt to redress the balance.

The terms "metalliferous coal" or "coal-hosted ore deposit" have been used to describe coals with practical economic significance for valuable metal production [3]. A significant number of coal-hosted metalliferous ore deposits have been discovered in China, including those containing Ge, Ga, Al, REY, Se, U, V, Zr, Nb, Mo, and Re [4] and Figure 8 in this publication [4] is of value in showing, on the periodic table, not only those elements exploited now and in the past, but also those elements considered promising, even highly promising, for future extraction. The possibility of coal ash becoming a source of Ge was recognised by Goldschmidt [1], but at that time there was no commercial use for Ge. This is not the case now and the Ge currently being extracted from Ge-rich coals in Russia and China amounts to more than 50% of the total industrial Ge production in the world [5]. In the period after World War 2 uranium-rich coals were an important source of uranium for the nuclear industry, both in the Soviet Union and in the USA [6].

In discussing the origin of rare (trace) elements in coals Goldschmidt [1] suggested several possible mechanisms, which he described as not necessarily mutually exclusive. The first was concentration during the life of the plants themselves as plant ashes were known to contain trace elements such as B. The second was concentration by removal of the more soluble material during the decay of the organic matter with some trace elements retained as insoluble hydroxides or due to formation of organo-metallic compounds and the third was post-depositional resulting from reaction with circulating aqueous solutions. In the review of valuable elements in Chinese coals by Dai et al., (2016) [6], a number of additional processes have been considered including the introduction into the peat at an early stage of more enriched solutions, such as from the leaching of pre-existing igneous rocks, typically granites or contemporaneous volcanics. The introduction of seawater, which has higher element concentrations, into the coal swamp at an early stage would fall in this category. In contrast to these early processes, classed as syngenetic or infiltration, there are later stages classed as epigenetic or exfiltration. The presence of mineralised cleats (joints) in the coal is evidence of later stage processes. Cleat mineralisation is known to be multistage and in the case of the coals featured in this work the main phases of cleat infill have been related to fluid evolution during burial diagenesis [7].

2. Sedimentology of the Coal Measures

In this paper we are exploring a possible link between trace element concentrations in coal and the presence of seawater in the depositional environment. This possibility requires a sedimentological explanation as the coals formed in a non-marine environment as opposed to the marine shales. The latter were deposited in a marine environment based primarily on the fauna. The Coal Measures (Pennsylvanian) in the North of England essentially consist of cyclic sequences composed of mudstones, siltstone, sandstone, seatearth and coal in that upward sequence [8]. Cycles vary in thickness, but few are more than 15 m, although some are 60 m thick and typically these have thick sandstone developments. There is significant lateral in variation both in the thickness of cycles and the relative proportions of the component lithologies. Many of the cycles owe their origin to a lateral variation in sedimentary facies superimposed on differential subsidence. However, at the base of some of the cycles the mudrocks are represented by marine shales. Up to 19 marine flooding events been identified in the Coal Measures of the North of England corresponding to global sea-level highstands [9,10]. Although most of the coal-bearing sequence is non-marine there are important marine incursions, which may have an influence within the sequence.

The depositional environment for the Coal Measures in the UK was a low-lying paralic delta plain colonized by abundant vegetation and traversed by major river distributaries. Breaching of the channels allowed crevasse channel and crevasse splay sands to be deposited in the interdistributary lagoonal areas containing mud, silt and plant debris [11]. Although the coalfields of northern England are now separated due to post-Carboniferous folding and erosion they were once continuous and mainly formed in a major depositional basin now referred to as the Pennine Basin (Figure 1) [12] which lies to the west of the Northwest European Carboniferous Basin [13]. To the east, coals in the Netherlands, Belgium and the Ruhr belong to the same basin.

In a predominantly non-marine sequence the marine bands provide a vital means of correlation, both within and between coalfields. The work of Calver [9] on the marine faunas within the marine bands showed that the lateral distribution of the different faunal facies was closely related to the form of the Pennine Basin, with the deeper water, more marine environment restricted to the centre of the basin reflecting the greater subsidence.

3. Role of Seawater on S and Cl Concentrations in British Coals

In the UK Carboniferous coals there is a regional variation in both the total S and the organic S concentrations. Data compiled by Wandless [14], and plotted by Spears et al. [15] (Figure 7), shows that the total S concentration is highest, with averages of over 2%, in an area of central England coinciding with the depocentre of the Pennine Basin. In the same area the organic S is also highest, averaging over 0.9%. The difference between the total S and the organic S is due to pyritic S as the sulphate S is negligible. In a summary of S in Yorkshire coals, all deposited within the Pennine Basin, Pearson [16] noted that the distribution of S is essentially random. The S is present in organic S, about 1%, and the rest, and generally the major part, is present in pyrite. However, an exception to the random S distribution is where coals are overlain by marine bands. These coals consistently have high S contents mainly due to pyrite, although the coals are generally thin and uneconomic. Although the accepted thinking within the coal industry at that time was that the S distribution was random, this had not been fully tested and not on a section by section basis within the seams. This became possible with British Coal's computerized data base in the early 1990s. (British Coal ceased to exist in 1994 and the records, including seam analyses, were transferred to the National Geological Records Centre at the British Geological Survey) Using the data base in a collaborative study with industry, and backed up with additional analyses, the distribution of S in what were at that time key economic seams (including the Parkgate Seam) was investigated by Cavender [17] and reported in Cavender and Spears [18] and Spears et al. [15]. It was found that the S contents of individual sections of the seam (plies) could be mapped and the distribution was not random as had been thought. The lateral variation in the S content is essentially due to pyrite. Furthermore the S distribution in one plie was unrelated to the plies above and below. The conclusion reached was that this was a depositional control and the time dependent changes, i.e., from one plie to the next, reflected changing conditions within the coal swamp and particularly the geometry of the swamp. The possibility that the S distribution was related to later features such as faulting or folding was tested and rejected. A depositional control on the S is consistent with the framboidal, early diagenetic, form of the pyrite. Sulphate bearing waters had access to the coal swamp and given the climate at that time it has been argued [15] that river water would be insufficiently saline and that seawater was the more likely source of the sulphate. Detailed mapping of the S concentrations in seams in the East Pennine Coalfield has also shown that S concentrations decrease away from areas of long-lived river channel systems [15], thus demonstrating that the channels provided a means of access into the coal-swamp. In summary the S rich-coals below marine horizons demonstrates the importance of seawater as a sulphate source and in those parts of the sequence away from the obvious marine influence a convincing case can be made that seawater entered the coal-swamp and that river channels provided a means of access. Although the organic S is subsidiary to the pyritic S it does vary laterally. However, the distance over which trends are discernible is much greater, with concentrations increasing towards the centre of the Pennine Basin where the marine influence was greatest. At the local scale, such as within colliery boundaries, this lateral variation is not apparent, whereas that of the pyritic S is and can be mapped [17]. The fact that there is this divergence on the scale of the lateral variation between organic S and pyritic S may possibly be related to the controls on the formation of pyrite. In a review of S in coals Chou [19] noted that the formation of pyrite involves the reaction of reduced S species and Fe^{2+} in the porewaters during diagenesis. The presence of reduced species results from the microbial destruction of the organic matter and the loss of oxygen from the system. The availability of sulphate in the overlying waters is one control on what is a complex reaction, but also important is the supply of Fe essentially from the detrital sediment. This could be related to the development of reducing conditions within the sediment or to the variations in the detrital input.

