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Rare earth element geochemistry of upper Ordovician cherts from the Southern Uplands of Scotland

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Abstract: Caradoc and Ashgill radiolarian cherts and siliceous mudstones from the Southern Uplands preserve primary rare earth element (REE) signatures which are comparable to those of more recent deposits from continental margin settings. This is incompatible with the widely held view of these rocks as open ocean deposits incorporated in an accretionary prism and reinforces the model of deposition on an extensional continental margin. The REE signatures can be used as fingerprints to differentiate between some of the fault-bounded formations within the area. They indicate the provenance of the mud grade siliciclastic material in these distal hemipelagites and are comparable with published REE data on greywackes in the same successions. This detailed analysis of the REE patterns in Lower Palaeozoic cherts demonstrates the usefulness of this approach in ancient orogens.

Keywords: Southern Uplands, Ordovician, chert, rare earth elements, geochemistry.

Determination of the rare earth element (REE) signatures of radiolarian cherts has become a very powerful tool in determining the environmental setting of Mesozoic and Cenozoic oceanic and ocean margin successions (see Murray 1994). It is also being used in conjunction with other geochemical data on Palaeozoic successions (Girty *et al.* 1996). The present study is the first systematic application of this approach to Early Palaeozoic rocks based purely on REE and is undertaken in a terrane of controversial origin, tectonic complexity and low grade (prehnite–pumpellyite) metamorphism. The study was undertaken in conjunction with biostratigraphical work which provides the temporal control on the geochemical samples. It shows that the use of REE geochemistry can be used to distinguish between various Ordovician formations within the Southern Uplands and to provide another valuable constraint on the plate tectonic history of this sector of the Caledonide Orogen.

Radiolarian chert geochemistry

Modern radiolarian oozes accumulate in a range of settings in nutrient rich upwelling zones which lead to high planktonic productivity. These occur along equatorial current divergences, subpolar convergences, the western edges of continental shelves and in some marginal seas (Hesse 1988). Similarly, Ordovician to Cretaceous radiolarian cherts are thought to have accumulated in high latitude east–west upwelling belts and in continental margin upwelling zones (Jones & Murchey 1986, p. 467).

Murray (1994) summarized the evidence for early diagenesis of cherts and showed that there is considerable chemical fractionation, most notably the addition of dissolved silica and the high mobility (addition or loss) of various elements. However, Al, Ti and Fe and the REE are largely immobile. Using an extensive database largely of Mesozoic and Caenozoic cherts from known depositional settings, Murray (1994) demonstrated that the REEs enable the distinction to be made between continental margin, proximal ridge and pelagic deposits. That analysis was restricted to cherts but earlier studies (Murray *et al.* 1990, 1991) showed that shales interbedded with the cherts gave similar REE patterns. The latter study also elegantly demonstrated the progressive change in REE chemistry with distance from the spreading ridge in a single succession. Using shale-normalized data from the Franciscan Complex of California, Murray *et al.* (1990) showed that the shale-normalized cerium anomaly [Ce_{sn}/Ce^* where $Ce^*=(La_{sn}+Pr_{sn})/2$] changes from extremely low values (about 0.29) for cherts and shales deposited near the spreading ridge, through values around 0.55 for those deposited in ocean basin settings and 0.90–1.30 for cherts and shales from continental margin settings estimated to be over 3000 km from the spreading ridge. Taking a larger data set, derived from DSDP and ODP cores from several oceans, Murray *et al.* (1992) obtained shale-normalized Ce_{anom} values between 0.12 and 1.69, but with clusters of samples at less than 0.50, between 0.5 and 0.8 and between 0.8 and 1.3 reflecting these three depositional settings. These Ce_{anom} signatures seem to be robust despite considerable discussion in the literature of potential variation in cerium and possibly europium anomalies as a function of oceanic redox conditions (Wilde *et al.* 1996, Holser 1997).

Murray *et al.* (1991, 1992) have shown that the variation in REE composition in marine cherts and mudrocks results from a combination of: (a) adsorption from sea water, (b) the composition of contained terrigenous particles and (c) the composition of contained metalliferous particles. The first of these results in the total REE abundance being controlled by sediment exposure time (i.e. burial rate). REE behaviour in sea water varies across ocean basins as a result of continental and spreading ridge influences and therefore can be used as an indicator both of oceanic environment and proximity to the continental shelf. Rivers are the main source of REE to the oceans (see Holser 1997) and strongly influence continental

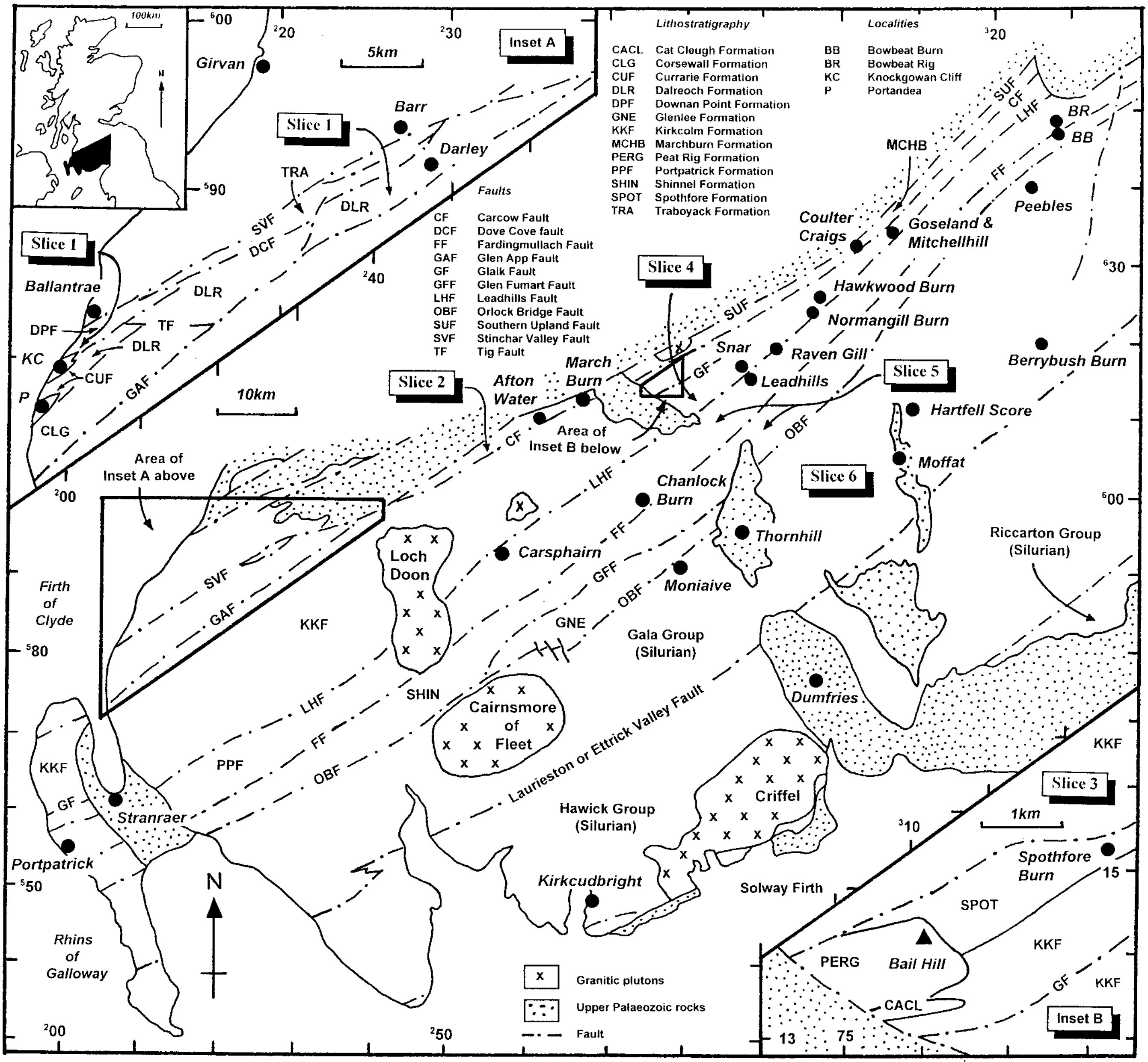


Fig. 1. Geological map of the Southern Uplands and southernmost Midland Valley of Scotland showing the localities mentioned in the text and the numbered fault-bounded slices from which upper Ordovician chert samples were obtained (based on Floyd 1996*a*, fig. 1). Detailed locality and lithological information on the samples is provided by Owen & Armstrong (1997).

shelf waters. Their REE signatures characteristically show little or no fractionation of Ce from the other REEs (Goldstein & Jacobsen 1988). In oxygenated ocean waters, oxidation of Ce(III) to the relatively insoluble Ce(IV) allows preferential removal of Ce from the water column, resulting in sea water with a pronounced negative Ce anomaly. (Elderfield & Greaves 1982; Holser 1997). Particulate Fe and Mn in hydrothermal plumes near spreading ridges preferentially scavenge still more Ce resulting in ridge influenced sea water having Ce anomalies lower than normal sea water (Klinkhammer *et al.* 1983). Eu anomalies in sea water most commonly reflect hydrothermal (positive) input (Elderfield 1988).

