Pergamon

Water-rock interaction in an acidic mine discharge as indicated by rare earth element patterns

F. Worrall* and D. G. Pearson

Department of Geological Sciences, Science Laboratories, University of Durham, South Road, Durham, DH1 3LE, United Kingdom

Abstract—The rare earth element (REE) composition of an acidic spring discharging at pH 2.7 was studied in relation to the REE composition of selected extracts of the coal-bearing strata hydrologically above the discharge. The low pH of the discharge and the access to the strata through which it flows provides an excellent opportunity to study the use of REEs as tracers of water-rock interaction. Extraction techniques were used to mimic the process of acidic groundwater generation in coal-bearing strata. Samples were treated to remove exchangeable ions and then treated sequentially with solutions buffered at pH 5.5, 3.6 and 1.6 in order to mimic the natural buffering systems of groundwaters. Finally, samples were oxidised with hydrogen peroxide in an attempt to remove the pyrite.

The results show that the composition of the spring is controlled by pyrite oxidation and buffering by Fe oxy-hydroxides, the latter with compositions inherited from carbonates from within the sequence. The similarity of REE patterns of the carbonate and the silicate extracts tends to obscure information concerning the relative roles of carbonate or silicate phases. The source strata of the spring has evolved over time and shows that different coal seams have a unique contribution. This distinct contribution appears more related to the mixture of sedimentary components (i.e. carbonates, silicates, etc.) in the coal seam and the combination of shale and sandstone layers surrounding coal seams than the composition of the components themselves.

The similarity between REE compositions of the sequential extracts suggests that relationships discovered for this spring will be applicable elsewhere in the basin. However, this very property will hamper the use of such lithophilic elements in cases where characterisation of the source area is not possible. *Copyright © 2001 Elsevier Science Ltd*

1. INTRODUCTION

Acidic mine discharges (AMD) represent a major source of water pollution in areas of present and former mining activity. The source of this pollution is taken as being the oxidation of pyrite (FeS_2), which creates groundwater with a low pH and high total dissolved solids (TDS), particularly metals and sulphate. However, many of the discharges from coal strata, associated with pyrite oxidation and termed *acidic mine discharges,* are circum-neutral (pH 6–7.5), implying extensive water-rock interaction before emergence. Carbonate minerals occur in coal measures, siderite being common and acting as an additional source of iron to these discharges (Younger, 1995). Quartz, feldspars, and clays also occur in coals and associated strata, providing further buffering capacity to these AMDs, and act as a source of trace elements. The extent to which these reactions control the composition of these discharges and their evolution has received comparatively little attention.

The purpose of this study is to identify the water-rock interactions that govern the composition of acidic groundwater discharges emanating from coal-bearing strata. This study will address a number of questions. First, can the phases that are being weathered by the highly acidic water produced be identified and their respective importance delineated? Second, can the source of the acidic groundwater be specifically identified, that is, which strata are contributing what to the discharge? Third, can the evolution of the discharge be predicted? With the

latter in mind it is important to consider the importance of buffering systems in controlling the composition of discharges and in their evolution. An easily accessible discharge at North-wood (National grid ref. –NZ 212 402; Fig. 1) allows a unique opportunity to study the development of acidic groundwaters. At this locality an acidic spring (pH 2.7) emerges from a perched water table on an isolated hillside within the West-phalian coal measures of the Durham basin (Fig. 1). The strata hydrologically above the spring at this site have been exposed by opencast mining of the area's coal seams, and therefore all the strata through which the spring water permeates can be sampled and analysed.

An examination of acidic mining lakes of eastern Germany suggests that three dominant buffering systems are operating (Geller et al., 1998): carbonates, Al-silicates, and Fe oxy-hydroxides. To understand the evolution of the discharge composition over time, it is necessary to consider the balance between the potential acid neutralisation/buffering reactions and the acid-producing, pyrite oxidation processes. If carbonates are present, the initial acid production will be buffered at circum-neutral pHs, but if acid production can outstrip the amount of carbonate available, the pH of the discharge will rapidly change as Al species become the major buffering system. These changes not only represent large shifts in pH but have consequences for element mobility that result in increased metal loads. Ultimately the system becomes self-buffering as one of the products of pyrite oxidation (i.e., Fe oxy-hydroxide) acts as the major buffering system. Although any given spring will conform to one or the other of these systems depending on which is dominant within the catchment of the spring, condi-

---

*Author to whom correspondence should be addressed (fred.worrall@durham.ac.uk).
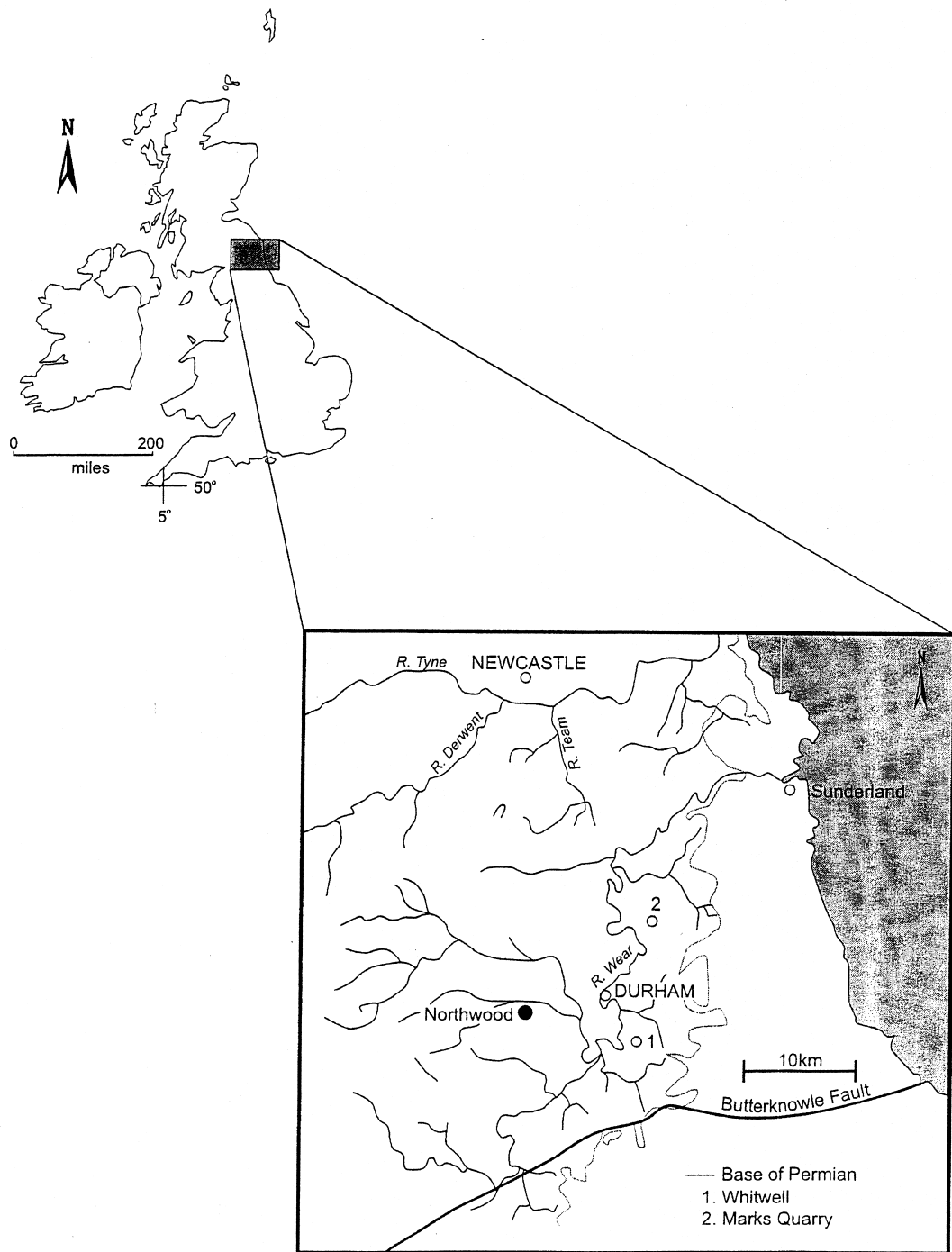
Fig. 1. Location map showing the site at Northwood and those sites from which coal-hosted pyrite could be sampled.

tions may be very heterogeneous with each of the buffering systems controlling water-rock interaction at different points in space and at differing scales. The balance of these buffering systems will control the overall emergent water quality of the discharge, and the spring will evolve as the balance of these local buffering systems shift. If chemical fingerprints of each of these buffering systems could be identified, then the balance and heterogeneity of the discharge's catchment could be as-

sessed. The heterogeniety of the catchment gives a measure of the likely evolution of the spring. For example, in a discharge that is about to become Al-dominated, the waters could be expected to show indicator ions of both Al and carbonate buffering systems.