Chlorine is another element in Yorkshire coals which is a significant impurity with concentrations reaching 1% in the coal in parts of the coalfield [16]. High concentrations, which these are, have a deleterious effect on the operation of power plants and methods of removal have been investigated. In the work of Caswell et al. [20,21] the Cl was found to be essentially present in pore waters within the coal. The composition of the porewaters within the coal are comparable with porewaters elsewhere in the sequence, but the coals have greater microporosity. The connate waters in the coalfield are essentially Na-Cl brines [22] and fit the general pattern of basinal brine evolution [23], with a progression from a Na-Cl to a Na-Ca-Cl brine. One way for the brine to evolve, a process subscribed to by Downing and Howitt [22] and others, was by a process of membrane filtration or reverse osmosis during burial in the Basin. Concentrations would rise during compaction and Cl as a conservative element would increase in concentration along with Na. This process would be greatly assisted if the original porewater was saline and of seawater derivation. Thus, in the case of Cl, the high concentrations found in the coals in northern England could well be due to a seawater influence in the Basin, although not as convincing, possibly, as the origin of the S in the system.

4. Role of Seawater on Trace Element Concentrations in British and Dutch Coals

4.1. South Wales

In work on coals from South Wales, Gayer et al. [24] sampled the Bute and the Amman Rider Seams, the former is above and the latter below one of the major marine bands in the Coal Measures, namely the Vanderbecki Marine Band. As would be predicted the S concentration in the seam with the marine roof is much higher than the other seam (4.19% as opposed to 1.09%). The trace element analyses by Gayer et al. [24] show (a) a Th/U ratio of below 2.9 for the Amman Rider, interpreted as indicative of enrichment of U from seawater; (b) Th/U values of between 2.5 and 4.9 for the Bute Seam indicative of "mild marine enrichment of U" (and this for a coal separated from the marine band by 3 to 4 m of rooted carbonaceous mudstones); (c) correlations between S and Pb, As, Cu and Ni in the Amman Rider were interpreted as due to pyrite and an origin from seawater and (d) enrichment in the Amman Rider coals of some of the environmentally sensitive elements by a factor of at least two compared with the global averages [25] whereas in the Bute Seam concentrations were less than the global average.

4.2. The Netherlands

In a study by Kombrink et al. [26] on the geochemistry of marine and lacustrine bands in the Upper Carboniferous of the Netherlands the underlying coals were also analysed using both inductively coupled plasma-atomic emission spectrometry (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS). The main focus of their work was in establishing the geochemical differences between the goniatite bearing shales, deposited in a distal and relatively deep marine environment and the proximal *Lingula* facies. Enrichment in redox-sensitive elements such as U, V and Mo was noted in the marine shales. Their discussion [26] covers the role of organic matter, the possible presence of anoxic bottom water and the rate of siliciclastic sedimentation. However, most pertinent to the present work are the important observations made on the geochemistry of the coals. It was observed that higher Mo and U concentrations in the coals may result from percolating seawater from above, in accordance with the findings of Gayer et al. [24], who, as noted above, also found enhanced U and Mo concentrations in marine influenced coals. The calculation of enrichment factors by Kombrink et al. [26] involved using the mean Al concentration of the average shale [27] for the mudrocks deposited in different salinity environments. Aluminium was used to normalize data to take into account changing clay proportions. In coals the enrichment was determined with respect to the mean trace element content of coals [24,25]. Aluminium was not used in the latter case because of its low concentration in coals. In addition some Al could be present in clay minerals which are not diagenetic, notably kaolinite, and coal macerals have also been recorded as containing organic Al [28]. This is particularly relevant if the enrichment factor is to be calculated to demonstrate the difference between the dominantly detrital mudrocks and the coals with a relatively small detrital fraction. In the present paper the approach adopted for the calculation of enrichment factors differs a little in that rather than using World mean/median values for coal and shale it is assumed that the non-marine mudrocks that occur in the sequence with the marine shales and the coals have element concentrations that closely reflect the detrital element contribution, i.e., that is the non-detrital fraction is relatively small. In other words the fine-grained siliciclastic sediment entering the depositional environment remains relatively unaltered and elements are not added from solution, whereas in the marine environment and possibly in the coal swamp this may not be the case.

On Figure 1 are plotted the enrichment factors for the marine shales in the work of Kombrink et al. [26]. The enrichment factors are calculated here as a ratio of the median of the element concentration in the marine shales divided by the median of the element concentration in the lacustrine (non-marine) shales. The majority of the elements show values for the ratio which are close to one, indicating that in the marine environment there has been very little transfer from solution into the sediment. For these elements the value of the ratio is in fact about 0.90 due to some dilution of the detrital fraction by the organic matter and elements added/retained from solution. Pyrite is one contributing mineral. The enrichment ratios could be normalised to eliminate the effect of dilution using the detrital elements but the correction is minor and has little effect on the values for those elements that are enriched. Values above unity on Figure 1 are noted for the elements highlighted by Kombrink et al. [26], namely V, Mo and U, but in addition there are other elements enriched including Ni, Cu, Zn, As, Pb and possibly Se, Cd, Sb and Tl. For the latter group values are closer to the analytical detection levels and percentage errors are higher.

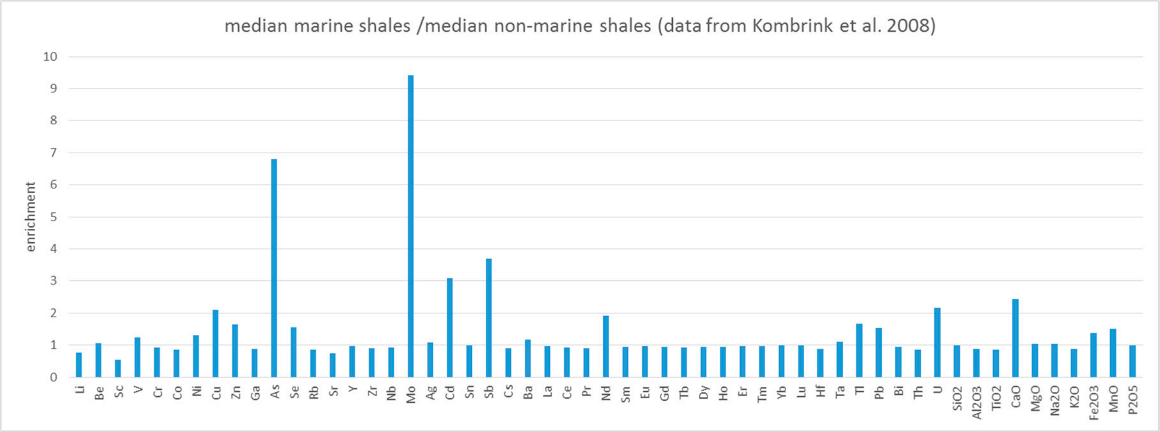

Figure 1. To show enrichment factors for Pennsylvanian marine shales in the Netherlands, based on median value marine shale/median value associated non-marine shale. Data from Kombrink et al. [26].