Under most circumstances, REE are largely transported from the weathering profile in particulate matter rather than in solution (Nesbitt 1979; McLennan 1989; Morey & Setterholm 1997). In some instances, REE may be diagenetically enriched in phosphatic fossils (Holser 1997 and references therein), in francolite overgrowths on detrital apatites in sandstones (Bouch *et al.* 1995), in diagenetic apatite (Ohr *et al.* 1994) or monazite nodules (Milodowski & Zalasiewicz 1991) in mudrocks; the mobilization of REE and their precipitation in these phosphates probably being mediated or modified by organic matter. Cullers *et al.* (1979) recognized that whilst most of the REE composition of siliciclastic sediments is found in the silt and clay size fractions, there is no direct correlation with clay mineralogy hence most clay minerals can accommodate the trivalent rare earths. Quartz has very low REE abundances and the REE content of the cherts and cherty

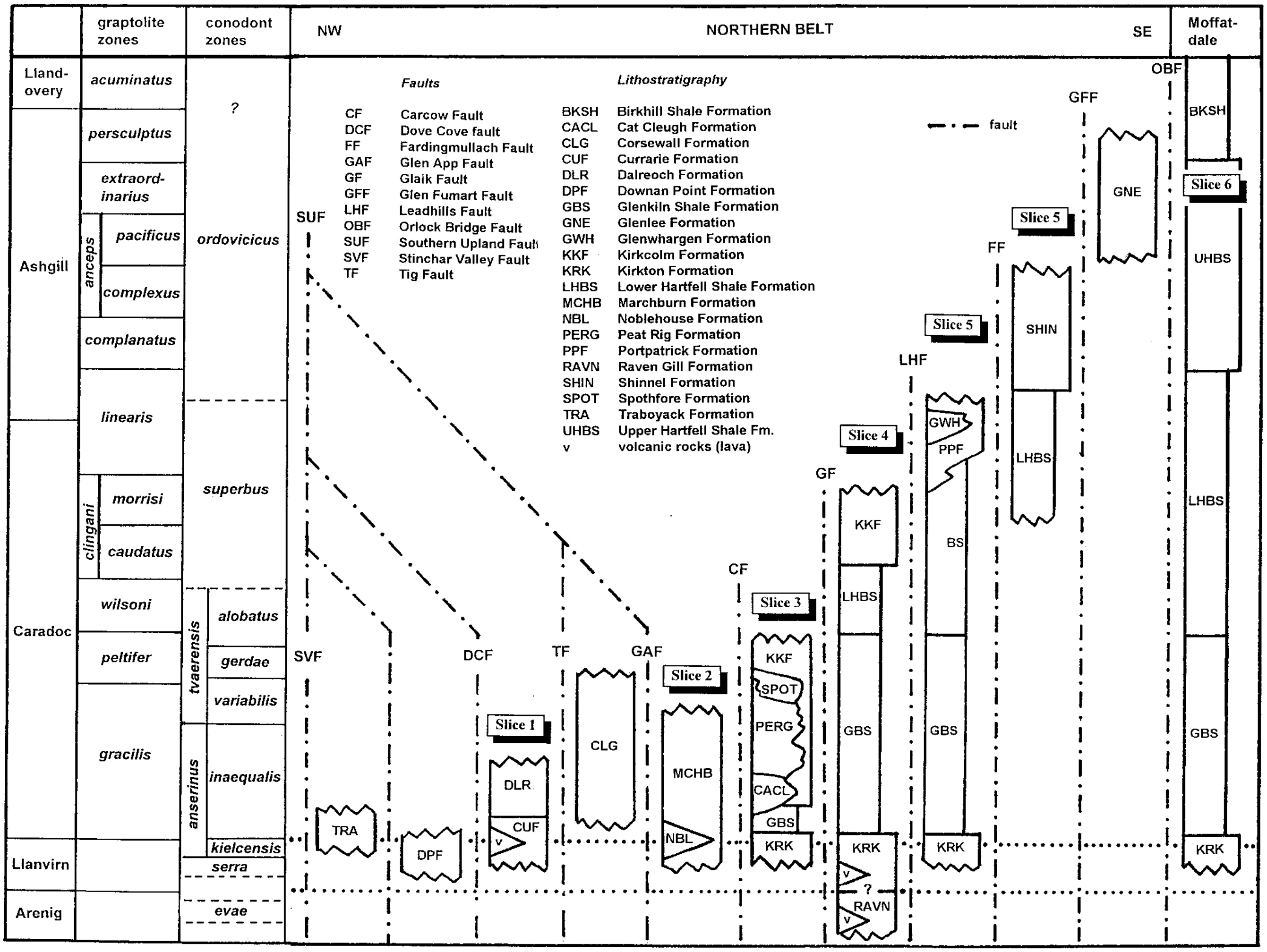


Fig. 2. The Ordovician lithostratigraphy of the Southern Uplands showing the fault-bounded slices from which upper Ordovician chert samples were obtained (based on Floyd 1996*a*, fig. 2). Note that the Kirkton and Raven Gill formations may be synonymous and of mid-Arenig age.

mudstones reflects the original clay composition plus any component derived from seawater adsorbed onto the clays or the biogenic component (Murray *et al.* 1992, p. 1897).

The dominance of the terrestrially derived detrital REE component in continental margin cherts means that it is appropriate to make comparisons with the now well established relationships between chondrite-normalized REE patterns and depositional environments of siliciclastic marine sediments. This approach was also adopted by Girty *et al.* (1996) in their analysis of cherts and argillites from the Ordovician to Devonian of the Sierra Nevada, California. McLennan (1989) and McLennan *et al.* (1990) showed that chondrite-normalized REE patterns of continental margin mudrocks commonly show the light REE (LREE) enrichment, negative Eu_{anom} [here calculated as Eu_{cn}/Eu^* where $Eu^* = (Sm_{cn} + Gd_{cn})/2$—see Murray *et al.* 1992, p. 1898 for a similar shale-normalised calculation] and flat heavy REE (HREE) distributions of mean shale. This may even be the case in arc settings where the dominant provenance is from old or recycled continental crust or from a fractionated igneous arc (i.e. with plagioclase removed). Under reducing conditions in the lower crust, Eu^{2+} substitutes for Sr in feldspar, especially calcic plagioclase, and thus in arc settings where there is a substantial contribution from an unfractionated source, the REE patterns of sediments containing unweathered Ca-plagioclase lack or have only a slight negative Eu_{anom} (Nance & Taylor 1977; McLennan 1989).

The Southern Uplands terrane

The Southern Uplands of Scotland comprises a series of SW–NE-striking slices of Ordovician and Silurian rocks, largely turbidites, at a low (prehnite–pumpellyite) grade of metamorphism (Merriman & Roberts 1996 and references therein) separated by strike-parallel faults (Fig. 1). Many of the these faults are used herein to define a series of numbered tectonic 'slices' within which sampling was undertaken in the present project (Figs 1, 2). Of these, 'tectonic slice 5' combines two major tectonic units as the REE data suggest some uncertainty about the lithostratigraphical assignment of some of the samples. The succession within each fault-bounded slice generally youngs to the north, but there is an overall southward younging across the belt as a whole. The area is bounded to the north by the Southern Upland Fault (see Floyd 1994) and whilst some authors have suggested that the Southern Upland Fault marks a line of considerable sinistral strike slip movement, faunal evidence suggests that no more than a few

Table 1. *Raw REE data, normalized cerium and europium anomalies and La/Yb ratios of cherts, cherty mudstones and shales analysed herein, arranged by tectonic slice*