Rare earth element (REE) patterns can record subtle geochemical processes in natural systems (Taylor and McLennan, 1988). Because of the lithophilic nature of REE, the source in

groundwaters is dominantly the surrounding strata, and hence the potential REEs have to be tracers of groundwater mixing, source regions, and water-rock interactions (Banner et al., 1989; Smedley, 1991; Fee et al., 1992; Johannesson et al., 1994; Banks et al., 1999). Recent work has suggested that the REEs may approach conservative behaviour in some groundwaters (McCarthy et al., 1996, 1998; Johanneson et al., 1997a). In addition, Johanneson et al. (1997b) have shown that REE patterns in groundwater retain a distinctive signal from different aquifers. Other studies have tended to focus on circumneutral or at least only slightly acidic waters (Smedley, 1991; Johannesson et al., 1997a). The low pH of the waters in the present study means that they are more likely to retain their metal content in solution and so make a good target for our study.

2. MATERIAL AND METHODS

2.1. Approach

The approach we use in this study is to compare the composition of groundwaters discharging from the Northwood spring, with selected extracts from the rock strata exposed above. Selective sequential extractions have been used for a wide variety of studies, including exploration geochemistry (e.g., Cardoso Fonseca and Martin, 1986), in environmental studies (e.g., Tessier et al., 1979), for assessing trace element mobility and availability in soils and sediments (e.g., Kersten and Förstner, 1995), and bioavailability of trace metals (e.g., Harrison, 1981). Chao (1984) has outlined the advantages of sequential over bulk analysis which include the following:

i.   understanding the mode of occurrence of elements of geochemical interest,
ii. evaluating leachability and mobility of elements,
iii. helping choose appropriate sample media and extraction procedures for analytical work,
iv. enhancing geochemical contrasts,
v.   highlighting the degree and extent of weathering, and
vi. aiding the interpretation of chemical data in relation to a broader chemical environment.

The series of sequential extractions used in the present study were chosen to correspond to the leachable phases believed to be present in the strata. Furthermore, the extracts were set to correspond to a pH just below levels of buffering by carbonates and Al-silicates (pH 5.5, 3.6 and 1.6 respectively) –as suggested by Geller et al. (1998). The latter was also set to guarantee that all acid-leachable phases are removed before extraction of oxidisable phases. Because the oxidation of pyrite produces acidity, it is important that the compositions of the oxidisable phases are not obscured by addition of REEs from acid-leachable phases, hence this determines the order of extraction. An initial extraction was used to remove the exchangeable ions before acid treatment.

2.2. Sample Collection

All strata in the Northwood section (Fig. 2) were sampled in triplicate with samples being taken at least two metres apart. An earlier study (Worrall and Pearson, in press-a) had shown that sampling in triplicate adequately reflected intrastrata variation, thus making interstrata comparisons possible. In addition, six separate samples of the Northwood spring were taken at times of minimum flow as chosen with reference to the records maintained by the opencast operator. The pH of the spring (pH 2.7–2.9) means that water samples did not require acidification nor filtration to remove ochreous precipitation. Samples of coal-hosted pyrite could not be found in the Northwood opencast but were available from other opencast coal mines in the same basin. Samples were taken from Whitwell (5/4 seam) and Mark's Quarry (mid leaf, High Main seam; Fig. 1).
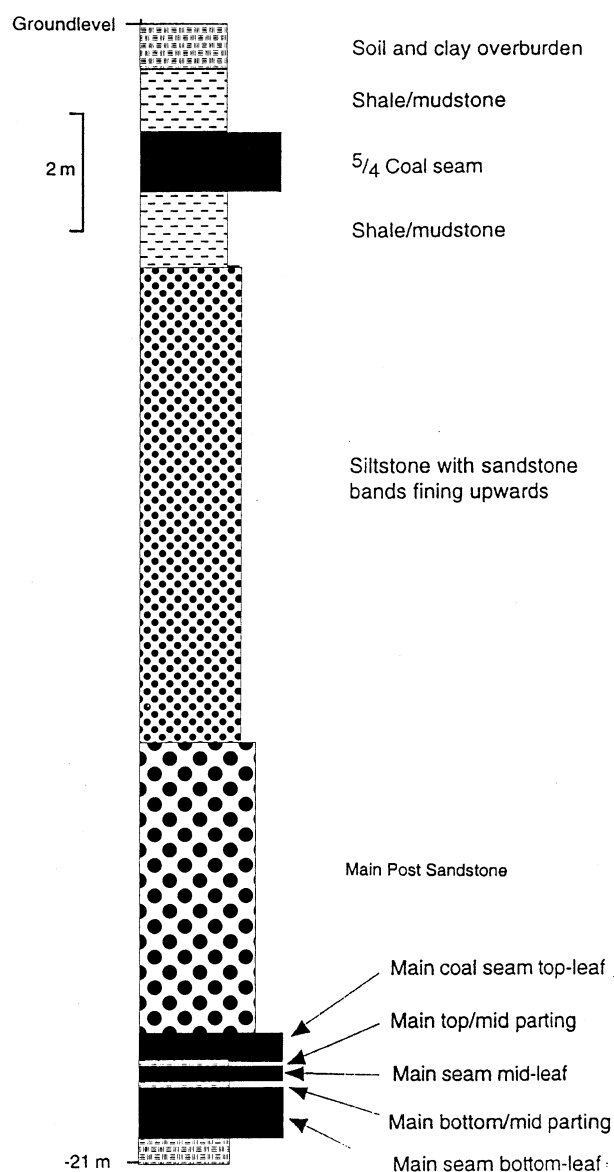

Fig. 2. The Northwood section showing all the strata sampled as part of the study. The base of the illustrated section indicates the level of the discharge at Northwood.

2.3. Sample Preparation

We crushed 2.5 g of each rock sample taken from the Northwood section to pass through 150-μm sieve before sequential extraction. The first phase of the sequential extraction procedure was removal of the exchangeable cations. In this case, 2.5 g of sample was mixed and left to stand overnight with 20 mL of 2 mol/L ammonium acetate buffered at pH 7. The mixture was filtered to 0.45 μm through a cellulose nitrate filter; the residue was washed with distilled, deionised water to make the filtrate up to 50 mL and was kept for analysis. The residue was dried at 105°C and kept for subsequent analysis.

Extraction of the carbonate phase was achieved using an acetate buffer set to a pH 5.5. All acetate buffer solutions used in this study were of sufficient ionic strength to ensure that complete dissolution of the phase concerned (carbonate or aluminosilicate), based on prior measurements of the acid neutralisation capacity, would not alter the solution pH by more than 0.1 pH units. For the extraction of carbonates the buffer was made up of equal volumes of 0.5 M acetic acid and 2.8

Table 1. Rare earth element concentrations (ppb) for the Northwood spring and the pryrite samples sampled from the Durham Basin in comparison with the limits of detection for this study.

Element	Northwood spring	Whitwell	Marks Quarry 1	Pyrite samples Marks Quarry 2	Marks Quarry 3	Marks Quarry 4	Limit of detection
La	2.69	0.13	0.06	0.18	0.05	0.17	0.002
Ce	10.71	0.38	0.17	0.67	0.13	0.76	0.000
Pr	2.25	0.07	0.03	0.16	0.04	0.19	0.002
Nd	10.70	0.25	0.11	0.76	0.19	0.93	0.008
Sm	3.80	0.05	0.02	0.27	0.07	0.33	0.004
Eu	1.30	0.01	0.00	0.08	0.02	0.10	0.004
Gd	6.25	0.06	0.03	0.35	0.07	0.38	0.002
Tb	0.94	0.01	0.00	0.06	0.01	0.06	0.002
Dy	5.80	0.06	0.01	0.35	0.06	0.35	0.015
Ho	0.93	0.01	0.00	0.06	0.01	0.06	0.002
Er	2.35	0.04	0.01	0.17	0.02	0.14	0.002
Tm	0.30	0.01	0.00	0.02	0.00	0.02	0.000
Yb	1.84	0.03	0.01	0.15	0.01	0.14	0.000
Lu	0.22	0.00	0.00	0.01	0.00	0.02	0.000

M sodium acetate. The crushed rock sample was mixed with the 20 mL of the buffer solution and left to stand overnight before being filtered as above; the residue was washed with distilled, deionised water to make the filtrate up to 50 mL and was kept for analysis. The residue was dried at 105°C, and 1.5 g of sample was kept for subsequent extraction.

Extraction of the aluminosilicate phases was achieved with an acetate buffer set at pH 3.6. This buffer solution was made up of equal volumes of 2 M acetic acid and 0.22 M sodium acetate. We mixed 1.5-g samples that had previously had been extracted for their exchangeable and carbonate phases with 20 mL of the buffer solution; these samples were allowed to stand overnight before being filtered as above. The residue was washed with distilled, deionised water to make the filtrate up to 50 mL and kept for analysis. The residue was dried at 105°C, and 1 g of sample was kept for subsequent extraction.

To ensure that all acid-leachable phases were extracted from the crushed rock samples before extraction of the oxidisable phases, 1 g of the residue of extraction at pH 3.6 was mixed with 20 mL of 0.01 M solution of H_2SO_4, measured as pH 1.6, and left to stand overnight. The samples were filtered as above and washed with distilled, deionised water to make the solution up to 50 mL for analysis. The residue was dried at 105°C, and 0.5 g was kept for subsequent analysis.

The remaining 0.5 g of sample was mixed with 20 mL of 3% hydrogen peroxide to remove the oxidisable phases. The samples were treated as above, being left overnight, filtered, and washed with distilled, deionised water to make the filtrate up to 50 mL for analysis. Two blanks were kept of each extraction solution, one of the extraction solution and one that has been processed as part of extraction step.