However, the main interest in the current work is not revisiting and confirming the findings of Kombrink et al. [26], for the marine shales, but in comparing the relative enrichments in the marine shales with the closely associated coals. Such a comparison is shown on Figure 2. In this case there is a need to normalize data and for the coals this has been based on a factor of 0.13, which is the approximate value of the concentrations of detrital elements in the coal as a ratio of the concentrations in the non-marine shale. The detrital elements can be recognized initially from the low values of their ratios, which is confirmed by the near unity plots on Figure 1 and the known geochemical behaviour of the respective elements. Elements with a ratio of 0.13 include Ga, Th, La, and Ce. The ratio for Li is 0.12, with Cr and Sn higher at 0.17 and Nb 0.19. Rubidium, on the other hand, gives a value of 0.03. The value of 0.13 is a reasonable compromise. A comparison of the enrichment factors on Figure 2 shows good agreement. If the elements are enriched in the marine shale then they are also enriched in the marine influenced coals and to a greater extent, demonstrating how efficient these coals are at fixing elements from solution. It might be argued that the overall higher values are simply an artefact of the normalisation calculation, but if so the detrital background level in the coals has been underestimated by at least a factor of two, which is most unlikely.

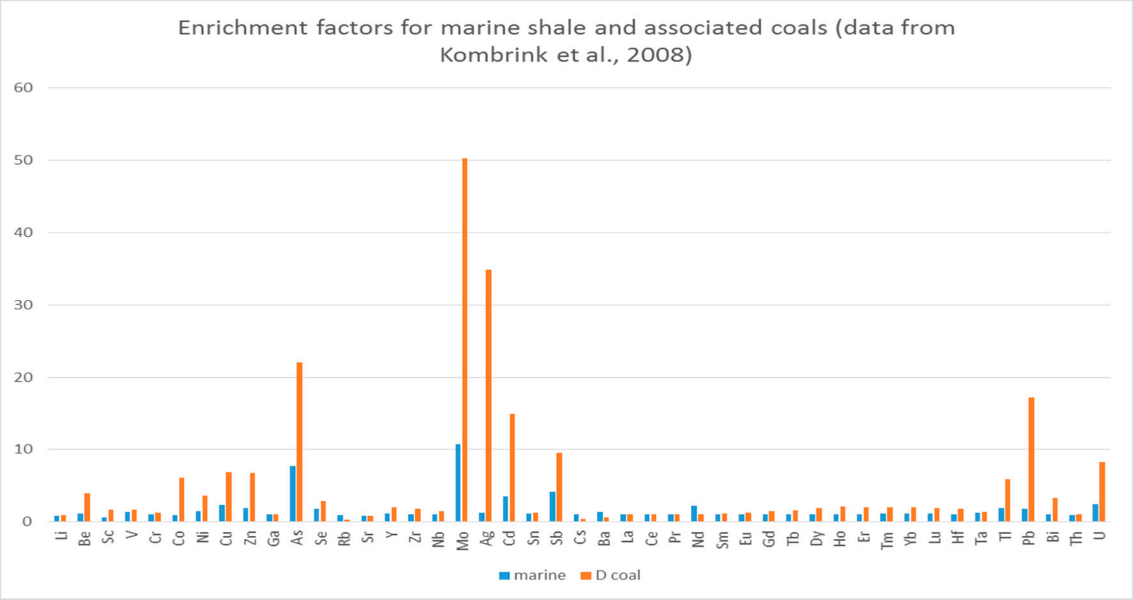

Figure 2. To show enrichment factors for Pennsylvanian marine shales and marine influenced coals in the Netherlands. Data from Kombrink et al. [26].

4.3. UK, Parkgate Coal

This is the coal that was sampled in the work of Cavender [17] and described earlier in this paper with respect to the S distributions. Samples were also comprehensively analysed by the USGS and described by Spears and Tewalt [29] and included in a review by Spears [12]. A summary of the analyses is shown on Table 1, including those of associated non-marine shales. As in the work of Kombrink et al. [26] analyses were made using both ICP-AES and ICP-MS, but with the inclusion of Hg determined by cold vapour atomic absorption spectrometry (CV-AAS) shown on column 3 Table 1 are the ratios of the median concentration in the coal to the median concentration in the shales. The trace elements identified as having low values for the ratio in the samples from the Netherlands above also show low values namely Ga (0.07), Th (0.08), Li (0.07), Cr (0.07) and Nb (0.08). Titanium is another element thought to be essentially detrital and the ratio is comparable (0.06). Cobalt also has a low ratio of 0.08 indicating that this element is also essentially detrital in origin, which is perhaps surprising. The value of 0.07 has been used to normalize the data to correct for the significantly smaller detrital input in the coals. This is a different value to that used in the calculations above because the detrital background is different. The resulting values are shown on Table 1, Column 4. Elements enriched by a factor greater than 3 are, in order, Se (35), Mo (30), As (16), Ge (22), Hg (17), Sb (15), Pb (6.1), Cd (5.4), Be (5.4), Cu (14.9), Tl (4.2), Ni (4.0) and U (3.1). All of the values are plotted on Figure 3 together with values from the marine influenced Dutch coals. Two elements not analysed in the first work, namely Ge and Hg, are also shown, and both are significantly enriched. The remaining elements are enriched in both data sets and to similar levels. It is concluded that the processes of enrichment are common to both groups and a key factor is the availability of trace elements in solution because of the presence of seawater. The Dutch coals analysed are marine influenced because they are overlain by marine strata. The comparable behaviour of the trace elements in the Parkgate Coal is convincing evidence that these too were marine influenced, which was also the conclusion reached from the S concentrations as discussed earlier.