				Slice 1 Currarie							Slice 1 Dalreoch			Slice 2				Slice 3					
Raw	At mass	Chondrite	Shale	AOW7	AOW8	AOW9	HOA2	HOA3	HOA5	AOW11	AOW13	AOW14	AOW15	AWO14	AOW35	AOW46	AOW47	AWO3	AWO4	AWO11	AWO12	AWO13	AWO16
La	139	0.31	41.00	22.30	18.66	13.23	16.04	24.09	12.38	20.54	14.87	16.20	16.46	24.01	19.62	9.47	26.24	6.96	9.91	5.94	5.83	7.76	4.60
Ce	140	0.81	83.10	45.33	44.88	32.21	37.77	53.30	25.53	45.56	32.30	40.62	38.38	47.45	42.87	21.14	55.46	14.36	21.18	13.92	12.96	18.21	8.93
Pr	141	0.12	10.10	5.32	5.45	3.34	4.79	5.93	2.42	5.34	3.34	4.08	3.94	4.83	4.70	2.18	5.97	1.33	2.10	1.45	1.28	1.75	0.85
Nd	143	0.60	38.30	23.18	23.91	13.83	20.58	23.57	9.50	22.26	13.11	17.03	16.32	20.42	18.07	8.50	23.27	5.62	8.94	5.65	5.45	7.33	3.60
Sm	147	0.20	7.50	5.19	5.60	2.93	5.17	5.08	1.79	4.94	2.55	3.57	3.45	3.36	3.58	1.67	4.71	0.98	1.61	1.14	1.05	1.33	0.66
Eu	151	0.07	1.61	1.49	1.57	0.70	1.33	1.22	0.38	1.27	0.56	0.87	0.85	0.59	0.84	0.36	1.00	0.24	0.36	0.23	0.23	0.31	0.15
Gd	157	0.26	6.51	5.11	5.35	2.81	4.92	4.98	1.85	4.87	2.27	3.56	3.43	2.98	3.44	1.68	4.61	0.92	1.57	1.08	1.04	1.30	0.65
Tb	159	0.05	1.23	0.83	0.88	0.42	0.86	0.80	0.27	0.77	0.31	0.54	0.54	0.30	0.51	0.25	0.75	0.12	0.21	0.15	0.15	0.18	0.09
Dy	161	0.32	6.51	4.74	5.03	2.43	5.19	4.76	1.62	4.50	1.74	3.05	3.18	1.52	2.98	1.48	4.50	0.72	1.15	0.88	0.80	1.06	0.53
Ho	165	0.07	1.34	1.00	1.06	0.52	1.09	1.03	0.34	0.93	0.36	0.62	0.68	0.33	0.63	0.31	0.96	0.15	0.22	0.17	0.16	0.21	0.11
Er	166	0.21	3.75	2.65	2.77	1.41	3.04	2.88	0.90	2.50	1.00	1.64	1.83	1.02	1.77	0.82	2.64	0.45	0.60	0.45	0.43	0.62	0.29
Tm	169	0.03	0.53	0.40	0.42	0.23	0.48	0.45	0.14	0.38	0.16	0.25	0.29	0.19	0.28	0.13	0.41	0.08	0.09	0.07	0.07	0.10	0.05
Yb	172	0.21	3.53	2.42	2.49	1.38	2.94	2.76	0.85	2.28	1.02	1.53	1.71	1.41	1.68	0.77	2.36	0.50	0.58	0.41	0.44	0.64	0.31
Lu	175	0.03	0.53	0.37	0.38	0.21	0.46	0.44	0.13	0.35	0.16	0.24	0.26	0.25	0.27	0.12	0.37	0.08	0.09	0.07	0.07	0.10	0.05
Tot REE				120.32	118.43	75.65	104.66	131.28	58.10	116.48	73.74	93.80	91.33	108.67	101.23	48.87	133.24	32.52	48.61	31.62	29.95	40.90	20.85
Chondrite normalized																							
Ce*				57.76	52.44	35.04	45.51	63.17	29.88	54.99	37.67	42.85	42.72	58.51	50.89	24.23	66.80	16.68	24.60	15.54	14.65	19.69	10.89
Ce/Ce*				0.97	1.06	1.14	1.03	1.04	1.06	1.03	1.06	1.17	1.11	1.00	1.04	1.08	1.03	1.07	1.07	1.11	1.09	1.15	1.01
Eu*				23.18	24.67	12.92	22.76	22.63	8.17	22.05	10.91	16.03	15.46	14.38	15.82	7.51	20.98	4.29	7.16	5.01	4.69	5.90	2.95
Eu/Eu*				0.87	0.86	0.74	0.79	0.73	0.63	0.78	0.70	0.73	0.75	0.56	0.72	0.65	0.65	0.76	0.68	0.62	0.66	0.71	0.69
La/Yb				6.21	5.06	6.45	3.67	5.89	9.82	6.08	9.85	7.13	6.48	11.48	7.85	8.26	7.51	9.35	11.43	9.72	8.95	8.21	10.11
Shale normalised																							
Ce*				0.54	0.50	0.33	0.43	0.59	0.27	0.51	0.35	0.40	0.40	0.53	0.47	0.22	0.62	0.15	0.22	0.14	0.13	0.18	0.10
Ce/Ce*				1.02	1.09	1.19	1.05	1.09	1.13	1.07	1.12	1.22	1.17	1.07	1.09	1.14	1.08	1.15	1.13	1.16	1.16	1.21	1.10
Eu*				0.62	0.60	0.36	0.72	0.72	0.26	0.58	0.35	0.44	0.43	0.45	0.50	0.24	0.67	0.14	0.23	0.16	0.15	0.19	0.09
Eu/Eu*				1.49	1.62	1.23	1.14	1.05	0.89	1.36	0.99	1.23	1.23	0.81	1.03	0.94	0.92	1.10	0.97	0.90	0.95	1.02	1.00
La/Yb				0.79	0.65	0.82	0.47	0.75	1.25	0.78	1.26	0.91	0.83	1.47	1.00	1.05	0.96	1.19	1.46	1.24	1.14	1.05	1.29

Table 1. *Continued*

	Slice 4							Slice 5								Slice 6					
Raw	AWO2	AWO9	AWO17	AOW16	AOW17	AOW30	AOW37	HFB55	HFB56	HFB59	HFB88++	AOW31++	AOW32	AOW33++	AOW34	AOW21	AAOW22++	AOW23++	AOW24++	AOW25	AOW27
La	10.34	8.12	6.53	6.58	11.16	33.82	4.56	24.90	22.18	21.90	14.94	2.40	5.28	5.23	5.63	15.85	16.65	17.31	11.17	9.16	7.67
Ce	22.57	16.01	13.06	15.58	24.35	75.08	10.31	63.06	44.21	49.20	35.78	4.55	12.05	8.88	13.04	39.82	36.87	40.65	23.92	25.29	15.16
Pr	2.27	1.89	1.58	1.60	2.61	7.94	1.27	6.49	5.38	5.36	3.75	0.56	1.34	1.37	1.40	3.76	4.21	4.63	2.75	1.99	1.24
Nd	9.52	7.13	6.34	6.27	10.28	30.32	5.31	25.11	19.89	19.89	13.98	2.23	5.47	5.83	5.64	14.64	16.78	18.72	10.53	7.26	4.38
Sm	1.73	1.31	1.34	1.20	2.02	5.66	1.14	5.25	3.76	3.70	2.78	0.44	1.21	1.19	1.15	2.61	3.00	3.32	1.70	1.24	0.69
Eu	0.36	0.33	0.28	0.26	0.42	1.16	0.26	1.17	0.84	0.79	0.59	0.17	0.68	0.41	0.45	0.49	0.61	0.67	0.35	0.28	0.18
Gd	1.68	1.26	1.34	1.14	1.82	5.41	1.10	5.92	3.63	3.42	2.56	0.44	1.14	1.21	1.17	2.34	2.63	2.78	1.50	1.37	0.76
Tb	0.23	0.15	0.21	0.15	0.26	0.76	0.16	0.94	0.51	0.48	0.37	0.07	0.17	0.18	0.18	0.33	0.37	0.40	0.22	0.20	0.12
Dy	1.25	0.87	1.23	0.88	1.43	4.40	0.83	5.22	2.90	2.75	2.07	0.42	0.99	1.15	1.04	2.06	2.32	2.41	1.38	1.24	0.84
Ho	0.25	0.16	0.24	0.18	0.30	0.93	0.16	1.04	0.58	0.54	0.42	0.09	0.21	0.25	0.21	0.43	0.52	0.52	0.32	0.26	0.21
Er	0.72	0.48	0.66	0.48	0.84	2.63	0.38	2.84	1.59	1.50	1.14	0.27	0.56	0.71	0.56	1.18	1.59	1.46	0.96	0.73	0.67
Tm	0.12	0.07	0.11	0.08	0.13	0.42	0.06	0.46	0.27	0.26	0.20	0.04	0.09	0.10	0.09	0.19	0.26	0.24	0.16	0.13	0.12
Yb	0.74	0.42	0.70	0.47	0.81	2.62	0.35	2.78	1.58	1.57	1.23	0.29	0.56	0.58	0.58	1.23	1.66	1.42	1.01	0.81	0.87
Lu	0.12	0.07	0.11	0.07	0.12	0.42	0.05	0.45	0.25	0.25	0.19	0.04	0.09	0.09	0.09	0.19	0.27	0.22	0.16	0.13	0.15
Tot REE	51.88	38.27	33.73	34.95	56.54	171.57	25.91	145.62	107.56	111.61	80.00	11.99	29.83	27.17	31.22	85.11	87.73	94.72	56.11	50.07	33.05
Chondrite normalised																					
Ce*	26.00	20.83	17.01	17.17	28.70	87.10	12.56	13.41	7.57	7.33	5.66	6.15	14.02	14.06	14.83	40.95	44.08	46.90	29.26	22.92	17.47
Ce/Ce*	1.07	0.95	0.95	1.12	1.05	1.07	1.02	1.05	1.09	1.09	1.06	0.91	1.06	0.78	1.09	1.20	1.04	1.07	1.01	1.37	1.07
Eu*	7.66	5.79	6.01	5.29	8.70	24.97	5.05	40.38	32.83	32.58	22.75	1.97	5.30	5.39	5.20	11.22	12.77	13.87	7.25	5.82	3.23
Eu/Eu*	0.64	0.78	0.63	0.66	0.65	0.63	0.70	0.64	0.69	0.66	0.66	1.17	1.75	1.03	1.18	0.59	0.65	0.65	0.66	0.64	0.76
La/Yb	9.46	12.93	6.27	9.46	9.30	8.71	8.88	6.04	9.47	9.40	8.19	5.65	6.31	6.06	6.60	8.72	6.77	8.24	7.47	7.67	5.96
Shale normalised																					
Ce*	0.24	0.19	0.16	0.16	0.27	0.81	0.12	0.62	0.54	0.53	0.37	0.06	0.13	0.13	0.14	0.38	0.41	0.44	0.27	0.21	0.16
Ce/Ce*	1.14	1.00	1.00	1.18	1.10	1.12	1.05	1.21	0.99	1.11	1.17	0.96	1.11	0.81	1.14	1.26	1.08	1.11	1.06	1.45	1.18
Eu*	0.24	0.18	0.19	0.16	0.27	0.79	0.16	0.80	0.53	0.51	0.38	0.06	0.17	0.17	0.17	0.35	0.40	0.43	0.23	0.19	0.10
Eu/Eu*	0.92	1.12	0.91	1.00	0.95	0.91	1.01	0.90	0.98	0.96	0.95	1.68	2.52	1.47	1.68	0.86	0.94	0.95	0.96	0.91	1.08
La/Yb	1.21	1.65	0.80	1.21	1.19	1.11	1.13	0.77	1.21	1.20	1.05	0.72	0.81	0.77	0.84	1.11	0.86	1.05	0.95	0.98	0.76