2.4. Analytical Method

Analysis for the REEs in each of the sequential extraction leachates was performed by solution-mode ICP-MS. The instrument used was a Perkin Elmer Elan 6000 (Perkin-Elmer corp., Norwalk, CT, USA), equipped with a standard cross-flow nebuliser and double-pass spray chamber. The methodology was optimised to minimise the influence of oxides and doubly charged ions, and oxide ratios were measured at the set up of each analytical run to make sure they were consistent with the correction methods being used. The isotopes to be measured were chosen as the most abundant for that element or to limit interferences. The following isotopes were analysed: [139]La, [140]Ce, [141]Pr, [143]Nd, [147149]Sm, [151, 153]Eu, [157]Gd, [159]Tb, [161163]Dy, [165]Ho, [166167]Er, [169]Tm, [172174]Yb, and [175]Lu. Special attention is paid to the influence of BaO on measured Eu concentrations. To counter this problem, both [151]Eu and [153]Eu were analysed to assess the influence of BaO interference above and beyond the established correction methods: no significant BaO interference was found. Dissolved samples were spiked with rhenium and rhodium as internal standards to monitor matrix effects. Calibration curves were established using NIST-traceable international standards, with standard concentrations set at 1, 5, and 10 ppb. One standard out of the four used is not included in the construction of the calibration curve, but is used as a check on the calibration curve. Standards were run at regular intervals throughout any given run to monitor instrumental drift. Detection limits were taken as three times the standard deviation in the blank and measurement error was assessed on the basis of sixfold replication of the Northwood spring sample. Detection limits are given in Table 1, and the maximum measurement error as ± 0.01 ppb where ppb is taken as $\mu g/kg$ and $\mu g/L$, depending on the nature of the sample.

Results were viewed as a multivariate data set and interpreted using principal components analysis and linear discriminant analysis.

3. RESULTS

The results of each of the extracts and water samples were chondrite normalised (Boynton, 1984). Normalisation against the REE composition of the Northwood spring does not reveal useful patterns because the composition is by its very nature a mixture of the compositions of these extracts.
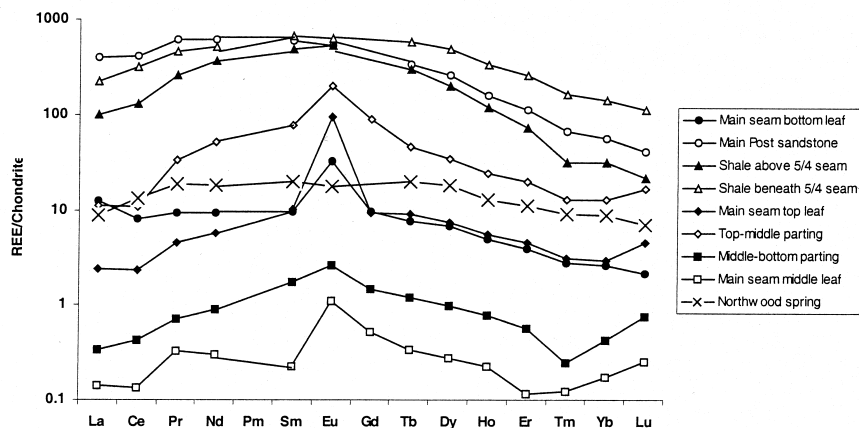
3.1. REE Patterns

The REE patterns of the extracts are illustrated in Figure 3a–e. Only complete patterns are shown (i.e., those where all measured REEs were above the detection limit). Patterns shown are the average for the particular stratigraphic layer and for that extraction technique. The average REE concentration of the Northwood spring is given in Table 1.

3.1.1. Exchangeable Phase Samples

The REE patterns of the exchangeable phases can be divided into two groups (Fig. 3a): those with and those without a strong Eu anomaly. Those without an Eu anomaly are those surrounding the 5/4 seam (shale above and beneath the 5/4 seam and the Main Post sandstone). Cerium anomalies are slight and are found only in those layers stratigraphically below the Main Post sandstone. The general pattern is enrichment to the mid-REE (MREE). The REE pattern for the Northwood spring is included and shows little or no Eu anomaly.

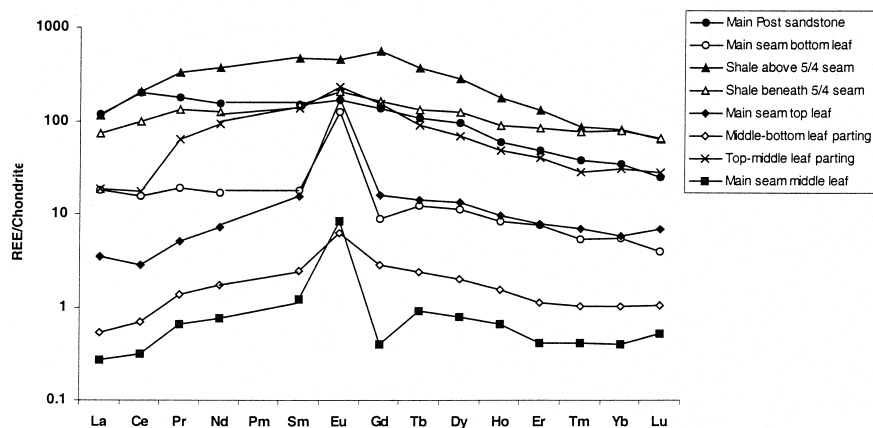a) Readily exchangeable phases

b) pH 5.5 leachates

Fig. 3. Rare earth element (REE) patterns for (a) exchangeable phases; (b) pH 5.5 leachates; (c) pH 3.6 leachates; (d) pH 1.6 leachates; and (e) hydrogen peroxide leachates. Promethium is included in these diagrams to complete the overall REE pattern, although it was not analysed for. Only complete patterns are shown (i.e., those for which all measured REEs were above the detection limit). Patterns shown are the average for that stratigraphic layer and for that extraction technique.

3.1.2. pH 5.5–Leached Samples

As above for the exchangeable phase extractions, the pH 5.5 leachate samples exhibit two groups with split between samples with and without an Eu anomaly (Fig. 3b). The same can be observed for the Ce anomaly.

3.1.3. pH 3.6–Leached Samples

Although a clear distinction can be observed between those with and without an Eu anomaly (Fig. 3c), the leachate from the shale beneath the 5/4 seam appears to have an Eu anomaly unlike above (Fig. 3a and 3b). This suggests that there is an Eu anomaly in some of the layers around the 5/4 seam and within a phase not mobilised at pH >3.6. The pH 3.6 leachate of the Main Post sandstone layer does not have an Eu anomaly. Both the Main Post sandstone and the Shale beneath the 5/4 seam appear to have positive Ce anomalies, whereas other layers do not.

3.1.4. pH 1.6–Leached Samples

These leachates do not show Eu anomalies of the scale previously observed (Fig. 3d). Distinct REE patterns are observed for these leachates including those that show a fractionation between light-REE (LREE) and heavy REE (HREE; e.g., Main seam bottom leaf), and secondly, those that show a MREE enrichment (e.g., middle bottom leaf shale parting).
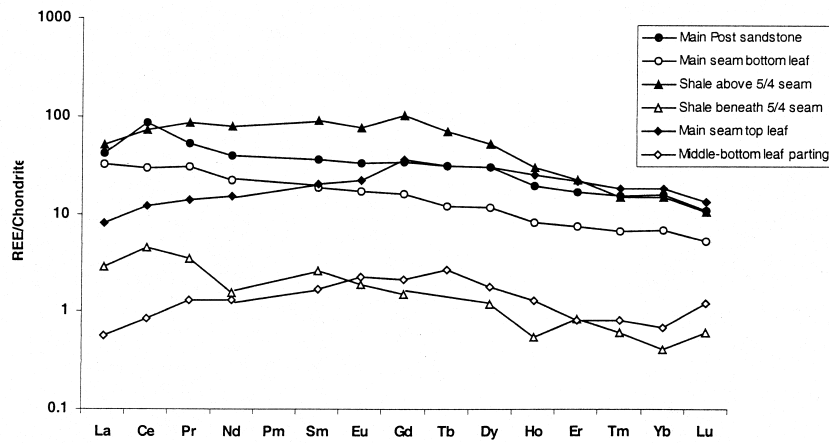
3.1.5. Peroxide-Leached Samples