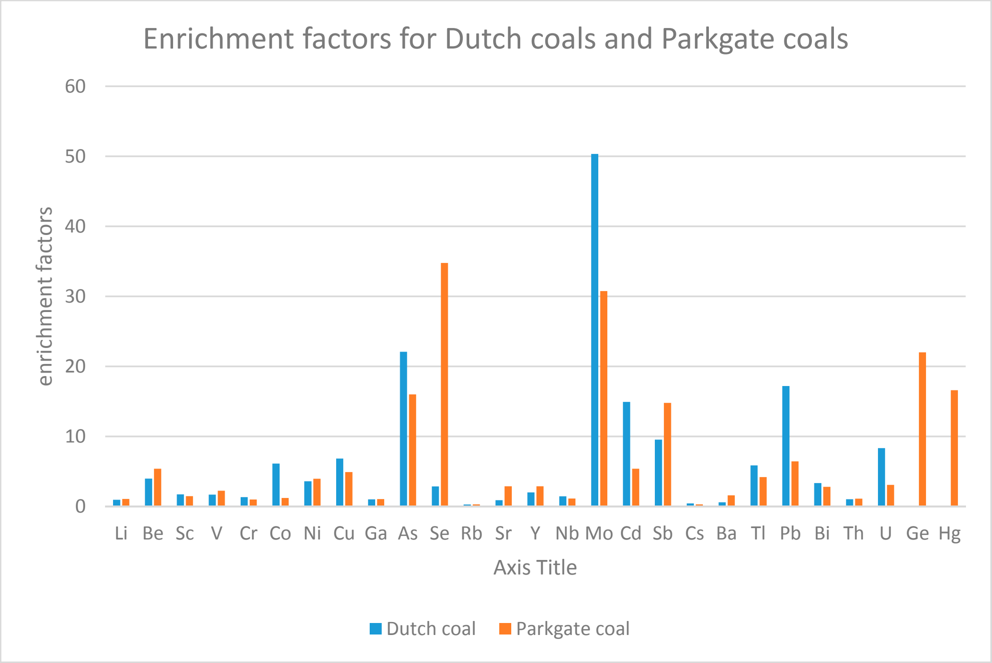

Figure 3. To show enrichment factors for marine influenced coals in the Netherlands and Parkgate coals in the UK. Data from Kombrink et al. [26] for the former and from Spears and Tewalt [29] and Spears [12] for the latter.

Table 1. Major and trace elements in Parkgate coals and associated mudrocks.

Elements	Unit	1	2	3	4
		Coal	**Shale**	**Enrichment Coal/Shale**	**Enrichment Coal/Shale (Scaled to 0.07)**
Si	Weight %	0.963	25.94	0.04	0.53
Al	Weight %	0.645	13.26	0.05	0.69
Ca	Weight %	0.171	0.19	0.9	12.86
Mg	Weight %	0.038	1.04	0.04	0.52
Na	Weight %	0.212	0.53	0.4	5.71
K	Weight %	0.072	3.44	0.02	0.3
Fe	Weight %	0.681	4.17	0.16	2.33
Ti	Weight %	0.03	0.53	0.06	0.81
P	Weight %	0.001	0.05	0.02	0.29
S*	Weight %	1.755	0.08	21.94	313.39
Ag	ppm	0.14			
As	ppm	11.5	10.3	1.12	16
Ba	ppm	84.1	760	0.11	1.58
Be	ppm	1.44	3.82	0.38	5.39
Bi	ppm	0.09	0.46	0.2	2.8
Cd	ppm	0.043	0.11	0.38	5.39
Cl	ppm	5850			
Co	ppm	2.34	27.9	0.08	1.2
Cr	ppm	8.94	130.6	0.07	0.98
Cs	ppm	0.28	14.5	0.02	0.28
Cu	ppm	29.7	86.5	0.34	4.91
Ga	ppm	2.01	27.3	0.07	1.05
Ge	ppm	5.52	3.59	1.54	21.99
Hg	ppm	0.086	0.074	1.17	16.65

Table 1. *Cont.*

Elements	Unit	1 Coal	2 Shale	3 Enrichment Coal/Shale	4 Enrichment Coal/Shale (Scaled to 0.07)
Li	ppm	10.02	134.1	0.07	1.07
Mn	ppm	24.4	645	0.04	0.54
Mo	ppm	2.8	1.3	2.15	30.75
Nb	ppm	0.78	9.87	0.08	1.13
Ni	ppm	24	86.9	0.28	3.95
Pb	ppm	12.75	28.3	0.45	6.44
Rb	ppm	3.67	182	0.02	0.29
Sb	ppm	1.68	1.62	1.03	14.78
Sc	ppm	2.13	20.8	0.1	1.46
Se	ppm	1.44	0.59	2.43	34.78
Sn	ppm	1.06			
Sr	ppm	35.1	175	0.2	2.87
Te	ppm	0.066			
Th	ppm	1	12.9	0.08	1.1
Tl	ppm	0.333	1.14	0.29	4.19
U	ppm	0.78	3.63	0.21	3.07
V	ppm	25.1	161	0.16	2.23
Y	ppm	4.59	22.7	0.2	2.88
Zn	ppm	7.6	79.4	0.1	1.37

Element concentrations in Parkgate coals and associated mudrocks UK is shown on Table 1. (Data from Spears and Tewalt, [29] and Spears, [12]). Column 1 shows median concentrations for the coals; column 2 shows median concentrations for the mudrocks; column 3 shows the ratio uncorrected for dilution of the detrital fraction in the coal and column 4 gives a corrected enrichment factor, taking in the dilution effect based on a scaling factor of 0.07. The derivation of this particular factor for this data is explained in the text.

5. Trace Element Locations in Parkgate Seam

There are a number of approaches, both direct and indirect, to determine the location of trace elements in coals. An indirect approach that has been widely used is based on a statistical analysis of a geochemical data base. An early application of this technique appears in the work of Goldschmidt [1], who argued that the inverse relationship between Ge concentrations in coals and the ash content is indicative of an organic association. Conversely, a positive relationship of elements with ash content demonstrates a relationship with one or more of the minerals present in the coals. It should be noted that the geochemical data base is a closed system in that elements sum to 100%. Thus in the case of Ge noted above, this is a two component system and as one increases the other must decrease. The variables are not independent and this influences the tests of significance. Chayes [30] was one of the first to note the problem. To overcome the problem a centred logratio transform was advocated by Aitchison [31,32] and applied to coal analyses by Drew et al. [33] and Spears and Tewalt [29]. A further improvement using a different log transform was proposed by Egozcue et al. [34] and applied to coals by Geboy et al. [35]. The log transforms do enable more rigorous statistical analyses to be conducted and will result in some changes (values of correlation coefficients, relative order of elements and significance levels), but the overall picture is unlikely to change [35], which is also the current author's experience.

The indirect approach for determining the locations of elements in the coal adopted here is based on the statistical analysis of a geochemical data base to produce, in the first instance, a correlation matrix and then to identify groups with a similar behaviour based on the correlation coefficients. Pairs of elements of interest are then plotted on x vs. y scatter plots. The value of the latter step was emphasized emphatically and eloquently by Anscombe [36] who showed it was possible for the relationships in data sets to differ fundamentally but for this not to be apparent from the calculated statistics, including the correlation coefficient. Outliers pose a particular problem as do non-linear relationships.

