Thermal effects on rare earth element and strontium isotope chemistry in single conodont elements

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Abstract—A low-blank, high sensitivity isotope dilution, ICP-MS analytical technique has been used to obtain REE abundance data from single conodont elements weighing as little as 5 μg. Sr isotopes can also be measured from the column eluants enabling Sr isotope ratios and REE abundance to be determined from the same dissolution. Results are comparable to published analyses comprising tens to hundreds of elements.

To study the effects of thermal metamorphism on REE and strontium mobility in conodonts, samples were selected from a single bed adjacent to a basaltic dyke and from the internationally used colour alteration index (CAI) "standard set." Our analyses span the range of CAI 1 to 8. Homogeneous REE patterns, "bell-shaped" shale-normalised REE patterns are observed across the range of CAI 1 to 6 in both sample sets. This pattern is interpreted as the result of adsorption during early diagenesis and could reflect original seawater chemistry. Above CAI 6 REE patterns become less predictable and perturbations from the typical REE pattern are likely to be due to the onset of apatite recrystallisation. Samples outside the contact aureole of the dyke have a mean $^{87}Sr/^{86}Sr$ ratio of 0.708165, within the broad range of published mid-Carboniferous seawater values. Our analysis indicates conodonts up to CAI 6 record primary geochemical signals that may be a proxy for ancient seawater. *Copyright © 2001 Elsevier Science Ltd*

1. INTRODUCTION

The geochemistry of conodonts, the phosphatic teeth of an extinct chordate, has come to be regarded as a potential proxy for original seawater chemistry during the Palaeozoic and an alternative model system to calcitic shells (Bertram et al., 1992). The incorporation of Rare Earth Elements (REE) into biogenic apatites is a complex process and the significance of the shape of REE patterns have been discussed extensively. Different models of incorporation (adsorption, substitution, diffusion, percolation, re-crystallisation) and potential sources (seawater, particulates, porewater, sediment) for REEs have been proposed (Bernat, 1975; Elderfield and Pagett, 1986; Grandjean et al., 1987; Grandjean et al., 1988; Sholkovitz et al., 1989; Grandjean-Lécuyer et al., 1993; Bertram et al., 1992; Reynard et al., 1999). Although the broad patterns of REE distributions from conodonts have been well established, the importance of late diagenetic and thermal alteration are still a concern for their use as geochemical tracers of original seawater chemistry (Elderfield and Pagett, 1986; 1987; Reynard et al., 1999).

If fossil apatite is to be useful in tracing ancient seawater chemistry then it must be demonstrated that REE uptake took place in a chemical environment representing seawater, that no significant elemental fractionation occurred during uptake and the mineral system remained closed following uptake. An increasing number of studies suggest that the trace element and isotopic composition of biogenic apatite can be preserved over geological timescales. In the marine realm, for example, Keto and Jacobsen (1987) suggested ε_{Nd} signatures in Cambrian and Ordovician conodonts and were able to distinguish palaeo-oceanic water masses. Wright et al. (1987) used the cerium anomaly in conodonts and ichthyoliths to reconstruct redox conditions in Palaeozoic. Grandjean et al. (1987) used REE profiles in ichthyoliths to reconstruct palaeobathymetry and changes in ocean circulation. Bertram et al. (1992) showed conodont apatite recorded ancient seawater $^{87}Sr/^{86}Sr$ values but samples with a conodont colour alteration index above 2.5 were suspect and even those below CAI 2.5 may be suspect, similar findings have been confirmed by other investigators (Diener et al., 1996; Ebneth et al., 1997; Veizer et al., 1999). Reynard et al. (1999) modelled the crystal-chemical controls on REE uptake by apatite from water by extrapolation of mineral/melt partition coefficients to lower temperature environments. They concluded that convex or "bell-shaped" REE patterns in fossil apatites are best explained by REE fractionation during uptake as the material recrystallises (even by small amounts ~0.2–1%) in the presence of fresh or ocean water during extensive late diagenesis and not a primary seawater signal.

In this paper we further evaluate the effects of increased thermal maturity on REE systematics and on strontium isotopes in conodont elements. To avoid possible "vital effects" and measuring multiple elements with varied history we have used a technique capable of measuring individual conodont elements.