Detailed geographical, stratigraphical and petrological information on the samples is given in Owen & Armstrong (1997). Note that sample AWO4, a clast from a monomict chert conglomerate in the Kirkcolm Fm in tectonic slice 3 is included for completeness. Suffice it to note here that its REE signature is identical to that of the bedded cherts from the same formation.

hundred kilometres of lateral displacement may have taken place (see Owen & Clarkson 1992; Armstrong *et al.* 1996; Scrutton *et al.* 1998).

The Southern Uplands was interpreted as an accretionary prism by McKerrow *et al.* (1977; see also Leggett 1987) and although this has become the generally accepted interpretation, alternative models have been proposed. Murphy & Hutton (1986) argued that only the Northern Belt of the area represents an accretionary prism, the remainder being a post-collision successor basin. Morris (1987) favoured a back-arc basin origin for the Northern Belt and a fore-arc setting for the Central and Southern belts. Stone *et al.* (1987) also proposed a back-arc setting for the Southern Uplands but Kelley & Bluck (1989, 1990) subsequently obtained mean cooling ages of 560 ± 50 Ma and 530 ± 10 Ma for clasts of andesitic and rhyolitic material respectively in very much younger Caradoc greywackes rich in arc derived material, indicating that an old rather than a contemporaneous arc periodically supplied sediment to the Northern Belt. Most recently, Armstrong *et al.* (1996) argued that the sedimentary history of the Northern Belt is closely linked to that of the Midland Valley to the north of the supposed terrane boundary with deposition taking place in a basin floored by continental crust and subsequently imbricated as part of a major transpressive flower structure, rooted along the Southern Upland Fault.

Fundamental to the Armstrong *et al.* (1996) model for the Southern Uplands is that none of the post-Arenig rocks originated in or oceanward of a subduction trench. This is in marked contrast to the accretionary prism model in which the cherts and shales beneath the Caradoc and younger greywacke units are assumed to have accumulated in an open ocean setting prior to their arrival at the trench (e.g. Bevins *et al.* 1992). Arenig volcanic and sedimentary rocks in the Leadhills Imbricate Zone, one of the major strike-parallel faults in the Southern Uplands, are enigmatic and their origins will be addressed by the present authors elsewhere.

The Ordovician lithostratigraphy of the Southern Uplands was revised by Floyd (1996*a*). Bedded cherts and cherty mudstones are a minor but widespread component of the Ordovician successions in the Northern Belt, principally occurring at two stratigraphical levels: the middle Arenig and lower Caradoc (Fig. 2). Associated conodont and graptolite faunas provide good biostratigraphical constraints on the cherts at several localities (e.g. Armstrong *et al.* 1990, 1996, in press; Armstrong & Dean 1996; Floyd 1996*a*). Abundant radiolaria have long been known from cherts in the Southern Uplands (e.g. Hinde 1890; Peach & Horne 1899; Smith 1907) and are present in most of the samples analysed herein. A recent pilot study by T. Danelian of Edinburgh University has demonstrated that they can be extracted from the rock, and thus amenable to modern analysis (pers. comm. 1996). This holds the prospect of further refinement of the stratigraphy, but a detailed Ordovician radiolarian biozonal scheme does not yet exist.

Analytical techniques

A British Geological Survey Technical Report (Owen & Armstrong 1997) includes a stratigraphical and geographical listing of all the samples used in this study as well as a commentary on each of the chert and cherty mudstone samples made prior to preparation for geochemical analysis. Several samples were deemed unsuitable for chemical analysis because of excessive weathering, fracturing or veining. All the remainder were analysed by XRD as a semiquantitative 'purity check'. Most of the cherts subsequently analysed by inductively coupled plasma–mass spectrometry (ICP-MS) contained at least 90% quartz (commonly much more than this); the remaining components mostly being clays and/or haematite with rarer feldspar. The colour of the chert seems to have no effect on the REE profile. As a further check, 18 samples were analysed for major and trace elements using XRF with the resultant Nb:Zr ratios of 1:1 suggesting no remobilisation of REE from heavy minerals (Owen & Armstrong 1997, appendix 9). All of the remaining rock samples and powders will be housed in the collections of the British Geological Survey.

Samples for REE analysis were dissolved in hot Aristar hydrofluoric and nitric acids. Most of those which did not fully enter into solution were excluded but a few were analysed for the reasons given in the relevant discussions below and indicated as such by a 'plus' sign after the sample number in the analysis data and plots. None are crucial to the conclusions of this paper but all support the results from the fully dissolved samples. At least some of the undissolved material is probably kerogen and thus not part of the mineralogy of the samples. The ICP-MS analysis was undertaken on the Perkin Elmer Sciex Elan 6000 machine in the Department of Geological Sciences at Durham University, calibrated using matrix matched standards to minimise matrix effects and internal Rh and Re standards were added to the samples prior to dilution. The limit of detection is $3 \times \sigma$ of the blanks and ranges from 0.7 to 7.3 ppb. The limit of quantification is $10 \times \sigma$ of the blanks and ranges from 1.8 to 13.8 ppb as shown by replicate analysis of the USGS reference rock standards SCo-1, W2, BCR1, BHVO1, RGM1 and x108 an internal laboratory quality control standard. The error bars fall within the symbols when plotted on the normalized distribution diagrams. A set of samples analysed as part of a pilot study using the ICP-MS facility at the Scottish Universities Research and Reactor Centre at East Kilbride was re-analysed as the first batch of samples at Durham as a (successful) test of the reproducibility of the technique on the Southern Upland cherts. The REE analyses were normalized against both a mean shale (following Murray *et al.* 1990, pp. 269–270) and CI carbonaceous chondrite (following Boynton 1984) to maximize the comparisons with published data on cherts and marine mudrocks respectively.

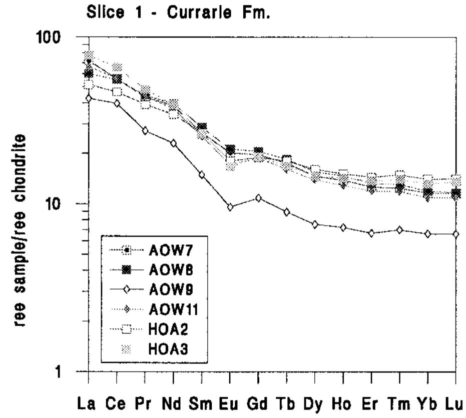
All analysed samples contain microveins of quartz and/or calcite and the inclusion of some of this material was inevitable in virtually all of the powders for REE analysis. The consistency of REE profiles within tectonic blocks and the distinct fingerprints of groups of cherts suggests that any REE input from these veins is either negligible or is an all pervasive background through which the original sediment REE profiles can still be recognized. A similar conclusion was reached by R. W. Murray (pers. comm. 1998) for the samples from the Franciscan Complex in California (Murray *et al.* 1990).

REE patterns of Southern Upland upper Ordovician bedded cherts

The REE data and normalized anomalies and ratios are given on Table 1. Two distinct REE patterns can be recognized, one broadly subdivisible into two. The patterns can be related to the stratigraphical and tectonic divisions within the Southern Uplands (Figs 1, 2).

Pattern 1

This is shown by all of the bedded cherts and cherty mudstones from tectonic slices 1–4, part of slice 5 and slice 6 (Figs 3–5). They have essentially flat shale-normalized patterns and chondrite normalized patterns which show LREE enrichment and a negative Eu_{anom}. Some differentiation may be possible within tectonic slice 1 where the Eu_{anom} is smaller in some of the samples from the Currarie Complex (0.74–0.87) (Pattern 1a) than in most of the remainder from that slice (0.63–0.75) and many of those from the other slices (0.59–0.79) (Pattern 1b, see Fig. 7). Considering the Pattern 1 samples slice-by-slice.