The peroxide leachates indicate that the phase is not the source of the Eu anomalies in the other leachates (Fig. 3e). Although the low concentrations in the peroxide leachates mean that few REE patterns are complete, comparisons with the leachates from pyrite samples show that a distinct sulphide signal can be observed (e.g., Main seam bottom leaf) and that

c) pH 3.6 leachates
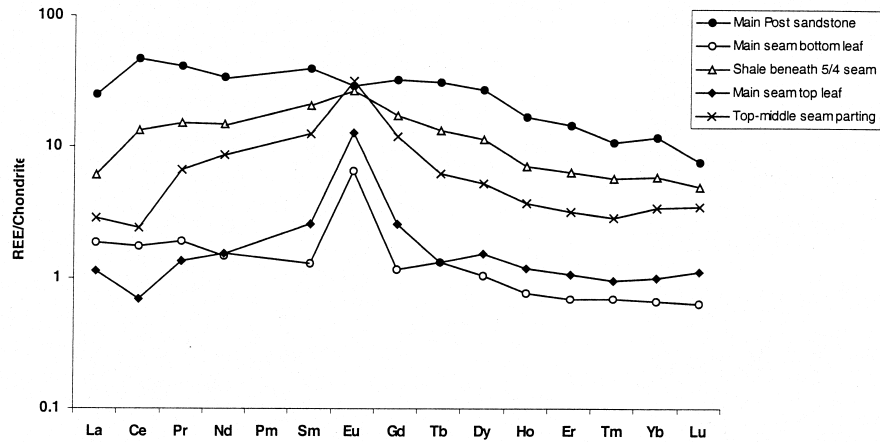
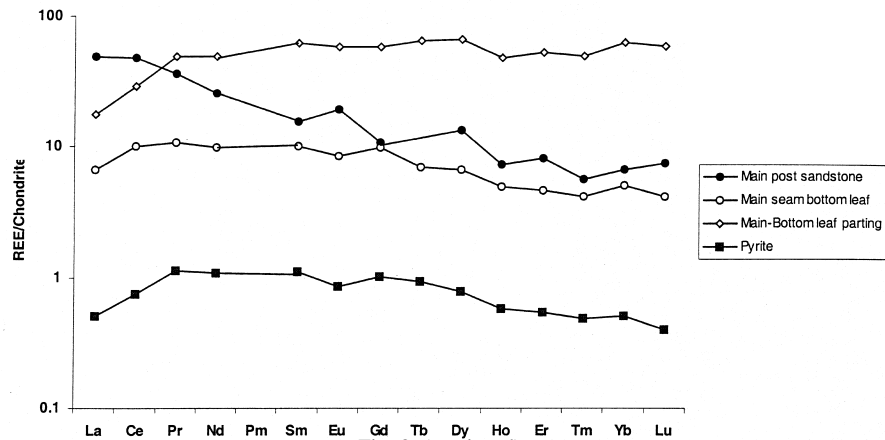

d) pH 1.6 leachates

e) Peroxide leachates

Fig. 3. (continued)

the Main Post sandstone appears to contain no such influences (Fig. 3e). The REE pattern of the peroxide leachate of the Main Post sandstone is very similar to that of the pH 1.6 leachate of the same sample, suggesting that strongly acidic conditions exist in these samples and that there is not necessarily complete removal of any given phase. These samples are compared with the average pyrite sample of those coal-hosted pyrites found elsewhere within the Durham Basin (Table 1).
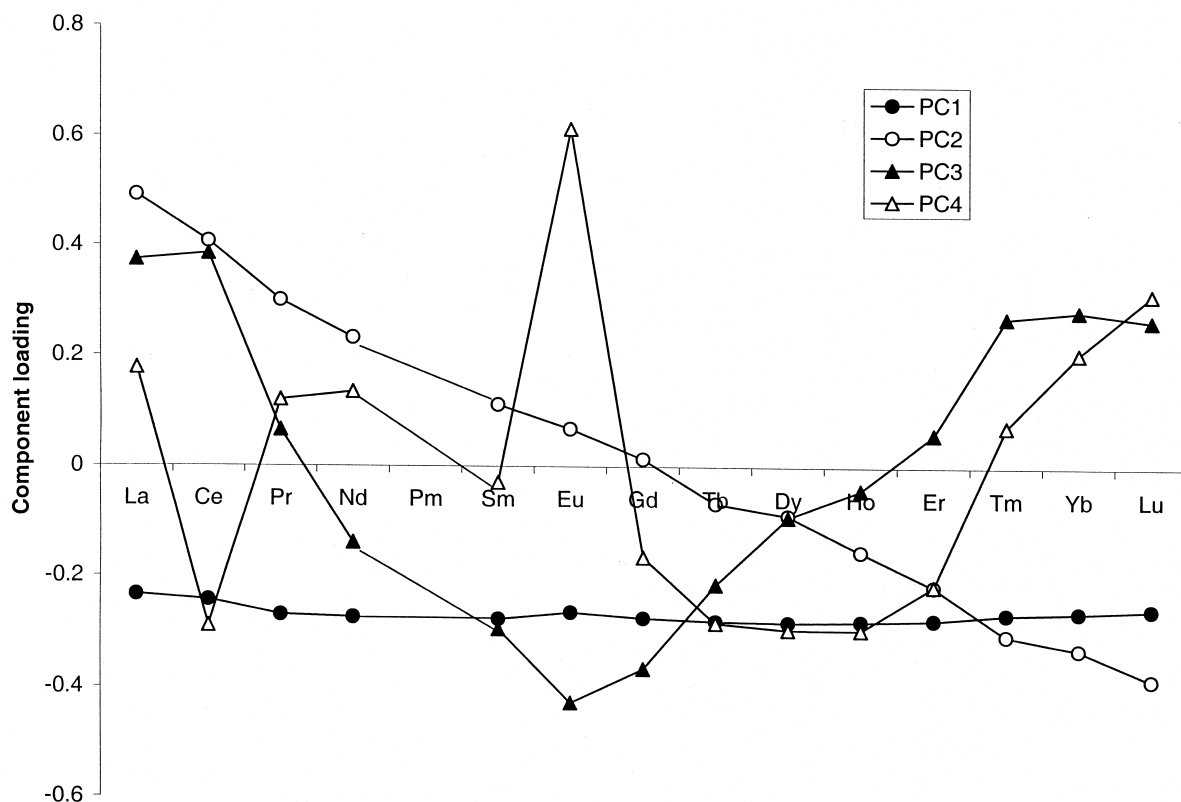
Fig. 4. Loadings of the first four principal components on the analysed rare earth elements.

3.2. Principal Component Analysis

Principal component analysis is an ideal technique for analysing multivariate data such as REE patterns. This method can be used to simplify data, to explore groups in data, and to visualise underlying controls in a multivariate data set (Tabachnick and Fidell, 1996). Principal component analysis recalculates the data in terms of multivariate components that better explain the variation in the data than the original variables. The number of calculated components will equal the number of variables included in the data set; however, the components are calculated in the order of the amount of variation in the data that they explain (i.e., the most important component first). This approach means that components that explain only a fraction of the variation can be explained, thus simplifying the data set. We performed principal component analysis using the maximum likelihood approach. The first four components explained 99% of the variation in the data. The loadings of the individual elements on these components act as a pseudo-REE pattern for that component (Fig. 4). The first component (PC1) explains 81% of the variation in the data and represents a general concentration component. The second component (10% of the variation in the data) represents a fractionation component across the series between light REE (La–Eu, LREE) and heavy REE (Gd–Lu, HREE), whereas the third component (PC3: 5% of the variation) represents the enrichment of the MREE with the maximum at Eu. The Eu and Ce anomalies are represented by the fourth component (PC4 to 3% of the variation). The first four components are chosen because, first, they

represent features of the data (e.g., Eu anomalies); second, they represent significant features of the data once PC1 is excluded (i.e., once the data is normalised for concentration differences); and, third, the first four components explain the 99% of the variation observed in the data. What these patterns represent may be discerned from the scores the extract samples have on these components (Figs. 5, 6, 7, and 8).

The lowest concentrations of REEs are found in the pyrite samples, plotted here as the average of those sampled from Whitwell and Mark's Quarry (Fig. 5). Two trends of increasing concentration are then discernible in Figure 5, both of which have pyrite as one end member. The average pyrite shows zero score on PC2, indicating that the REE composition of pyrites in the Durham basin and in the Northwood stratigraphic sequence are marked by essentially no fractionation between the LREE and HREE. The high-concentration end member of trend A (Fig. 5) is represented by the pH 5.5 extract of the Main Post sandstone, which passes through the composition of many of the pH 1.6 extracts before reaching the average pyrite. This trend also represents a fractionation of LREEs over HREEs. The close association between the pH 5.5 leachates and the pH 1.6 leachates suggests that the REE pattern of the phases being leached is controlled by a similar mechanism and may be inherited either from the same source or from another. This close association suggests little fractionation between these phases. The fact that this trend is defined by the pH 1.6 leachates and not one of the other leachates suggests that the end member is neither carbonate nor silicate but rather a
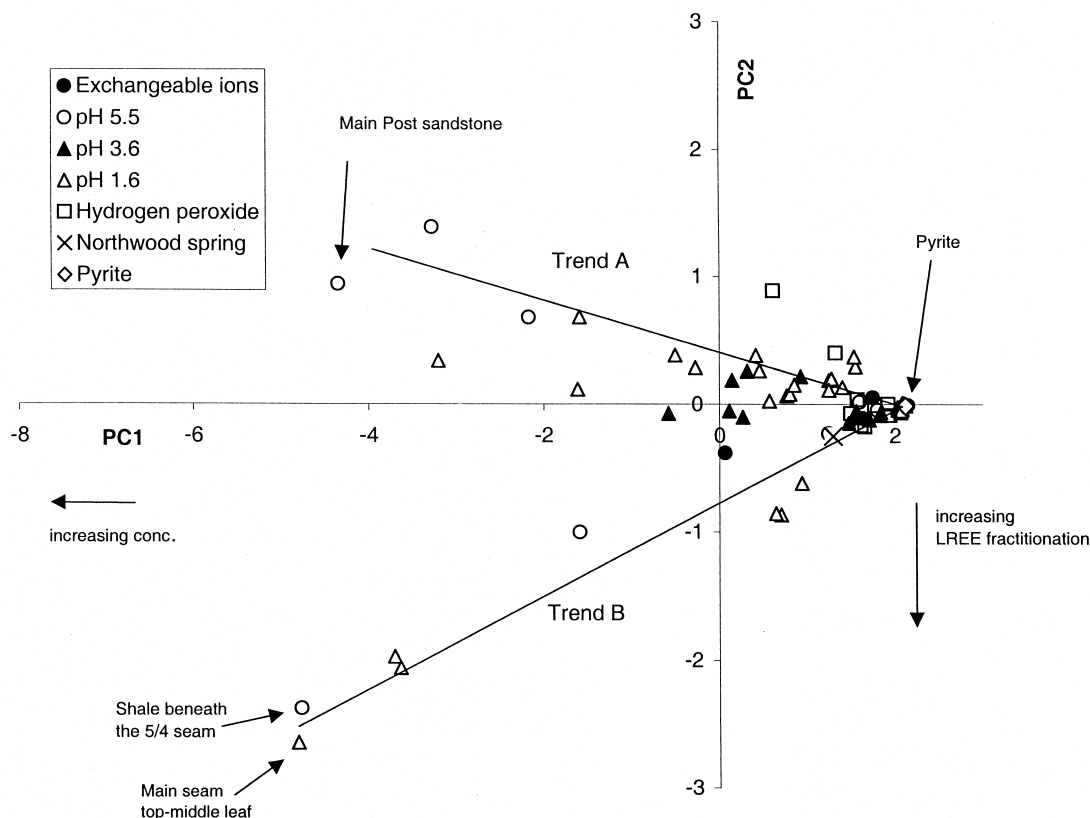
Fig. 5. Principal component 1 (PC1) vs. principal component 2 (PC2).