2. MATERIAL AND METHODS

2.1. Sampling

Conodont elements were separated from the host rock using standard preparation techniques (Stone 1987). Two sample sets have been analysed (Table 1). The first includes selected elements from the conodont colour alteration index (CAI) standard set provided by Anita Harris (United States Geological Survey) hereafter the standard set. These specimens, from a variety of strata and depositional settings, exhibit thermal alteration from CAI 1 to 8, reflecting temperatures of matura-

Table 1. Raw abundance data in ppm for the studied sample sets.

Dyke samples	CAI	Ce	Nd	Sm	Eu	Gd	Dy	Er	Yb
bdr5	CAI2	82.9	61.6	13.3	3.1	13.9	7.9	4.1	n.d.
bdr2	CAI6	49.3	47.5	10.3	2.7	10.3	6.0	2.9	n.d.
bdr3	CAI5	48.5	38.1	7.9	2.3	7.1	4.3	2.2	n.d.
bd3	CAI5	60.2	43.1	9.2	2.3	9.3	5.7	2.3	n.d.
bdr1	CAI6	25.8	20.8	5.0	1.6	4.7	3.1	1.2	n.d.
Standard Set									
CAI1a		17.8	16.9	3.5	0.8	3.4	2.9	1.4	n.d.
CAI1.5		3.5	7.1	1.2	0.3	1.7	1.5	0.7	0.2
CAI2		13.8	8.2	1.2	0.3	1.5	1.3	0.6	0.2
CAI3		32.3	36.1	7.4	1.6	7.1	5.9	1.9	0.8
CAI4		22.9	52.1	10.1	2.5	13.5	11.2	3.9	1.5
CAI 4.5		152.5	239.8	45.5	11.8	49.0	29.4	7.2	1.9
CAI5		38.6	45.0	9.9	2.5	11.6	10.4	4.0	1.9
CAI5.5		26.0	24.9	5.3	1.5	6.5	5.5	1.9	0.7
CAI6		17.7	33.5	7.0	1.5	9.1	7.0	1.8	0.5
CAI6.5		185.0	179.6	28.4	8.3	31.1	22.4	5.4	1.3
CAI5		38.6	45.0	9.9	2.5	11.6	10.4	4.0	1.9
CAI5.5		26.0	24.9	5.3	1.5	6.5	5.5	1.9	0.7
CAI6		17.7	33.5	7.0	1.5	9.1	7.0	1.8	0.5
CAI4.5		152.5	239.8	45.5	11.8	49.0	29.4	7.2	1.9
CAI7		115.5	155.4	51.0	10.0	42.7	23.1	4.6	1.5
CAI8		171.9	107.9	18.6	3.0	16.5	12.7	4.3	2.2
Mean shale		83.0	38.0	7.5	1.6	6.4	5.5	3.8	3.5

All analyses are for single conodont elements. Dyke samples were as collected by Armstrong and Strens (1987) from a single bed of the Acre Limestone, Beadnell Bay at the following distances from the beadnell dyke: bdr1 = at the contact of the dyke; bdr2 = 0.5 m; bdr3 = 1 m; bdr3 = 1 m; bdr5 = 3 m. The CAI standard set samples were provided by Dr. A. G. Harris (U.S.G.S.): CAI 1 = Upper Carboniferous, Wyoming; CAI 1A-2 = Mid-Permian, Kiabab Limestone, Nevada; CAI 3 = Mid-Permian, Ely Limestone, Nevada; CAI 4 = Lower Carboniferous, Monte Cristo Group, Nevada; CAI 4.5 = Lower carboniferous, Joana Limestone, Nevada: CAI 5–6.5 = Lower Carboniferous, central Sonora; CAI 7 = Experimentally induced specimens from the Independence Shale, Iowa; CAI 8 = Upper Devonian Kellwasser Limestone, Harz Mountains, Germany. Mean shale = mean of the NASC, European and Russian shale standards from Owen et al. (1999).

tion from <5°C to >600°C (Epstein et al., 1977; Rejebian et al., 1987). Dry heating in the laboratory produced specimens with CAI 7 from the standard set (Dr. A. G. Harris personal communication).