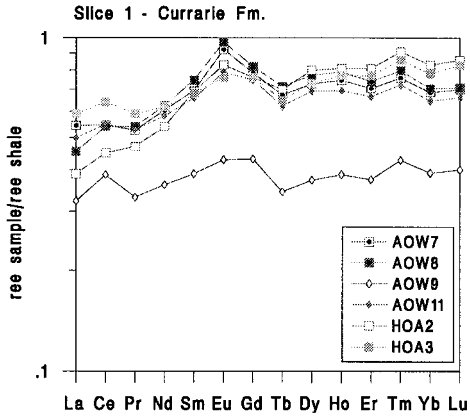


Fig. 3. Chondrite- and shale-normalized Pattern 1a REE compositions of cherts and siliceous mudstones from the Currarie Formation (see Armstrong *et al.* in press for stratigraphy) around Knockgowan Cliff (AOW 7-8, HOA 2-3), Portandea (AOW9) and Big Park Farm (AOW11); tectonic slice 1, between the Stinchar Valley and Glen App faults.

Slice 1: between the Stinchar Valley and Glen App faults (Figs 3, 4a). Samples of bedded cherts from the Currarie Formation along the coast and from the overlying Dalreoch Formation inland at Darley, near Barr have REE compositions which are assigned to patterns 1a and 1b.

Most of the Currarie Formation samples are of red siliceous mudstone with scattered radiolaria and show chondrite-normalized profiles with a fairly small Eu_{anom} (0.74–0.87) and hence Eu peaks on the shale-normalized plots (Fig. 3). The La/Sm ratios of 2.1–2.85 indicate fairly low LREE enrichment. This is REE Pattern 1a (see above).

The red siliceous mudstones with scattered radiolaria from the Dalreoch Formation show shale-normalized plots which are essentially flat and chondrite-normalized LREE enrichment (La/Sm=2.85–3.0) and a distinct negative Eu_{anom} (0.70–0.75) (Fig. 4a. This is REE Pattern 1b and is also shown by one of the samples of red chert (HOA5) from the Currarie Formation at Portandea.

Slice 2: between the Southern Upland and Carcow faults (Fig. 4b). Samples of red radiolarian chert and siliceous mudstones with scattered radiolaria from the Marchburn Formation show a type 1b REE signature with a shale-normalized Ce_{anom} of 1.0–1.08 and a chondrite–normalized Eu_{anom} of 0.65–0.72.

Slice 3: between the Carcow and Glaik faults (Fig. 4c). The stratigraphy of the area reflects the complex interplay between members of the Kirkcolm Formation and the Bail Hill Volcanic Group (Hepworth *et al.* 1982; Floyd 1996*a*) (Figs 1, 2). The chert samples are from the Kirkcolm Formation including one from what has been interpreted as an olistolith of chert (AWO16) (see Floyd 1996*b*) from the Spothfore Member. All of the cherts, irrespective of colour or possible allochthonous position, show REE Pattern 1b. The shale- and chondrite-normalized Ce_{anom} are 1.10–1.21 and 1.01–1.15 respectively and the chondrite–normalized Eu_{anom} range from 0.62 to 0.76.

Slice 4: between the Glaik Fault and the Leadhills Imbricate Zone (Fig. 5a). Cherts and cherty mudstones in this tectonic slice come from at least two stratigraphical settings.

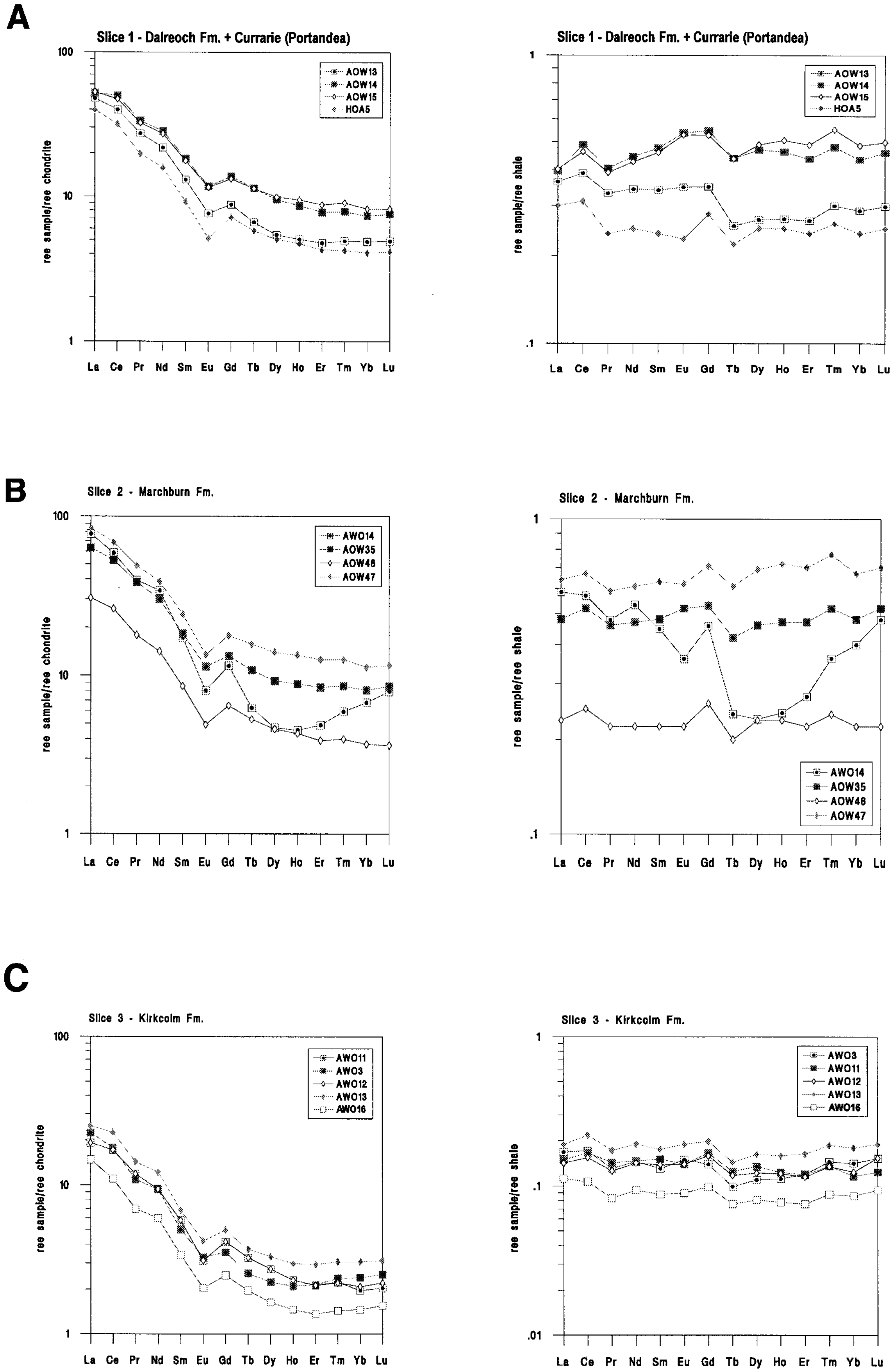
(i) From within the greywackes of the Kirkcolm Formation, from Mitchelhill and the headwaters of the Snar Water, probably below the level of the middle Caradoc fossiliferous conglomerate (Clarkson *et al.* 1992; Owen & Clarkson 1992).

(ii) From red siliceous mudstones above volcanic rocks, including pillow lavas in the Hawkwood Burn and at Goseland Farm, near Kilbucho. The siliceous mudstones yield *P. anserinus* Biozone conodonts and those in the Hawkwood Burn section were designated by Floyd (1996*a*, p. 158) as a reference section for the Kirkton Formation which, together with the Raven Gill Formation (Fig. 2), has its type development along the Leadhills Imbricate Zone (see Leggett *et al.* 1979; Hepworth *et al.* 1982; Leggett & Casey 1982 for discussion of structure). A second reference section was also designated in Normangill Burn which may lie within that tectonic zone and a sample of grey chert (AOW37) was analysed from bedded cherts with thin shale interbeds here. These beds pass northwards into grey cherts and black shales yielding diplograptids which may mark the Moffat Shale Group assumed to be above the Kirkton Formation (Floyd 1996*a*, p. 158) or simply shaly intercalations within the cherts. The REE geochemistry of cherts undoubtedly from the Leadhills Imbricate Zone and associated with mid-Arenig conodont faunas (Armstrong & Dean 1996) are being assessed as part of a wider study by the present authors.

Despite their different stratigraphical settings, the lower Caradoc cherts between the Glaik Fault and Leadhills Imbricate Zone, and the sample from Normangill Burn all have type 1b REE patterns. The shale- and chondrite-normalized Ce_{anom} are 1.00–1.18 and 0.95–1.12 respectively and the chondrite-normalized Eu_{anom} range from 0.63 to 0.79.

Slice 5: between the Leadhills Imbricate Zone and the Orlock Bridge Fault (Fig. 5b). Samples from below the Moffat Shale Group below the Portpatrick Formation along the Fardingmullach Line in Chanlock Burn, including one which did not fully enter into solution, show type 1b REE patterns. Importantly, this contrasts with other samples from this tectonic slice which have Pattern 2 signatures (see below).