residual weathering product with an REE composition inherited from carbonates (i.e., pH 5.5 extracts of the Main Post sandstone). The most likely candidate for such a weathering product would be iron oxy-hydroxides (ochres), although this is unlikely to be the sole constituent of this material. It has been demonstrated (Worrall and Pearson, in press-a) that ochres show no systematic fractionation of REE with respect to the waters from which they precipitate and that they are highly efficient scavengers of elements from solution. Ochres thus concentrate REEs and provide a mechanism for REE patterns to be inherited from an easily leached phase (i.e., pH 5.5 leachates) to residual weathering products (i.e., ochres). Therefore, ochre precipitates within the Main Post sandstone would have very similar REE composition to the material that has been leached into the solution.

Trend B also shows a close association between pH 5.5 and pH 1.6 leachates. The high-concentration end member of this trend represents the pH 5.5 extractable phases of the shale beneath the 5/4 seam, and the pH 1.6 extractable phases of the top-middle leaf parting of the Main seam. These relationships confirm the observation made for trend A that the REE pattern of easily weatherable material (pH 5.5 extracts) is transferred to less easily weathered precipitates (i.e., ochres; pH 1.6 extracts). Trend B is one of increasing fractionation with increasing atomic mass across the REE series, rather than decreasing mass as with trend A. This trend includes the composition of the Northwood spring, giving a mixing line that suggests the REE pattern of the spring is 88% pyrite and 12% residual weathering

products. If it is assumed that the end members of these trends represent precipitates, then there appears to be two sources giving rise to the two distinct trends A and B. The REE composition of the pH 1.6 leachates from the Main Post sandstone suggests weathering associated with pyrite oxidation in the 5/4 seam that both leached and deposited material in the Main Post sandstone. This source has either ceased or does not add significantly to the composition of the spring. The existence of two trends does suggest that different seams will give distinguishable signatures to the groundwaters. The hydrogen peroxide extract of the 5/4 seam was below detection for a number of the elements analysed and so could not be included in this analysis. Thus it is not possible to examine whether the pyrite in this seam had a distinct composition (i.e., substantially different from the basin average). Analysis of pyrites from Whitwell and the Mark's Quarry suggests that the composition of pyrite in this sequence is comparatively uniform. Therefore, differences between these trends (trends A and B; Fig. 5) are likely due to the nonpyrite mineral content and the differences between the stratigraphic setting of the coal seams, that is, the combination of shales and sandstones hydrologically beneath the coal seam or source of the pyrite oxidation. Noninvolvement of the Main Post sandstone in trend B suggests that the source of the Northwood spring is from either the main top leaf or the top-mid leaf parting of the Northwood section and that production of acidic water leaches the shale parting.

A different perspective on this relationship can be viewed by plotting PC1 vs. PC3 (Fig. 6). The similar trends as in Figure
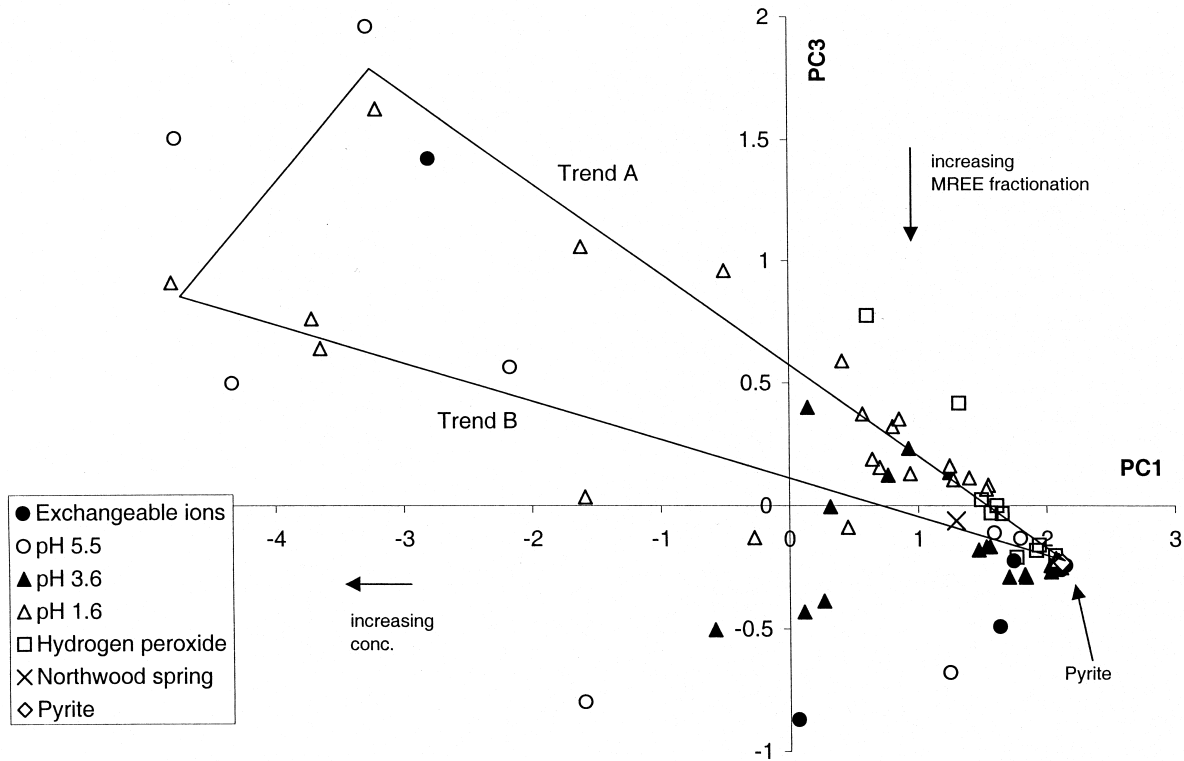
Fig. 6. Principal component 1 (PC1) vs. principal component 3 (PC3).

5 are visible. Both trends show no fractionation in the MREEs. The position of the Northwood spring relative to these trends is more ambiguous on the PC1 vs. PC3 plot. On trend B, the Northwood spring represents a mixture of 91% pyrite and 9% of the residual material. The composition of the Northwood spring also can be expressed as a ternary mixture composed of 87% pyrite, 8% residual product B, and 5% residual product A, where A and B refer to the end members of the respective trends. If this ternary interpretation is accepted, then a small contribution from the weathering of the strata around the 5/4 seam is implied.

The comparison of PC2 and PC3 shows the same trend as described above (trend B; Fig. 7); however, the plot of PC2 vs. PC3 also shows a broad trend composed of the bulk of the samples. The comparison of PC2 and PC3 is independent of PC1. Because PC1 represents the REE concentrations of the samples, the plot of PC2 vs. PC3 is independent of the concentration of the samples. On the plot PC2 vs. PC3, compositions of extracts and spring waters plot together and thus confirms that water and rock can be compared directly as discussed above (Figs. 5 and 6). The confirmation that water and rock composition can be directly compared suggests a water-rock interaction ratio on the order of one litre of groundwater to one kilogram of rock.