The second sample set was collected from the Acre Limestone, adjacent to the Beadnell dyke, Northumberland, England (Armstrong and Strens 1987). The Beadnell dyke was intruded as part of the feeder system to the Whin Sill, which has been radiometrically dated at 295Ma (K-Ar, Fitch and Miller 1967; in agreement with a baddelyite ^{238}U-^{206}Pb age, Hamilton and Pearson, unpublished data). Thermal alteration of these samples occurred some 45 million years after deposition of the host sediment. Armstrong and Strens (1987) showed that conodonts adjacent to the dyke metamorphosed and equilibrated in a relatively short time (<1 month). They interpreted the complex pattern of maturation that occurred away from the dyke, to be associated with hydrothermal fluid circulation close to the dyke.

2.2. Strontium Analysis

In the past, instrumental limits of detection for REE have necessitated the use of bulk samples of tens to hundreds of conodont elements to obtain reproducible results. Moreover careful cleaning protocols have had to be employed to remove adhering mineral and adsorbed cations. Recent work (Griselin et al., 1999) has indicated that combined ICP-MS analysis and isotope dilution techniques are sufficiently sensitive as to allow the REE and trace element analysis of individual and possibly parts of a single conodont element.

Samples were weighed on a Metter UMT-2 micro-balance (precison 0.1 μg) followed by spiking (for REE) and dissolution in 3N HNO3 (0.1 ml/100 mg), the samples were centrifuged and loaded onto the columns. Sr was separated first using Sr-spec-resin (EIChroM©, 100–150 μm) in cleaned 0.17 ml quartz columns. After elution of the prefraction, with 30 cv of 3N HNO$_3$, Sr was collected with 10 cv of milliQ-water (or 0.05N HNO$_3$). The HNO$_3$ prefraction was collected and used for REE separation (see below). Once dried down and nitrated the samples were ready for mass-spectrometry measurements. The total

blank procedure for Sr varied between 250 to 350 pg at the time of analysis.

The Sr isotope compositions were measured on a MAT-Finnigan 262 RPQ-plus multicollector mass spectrometer at the Vrije Universiteit (Amsterdam). The samples were loaded on a single annealed rhenium filament with TaCl$_5$. The five Sr masses (84–88) were determined using a static routine and were corrected on-line for ^{85}Rb interferences and mass-fractionation correction (using ^{86}Sr/^{88}Sr = 0.1194). During the time of analysis, 50 to 200 ng Sr international standards (NBS 987) were measured and gave the following average values for the ^{87}Sr/^{86}Sr isotope ratio: 0.710241 ± 0.000035 (2σ, n = 31). The standards measured for this study gave a ^{87}Sr/^{86}Sr ratio equal to 0.710250 ± 0.000011 (2σ, n = 4) and are therefore within error of the long term value for the NBS 987 international standard.

2.3. REE Analysis

We have employed a low-blank, high sensitivity isotope dilution REE analytical technique developed at Durham University (Griselin et al., 1999). The technique has blank levels of <<1 pg for most REE and detection limits of ~1 ppt in solution. Elements analysed are Ce, Sm, Nd, Eu, Gd, Dy, Er and Yb using a mixed REE spike (^{142}Ce, ^{147}Sm, ^{145}Nd, ^{153}Eu, ^{155}Gd, ^{161}Dy, ^{167}Er and ^{171}Yb) specifically tailored to conodont analysis before dissolution all samples were ultrasonically washed in 0.1 mol/L ammonium chloride solution (99.999% Alfa) to remove surface and loosely bound, non-lattice held material and then rinsed with pure water.

REEs were separated from the HNO$_3$ prefraction using a REE specific Truspec®AE resin in a single column pass. Samples were measured for REE at the University of Durham, Department of Geological Sciences, on a Perkin Elmer Sciex Elan 6000 ICP-MS using either a CETAC MCN-6000 or a CETAC Aridus micro-concentric desolvating nebuliser. Uptake rates were between 50 and 80 μL per minute. Since REEs are not separated individually interferences of LREE oxides on MREE and HREE isotopes occur during measure-