The ash content resulting from coal combustion is essentially derived from detrital and diagenetic minerals, with the organic matter making a negligible contribution to the major elements. An improved understanding of a trace element's location can be achieved by using major elements to quantify mineral abundances. This is illustrated on Figure 4a, where in the first instance Fe is plotted against the total S content in the Parkgate coals based on analyses in Spears and Tewalt [29]. This shows a positive relationship with the increases in both elements corresponding to variations in the amount of pyrite. (The slope of the regression equation corresponds to a composition of Fe $S_{1.90}$ which is close to the theoretical composition of pyrite). Also note that when the Fe content tends to zero there is a positive intercept on the S axis, which is the S independent of the pyrite, namely the organic S. The Fe content in the coals is closely related to the abundance of pyrite and if trace elements are contained by pyrite this should be revealed in correlations involving trace elements and Fe. Significant correlations with Fe are observed for 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). (Figures included in brackets for each element are the product moment coefficient of correlation r). The Fe vs. Tl scatter plot is shown on Figure 4b, which shows that pyrite is a major host for Tl. It is possible to go further and conclude, from the lack of a significant intercept value of the regression equation on either axis, that other sources for Tl are negligible. Mercury, Pb, As and Se are also similar in not showing significant intercept values when plotted against Fe, demonstrating that these elements are present in pyrite to the exclusion of other significant sources. The plot of As vs. Tl (Figure 4c) shows these two elements are closely related as are Tl and Hg (Figure 4d). Molybdenum, Cd, Ni and Sb also show significant correlations with Fe, but with lower values of the correlation coefficients. These elements occur predominantly in pyrite, but with possible contributions from other minor sources, which is not the case for Hg, Tl, Pb, As and Se where it is estimated that more than 90% of the element is contained in pyrite.

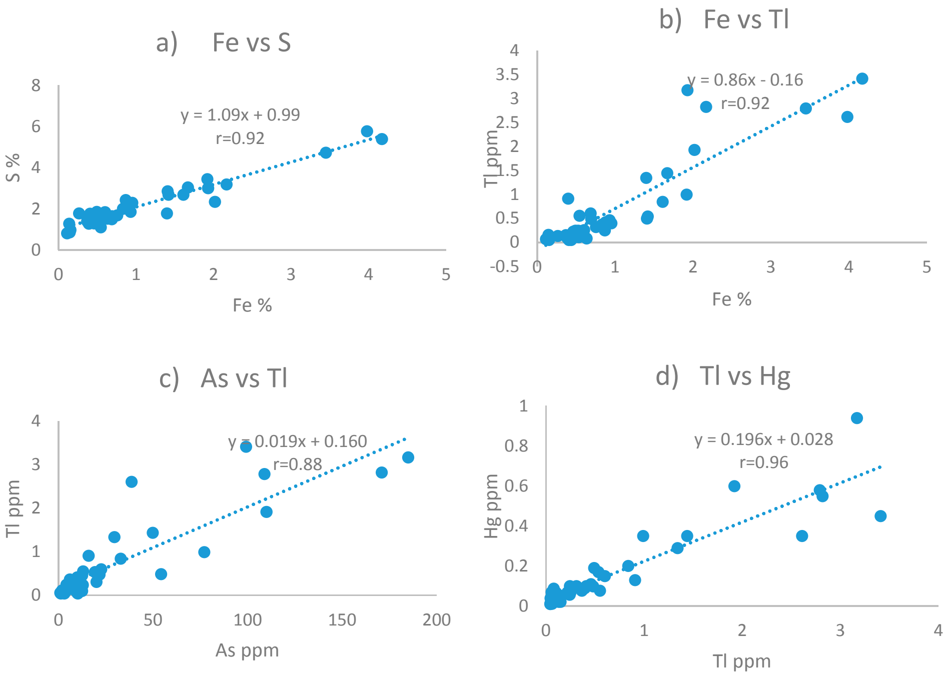

Figure 4. To show bivariate plots for elements in the Parkgate coals (UK). (**a**) Fe vs. S; (**b**) Fe vs. Tl; (**c**) As vs. Tl; (**d**) Tl vs. Hg. Regression equations and product moment correlation coefficients shown.

The discussion for the trace elements has dealt with relationships with Fe and inter-relationships between the trace elements. It is worth noting that correlations of trace elements with S are similar to those with Fe [29] but show marginally lower values of the correlation coefficients, although still statistically significant. This is due to proportionally more S being in another source than Fe. Nevertheless, plots of Hg, Tl, Pb, As and Se against S all show similar intercepts on the S axis as does Fe.

It has been noted earlier that elements are enriched in the Parkgate coals compared with the non-marine mudrocks in the sequence and that the levels of enrichment are comparable with marine influenced Dutch coals [26]. The elements contained within the pyrite are all identified as being enriched. There are some exceptions, notably Ge with a possible organic association, and elements which show moderate enrichment such as Cu and U for which may be present in pyrite, but cannot be demonstrated, in this case, from the statistics.

In order to calculate enrichment factors the data was normalized by using values for elements with minimum enrichments on the assumption that these are the detrital elements. This can be verified from the statistical analysis of the Parkgate coals [12,29] by looking for correlations involving the major elements Si, Al and K. The detrital minerals consist of quartz and the clay minerals including some diagenetic kaolinite. As this is an aluminium silicate the best measure of the detrital minerals is achieved by using K, which is present primarily in illite. In the Parkgate coals [12,29], trace elements correlating with K at the 99% significance level 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).

The plot of Rb vs. K [29] (Figure 3) not only has a very high correlation coefficient ($r = 0.998$), but also the linear regression equation passes very close to the origin on the bivariate plot and the intercept value is not significantly different to zero. Elements similar in behaviour to Rb are Cs, Li, Ga, Cr, Sc, Th and possibly Nb, and a predominantly detrital origin is indicated. What this means is that as the amount of clay in the coals increases so to do the concentrations of these elements. The detrital nature of these elements is demonstrated, which validates the procedure adopted here for the calculation of the enrichment factors.

The scaling factor used excludes values for K and Rb which are lower than the norm (Table 1). It is possible that these values are lower because there is some loss of K and Rb from their main location, which is the interlayer site in illite. Cation exchange with the NH_4 ion is one possibility, which is a reaction associated with the maturation of organic matter [37].

Vanadium also correlates with K, indicating a clay association, but there is a significant intercept value on the regression equation demonstrating that V is also present in another source in the coal, which is presumably the organic matter. Similar in behaviour to V, in correlating with K, are Cu, U, Sn, Y and Bi demonstrating a detrital control but with again a significant input from another source, possibly the organic matter.

Although an organic association for some elements, notably V, is indicated from the statistical analysis of the Parkgate data, inverse correlations with ash content were not observed because the organic matter is not the only source. One exception is Ge, which in line with Goldschmidt's findings [1], does show an inverse correlation with ash content, but one that is below the 95% significance level. Another element of interest is Be which shows a significant correlation with Ge and an organic association is suspected.