The broad trend observed for the bulk of the samples (Fig. 7) is bounded by pH 5.5 leachates of the Main Post sandstone and the Shale above the 5/4 seam. Previous work (Worrall and Pearson, in press-b) indicates that carbonates in shale above the 5/4 seam are the most sideritic in the Northwood sequence, suggesting that this end member represents the REE composi-

tion of siderite (i.e., enriched in MREE; Fig. 3b). The other end member lies at the end of a trend defined by the pH 1.6 leachates, reinforcing the idea that there are carbonates in the Main Post sandstone with compositions that are inherited by ochres. This trend is also followed by the pH 3.6–leached samples. The high PC3 end member of this trend is again the Main Post sandstone, and similarly the low PC3 end member is the pH 3.6 extract from the shale above the 5/4 seam. Again, this highlights the similarity of the REE patterns of the different sedimentary components in this sequence.

It is possible to interpret a point on this broad trend as an end member of trend B (Fig. 7): however, this would require ignoring the role of pyrite weathering as a REE source. The composition of pyrite and the hydrogen peroxide–leached samples lie on this same broad trend, implying that the REE compositions of the various stratigraphic components—be it carbonate, silicate, or pyrite—have very similar REE patterns. Elements of the REE pattern could be inherited from a common source originating at the sedimentation of these coal measures, with the potential that this pattern is passed on through diagenesis and even acid weathering.

PC4 describes the Eu and Ce anomalies (Fig. 8). Large positive Eu or large negative Ce anomalies do not distinguish the Northwood spring. The largest Eu anomalies are observed for the exchangeable ions leachates, which also have well-developed negative Ce anomalies. The samples with a positive Eu anomaly are those strata associated with the Main seam, whereas those with a slight negative Eu anomaly are those around the 5/4 seam and the Main Post sandstone. The Northwood spring shows a negative Eu anomaly and a positive Ce
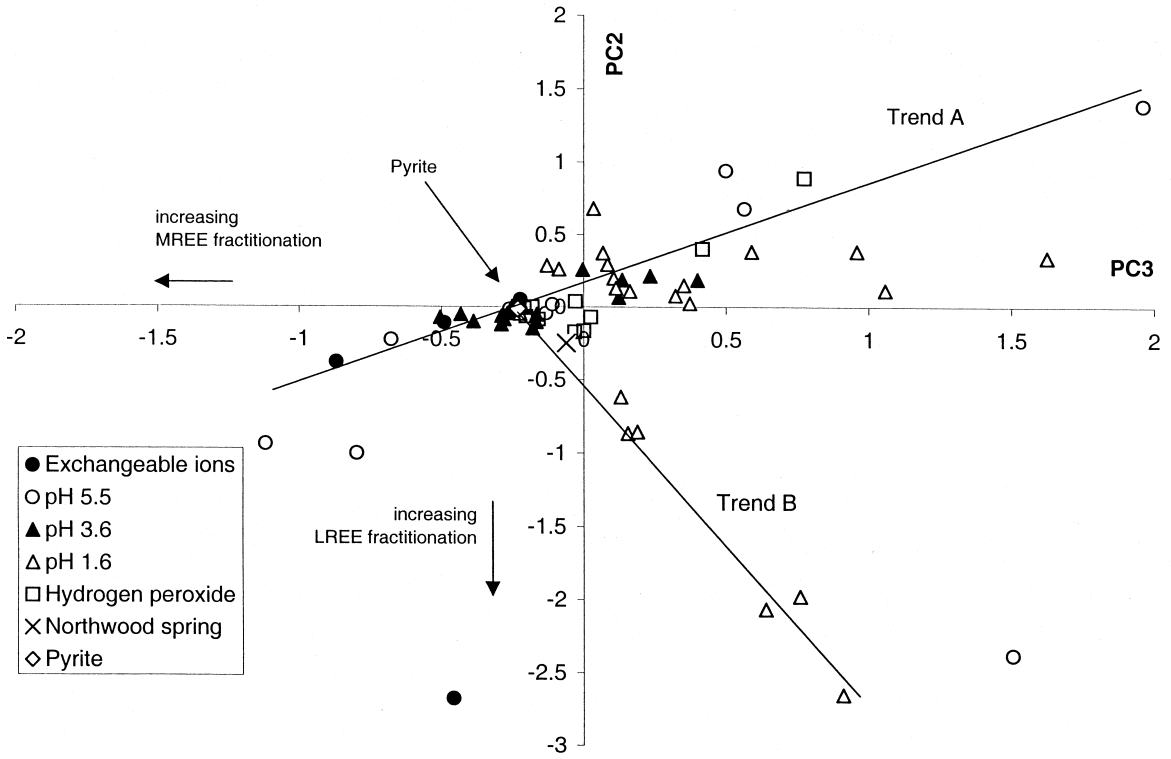
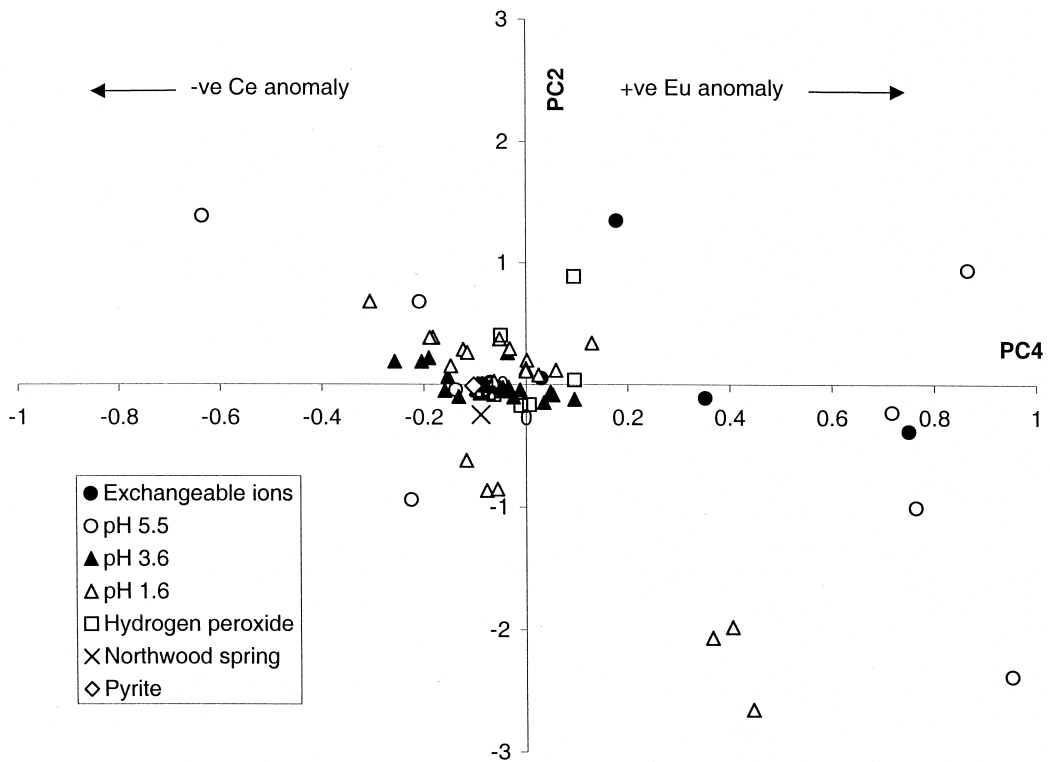Fig. 7. Principal component 1 (PC3) vs. principal component 2 (PC2).

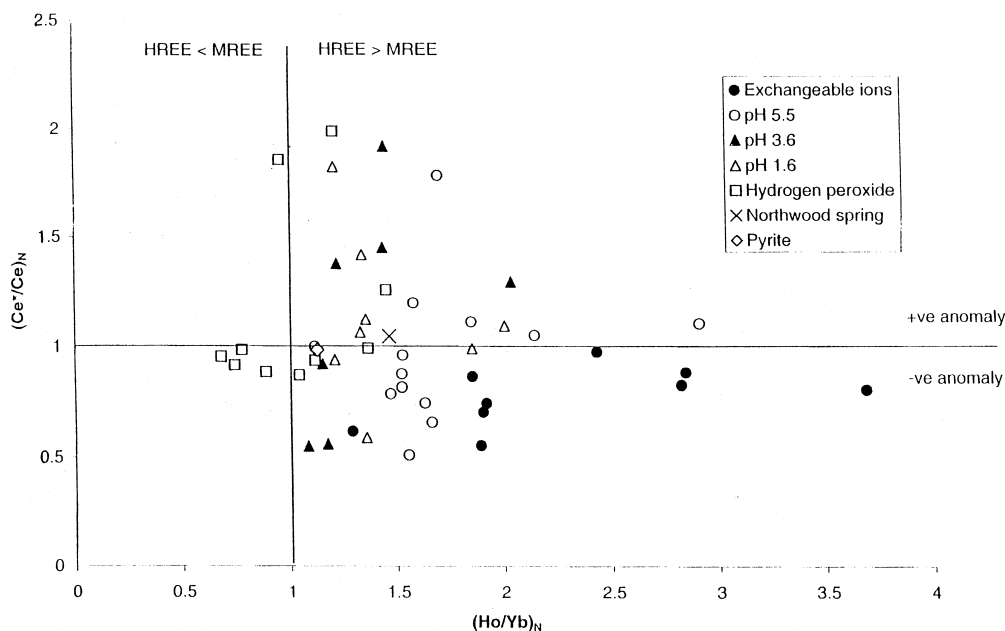Fig. 8. Principal component 1 (PC4) vs. principal component 2 (PC2).