ment. Therefore oxides were corrected for during all determinations. Oxide and mass bias correction factors were determined using standard solutions, before each batch of sample analysis and also following analysis to monitor instrumental drift. 27 masses were measured including ^{131}Xe, ^{137}Ba and ^{138}La, which are used to make relevant oxide corrections. Oxide levels for both nebulisers varied between 0.02 and 0.1% for CeO^+/Ce^+, depending on day-to-day operating parameters, thus minimising oxide interference problems. Measurement time was circa 8 min per sample with peak dwell times of 20 ms and 30 sweeps of the mass range were repeated 30 times. Typical wash-out times varied from 5 to 20 min. On-peak backgrounds were measured before each sample run by injecting 1 mL of 3.5% HNO_3 and making 5 replicate measurements. Some problems with sample memory were encountered for high abundance samples, particularly for Ce, which required some of the longer rinsing times between samples. Sample data was only taken when the ^{142}Ce background was below 50 counts per second. The data were corrected off-line for mass-interferences and blanks/background, and then used for simple ID calculation of concentrations. The international rock standards PCC1 and DTS-1 and sample duplicates were also measured. The concentrations measured for the international standards are in accordance with the recommended values and other data published in the literature (Eggins et al., 1997; Niu and Hekinian, 1997). Reproducibility and accuracy of the REE data with reference to international rock standards are given in Griselin et al. (in press). At the concentration level recorded in the individual conodont elements, replicate analyses of silicate rocks were reproducible to better than 5% (2σ). Our current spike does not contain La and this limits our ability to resolve Ce anomalies.

3. RESULTS

3.1. Rare Earth Elements

Absolute REE concentrations throughout the CAI range are extremely variable, e.g., (Nd)$_n$ 0.2 to 7.9 (Figs. 1, 2). Despite this the slopes of shale normalised patterns are remarkably homogeneous and "bell–shaped" across all the CAI values (Figs. 1A, 2). The apparent convexity of the curves may have been exaggerated by the lack of La data from our samples, in that ant Ce anomaly will increase the apparent LREE/MREE fractionation. The typical REE pattern throughout the CAI range is characterised by middle Rare Earth (MREE) enrichment, minor Ce depletion and a tendency towards heavy Rare Earth (HREE) depletion, particularly Er and Yb, relative to light Rare Earth's (LREE). There is no systematic change in the shape of the patterns with CAI but there is an apparent increase in REE abundance with increasing CAI in the standard set samples (Fig. 1A) whilst the converse is true for samples adjacent to the dyke (Fig. 2). Sample bdr1 from within the contact aureole of the dyke shows reduced concentrations compared to the other samples.

3.2. Strontium Isotopes

$^{87}Sr/^{86}Sr$ ratios of samples away from the contact aureole of the dyke are constant (within error) with a mean value of 0.708165 (min. 0.708152 ± 10—max. 0.708172 ± 11; Table 1, Fig. 3. Sample bdr1, closest to the dyke, has a significantly less radiogenic value of 0.708027.

4. DISCUSSION

4.1. Rare Earth Elements

Our analysis of single conodont elements has revealed a homogeneous "bell-shaped" REE pattern that remains stable up to CAI 6; above this value the shape of the pattern becomes less predictable. Samples adjacent to the Beadnell dyke show a general decrease in REE abundance with increasing CAI.

Kolodny et al. (1996) recognised that fossil biogenic apatites contain 5 to 6 times the concentration of REEs than found in seawater and that the patterns obtained must be the result of diagenetic alteration. Two mechanistic hypotheses have been proposed to explain the abundances of REEs and the isotopic compositions of elements such as Sr and Nd in biogeneic apatite. The first, that they are the consequence of adsorption during the early diagenetic reorganisation from calcium hydroxy-apatite to francolite (Trueman, 1999) and thus reflect original seawater chemistry (Grandjean et al., 1987; Grandjean-Lécuyer et al., 1993). Or secondly, that they result from substitution reactions during recrystallisation in the presence of seawater (Wright et al., 1987; Shemesh, 1990; Bertram et al., 1992; Reynard et al., 1999). Our data shed new light on which of these hypotheses is more appropriate for explaining the REE patterns in conodonts.

The REE abundance patterns we have obtained for single elements are comparable to those published for bulk samples containing tens or hundreds of elements (Grandjean-Lécuyer et al., 1993; Wright et al., 1984; 1987; Bertram et al., 1992; Reynard et al., 1999). Conodont apatite shows consistent MREE enrichment producing "bell-shaped" REE patterns on abundance plots. In both our datasets there is no change in this pattern from CAI 1 to 6 indicating a REE pattern established in early diagenesis remains unaltered over a temperature range of <50 to ~550°C.

