CHEMICAL FINGERPRINTING OF ACID MINEWATERS: THE USE OF RARE EARTH ELEMENTS (REE) PATTERNS

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ABSTRACT

There has been coal mining in County Durham (N.E. England) since Roman times. In the middle of the last century the invention of pumping engines meant that deep mining of coal could start and this continued until 1993 when the last mine in the basin closed, although opencast operations continue to this day. With the closure of the last deep coal mines it has been suggested that the network of pumping stations that suppressed the water table in the basin to depths of up to 250 feet (approximately 80m) be decommissioned and pumping turned off. It has been estimated that within 15 years of the cessation of minewater pumping the basin will be entirely flooded (Sherwood and Younger, 1993), with new springs and seeps appearing progressively over that period. With the rebound of the water table coal-bearing strata that has been exposed to oxidation for well over a century will be flushed out potentially bringing acidic, ferruginous groundwaters to the surface. This represents a major driver for acid mine discharge research in Durham coalfield and particular the better understanding of potential emergent water quality. Despite the dewatering of the basin many discharges are known and documented in the region. These discharges are associated with spoil heaps, perched water tables or the fringe of the dewatered area. These discharges allow an opportunity to study the range of possible water qualities and understand the controls on their chemistry.

The primary source of the acidity and pollution in these groundwater is taken as the oxidation of pyrite and other sulphide minerals. The highly acidic water generated from such reactions will have a high weathering potential capable of leaching metals from the surrounding strata. Indeed, many of the identified mine water discharges in the region, although described as acidic, are often circum-neutral implying extensive water-rock interaction. Among these water-rock interactions could be the reaction with mineral siderite, a common carbonate phase within coal-bearing sequences, its dissolution would release additional iron into the environment. Therefore, this project has set out to:

- *develop techniques capable of identifying the source layers for the discharges;*
- *identify the phases contributing to the composition of any spring; and*
- *assess the evolution of the acid mine discharges.*

METHODOLOGY

The project sought to achieve the above aims by means of chemically fingerprinting the seams and non-coal-rocks of coal-bearing strata of the Durham district and comparing these with the fingerprint of discharging waters and their associated ochre deposits. The chemical fingerprints were generated by means of both inductively coupled plasma optical emission spectroscopy (ICP-OES) and inductively coupled plasma mass spectroscopy (ICP-MS). This combination of instrumentation meant that a suite of elemental analysis could be generated that encompassed: Al, Si, Na, Ca, K, Na, Mg, Mn, Fe, S, Cd, Cu, B, Sc, Ni, Ti, As, Ga, Rb, Sr, Y, Zr, Cs, Ba, rare earth elements (REE), Pb, Th, and U. This paper will focus solely on the interpretation of the REE patterns. A total dissolution of coal and shale samples was achieved by using an adaptive microwave digestion strategy involving treatment with nitric, sulphuric and perchloric acids. This work was particularly focused on the opencast at Northwood (Figure 1) where a perched water table on an isolated hillside generates a spring line. The pH of the emergent water quality has been recorded as being as low as pH 2.5, low enough such that no ochre has deposited out of this water hence preserving the chemical fingerprint. The presence of an opencast at this site means that coal seams and associated layers that lie stratagraphically above the spring are exposed and can be sampled. All exposed layers above were analysed. Samples from each layer were leached with both acid at pH 2 and a mild peroxide solution. These separate leachates of the sample were taken to mimic the oxidation and acid weathering processes that generate the observed discharges.

RESULTS

A comparison between the REE whole rock and emergent water composition shows that there is little correspondence suggesting that waters percolating through the strata equilibrate with only particular fractions of the rock. A far greater correspondence is observed with between the emergent water compositions and the acid leachates from certain strata (Figure 2).

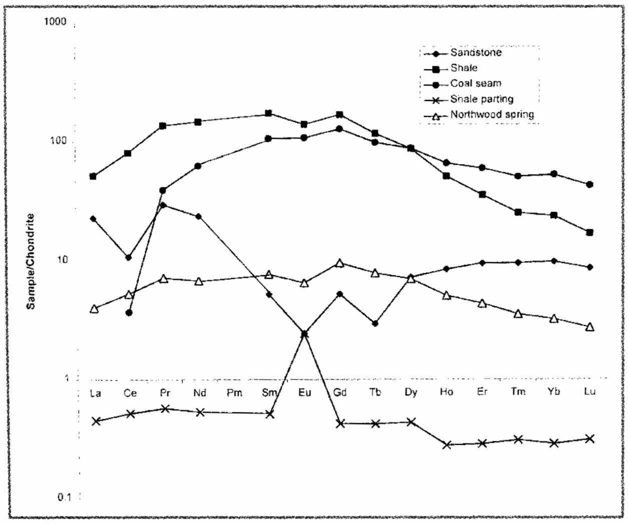

Figure 1. Comparison of rare earth elements (REE) patterns from acid leachates of sampled strata and the Northwood spring.

Expressing the REE pattern in terms of elemental ratios shows that the composition of the waters at Northwood can now be expressed in terms of mixing lines between end member compositions (Figure 3). The trend in the sampled acid minewaters parallels those for the selective leachates. The lateral shift can be ascribed to the increased influence of oxidation products, especially pyrite. The trend to increasing Yb/Gd and La/Gd is towards increasing weathering products (point A – Figure 3) with the other end-member being residual weathering products (point B – Figure 3). This trend suggests that the Northwood spring is the most highly weathered of the sampled discharges whilst those at Quaking Houses and Helmington Row, where the pH is 4 –5, have a very significant contribution from silicate weathering.