Slice 6: south of the Orlock Bridge Fault (Fig. 5c). The Ordovician succession in the Central Belt is composed largely of shales of the Moffat Shale Group. Samples of chert and, for comparative purposes, shale from two localities were analysed: (i) The '*peltifer*' to *linearis* biozones in the Glenkiln and Lower


A
Slice 1 - Dalreoch Fm. + Currarie (Portandea)
AOW13
AOW14
AOW15
HOA5
ree sample/ree chondrite
ree sample/ree shale
La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
B
Slice 2 - Marchburn Fm.
AWO14
AOW35
AOW46
AOW47
ree sample/ree chondrite
ree sample/ree shale
La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
C
Slice 3 - Kirkcolm Fm.
AWO11
AWO3
AWO12
AWO13
AWO16
ree sample/ree chondrite
ree sample/ree shale
La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

Hartfell Shale formations at Hartfell Score and (ii) the probable *gracilis* Zone at Berrybush Burn (see Floyd 1996*a*; Finney & Bergström 1986).

All of the samples have type 1b REE patterns, even the shales which did not fully enter into solution but are included here to provide a fuller suite of REE than the Moffat Shale Group samples analysed by Merriman & Roberts (1990) and Wilde *et al.* (1996). The only slightly unusual profile is that of AOW27, a very pure chert with exquisitely preserved radiolaria from Berrybush Burn which has a markedly concave shale-normalized profile. This is also reflected in the chondrite-normalized La/Sm and Gd/Yb ratios which are unusually high (7.02) and low (0.71) respectively.

Pattern 2

This is typified by a positive chondrite-normalized Eu_{anom} (1.03–1.75) and is shown by four of the samples from slice 5 (Fig. 6). Two of these did not fully enter into solution and are therefore inherently suspect. The concordance between the REE patters of the Moffat Group shales from the Central Belt which did not fully enter into solution and the cherts from there which did, provide some justification for at least presenting all four samples ascribed to Pattern 2. They comprise: (i) a black, radiolarian rich, cherty shale (AOW31) from shales with cherty ribs and wackes of the Moffat Shale Group and basal Portpatrick Formation along the Fardingmullach line on western slopes of Bowbeat Rig north of Peebles (Hughes & Boland 1995, p. 8) and (ii) green, black and grey radiolarian cherts (AOW32-34) between the Fardingmullach Line and the Orlock Bridge Fault in Bowbeat Burn from a succession of shales, cherts and chert breccias ascribed to the Shinnel Formation of probable Ashgill age (Floyd 1996*a*; Floyd & Rushton 1993) by Hughes & Boland (1995, pp. 9–10).

The positive Eu_{anom} suggests an input of undifferentiated material, in particular, calcic-plagioclase. This would be commensurate with the abundance of andesitic material in the greywackes of the Portpatrick Formation but is surprising for the Shinnel Formation which has a dominantly more mature provenance (Floyd 1982; Floyd & Trench 1989). Either the Bowbeat Burn samples have been ascribed to the wrong stratigraphical unit or, at times of low siliciclastic sediment input, the 'background' detrital mud component was being sourced from an andesitic hinterland. One of the Bowbeat Burn samples (AOW33) which did not enter fully into solution has a larger negative Ce_{anom} (0.81 shale-normalized) than is seen in other Southern Upland samples but it is not of the same order of magnitude as that of cherts which accumulated in open ocean settings. The Bowbeat Rig sample which did not fully enter into solution (AOW31) has a lower overall REE content but an elemental distribution pattern similar to that of AOW32 and AOW34.

Europium and cerium anomalies

In addition to the diagrams showing the overall REE patterns, a plot of chondrite-normalized Eu_{anom} against Ce_{anom} (Fig. 7) provides the clearest discrimination of the Pattern 2 cherts, with their positive Eu_{anom} from Pattern 1b. The Currarie Formation samples showing Pattern 1a have only a slight overlap with the upper part of the cluster of Pattern 1b samples.

Total REE abundances

The absolute abundance of REE in cherts is at least partly a reflection of dilution by quartz which has only a very low REE content (Murray 1994; Girty *et al.* 1996) and partly a result of deposition rate, i.e. exposure time to seawater. Despite this, the total REE data for the Southern Upland cherts are presented here (Table 1, Fig. 8) and allow limited further clarification of the patterns recognised above namely: (i) The Pattern 2 samples (AOW31-34) show some of the lowest values in the whole data set (11.99–31.22 ppm) and are considerably less than those of the Pattern 1b samples from the Fardingmullach line (prefixed HFB–80.00–145.62 ppm) in the same tectonic slice as used herein. (ii) The Pattern 1a and 1b samples in Slice 1 have relatively high (75.65–131.28 ppm) and low (58.10–93.80 ppm) REE abundances respectively with very little overlap between the two. However, Pattern 1b samples from outside Slice 1 have total REE abundances comparable to those of Pattern 1a. (iii) The Kirkcolm Fm, values and most of those from the supposed Kirkton Fm in slices 3 and 4 are identical (34.95–56.54 ppm) and very low although one sample (AOW30) from the cherts associated with volcanic rocks in slice 4 has the highest REE content of all (171.57 ppm).

Interpretation of chert REE data

The normalized REE diagrams for all of the Southern Upland Caradoc and Ashgill radiolarian cherts and cherty mudstones are comparable to those of Mesozoic and Cenozoic deposits from continental margin settings (Murray 1994; Murray *et al.* 1990, 1991, 1992). They have essentially flat shale-normalized REE distributions, lacking the distinct negative Ce anomalies characteristic of open ocean and mid-ocean ridge environments. The shale-normalized Ce anomalies are close to 1, and 33 of 38 La/Yb values are between 0.7 and 1.3 (total range 0.47–1.65, mean 1.15). This is typical of continental margin settings, such as those of the present Atlantic, in which the REE patterns reflect a significant contribution from the terrigenous input but also some adsorption from seawater (see Murray *et al.* 1992).

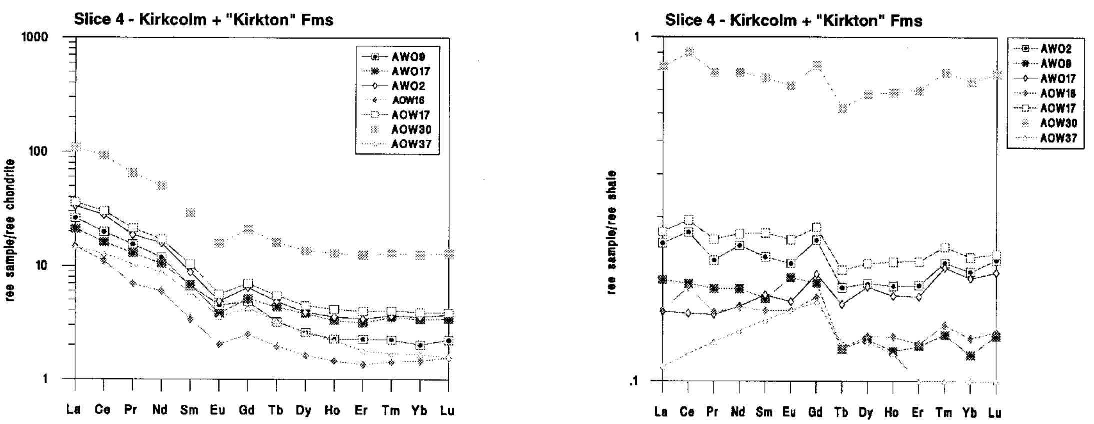
The chondrite-normalized diagrams show LREE enrichment and, in most instances, a negative Eu_{anom}. The small negative Eu_{anom} in Pattern 1b and positive Eu_{anom} of Pattern 2 is consistent with an immature andesitic source periodically supplying sediment to the basin.

Comparison with greywacke REE patterns in the Southern Uplands

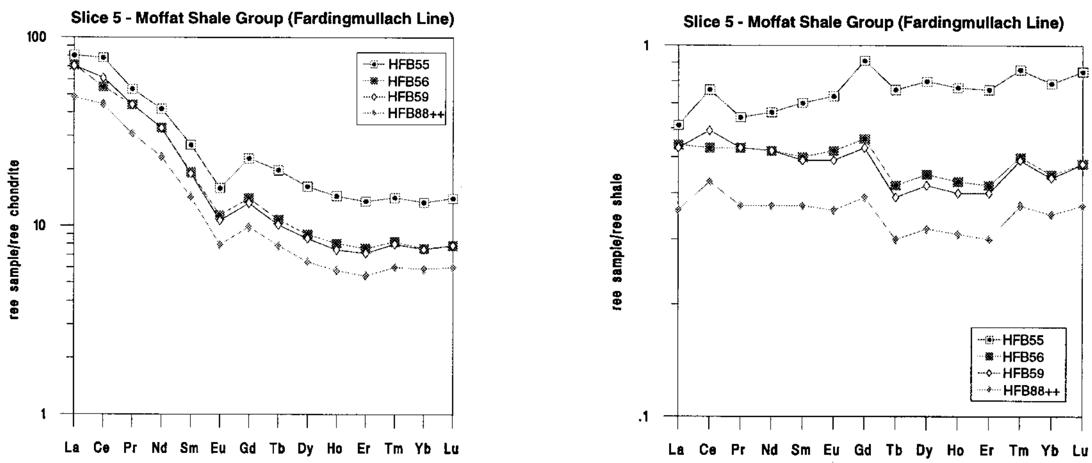
Variation in REE geochemistry has been successfully used to characterize and delimit provenance in modern turbidites

Fig. 4. Chondrite- and shale-normalized Pattern 1b REE compositions of cherts and siliceous mudstones from: (**a**) the Currarie Formation (see Armstrong *et al.* in press) at Portandea (HOA5) and the Dalreoch Formation (see Ince 1984; Floyd 1996*a*) near Darley (AOW 13-15); tectonic slice 1, between the Stinchar Valley and Glen App faults. (**b**) the Marchburn Formation at March Burn (AWO14) (see Floyd 1982), Coulter Craigs (AOW35) and the Afton Water (AOW46,47) (see Floyd 1996*b*); tectonic slice 2, between the Southern Upland and Carcow faults. (**c**) the Kirkcolm Formation around Bail Hill (see Floyd 1996*a*); tectonic slice 3, between the Carcow and Glaik faults.