Conodont element crowns are composed of enamel or enamel homologues that have a coarse primary crystalline structure with crystallites commonly up to 4 μm in length (Sansom et al. 1992). The preservation of this histology in specimens heated to CAI 5 (Armstrong and Smith, unpublished data) also indicates that bulk re-crystallisation of apatite is not occurring during high temperature diagenesis.

Prominent elemental zoning has been found in some conodonts (Bruhun et al., 1997) and fish teeth (Toyoda and Tokonami, 1990) whilst other conodont samples lack zoning (e.g., Grandjean-Lécuyer et al., 1993). The absence of zoning would support early diagenetic homogeneous REE adsorption involving the bulk of the phosphatic material and the system remaining closed during later diagenesis (Grandjean-Lécuyer and Albarède, 1989; Grandjean-Lécuyer et al., 1993). The presence of elemental zoning in some samples may thus be used as a criterion to indicate that they are inappropriate for seawater tracing.

We conclude that REE uptake in conodonts occurred during early diagenesis and potentially record a primary chemical record of the aqueous environment in which they had grown. The MREE enrichment observed in conodont elements is also found in deep-sea Fe-rich nodules (Piper, 1974; Elderfield et al., 1981; Aplin, 1984; Ingri and Ponter, 1987; De Carlo and McMurtry, 1992) and estuarine seawater (Hoyle et al., 1984). All conodonts analysed to date have come from shallow marine shelf limestones and uptake of REE from estuarine waters may dominate the observed pattern. Hoyle et al. (1984) reported MREE enrichment in water from the estuary of the River Luce, S. W. Scotland (Fig. 4). In this organic rich, acidic system preferential removal of HREE (~95%) relative to LREE (~60%) was chiefly associated with Fe rich organic colloids
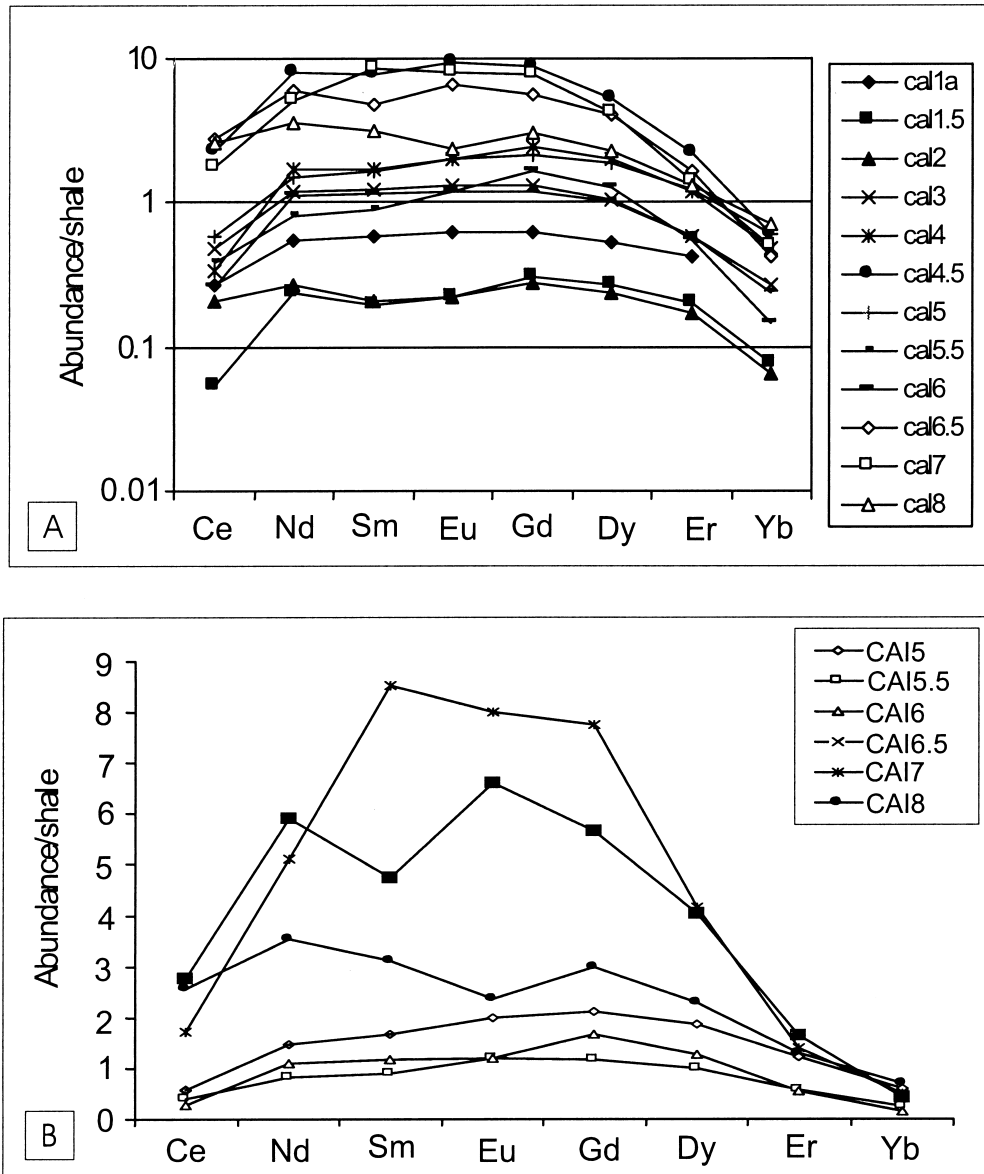
Fig. 1. Shale normalised REE abundance plots based on data in Table 1. Fig. 1A: CAI standard set, Fig. 1B: Normalised abundances for samples CAI 5 to CAI 8 re-plotted on a linear scale to emphasize the change in shape of the patterns above CAI 6.