In order to determine the maceral association of those elements with a suspected organic host, representative samples were analysed for petrography and trace elements [28], the latter using laser ablation inductively coupled mass spectrometer (LA-ICP-MS). Polished sections of coal were analysed using a beam diameter of 20 μm in transects of about 10mm. The elements chosen for analysis, based on probable/possible organic association, were V, Ge, Ni, Cu, Sr and Ba with Fe and Al as controls on the mineralogy. The element profiles reflect the petrography with spikes for Cu and Ni due to micron-sized pyrite grains and broader increases corresponding to specific macerals. The Cu/Ni ratio is relatively constant for the pyrite and although statistically the sample size is small there is an indication of constant fluid compositions, which is again consistent with the presence of seawater. Vitrinite is the maceral containing most of the Ge and V, however there is evidence of some mobility during diagenesis, particularly for Ge. Although Al was included in the suite of elements analysed as a measure of the detrital clay another V vs Al relationship was discovered linked to the vitrinite [28] (Figure 7), which indicates that this Al is present in the organic matter. In some samples Ge is similar in behaviour to V and Al, but in others concentrations are uniformly low in the vitrinite, leading to the suggestion of greater mobility during diagenesis. This is borne out when element profiles through the seam are investigated. The enrichment of Ge near the margins of coal and within the partings of seams have been well documented [38]. In the Parkgate Seam Ge and Be show this pattern with concentrations higher at the margins of the seam [12] (Figure 7). Vanadium, on the other hand, only shows this distribution in some seam profiles. Enrichment at the upper and lower boundaries of the seam contrasts with the S distribution, which can be related to depositional processes. The seam profiles of Ge and Be, and V to a lesser extent, implies movement of ions during diagenesis. The question which is difficult to resolve is whether this is a redistribution within the seam or the introduction to a lesser or greater extent of ions originating outside the seam.

6. Discussion

The elements that are enriched in the coals considered in this work fall into two groups; one that is present in pyrite and the other present in the organic matter and vitrinite in particular. These two modes of occurrence are discussed further in the following text. There are a number of lines of evidence supporting the contention that the elements in pyrite were added at the time the peat was accumulating and that seawater was the ultimate source of these elements. The pyrite in question has an early diagenetic form and its distribution in seams can be mapped on a plie (bench/bed) basis within the seam. The distribution relates to depositional processes and not to post-depositional events such as folding or faulting. The elements that are pyrite related and enriched in the coals show similar patterns of enrichment to coals overlain by marine shales and indeed to the marine shales themselves. It is noteworthy that the degree of enrichment for the coals is greater than that for the marine shales, which is an indication of how efficient coals, or rather their precursors, can be in fixing elements from solution. In the preceding discussion the focus has been on the early form of pyrite, because this is volumetrically the dominant form, and not on later pyrite such as that present in the cleat (joints). The petrography of the latter is multistage and the mineralisation has been linked by Spears and Caswell [7] (Table 6) not only to fluid evolution in the basin during diagenesis, but also to elements released from the coal itself during coalification. More recently Kolker [39] has reviewed minor element distribution in iron disulphides in coals and has stressed the complex reactions involved in the formation of pyrite and marcasite within the coal and the different times of formation. The complex nature of the reactions involving the formation of reduced sulphur species and precipitation of Fe monosulphides in early diagenesis has been noted by Chou [19].

In another review publication Diehl et al. [40], noted the multistage formation of pyrite and the differing compositions in Pennsylvanian coals from the Appalachian region. This is not at variance with results of the present work which relates to the early formed pyrite rather than that which is post-compaction. In the coals from Alabama and Kentucky As, Se, Mo, Sb, Tl, Cu, and Hg are unusually concentrated in constituent pyrite [40]. There is broad agreement here with the present work in which it has been noted that As, Se, Hg, Tl and Pb are present in pyrite to the apparent exclusion of other sources (probably $> 90\%$). Pyrite is also a major host for Mo, Cd, Ni, Sb and Cu (the latter based on LA ICP-MS) but with a detectable contribution (probably $< 50\%$) from other sources.

In the studies on the coals in the Appalachian Region [40], it has been proposed that the metal-bearing pyrites were formed from hydrothermal solutions that were introduced into the coal beds along sets of NW–SE trending normal faults and structural discontinuities structures during the Alleghenian Orogeny. In the UK, Goldschmidt [1] suggested that element enrichment in the coals from

Northumberland (Hartley Colliery) might perhaps be linked to ores in the Lower Carboniferous in the nearby northern Pennines. Dewatering of adjacent basins as a source of hydrothermal fluids in the North Pennine Orefield has been considered by a number of authors over the years, including Dunham [41]. More recently Cann and Banks [42] have argued dewatering of the adjacent basins did not contributed significantly to the hydrofluids of the orefield and that the main phase of ore generation took place post-Carboniferous, during a Late Permian extension, which allowed saline waters, probably from the Zechstein Sea, to penetrate deep into the basement. Element enrichment in the coals of the Pennine Basin are therefore believed to be unrelated to the mineralisation in adjacent areas. On a more historical note it was originally thought the orefluids originated from contemporaneous granites below the stable blocks that are a key feature of much of the northern Pennines. Although exploratory work [41] discovered the granites they proved to be pre-Carboniferous age in age. Nevertheless, the granites are now thought to provide a heat flux which would drive fluid movement [42]. There is no doubt that fluid flow was complex and has been demonstrated by Bouch et al. [43] who identified earlier pervasive dolomitization and ankeritization, which took place in the presence of a high salinity brine, possibly one which was expelled from progressively maturing basinal shales over a period extending from the Late Carboniferous into the Early Permian. In summary, therefore, there is no convincing evidence from the orefield that the hydrothermal fluids were related to the metal enrichment in the coals, which is consistent with the present work where it is thought the enrichment was depositional. Not covered in the present paper, but considered in earlier work [7], is the timing of the cleat (joint) infill, which consists of (a) sulphide; pyrite and marcasite mainly with minor sphalerite and galena; (b) silicate; quartz and kaolinite and (c) carbonate; ankerite and ferroan calcite. There is a paragenetic sequence from (a) to (c) which has been linked to the diagenetic sequences in the associated clastic sediments and to have taken place during normal burial diagenesis. The ions necessary for these minerals are thought to have originated in both the coal and the associated clastic sediments [7] (Table 6) and therefore some post-depositional addition of elements to the coal is envisaged, but the amount is minor and has little influence on the whole rock geochemistry and its statistical analysis.

Finally, we return to the Ge enrichment in the coals. Goldschmidt [1] deduced that the Ge was organically related from the inverse relationship with ash content and this indirect, statistical approach to element-association has subsequently been developed, as in this work, to obtain detailed location information on many elements. Direct analyses show that Ge is concentrated in vitrinite, but not uniformly compared with V and Al, which could be due to Ge mobility during diagenesis. This is consistent with the common observation from coal seam profiles that Ge concentrations are higher at the upper and lower boundaries of the seam. Goldschmidt [1] suggested that Ge and other elements were possibly concentrated during the life of the plants and he demonstrated [1] (Table 4) that Ge was present in the ash of leaves and was higher in forest floor humus by a factor of at least 10. Germanium is now an element of technological and environmental importance and a wide-ranging review by Rosenberg [44] includes a detailed account of the biogeochemistry. Germanium is noted as being a very conservative element in biogeochemical terms and is similar in behaviour to Si, although the molar ratio deviates where Ge is complexed and transported, as for example by humic rich waters. Nevertheless, it has a high affinity for organic matter, as is demonstrated by the enrichment in coals. Specific information on the Ge behaviour in plants is provided by Delvigne et al. [45]. In their work two silica accumulating plants were studied to determine if there is partioning of Si and Ge in the plant pathways. Their results show equal uptake of both elements into the roots, but then Ge is preferentially retained in the roots. Consequently the Si/Ge is lower elsewhere in the plants, including in the opaline phytoliths, which are eventually recycled through the underlying litter and thus increasing the element fractionation. An important aim of the authors [45] was to understand more fully the Si flux into the oceans. In the present work of particular interest is the fact that Ge is retained within the plants, and moreover in horsetails, which are common in the Carboniferous. There is therefore support for Goldschmidt's [1] contention that Ge could be enriched in coals because of accumulation by the original plants. However, during coal maturation the evidence points to movement of Ge within the coal leading to enrichment in some vitrinites, but not all, and enrichment of Ge at the margins of the seam. Mobilisation of Ge from plant debris in the clastic sediments could be a contributing factor to enrichment of Ge at the margins of seams.