Fig. 9. $(Ho/Yb)_N$ vs. $(Ce/Ce*)_N$.

anomaly. All the samples stratigraphically below the Main Post sandstone have a REE pattern for their exchangeable phase leachates that exhibit a negative Ce anomaly. For the pH conditions of the Northwood spring (~pH 2.7), Eu and Ce will both occur in solutions as the +3 ion (Brookins, 1989). The negative Ce anomaly of most sedimentary minerals is a consequence of depletion due to the presence of Ce(IV) in oxic, aqueous solutions (Brookins, 1989). Minerals weathering in this solution may pass their negative Ce anomaly into the solution, but at the Eh-pH conditions of the Northwood spring the Ce will likely be reduced to Ce(III). This is more mobile than Ce(IV), so even with cation exchange there is a slight Ce enrichment in the spring leading to positive Ce anomalies.

In previous studies of sedimentary sequences, positive Eu anomalies in whole rock samples have often been associated with the presence of plagioclase (McClennan, 1989). Thus, in sequences where plagioclase is being weathered, positive Eu anomalies may be expected in the resulting solution. It is also possible that cation exchange will remove Eu from solution; however, to obtain a negative Eu anomaly would require the preferential removal of Eu from solution relative to the other MREEs. A small negative Eu anomaly may be ascribed to less-than-perfect oxide correction on Gd during analysis, which cause the Gd concentrations to be enhanced.

The samples leached with peroxide plot close to the pyrite, suggesting that they are, as planned in the extraction protocol, dominantly of pyritic composition (Fig. 5). However, two samples show a distinct pattern characterised by steep declines across the LREEs and low levels of unfractionated HREEs, with no Ce or Eu anomalies. These samples are both from the Main Post sandstone. It is difficult to understand what phase this represents as levels of pyrite in sandstone are zero, and although there are trace levels of organic matter in this sandstone, it is insignificant compared with the shale and coal layers.

3.3. Discriminant Analysis

Discriminat analysis is a technique for calculating the best function for separating two predefined groups of data (Tabachnick and Fidell, 1996). Discriminant analysis was performed on sets of analyses from pairs of extraction methods (e.g., pH 5.5 leachates vs. pH 3.6 leachates), and the results were examined to suggest possible pairs of discriminators. For all the steps in the sequential extraction, the analysis suggests that the Ce anomaly and ratios of LREE/MREE and MREE/HREE would be the best combinations for discriminant analysis. For discrimination, the Ce anomaly is calculated as $Ce/Ce* = (Ce)_N / [\sqrt{((La)_N (Pr)_N)}]$, previously $Ce/Ce*$ was merely identified in the principal component (Fig. 8). Plotting these combinations shows that the best discriminator between the sequential extracts is $(Ho/Yb)_N$ (Fig. 9). Using this criteria, the most fractionated extracts are the exchangeable ions, and the least fractionated are hydrogen peroxide–leached samples. However, the actual discrimination is not clear-cut, and there are separate groupings of samples within those for each extraction. The highest $(Ho/Yb)_N$ values are observed for the extracts from the shale above the 5/4 seam, closely followed by extracts of the Main Post sandstone. Samples from around the Main seam have $(Ho/Yb)_N = 1.9$. In comparison to the composition of their respective pH 5.5 extracts, all plot at higher $(Ho/Yb)_N$ values. Equally, the pH 1.6 extracts compositions of all the other extracts plot at lower $(Ho/Yb)_N$ values than their respective pH 5.5 extracts. In general, the hydrogen peroxide–leached samples and the pyrite samples have the lowest values of $(Ho/Yb)_N$. An exception is the hydrogen peroxide–leached samples from the Main Post sandstone, which have already been discussed, that have positive Ce anomalies.

Acid leaching of the carbonate phase appears to result in fractionation of REEs with MREE being preferentially adsorbed by cation exchange. This could be expected, considering

the decrease in charge density of ions with increasing atomic number across the REE series. Indeed, Benedict et al. (1997) showed that REE adsorption to alluvium was stronger for LREE than for HREE and the trend across the series was approximately log linear. This effect should pertain across the whole of the REE series, and so a similar fractionation would be expected for the LREE, but no such fractionation is observed (Fig. 9). The preferential adsorbance of MREE leaves a solution relatively enriched in HREE as is reflected in the composition of the pH 1.6 leachates, identified here as the ochre deposits, which would precipitate from these solutions.

An alternative explanation is to consider complexation as explanation for the observed fractionation behaviour of the REEs in solution. Many inorganic and organic ligands form preferentially stronger solution complexes with HREE than LREE (Cantrell and Byrne, 1987; Lee and Byrne, 1993; Millero, 1992; and Byrne and Sholkovitz, 1996). Johannesson et al. (1999) demonstrated that observed HREE enrichment in groundwaters from an alluvial aquifer were due to changes in complexation strength. Carbonate complexes may well dominate in these groundwaters when they are carbonate buffered, but this is unlikely to be the case as pH and alkalinity drops. Alternatively, phosphate has been shown to be a significant complexing agent for REE (Johannesson et al., 1996); however, in Fe-rich solutions the low levels of phosphate may be readily precipitated and indeed may form a scavenging mechanism for removing REE rather than complexing REEs. Organic ligands have been shown to have strong associations with REE (McCarthy et al., 1996, 1998), but concentrations of dissolved organics in this system are likely to be low in comparison with inorganic ligands. An alternative possibility is complexation by the abundant sulphate found in these groundwaters.

This chain of events could be reversed (i.e., the precipitation of ochre may preferentially remove HREE leaving a solution enriched in MREE to undergo cation exchange). Grandjean-Lecuyer et al. (1993) have suggested that Fe oxy-hydroxides will remove LREEs in the aqueous environment. There is no evidence for this mechanism from our study. Equally, Worrall and Pearson (in press-a) showed that there was no evidence for this mechanism of REE fractionation in a study of other acidic discharges in the same basin. The pH 3.6–leached samples overlie the pH 1.6–leached samples, suggesting noninvolvement in this fractionation process, either because the silicate phases are not being weathered or because ochre precipitation and/or cation exchange from these solutions does not preferentially remove HREE or MREE.

The Northwood spring plots between the pH 5.5– and 1.6–leached samples and could easily fall along a mixing line between acid leachable material of various origins and pyrite or at least hydrogen peroxide leachates. The samples from around the 5/4 seam are more widely differentiated and fractionated along the $(Ho/Yb)_N$ axis than are those from the Main seam. This could imply that these strata are more extensively weathered and that their weathering was, and is, more heterogeneous than in the Main seam. The variation along the $(Ce/Ce^*)_N$ axis of the 5/4 seam is remarkably restricted and follows the same trend as the spring composition, pyrite, and the majority of the hydrogen peroxide leached samples. Samples from the strata associated with the Main seam are differentiated along the Ce

anomaly axis, but whatever controls this does not appear to be important for the composition to this spring.

4. DISCUSSION

To what extent is it possible to delineate the lithological controls on the composition of the Northwood spring using REE compositions? The principal component analysis shows clear mixing lines for the Northwood spring. These mixing lines suggest a composition controlled by pyrite oxidation and buffering against iron ochres. The iron ochres inherit their composition from the weathering of carbonates within the sequence, suggesting a weathering cycle where REE compositions show significant inheritance through a sequence of carbonate dissolution and ochre precipitation. Within this sequence there is little evidence for a significant role of a silicate phase, either directly by buffering the solution or through ochres that have precipitated from such a solution. However, the similarity of the REE composition between carbonate and silicate phases may well obscure such a signal in this case. The REE data do provide substantial evidence for the source and evolution of the groundwaters issuing from the Northwood spring. The source of the spring cannot be the strata around the 5/4 seam, because this seam did produce acidic groundwater at one stage that had a distinct composition from that of the present discharge. The present discharge appears buffered by the Fe oxy-hydroxides of the very top layers of the Main seam. This suggests significant acid production in the top leaf of the Main seam. The fact that lower strata do not appear to contribute to the spring's composition suggests that the spring still has a significant time period before the acid producing potential becomes exhausted. One possible explanation of this observation is that before opencasting, the perched water table that must have fed this spring may well have kept parts of the Main seam saturated and thus limited pyrite oxidation of these strata.

Do REE patterns enable us to distinguish between the influence of the various possible buffering systems within the catchment of a borehole? The discriminant analysis shows that it is difficult to discern particular combinations of REE or anomalies that would enable us to clearly distinguish one extract from another. The variation in the fractionation of HREE does, however, suggest that there might be a discernible evolution in discharges distinguished by a trend in $(Ho/Yb)_N$. Young discharges will be characterised by highly HREE fractionated patterns. This fractionation decreases over time as the spring either evolves towards the composition of pyrite or towards being buffered by Fe oxy-hydroxides.