which flocculate during estuarine mixing of river and seawater, but no Ce anomaly is developed. These processes leave estuary water relatively enriched in MREE, with a "bell-shaped" pattern on shale normalised abundance plots (Fig. 4) that are similar to patterns obtained for conodonts.

Above CAI 6 the generation of a bell-shaped REE pattern becomes less predictable (Fig. 1B). Sample CAI 7 from the standard set exhibits a similar degree of MREE enrichment to that reported from Devonian conodonts from the Montagne Noire region, France (Grandjean-Lécuyer et al., 1993). Reynard et al. (1999) modelled this highly fractionated pattern by invoking variable REE substitution during c. 0.6 to 0.8% recrystallization. Above CAI 6 conodonts change colour from medium dark grey (CAI 6) through white (CAI 7) to colourless

(CAI 8) with a mottled patterning indicating the migration of carbon out of the element during recrystallization (Rejebian et al., 1987). These observations suggest perturbations from the typical REE pattern above ~550°C are the result of apatite recrystallisation.

Published REE abundances in conodonts show considerable variation. These might be attributed to the variations in original seawater chemistry, could be "vital effects" related to species or the result of variations in late diagenetic conditions. We observe a general decrease in REE abundance with increasing CAI for samples adjacent to the dyke and an increase through the standard sample dataset. The dyke samples are taken from the same strata and thus vary only in CAI, indicating gradual loss of REEs with increasing temperature whilst retaining the
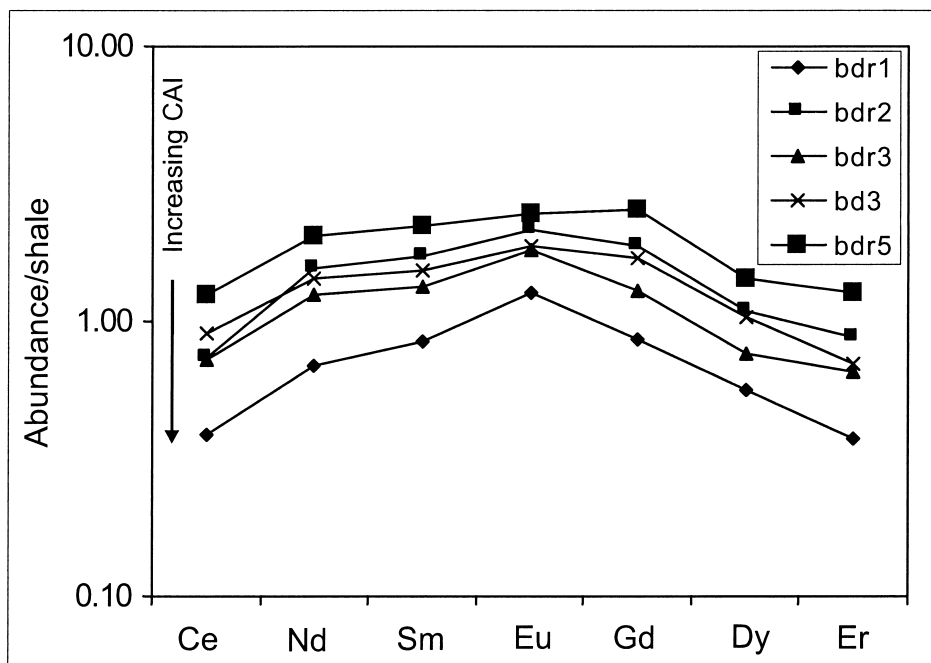
Fig. 2. Shale normalised REE abundance plots for samples collected adjacent to the Beadnell dyke. All samples show a decrease in REE abundance with increasing CAI with the exception of bd2.

