Chemostratigraphy, K-Ar ages and illitization of Silurian K-bentonites from the Central Belt of the Southern Uplands–Down–Longford terrane, British Isles

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Abstract: The Central Belt of the Southern Uplands Terrane, in both Scotland and Ireland, is a faulted and imbricated sequence of Caradoc to Llandovery shales and Llandovery turbidites with numerous interbedded K-bentonites. The bentonites are composed dominantly of R3-ordered mixed-layer illite/smectite (I/S) containing 90–95% illite, and represent the product of illitization during low-grade metamorphism. K-Ar age determination on the <0.5 µm size fraction gave a range from 379 ± 10 to 406 ± 10 Ma. The fixed K is thought to have originated in the precursor ash, and was remobilized during the transformation of smectite to I/S. K-Ar ages record a retrograde thermal event that post-dates Wenlock prehnite–pumpellyite facies metamorphism and is contemporaneous with cooling and uplift during the end-Silurian–early Devonian collision of Laurentia with the East Avalonian terrane. Differences in Rb and other trace elements between the K-bentonite beds are due, in part, to differences in original ash composition, and can be used to group the beds within biostratigraphically-defined boundaries. The chemical identification of groups of K-bentonite beds offers additional criteria for their stratigraphical correlation on a regional scale.

The Lower Palaeozoic rocks of the Southern Uplands of Scotland continue WSW across the North Irish Sea into Ireland through County Down to Counties Cavan and Longford (Bryce 1852; Anderson & Cameron 1979), and in so doing compose a major fault-bounded terrane on the northern margin of the paratectonic Caledonides (Hutton 1989). Peach & Horne (1899) divided the Southern Uplands into Northern, Central, and Southern Belts consisting, respectively, of Ordovician, mainly Llandovery, and Wenlock strata. The division remains generally operative in Scotland and can be readily applied in Ireland. The rocks of the terrane have a highly distinctive lithological and structural style (e.g. Anderson & Cameron 1979; Leggett & Casey 1982). The widely accepted interpretation of the entire terrane as an accretionary prism developed above a subduction zone on the northwestern edge of Iapetus (Mitchell & McKerrow 1975; McKerrow et al. 1977) has recently been challenged by publication of an alternative back-arc and foreland basin thrust-duplex model (Stone et al. 1987). In both models the palaeogeographical relationship to a contemporaneous volcanic arc, or arcs, supplying detritus, remains controversial (Murphy & Hutton 1986; McKerrow 1987; Morris 1987; Stone et al. 1987; Kelling et al. 1987).

The Llandoverian Central Belt, in Scotland and in Ireland, consists of a thin (<100 m) formation of black, graptolitic shales (Birkhill Shales), overlain by a thick (>500 m) succession of sandy and silty turbidites (Gala and Hawick Groups) (Barnes et al. 1987). Both black shales and turbidites contain numerous K-bentonite beds, ranging from a few millimetres, up to about 1 m in thickness. These beds represent explosively erupted ash of intermediate to felsic composition and may be related to subduction of the closing

Iapetus Ocean (Batchelor & Weir 1988; Huff et al. 1988; Merriman & Roberts 1990). The timing of that closure is variously estimated between late Ordovician and early Devonian, with recent analysis suggesting a Wenlock collision (Barnes et al. 1989). Conodont and graptolite reflectance measurements together with illite crystallinity values in both the Southern Uplands and Longford-Down areas indicate maximum temperatures of 300 °C to 400 °C, equivalent to prehnite–pumpellyite facies metamorphism (Oliver 1978; Bergström 1980). Interpretation and structure are both complicated by sinistral transpressive movement during and after plate collision (Anderson & Cameron 1979; Leggett 1980; Soper & Hutton 1984; Knipe & Needham 1986).

Stratigraphical correlation between the tectonic slices of Longford–Down and the Southern Uplands is difficult in the absence of recognizable key beds and well-defined biostratigraphical markers. Graptolite zonation provides a medium-resolution stratigraphical framework (Toghill 1968), but zone boundaries are frequently indistinct due to deformation of the shales, and their lateral continuity is difficult to trace.

K-bentonites could serve as ideal time planes, provided that they can be distinguished from one another on a regional scale. Recent studies of Ordovician K-bentonites in the eastern midcontinent of North America have shown that altered vitric ashes retain a sufficient portion of their original chemistry to permit their regional identification and correlation by chemical fingerprinting (Kolata et al. 1986, 1987). In this paper we present evidence that K was remobilized in Llandovery K-bentonites during Silurian metamorphism with the resultant transformation of bentonitic smectite to illite/smectite and that Rb, which also

originated in the ash beds, retained its relative distribution between beds and thus serves along with some immobile trace elements as a reliable chemostratigraphic parameter.