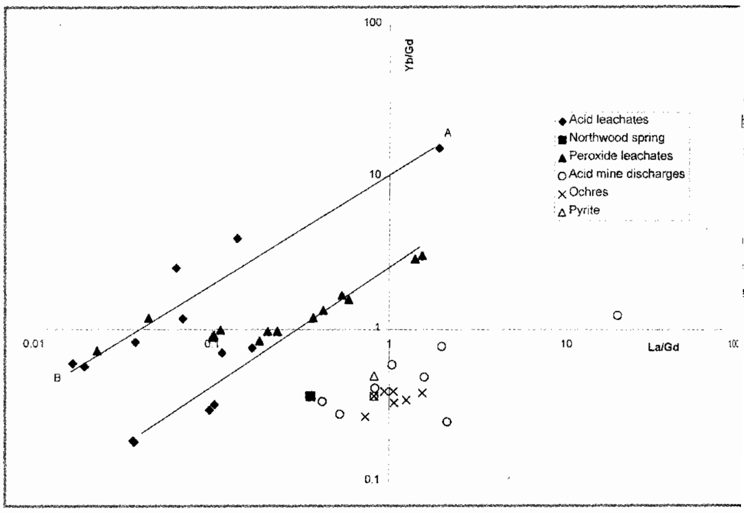

Figure 2. (Yb/Gd)N vs. (La/Gd)N for all samples taken in this study.

Ce and Eu anomalies can be calculated from REE patterns (Figure 4). This means that the data can plot in one of four regions defined by whether samples have a positive or negative Ce anomaly and/or a positive or negative Eu anomaly. Positive Eu anomalies are associated with substitution of Eu for Sr in plagioclase. This then acts as a marker for the involvement of silicate phases in the generation of acidic mine discharges. Those discharges which have positive Eu anomalies tend to have pH < 6. The Ce anomaly is normally associated with the scavenging out of Ce due to the redox behaviour of Ce(III) versus Ce(IV), however, the Eh/pH conditions of the discharges suggests that this transition cannot explain the anomalies observed. Alternatively, positive Ce anomalies are observed for those springs where the total REE concentrations are relatively low and Nesbit (1979) showed that positive Ce anomalies could occur for highly weathered rocks. Thus positive Ce anomalies appear indicative of springs sources from highly weathered, depleted horizons. The largest negative Ce anomalies are observed for the acid leachates of the sandstones within the sampled sequences suggesting that the lower Ce anomalies represent an increased signature from the original sediments.

DISCUSSION

It is possible to classify acid mine discharges in a number of ways. Younger (1995) has suggested a system on the basis of alkalinity and sulphate/chloride ratio in order to get around the problems of representing acid mine discharges on Piper diagrams. For lakes receiving acid minewater, Geller et al. (1998) have suggested a system based on the dominant buffering system operating. Our results show differing chemical signatures depending on the pH of the discharges. Those discharges showing positive Eu anomalies are only found for those discharges with pHs between 6 – 4.5 the region where we would expect silicates to be the main source of buffering. Equally, Eu anomalies were not observed for those springs with pH's above and below this range where carbonate and iron buffering system will be operating. The above chemical fingerprints go beyond such distinctions and are able to show the degree of involvement of silicates and also the relative degree of weathering. Thus, the possibility exists that a classification can now be given both in terms of pH buffering, but also in terms of extent of weathering. The extent of weathering can be judged both in terms of the relative involvement of silicates but also in terms of the degree of weathering. The possibility of using chemical fingerprints to judge the evolution and potential longevity of minewater discharges can now be considered.

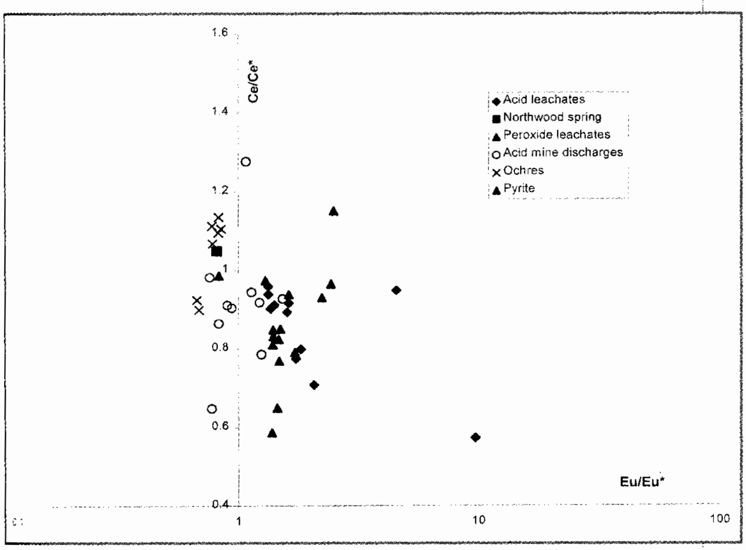

Figure 3. Eu anomaly vs. Ce anomaly for all samples taken in this study.

CONCLUSION

- Selective extracts provide a good fingerprinting technique for emergent waters whereas whole rock compositions do not;
- Relative changes in La/Gd and Yb/Gd indicate increased influence of weathering and oxidation on the composition of discharges;
- The presence of a positive Ce anomaly indicate increased influence of residual weathering product; and
- The presence of Eu anomaly is indicative of the reaction of the groundwaters with plagioclase.

These fingerprinting techniques provide a better understanding and more complex classification of acid mine discharges than previously possible. There is a great potential for fingerprinting techniques to help us understand the evolution and potential longevity of discharges.

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