primary relative abundance pattern. Conodonts from the contact aureole of the dyke show marked REE depletion compared to the other samples from this set, with preferential depletion in LREEs. This suggests that in such extreme environments of thermal metamorphism and fluid circulation, re-crystallisation

and/or hydrothermal fluids in the contact zone can alter conodont element chemistry. The standard set samples included specimens from a wide range of ages and depositional envi-
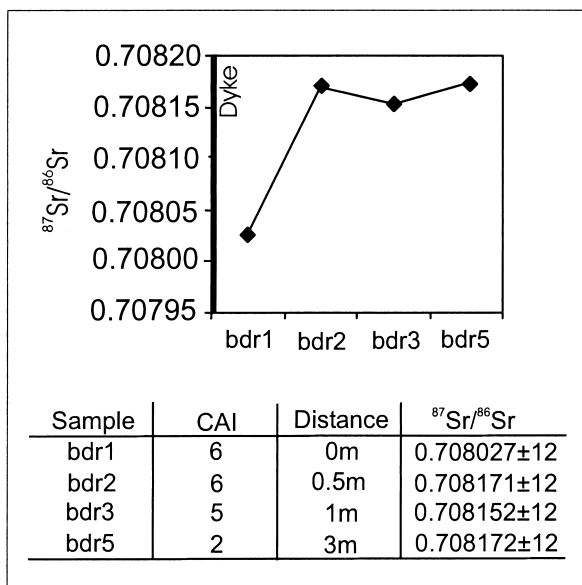

Sample	CAI	Distance	$^{87}Sr/^{86}Sr$
bdr1	6	0m	0.708027±12
bdr2	6	0.5m	0.708171±12
bdr3	5	1m	0.708152±12
bdr5	2	3m	0.708172±12

Fig. 3. Strontium isotope values of samples collected from adjacent to the Beadnell dyke. Points are scaled to include the error bar (2σ). All samples fall within the broad published range of Lower Carboniferous seawater values measured from calcitic brachiopods (Bruckschen et al.1995; Bruckschen et al. 1999.
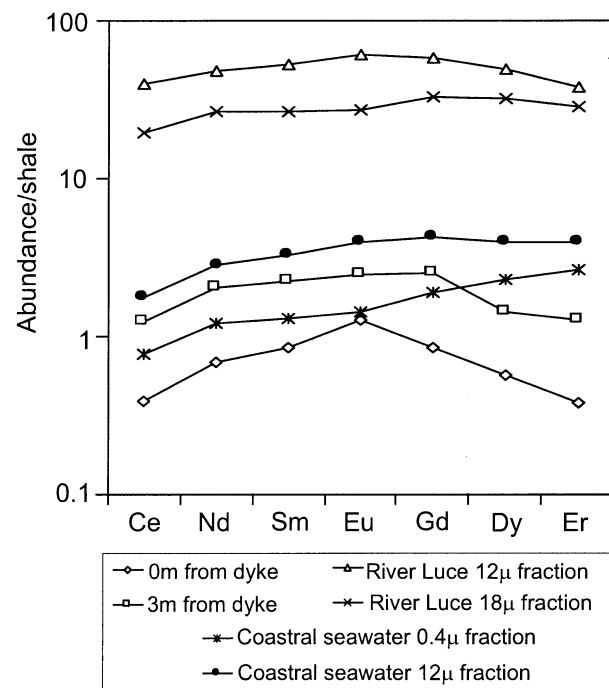