Materials and methods

Samples

Twenty K-bentonite beds were sampled from the Birkhill Shale Formation, Gala and Hawick Groups at six locations in both County Down in Northern Ireland and Dob's Linn in the Southern Uplands (Fig. 1). The beds ranged in age from early to late Llandovery (*A. acuminatus* to *M. crenulata* biozones) and occur in three age groups defined by graptolite zonation, Rhuddanian, Idwian, and Telychian (Fig. 2). Samples were selectively collected from the thicker and more prominent beds, since some sequences, particularly at Dob's Linn, have many closely-spaced K-bentonite beds 1–2 mm in thickness. The petrology and whole-rock mineralogy of the K-bentonites at Dob's Linn has been described by Merriman & Roberts (1990). Biostratigraphical location of the K-bentonites was based on the work of Toghill (1968) and Williams (1983) at Dob's Linn, and Cameron & Anderson (1980) and Anderson (1978) in County Down.

Analytical methods

A portion of each sample was dried overnight at 65 °C, then ground to <400 mesh in an agate mill and analysed for major and trace elements by instrumental neutron activation analysis (INAA) and wavelength dispersive X-ray fluorescence spectroscopy (XRF). Separate, unground portions of each sample were suspended in distilled water after particle separation by ultrasonic disaggregation. The <0.5 μm size fraction was recovered by ultracentrifugation and a portion set aside for K-Ar age determination. The remainder was used to make orientated slides by the smear technique for powder X-ray diffraction (XRD) analysis. After drying and vapour-saturation with ethylene glycol for 48 hours at 50 °C, the slides were analyzed by powder X-ray diffraction using a Siemens D-500 automated powder diffractometer. Slides were scanned at $0.2°2\theta$/minute using CuKα radiation and a graphite monochromator. Powder diffraction patterns of illite/smectite were modeled using the NEWMOD computer program of Reynolds (1985).

Potassium was analysed in duplicate using mixed-acid digestion followed by flame photometry with lithium as the internal standard. The minimum error of ±1% was based on replicate analyses of

standards. Argon was analysed by the isotope dilution technique using an enriched ^{38}Ar spike in a VG-Isotopes MM1200 mass spectrometer and argon extraction line. Analyses of standard glauconite GL-0 yielded 25.08 nl/gm ^{40}Ar and 6.64% K$_2$O, compared to recommended values of 24.8 and 6.59, respectively. The quoted errors are compounded from errors in the spike calibration and the isotope ratio measurements, and incorporate any error enhancement due to correction for atmospheric argon contamination. Constants used in the age calculations are as recommended by Steiger & Jager (1977).

Clay mineralogy

Powder X-ray diffraction data from the <0.5 μm size fraction of Llandovery K-bentonites indicated that all samples consist of regularly mixed-layer, R3-ordered illite/smectite varying between 90% and 95% illite in the I/S (Table 1), and some samples contain minor (5–15%) amounts of chlorite. Chlorite has weak first-order (14 Å) and third-order (4.7 Å) reflections indicating that it is an iron-rich variety (Brindley & Brown 1980). Interpretation of illite/smectite powder diffraction data was made following the methods of Reynolds (1980, 1985), Veblen *et al.* (1990), and Ahn & Buseck (1990). The observed first order reflections between 9.95 Å and 10.07 Å, and second order reflections between 5.1 Å and 5.07 Å are very close to a pure clay mica (illite) at 10 Å and 5 Å, respectively. However, the asymmetry of the first-order reflection on the low-angle side and the elevated background beneath it, together with the slightly shifted position are characteristic of ISII or R3-ordering (Środoń 1984). This is confirmed by computer simulation using the NEWMOD program of Reynolds (1985).