7. Conclusions

Coals occurring below marine bands in the UK have higher S concentrations, demonstrating the importance of seawater as a sulphate source.

(1) In the Parkgate Seam from the East Pennine Coalfield the variation in the S concentrations, due essentially to the amount of pyrite, can be mapped on a plie by plie basis. Adjacent plies, i.e., sections of coal above and below, have different distributions, indicating a depositional control which is consistent with the dominant form of pyrite, namely early diagenetic framboids.

(2) Seawater is thought to have gained access to the coal swamp via long-lived river channels. Ingress of high sulphate bearing waters from other sources is thought unlikely.

(3) Goldschmidt and his coworkers (summarized in English in 1 and 2) highlighted the enrichment of trace elements in coal ashes, including samples from the UK and postulated possible mechanisms of enrichment, including incorporation in the original plants and also the possible role of epigenetic ore-fluids associated with the North Pennine Orefield. The origin of the latter is now not thought to be related to the trace element enrichment in the coals, for which, in any case, a depositional origin is proposed.

(4) The enrichment of trace elements in the Parkgate Seam is demonstrated by comparison with the analyses of non-marine mudrocks in the sequence. Elements significantly enriched are Se (35), Mo (30), As (16), Ge (22), Hg (17), Sb (15), Pb (6.1), Cd (5.4), Be (5.4), Cu (14.9), Tl (4.2), Ni (4.0) and U (3.1).

(5) Coals from the Netherlands, which are of a comparable age to coals in the UK, were analysed by Kombrink et al. [26] together with associated marine and non-marine shales. The enrichment factors for the coals and the marine shales are comparable and are also comparable for the elements in common with the Parkgate Seam in the UK. This is compelling evidence that the Parkgate Coal is marine influenced even though most of the sequence is non-marine.

(6) The inverse relationship between Ge concentration and ash content noted by Goldschmidt (1), indicating a Ge-organic association, is an early example of an indirect method of determining element associations; a statistical approach which is widely used today. However, statistics can be misleading in some cases, as Anscombe [36] demonstrated, and bivariate plots are important. It should also be recognized that geochemical data sums to 100% and significance tests are influenced by the closed system. Several log-transforms have been proposed to overcome this problem.

(7) In line with Goldschmidt's findings [1] Ge in the Parkgate samples shows an inverse relationship with the organic matter, but one that is not significant at the 95% level. Direct analyses (LA ICP-MS) show Ge is concentrated in vitrinite, along with V and Al, but the former's concentrations are more variable suggesting greater mobility of Ge during diagenesis. This is borne out by element profiles through the seam showing enrichment of Ge at the margins of seam. This could be redistribution within the seam or later additions possibly from solutions with a contribution from plant debris in the clastic sediments.

(8) Ge is organic associated in the Parkgate coals and the possibility of derivation from plant material, as suggested by Goldschmidt [1], is supported by more recent work on silica accumulating plants, including horsetails [45], which show fractionation of Si and Ge with Ge preferentially retained in the roots.

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References

1. Goldschmidt, V.M. *The Occurrence of Rare Elements in Coal Ashes*; Published lecture to British Coal Utilisation Research Association (BCURA): Newcastle, UK, 1943.
2. Goldschmidt, V.M. *Geochemistry*; Oxford University Press: Oxford, UK, 1954.
3. Seredin, V.; Finkelman, R.B. Metalliferous coals: A review of the main genetic and geochemical types. *Int. J. Coal Geol.* **2008**, *76*, 253–289. [CrossRef]
4. Dai, S.; Yan, X.; Ward, C.R.; Hower, J.C.; Zhao, L.; Wang, X.; Zhao, L.; Ren, D.; Finkelman, R.B. Valuable elements in Chinese coals: A review. *Int. Geol. Review.* **2016**, *2016*, 1–31. [CrossRef]
5. Dai, S.; Seredin, V.V.; Ward, C.R.; Jiang, J.; Hower, J.C.; Song, X.; Jiang, Y.; Wang, X.; Gornostaeva, T.; Li, X.; et al. Composition and modes of occurrence of minerals and elements in coal combustion products derived from high-Ge coals. *Int. J. Coal Geol.* **2014**, *121*, 79–94. [CrossRef]
6. Kislyakov, Y.M.; Shchetochkin, V.N. Hydrogenic ore formation. *Mosc. Geoinform.* **2000**, *608*. (In Russian)
7. Spears, D.A.; Caswell, S.A. Mineral matter in coals: Cleat minerals and their origin in some coals from the English Midlands. *Int. J. Coal Geol.* **1986**, *6*, 107–125. [CrossRef]
8. Gossens, R.F.; Smith, E.G.; Calver, M.A. Westphalian. In *The Geology and Mineral Resources of Yorkshire*; Rayner, D.H., Hemingway, J.E., Eds.; Yorkshire Geological Society Occasional Publication: Leeds, UK, 1974; pp. 87–114.
9. Calver, M.A. Distribution of Westphalian marine faunas in northern England and adjoining areas. In *Proceedings of the Yorkshire Geological Society*; Yorkshire Geological Society Occasional Publication: Leeds, UK, 1968; Volume 37, pp. 1–72.
10. Waters, C.N.; Waters, R.A.; Barclay, W.J.; Davies, J.R. *A Lithostratigraphical Framework for the Carboniferous Successions of Southern Great Britain (Onshore)*; British Geological Survey: Nottingham, UK, 2009.
11. Guion, P.D.; Fielding, C.R. Westphalian A and B sedimentation in the Pennine Basin, UK. In *Sedimentation in a Synorogenic Basin Complex: The Upper Carboniferous of North-West Europe*; Besly, B.M., Kelling, G., Eds.; Blackie: Glasgow, UK; London, UK, 1988; pp. 153–177.
12. Spears, D.A. The geochemistry and mineralogy of high-S coals, with examples mainly from the East Pennine Coalfield in Yorkshire and Nottinghamshire, UK: An overview. *Proc. Yorks. Geol. Soc.* **2015**, *60*, 204–226. [CrossRef]
13. Ziegler, P.A. *Geological Atlas of Western and Central Europe*, 2nd ed.; Shell Internationale Petroleum Maatschappij B.V: Hague, The Netherlands, 1990.
14. Wandless, A.M. The occurrence of sulphur in British coals. *J. Inst. Fuel* **1959**, *32*, 258–266.
15. Spears, D.A.; Rippon, J.H.; Cavender, P.F. Geological cosntrols on the sulphur distribution in British Carboniferous Coals: A review and reappraisal. *Int. J. Coal Geol.* **1999**, *40*, 59–81. [CrossRef]
16. Pearson, H.W. Coal. In *The Geology and Mineral. Resources of Yorkshir*; Rayner, D.H., Hemingway, J.E., Eds.; Yorkshire Geological Society Occasional Publication: Leeds, UK, 1974; Volume 2, pp. 309–327.
17. Cavender, P.F. Sulphur Distribution in Key British Coals and the Trace Element Concentrations in Sulphide Minerals. Ph.D. Thesis, University of Sheffield, Sheffield, UK, 1995.
18. Cavender, P.F.; Spears, D.A. Sulphur distribution in a multi-bed seam. In *European Coal Geology and Technology*; Gayer, R.A., Pesek, J., Eds.; Geological Society: London, UK, 1997; Volume 125, pp. 245–260.
19. Chou, C.L. Sulfur in coals: A review of geochemistry and origins. *Int. J. Coal Geol.* **2012**, *100*, 1–13. [CrossRef]
20. Caswell, S.A.; Holmes, I.F.; Spears, D.A. Water-soluble chlorine and associated major cations from the coal and mudrocks of the Cannock and North Staffordshire coalfields. *J. Inst. Fuel* **1984**, *63*, 774–781. [CrossRef]
21. Caswell, S.A.; Holmes, I.F.; Spears, D.A. Total chlorine in coal seam profiles from the South Staffordshire (Cannock) Coalfield. *J. Inst. Fuel* **1984**, *63*, 782–787. [CrossRef]
22. Downing, R.A.; Howitt, F. Saline groundwaters in the Carboniferous rocks of the English East Midlands in relation to the geology. *Quart. J. Eng. Geol.* **1969**, *1*, 241–269. [CrossRef]