Fig. 4. Shale normalised REE abundance plots from samples adjacent to the Beadnell dyke and the River Luce (from Hoyle et al., 1984). River Luce data are discriminated by particulate size in microns.

ronments making cause and effect relationships between REE abundance and CAI impossible to elucidate.

4.2. Strontium Isotopes

Data from adjacent to the Beadnell dyke show constant $^{87}Sr/^{86}Sr$ ratios within analytical error in all but the sample closest to the dyke. This sample has experienced temperatures of approximately 650°C (Armstrong and Strens, 1987). Bertram et al. (1992) found that conodonts of the same age with low CAI values have much lower $^{87}Sr/^{86}Sr$ ratios than samples with high CAI values. They concluded that the process of thermal maturation had resulted in the incorporation of Sr into the conodont lattice that is more radiogenic than the seawater, by exchange with diagenetic fluids; a conclusion supported by more recent studies (Diener et al., 1996; Ebneth et al., 1997; Veizer et al., 1999). Textural and proton-induced X-ray emission (PIXE) trace element studies (Bruhn et al., 1997) have showed that conodonts exchange about one third of their Sr with the surrounding rock matrix. In pure carbonates they may still retain their near seawater $^{87}Sr/^{86}Sr$ values, but mostly values are $\sim 5 \times 10^{-5}$ more radiogenic (Ebneth et al., 1997). The strontium isotope record as measured in calcitic brachiopods shows an Early Carboniferous decline from ~ 0.7083 to a mid-Visean minimum of 0.7077 followed by a sharp rise to the mid-Pennsylvanian (Bruckschen et al., 1995; Bruckschen et al., 1999). The values obtained from the Beadnell conodont samples fall within the broad range for the Early Carboniferous and may plausibly record ambient seawater $^{87}Sr/^{86}Sr$. However, taking the minimum $^{87}Sr/^{86}Sr$ value of 0.7077 for Visean seawater then our values are 4.65×10^{-4} times more radiogenic than background. The less radiogenic $^{87}Sr/^{86}Sr$ value recorded by the sample within the aureole of the dyke may reflect chemical exchange with hydrothermal fluids associated with dyke during intrusion and cooling.

5. CONCLUSIONS

The newly developed analytical procedures produce analyses of single conodont elements as small as 5 μg that compare well with published results from bulk samples of tens to hundreds of elements. This technique has the potential to greatly increase the range of samples suitable for analysis and provide a way to rapidly screen bulk samples for the effects of alteration processes.

Homogeneous, "bell-shaped" shale normalised REE patterns in conodonts across the range of CAI 1 to 6 argue for, REE immobility and adsorption during early diagenesis and against a progressive enrichment through percolating diagenetic or hydrothermal fluids or REE fractionation due to recrystallisation. It is likely that REE uptake occurred during the phase transition from the unstable calcium hydroxy-apatite to the more stable francolite, shortly after death. The REE pattern obtained from conodonts is comparable to that of estaurine water where mixing of fresh and seawater induces Fe flocculation and depletion of HREE and to a lesser extent, LREE relative to MREE.

Samples from adjacent to the Beadnell dyke show a gradual decrease in REE abundance with increasing CAI, whilst retaining the "bell-shaped" pattern. This could be due subtle changes

in the francolite lattice with increasing temperature or reactions associated with devolatalisation during thermal maturation of the organic matrix of the conodont element. Above CAI 6 REE patterns are less predictable and perturbation from the typical REE abundance pattern are likely to be due to the onset of recrystallisation.

Conodont samples outside the thermal aureole of a basaltic dyke and within the range of CAI 1 to 5 fall within the predicted broad range of Early Carboniferous $^{87}Sr/^{86}Sr$ ratios and could plausibly recording ambient seawater. Alternately our data support the conclusions of others that strontium in conodont elements is more radiogenic than background.

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