To what extent are these results applicable to other AMD discharges? The Northwood spring is easily characterised due to access to the strata from which it originates. It is unclear, however, how the Northwood Spring applies to discharges in the rest of this basin or to other such basins where the source area cannot be examined? This is a question of whether the compositions of carbonate and silicate phases are uniform across the basin as the behaviour of the exchangeable phase and the ochres can be considered to follow on directly from what is available in solution from these sources. Two pieces of evidence from this study suggest that the results may be generally applicable. First, because the composition of coal-hosted pyrite from opencasting operations elsewhere in the basin is similar to

that found for the hydrogen peroxide leached samples, it is possible that despite geographical separation, the REE composition of pyrite in the basin has a common source. Second, the compositions of the pH 5.5 and 3.6 extracts follow the same broad trend in the principal component analysis, suggesting similar sources and controls on the their REE composition and therefore indicating that REE compositions throughout the basin are very similar. However, differences are evident between the two seams (5/4 and Main). For example, the difference in the composition of pH 5.5 extracts (cf. trend A and trend B; Fig. 5) and beyond that due to their weathering (Fig. 6). Differences in the REE composition of the two seams suggests that some first-order similarities in the composition across the basin are complicated by changes in sedimentological conditions. Changes in the proportions of the carbonate and silicate phases, as well as the nature and succession of strata through which the groundwaters will pass before discharge, may explain differences in REE composition. Such differences mean that influence of the individual coal seams will be differentiable.

5. CONCLUSIONS

We examined the REE composition of an acidic spring where the pH of the discharge (pH 2.7) allows for careful study because the chemical signal is not confused by the precipitation of iron ochres. The study of sequential extracts of the strata through which the groundwater passes shows that the composition of the spring is controlled by the composition of pyrite and buffering by Fe oxy-hydroxides but that these ochres have an inherited composition from carbonates within the sequence. The spring has evolved from weathering high in the sequence to being sourced in the lower coal seam. The spring could continue to flow for a substantial time because much of the lower coal seam has yet to make a significant contribution to acid production. The spring is also evolving in terms of HREE fractionation, such that decreasing fractionation is observed as the spring evolves away from being carbonate buffered and towards Fe oxy-hydroxide buffering or the composition of pyrite. It is not possible to say whether this fractionation is due to adsorption or to precipitation of ochres.

However, the general lithophilic character of REEs suggests that the compositions of the phases in the sequence are very similar, and as such it becomes difficult to distinguish a role for each of the extracts, especially the silicate phase. This characteristic will limit the use of REE in understanding groundwater composition in aquifers with relatively homogeneous sedimentary sources or in relatively small-scale studies where flow paths do not sample a variety of rock types. REE will be of more use in aquifers with a wide variety of rock types (e.g., limestone and sandstones).

Associate editor: T. Paces

REFERENCES

Banks D., Hall G., Reimann C., and Siewers U. (1999) Distribution of rare earth elements in crystalline bedrock groundwaters: Oslo and Bergen regions. *Appl. Geochem.* **14,** 27–39.

Banner J. L., Wasserburg G. J., Dobson P. F., Carpenter A. B., and Moore C. H. (1989) Isotopic and trace element constraints on the origin and evolution of saline groundwaters from central Missouri. *Geochim. Cosmochim. Acta* **53,** 383–398.

Benedict F. C., Jr, DeCarlo E. H., and Roth, M. (1997) Kinetics and thermodynamics of dissolved rare earth elements by alluvial materials from the Nevada test site, southern Nevada, U.S.A. In *Geochemistry; Proceedings of the 30th International Geol. Congress, VSP* (ed. X. Xuejin), Vol. 19, pp. 173–188, Utrecht, The Netherlands.

Boynton W. V. (1984) Geochemistry of the rare earth elements: Meteorite studies. In *Rare Earth Element Geochemistry* (ed. P. Henderson), pp. 63–114, Elsevier, Amsterdam.

Brookins D. G. (1989) Aqueous geochemistry of rare earth elements. In: B. R. Lipin, G. A. McKay (eds.), *Geochemistry and Mineralogy of Rare Earth Elements. Reviews of Mineralogy,* **21,** 201–225.

Byrne R. H. and Sholkovitz E. R. (1996) Marine chemistry and geochemistry of the lanthanides. In *Handbook of Physics and Chemistry of the Rare Earths* (eds. K. A. Gschneider Jr and L. Eyring), Vol. 23, pp. 497–593, Elsevier, Amsterdam.

Cantrell K. J. and Byrne, R. H. (1987) Rare earth element complexation by carbonate and oxalate ions. *Geochim. Cosmochim. Acta* **51,** 597–605.

Cardosa Fonseca E. and Martin H. (1986) The selective extraction of Pb and Zn in elected mineral and soil samples, application in geochemical exploration (Portugal). *J. Geochem. Explor.* **26,** 231–248.

Chao T. T. (1984) Use of partial dissolution techniques in geochemical exploration. *J. Geochem. Explor.* **20,** 101–135.

Fee J. A., Gaudette H. E., Lyons W. B., and Long D. T. (1992) Rare earth element distribution in the Lake Tyrell groundwaters, Victoria, Australia. *Chem. Geol.* **96,** 67–93.

Geller W., Klapper H., and Schultze M. (1998) Natural and anthropogenic sulfuric acidification of lakes. In *Acidic mining lakes* (eds. W. Geller, H. Klapper, and W. Salomons), pp. 3–14, Springer-Verlag, Berlin.

Grandjean-Lécuyer P., Feist R., and Albarède F. (1993) Rare earth elements in old biogenic apatites. *Geochim. Cosmochim. Acta* **57,** 2507–2514.

Harrison R. M. (1981) Chemical association of lead, Cd, Cu and Zn in street dusts and roadside soils. *Environ. Sci. Technol.* **15,** 1378–1383.

Johannesson K. H., Farnham I. M., Guo C., and Stetzenbach, K. J. (1999) Rare earth element fractionation and concentration variations along a groundwater flow path within a shallow, basin-fill aquifer, southern Nevada, USA. *Geochim. Cosmochim. Acta* **63,** 2697–2708.

Johannesson K. H., Lyons W. B., Fee J. A., Gaudette H. E., and McArthur J. M. (1994) Geochemical processes affecting the acidic groundwaters of Lake Gilmore, Yilgarn Block, Western Australia: A preliminary study using neodymium, samarium, and dysoprosium. *J. Hydrol.* **154,** 271–289.

Johannesson K. H., Lyons, W. B., Yelken, M. A., Gaudette, H. A., and Stetzenbach, K. J. (1996) Geochemistry of rare-earth elements in hypersaline and dilute acidic natural terrestrial waters: Complexation behavior and middle rare-earth element enrichments. *Chem. Geol.* **133,** 125–144.

Johannesson K. H., Setzenbach K. J., and Hodge V. F. (1997a) Rare earth elements as geochemical tracers of regional groundwater mixing. *Geochim. Cosmocim. Acta* **61,** 3605–3618.

Johannesson K. H., Setzenbach K. J., Hodge V. F., Kreamer D. K., and Zhou X. (1997b) Delineation of groundwater flow systems in the southern Great Basin using aqueous rare earth element distributions. *Ground Water* **35,** 807–819.

Kersten M. and Förstner U. (1995) Speciation of trace metals in sediments and combustion waste. In *Chemical Speciation in the Environment* (eds. A. M. Ure and C. M. Davidson), pp. 234–275, Chapman and Hall, London.

Lee J. H. and Byrne R. H. (1993) Complexation of trivalent rare-earth elements (Ce, Eu, Gd, Tb, Yb) by carbonate ions. *Geochim. Cosmochim. Acta* **57,** 295–302.

McCarthy J. F., Stafford P. L., and Toran L. E. (1996) Colloid-facilitated field-scale transport of lanthinides and actinides in fractured saprolite. *EOS.* **77,** F212.

McCarthy J. F., Sanford W. E., and Stafford P. L. (1998) Lanthanide field tracers demonstrate enhanced transport of transuranic radionuclides by natural organic matter. *Environ. Sci. Technol.* **32,** 3901–3906.

McClennan S. M. (1989) Rare earth elements in sedimentary rocks: Influence of provenance and sedimentary processes. In *Geochemistry and mineralogy of rare earth elements* (eds. B. R. Lipin and G. A. McKay). *Reviews in Mineralogy,* **21,** 169–200.

Millero F. J. (1992) Stability constants for the formation of rare earth inorganic complexes as a function of ionic strength. *Geochim. Cosmochim. Acta* **56,** 3123–3132.

Smedley P. L. (1991) The geochemistry of rare earth elements in groundwater from the Carnmenellis area, southwest England. *Geochim. Cosmochim. Acta* **55,** 2767–2779.

Tabachnick B. G. and Fidell L. S. (1996) *Using Multivariate Statistics.* Harper Collins College, New York.

Taylor S. R. and McClennan S. M. (1988) The significance of the rare earths in geochemistry and cosmochemistry. In *Handbook on the Physcis and Chemistry of the Rare Earths* (eds. K. A. Gschneidner Jr and L. Eyring), Vol. 11, pp. 465–479, Elsevier, Amsterdam.

Tessier A., Campbell P. G. C., and Bisson M. (1979) Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* **51,** 844–850.

Worrall F. and Pearson D. G. (2001) The development of acidic groundwater in coal-bearing strata: Part I. Rare earth element fingerprinting. *Appl. Geochem* **16,** 1465–1480.

Worrall F., and Pearson D. G. (in press-b) Controls on the composition of acidic mine discharges from coal-bearing strata: Trace element composition. *Appl. Geochem*.

Younger, P. L. (1995) Hydrogeochemistry of minewaters flowing from abandoned coal workings in County Durham. *Quat. J. Eng. Geol.* **28,** 101–113.