23. Hanor, J.S. Porewaters in sediments. In *Encyclopedia of Sediments and Sedimentary Rocks*; Middleton, G.V., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands; Boston, MA, USA; London, UK, 2003; pp. 537–542.
24. Gayer, R.A.; Rose, M.; Dehmer, J.; Shao, L.-Y. Impact of sulphur and trace element geochemistry on the utilization of a marine-influenced coal—Case study from the South Wales Variscan foreland basin. *Int. J. Coal Geol.* **1999**, *40*, 151–174. [CrossRef]
25. Swaine, D.J. *Trace Elements in Coal*; Butterworth: London, UK, 1990.
26. Kombrink, H.; Van Os, B.J.H.; Van Der Zwan, C.J.; Wong, Th.E. Geochemistry of marine and lacustrine bands in the Upper Carboniferous of the Netherlands. *Neth. J. Geosci.* **2008**, *87*, 309–322. [CrossRef]
27. Taylor, S.R.; McLennan, S.M. *The Continental Crust: Its Composition and Evolution*; Blackwell: Oxford, UK, 1985.
28. Spears, D.A.; Borrego, A.G.; Cox, A.; Martinez-Tarazona, R.M. Use of laser ablation ICP-MS to determine trace element distributions in coals, with special reference to V, Ge and Al. *Int. J. Coal Geol.* **2007**, *72*, 165–176. [CrossRef]
29. Spears, D.A.; Tewalt, S.J. The geochemistry of environmentally important trace elements in UK coals, with special reference to the Parkgate Coal in the Yorkshire—Nottinghamshire Coalfield, UK. *Int. J. Coal Geol.* **2009**, *80*, 157–166. [CrossRef]
30. Chayes, F. *Ratio Correlation*; The University of Chicago Press: Chicago, IL, USA, 1971.
31. Aitchison, J. *The Statistical Analysis of Compositional Data*; Chapman and Hall: London, UK, 1986.
32. Aitchison, J. Logratios and natural laws in compositional data analysis. *Math. Geol.* **1999**, *31*, 563–580. [CrossRef]
33. Drew, L.J.; Grunsky, E.C.; Schuenemeyer, J.H. Investigation of the stucture of geological process through multivariate statistical analysis—The creation of a coal. *Math. Geosci.* **2008**, *40*, 789–811. [CrossRef]
34. Egozcue, J.J.; Pawlowsky-Glahn, V.; Mateu-Figueras, F.; Barcelo-Vidal, C. Isometric logratio transformations for compositional data analysis. *Math. Geol.* **2003**, *35*, 279–300. [CrossRef]
35. Geboy, N.J.; Engle, M.A.; Hower, J.C. Whole-coal versus ash basis in coal geochemistry: A mathematical approach to consistent interpretations. *Int. J. Coal Geol.* **2013**, *113*, 41–49. [CrossRef]
36. Anscombe, F.G. Graphs in statistical analysis. *Am. Stat.* **1973**, *27*, 17–21.
37. Williams, L.B.; Ferrell, R.E. Ammonium substitution in illite during maturation of organic matter. *Clays Clay Miner.* **1991**, *39*, 400–408. [CrossRef]
38. Yudovich, Y.E. Notes on the marginal enrichment of Germanium in coal beds. *Int. J. Coal Geol.* **2003**, *56*, 223–232. [CrossRef]
39. Kolker, A. Minor element distribution in iron disulphides in coal: A geochemical review. *Int. J. Coal Geol.* **2012**, *94*, 32–43. [CrossRef]
40. Diehl, S.F.; Goldhaber, M.B.; Koenig, A.E.; Lowers, H.A.; Ruppert, L.F. Distribution of arsenic, selenium, and other trace elements in high pyrite Appalachian coals: Evidence for multiple episodes of pyrite formation. *Int. J. Coal Geol.* **2012**, *94*, 238–249. [CrossRef]
41. Dunham, K.C. Pennine mineralisation in depth. *Proc. Yorks. Geol. Soc.* **1988**, *47*, 1–12. [CrossRef]
42. Cann, J.R.; Banks, D.A. Constraints on the genesis of the mineralization of the Alston Block, Northern Pennine Orefield, northern England. *Proc. Yorks. Geol. Soc.* **2001**, *53*, 187–196. [CrossRef]
43. Bouch, J.E.; Naden, J.; Shepherd, T.J.; McKervey, J.A.; Young, B.; Benham, A.J.; Sloane, H.J. Direct evidence of fluid mixing in the formation of stratabound Pb–Zn–Ba–F mineralisation in the Alston Block, North Pennine Orefield (England). *Miner. Depos.* **2006**, *41*, 821–835. [CrossRef]
44. Rosenberg, E. Germanium: Environmental occurrence, importance and speciation. *Rev. Environ. Sci. Technol.* **2009**, *8*, 29–57. [CrossRef]
45. Delvigne, C.; Opfergelt, S.; Cardinal, D.; Delvaux, B.; André, L. Distinct silicon and germanium pathways in the soil-plant system: Evidence from banana and horsetail. *J. Geophys. Res.* **2009**, *114*, G02013. [CrossRef]