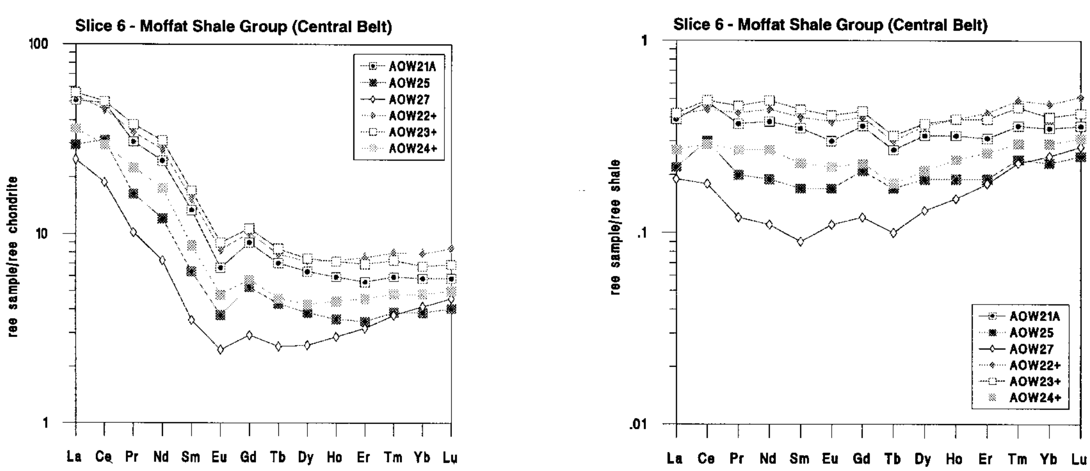
A


Slice 4 - Kirkcolm + "Kirkton" Fms
ree sample/ree chondrite
AWO9
AWO17
AWO2
AOW16
AOW17
AOW30
AOW37
La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Slice 4 - Kirkcolm + "Kirkton" Fms
ree sample/ree shale
AWO2
AWO9
AWO17
AOW16
AOW17
AOW30
AOW37
La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

B


Slice 5 - Moffat Shale Group (Fardingmullach Line)
ree sample/ree chondrite
HFB55
HFB56
HFB59
HFB88++
La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Slice 5 - Moffat Shale Group (Fardingmullach Line)
ree sample/ree shale
HFB55
HFB56
HFB59
HFB88++
La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

C


Slice 6 - Moffat Shale Group (Central Belt)
ree sample/ree chondrite
AOW21A
AOW25
AOW27
AOW22+
AOW23+
AOW24+
La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Slice 6 - Moffat Shale Group (Central Belt)
ree sample/ree shale
AOW21A
AOW25
AOW27
AOW22+
AOW23+
AOW24+
La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

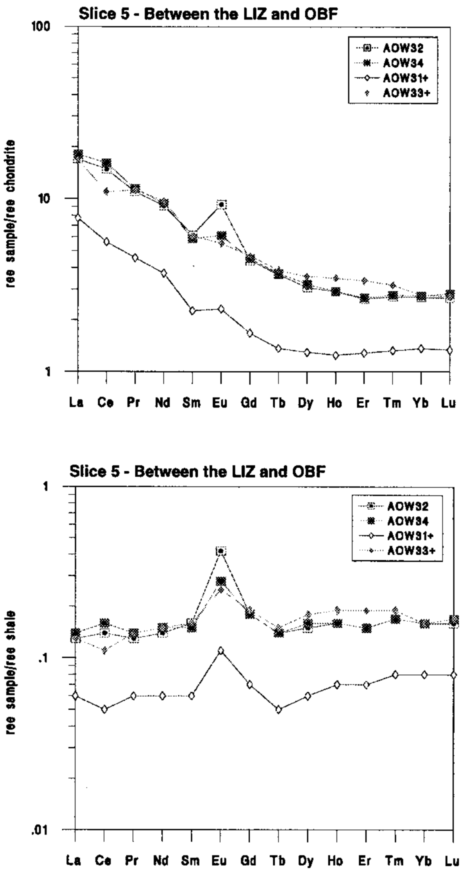


Fig. 6. Chondrite- and shale-normalized Pattern 2 REE compositions of cherts and siliceous mudstones from the Moffat Shale Group/basal Portpatrick Formation along the Fardingmullach Line west of Bowbeat Rig (AOW31) and strata ascribed to the Shinnel Formation in Bowbeat Burn (AOW32-34); tectonic slice 5 between the Leadhills Imbricate Zone and Orlock Bridge Fault.

(McLennan *et al.* 1990). This approach was followed by Duller & Floyd (1995) as part of an extensive analysis of greywacke geochemistry in the Southern Uplands and by Williams *et al.* (1996) in a more restricted study of the REE composition of greywackes in selected turbidite formations from the Southern Uplands and Lake District. Both studies highlighted the contrasting REE patterns of the mature continentally derived material and the juvenile volcanogenic source which provided sediment to the Southern Uplands at various times.

The only Ordovician greywackes analysed by Williams *et al.* (1996) were from the Kirkcolm and Portpatrick formations. The differing provenance characteristics of these units are well known from petrographical studies (e.g. Floyd 1982; Stone *et al.* 1987) and the principal geochemical characteristics of the stratigraphical units of the Southern Uplands are known from the Geochemical Survey Programme of the BGS (see Stone *et al.* 1993; BGS 1993). Both lines of evidence show

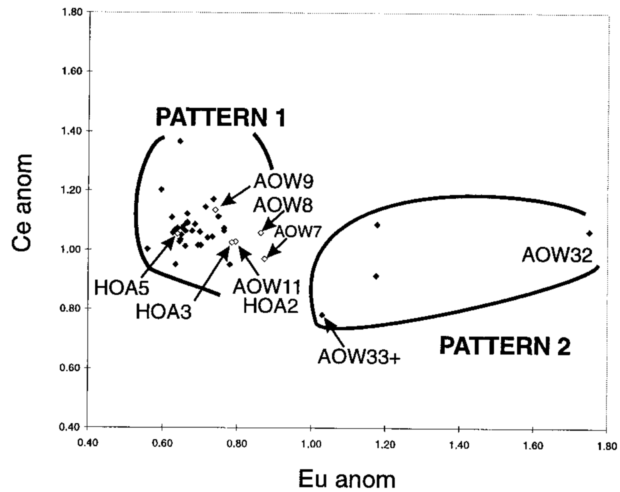


Fig. 7. REE discriminant plot of chondrite-normalized Ce_{anom} against Eu_{anom} for upper Ordovician cherts, siliceous mudstones and shales from the Southern Uplands. Open diamonds represent samples from the Currarie Formation. Most of these comprise Pattern 1a but one (HOA5) is assigned to Pattern 1b.

provenance variations consistent with the simultaneous fluxes of mature continental and arc detritus (signified by low Rb/Sr and intermittently high Ni, Mg, Fe and Cr) into the basin. The Kirkcolm Formation, the greywacke formation in slices 3 and 4, contains quartzose greywackes which show more uniform LREE and a distinct negative chondrite-normalized Eu_{anom}. The more pyroxenous Portpatrick Formation greywackes (slice 5) have relatively flat mid-REE profiles and only a very slight Eu_{anom} depletion (Williams *et al.* 1996). Williams *et al.* argued that the juvenile volcanogenic component supported the model of Ordovician deposition in a back-arc basin (Stone *et al.* 1987). They also showed that samples from the progressively younger and more southerly turbidites showed a trend to more evolved ‘granitic’ REE patterns.