These data agree with the observations of Cameron & Anderson (1980) for Coalpit Bay K-bentonites with respect to the high illite content of the illite/smectite and subsidiary amounts of chlorite, but not with their finding of R0 or random-ordered illite/smectite. Nor do our data support the conclusions of Batchelor & Weir (1988) that the Dob's Linn bentonite clays are randomly mixed-layer illite/smectite with subsidiary free illite. It is possible that some of the disparity in clay mineralogy results from the difference in particle size fractions studied by the various authors (Coarse 1–2 μm) clay fractions are more likely to contain detrital illite and a higher proportion of smectite in I/S than finer (0.1–0.5 μm)
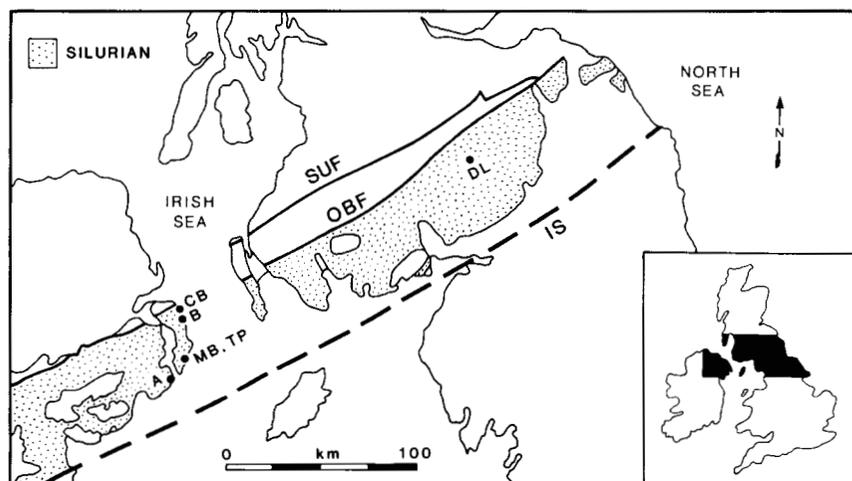

Fig. 1. Geological map of the Southern Uplands and County Down showing the distribution of Silurian rocks (stippled) and Llandovery K-bentonite sample localities. DL, Dob's Linn; CB, Coalpit Bay; B, Ballywhiskin; MB, Millin Bay; TP, Tara Point; A, Ardglass; IS, Iapetus suture; OBF, Orlock Bridge fault; SUF, Southern Uplands fault.

Period	Epoch	Age	Biostratigraphic correlation			K-BENTONITE
Silurian	Llandovery	Telychian	Monoclimacis crenulata		C₆	NI3, NI5
			Monoclimacis griestoniensis		C₅	NI4
			Monograptus crispus		C₄	NI1
		Fronian	Monograptus turriculatus		C₂₋₃	B17-6
			Monograptus sedgwickii		C₁	CB2, CB4
		Idwian	Monograptus convolutus		B₃ B₂	CB5, NI2
			Coronograptus gregarius	argentus magnus triangulatus	B₁	B17-4, B17-5
		Rhuddanian	Coronegraptus cyphus	cyphus acinaces	A₄	CB6, B17, B17-3
			Cystegraptus vesiculosus		A₃	CB7 CB8, B17-0, B17-1, B17-2
			Akidograptus acuminatus		A₂	CB9
			Glyptograptus persculptus		A₁	

Fig. 2. Silurian stratigraphical section for the Southern Uplands and the Longford–Down Massif. K-bentonite samples are listed according to graptolite zone boundaries. Geographic locations are as follows: NI1, *M. crispus* zone, Ballywhiskin, Co. Down, (J614735) (=sample B1 in Cameron & Anderson 1980); NI2, *C. gregarius* zone, Coalpit Bay, Co. Down, (J59487884); NI3, *M. crenulata* zone, Tara Point, Co. Down, (J63674911); NI4, *M. griestoniensis* zone, Millin Bay, Co. Down, (J63214911); N15, *M. crenulata* zone, Ardglass, Co. Down, (J563368); B17-0 to B17-2, *C. vesiculosus* zone, Dob's Linn, Southern Uplands, (NT196158) (ref. Toghill 1968); B17, B17-3, *C. cyphus* zone, Dob's Linn; B17-4, B17-5, *C. gregarius* zone, Dob's Linn; B17-6, *M. convolutus* zone, Dob's Linn; CB2, CB4, CB5, *C. gregarius* zone (*L. argentus*), Coalpit Bay, Co. Down, N.I. (J594788) (ref. Cameron & Anderson 1980); CB6 to CB9, *A. acuminatus* to *C. cyphus* zone, Coalpit Bay.