The chondrite-normalized diagrams of both Duller & Floyd (1995) and Williams *et al.* (1996) together with the discriminant plots of the latter authors show close parallels to the chert REE analyses detailed herein. The Kirkcolm Formation samples have LREE enrichment, more uniform LREE and distinct negative Eu_{anom}. These are typical of sediments sourced by mature continental material and are essentially those of Pattern 1 in the Southern Upland chert samples (which includes cherts from the Kirkcolm Formation). The shales from the Moffat Group in the Central Belt analysed herein (AOW22-24, Fig. 5c) also show this pattern. Portpatrick Formation samples in comparison have relatively flat patterns and very slight Eu_{anom}. Pattern 2 amongst the Southern Upland cherts extends this to the more extreme condition in which there is a significant positive Eu_{anom}. This group includes at least one sample from the basal part of the Portpatrick Formation. Shale-normalized plots of the data presented by Williams *et al.* show the Kirkcolm Formation to

Fig. 5. Chondrite- and shale-normalized Pattern 1b REE compositions of: (**a**) cherts and siliceous mudstones from the Kirkcolm Formation and Caradoc strata previously ascribed to the Kirkton Formation from Mitchelhill (AWO2, AOW16,17), Goseland farmtrack (AOW30), Snar Water (AWO9), Normangill Burn (AOW37) and Hawkwood Burn (AWO17); tectonic slice 4, between the Glaik Fault and Leadhills Imbricate Zone (see Armstrong et al. 1990; Clarkson *et al.* 1993); (**b**) cherts and cherty mudstones from along the Fardingmullach Line in Chanlock Burn; tectonic slice 5 between the Leadhills Imbricate Zone and Orlock Bridge Fault; (**c**) chert from the Glenkiln Formation (AOW21) and shales (AOW22-24) from the Hartfell Shale Formation (Moffat Shale Group) at Hartfell Score (see Zalasiewicz *et al.* 1995) and cherts from the Glenkiln Formation at Berrybush Burn (AOW25, 27) (see Floyd 1996*a*); tectonic slice 6, south of the Orlock Bridge Fault.

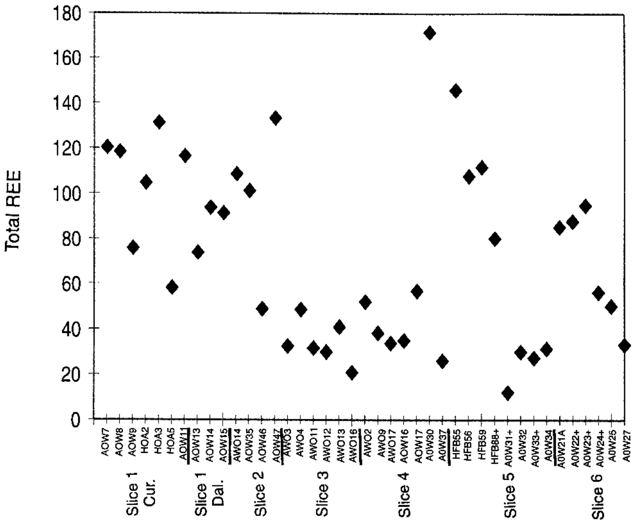


Fig. 8. Absolute abundance (in ppm) of REE in cherts, cherty mudstones and shales of the Southern Uplands. Samples are arranged tectonostratigraphically, in the same order as on Table 1. Note that sample HOA5 shows REE pattern 1b whereas the remaining samples from the Currarie Formation are assigned to Pattern 1a.

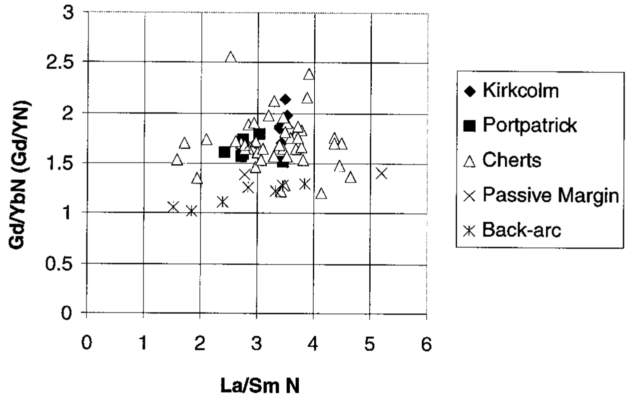


Fig. 9. REE discriminant plot of chondrite-normalized ratios of Gd/Yb (or Gd/Y for greywacke data taken from Williams *et al.* 1996) against La/Sm for the upper Ordovician cherts cherty mudstones and shales described herein, greywackes from the Kirkcolm and Portpatrick formations and mudrocks from known back-arc and passive settings (from McLennan *et al.* 1990). Note that this plot provides no distinction between the Southern Upland chert and shale samples analysed in this study: the Pattern 2 samples have Gd/Yb and La/Sm ratios of 1.23–1.68 and 2.76–3.42 respectively. Most significantly all but two of the Southern Upland samples plot as a separate cluster, away from the back-arc field. The two Southern Upland samples which plot on the margins of the back-arc field are AOW 31 the Pattern 2 cherty shale from near the base of the Portpatrick Formation and AOW22 one of the black shales from the lower Hartfell Shale Formation.

have very flat patterns emphasizing the close similarity to post-Archaean mean shale. Portpatrick Formation greywacke samples on the other hand consistently show peaks for Eu and Tm.

The Eu_{anom} against La/Sm discrimination plot of Williams *et al.* (1996, Fig. 4) resolves the Kirkcolm and Portpatrick formations into two clearly defined fields with little overlap in exactly the same way that the Eu_{anom} separates the chert data into fields representing Pattern 1 and Pattern 2 (Fig. 7). Both the chert Pattern 2 and the plot of the Portpatrick Formation greywackes are distinguished by high Eu_{anom} values which is compatible with a high andesitic/feldspar detrital component.

Williams *et al.* (1996, Fig. 5) used Y as a surrogate for Yb and plotted chondrite-normalized Gd/Y against La/Sm to contrast the REE compositions of their Southern Upland and Lake District greywacke formations with those of known tectonic settings described by McLennan *et al.* (1990). Williams *et al.* noted that Taylor & McLennan (1985) had identified systematic differences between the HREE patterns of Archaean and modern turbidites, thought to reflect crustal evolution. However, McLennan (1989) subsequently considered that there may be no significant change in well mixed sedimentary REE patterns through time and that any such differences may be the result of biased sampling or preservation. The greywacke formation data of Williams *et al.* (1996) are plotted herein (Fig. 9) together with Gd/Yb and La/Sm ratios from the Southern Upland cherts and data from back-arc and continental margin settings given by McLennan *et al.* (1990). The Kirkcolm and Portpatrick Formation samples together with virtually all of the cherts plot with the albeit limited data from known passive margins in a separate field from the back-arc data. Contrary to the overall conclusions of Williams *et al.* (1996) there is no evidence from this REE discrimination plot for a back-arc environment in the Southern Upland material. The close similarity of the chert REE data to those of the greywacke units suggests that the cherts are the hemipelagic components of extremely distal greywacke deposits.

Conclusions

The following REE patterns can be recognized in the upper Ordovician cherts and cherty mudstones in the Southern Uplands.

Pattern 1. Shows an essentially flat shale-normalized REE profile and chondrite normalized profiles which show LREE enrichment and a negative Eu_{anom}. Some samples, notably from the Lower Caradoc Currarie Formation, have a smaller Eu_{anom} (0.74–0.87) (Pattern 1a) whereas a larger negative Eu_{anom} (0.59–0.79) is typical of Pattern 1b and is shown by: red and grey cherts and cherty mudstones of the Lower Caradoc Dalreoch, Marchburn and Kirkcolm formations, red chert of the Currarie Formation at Portandea, red mudstones associated with volcanic rocks to the north of the Leadhills Imbricate Zone (Lower Caradoc), grey cherts of uncertain age along the Fardingmullach Line and dark grey Caradoc cherts south of the Orlock Bridge Fault.

Pattern 2. Shows a positive chondrite-normalized Eu_{anom} (1.03–1.75) and is shown by black cherty shale of the basal transition to the Upper Caradoc Portpatrick Formation and grey, green and black cherts thought to belong to the Shinnel Formation of probable Ashgill age.

This is the first detailed analysis solely of REE patterns in Lower Palaeozoic cherts. Despite their age, prehnite–pumpellyite metamorphism and structural complexity, upper Ordovician radiolarian cherts and siliceous mudstones from the Southern Uplands preserve primary REE signatures which: (i) are comparable to those of more recent cherts and mudrocks from known tectonic settings; (ii) can be used as fingerprints to differentiate between some of the tectonic slices/formations within the area; (iii) indicate the provenance of the mud grade siliciclastic material in these distal hemipelagites; (iv) are comparable with published REE data on greywackes from some of the associated turbidite formations.

The REE data indicate that all of the upper Ordovician cherts accumulated at, or close to, a continental margin with none showing the pronounced negative Ce_{anom} present in shale-normalized cherts from open ocean and mid-ocean ridge environments. Most of the samples have REE compositions (Pattern 1b) which indicate that their detrital components were sourced from a mature continental block. The virtual absence of a negative Eu_{anom} in samples from the Currarie Formation (Pattern 1a) represents an intermediate condition to that of Pattern 2 in which there is Eu enrichment, indicating an andesitic component in the sediment source area. This is also reflected in the petrography and the geochemistry of mudstones in some of the associated greywackes, although the nature of this source block remains enigmatic.

The REE data lend further support to the Armstrong *et al.* (1996) model of deposition at an extending continental margin and are contrary to the formation of the cherts within the open ocean envisaged in the widely accepted accretionary prism hypothesis.

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