fractions (Hower *et al.* 1976). Both Cameron & Anderson (1980) and Batchelor & Weir (1988) reported data for the $<2\,\mu m$ size fraction of K-bentonites while our data are for the $<0.5\,\mu m$ fraction. The finer fraction is generally considered to reflect the diagenetic history of the clay more accurately, and is less likely to contain detrital contamination (Hower *et al.* 1976). The transition of illite/smectite to R3 ordering occurs during burial metamorphism at about 150–175 °C, and under equilibrium conditions would go to illite at about 250 °C (Hoffman & Hower 1979; Eslinger & Savin 1973). The fact that R3 I/S survived a rather brief but intense period of low-grade metamorphism at peak temperatures near 400 °C in the Southern Uplands–Down–Longford terrane without converting completely to illite, may indicate there was insufficient time for K equilibration. Under conditions of low-grade metamorphism the slowness

of reaction kinetics often results in geochemical and mineralogical disequilibrium (Hunziker 1986). In addition, evidence from K-Ar age measurements shows the system remained open to Ar diffusion during peak metamorphism.

K-Ar age determination

The $<0.5\,\mu m$ size fraction of nine Llandovery K-bentonite samples from Dob's Linn and County Down were dated by K-Ar methods and gave a range of ages from 379 ± 10 Ma to 406 ± 10 Ma for all samples, with a mean of 390 ± 6 Ma (Table 1). The relatively narrow range in ages is greater than routine analytical error but does not appear to correlate with K content or stratigraphical age of the host rocks. It is possible that particle size is an important factor. Hay *et al.* (1988) determined K-Ar ages on both coarse

Table 1. *Clay mineralogy and K–Ar ages of Llandovery K-bentonites*

Sample	Biostratigraphic age	Location	Clay mineralogy		%K	%Atmos ^{40}Ar	K/Ar age (Ma) $\pm 2\sigma$
NI3	*M. crenulata*	Tara Pt.	R3	I/S (+Ch)	7.64	12.1	386 ± 10
NI5	*M. crenulata*	Ardglass	R3	I/S	7.22	22.1	389 ± 10
NI4	*M. griestoniensis*	Millin Bay	R3	I/S (+Ch)	6.91	14.1	383 ± 10
NI1	*M. crispus*	Ballywhiskin	R3	I/S (+Ch)	7.32	15.9	403 ± 8
CB2	*M. convolutus*	Coalpit Bay	R3	I/S (+Ch)	7.11	7.8	383 ± 10
B17-4	*C. gregarius*	Dob's Linn	R3	I/S (+Ch)	5.79	14.2	379 ± 10
NI2	*C. gregarius*	Coalpit Bay	R3	I/S (+Ch)	6.65	6.5	406 ± 10
B17	*C. cyphus*	Dob's Linn	R3	I/S	5.26	13.6	396 ± 7
CB7	*C. vesiculosus*	Coalpit Bay	R3	I/S (+Ch)	6.74	20.9	383 ± 10
							Mean 390 ± 6

I/S, illite/smectite, Ch, chlorite.

(0.2–2.0 μm) and fine (<0.1 μm) fractions of Ordovician K-bentonite and found that the former gave younger ages, on average, by about 15 Ma. The reverse pattern is usually observed (Odin et al. 1986). Hay et al. (1988) suggested that their results might be due to Oswald ripening, in which crystal size increases through time with dissolution of the fine fraction. The net effect would be to give older ages for small particles and younger ages for the large ones. Our studies were confined to the <0.5 μm fraction, and any particle size variation between samples might also be reflected in slight variations in the ages determined. The relatively close agreement between the ages suggests that such effects are minor and the mean result probably represents the best estimate of the K-Ar age.

Chemical stratigraphy

Previous studies have found that, even after post-depositional alteration, Palaeozoic K-bentonites retain a chemical fingerprint of their original ash composition which allows identification and correlation on a regional scale (Kolata et al. 1986, 1987). Analysis of variance and discriminant function analysis can be used to rank chemical elements according to their power to discriminate between individual or groups of K-bentonite beds. The samples in this study were divided into groups on the basis of graptolite zone membership. Analytical data for Llandovery K-bentonites (Table 2) were treated by analysis of variance in order to calculate the ratio of the mean between-group variance to mean within-group variance, or F-ratio statistic, for each element. Those elements with the highest F ratios, or greatest individual discriminating ability, are listed in Table 2. A bivariate plot of two of the higher ranked elements show a tendency toward clustering of samples as a function of biostratigraphical position (Fig. 3). However, the overlap between clusters detracts from their use as parameters for the unequivocal assignment of unknown samples, and thus limits their stratigraphic value.

Further separation of the groups is possible by the use of discriminant function analysis (Huff & Kolata 1989). The process of achieving optimal discrimination requires finding the linear combination of group variables (in this case, chemical elements) which produces the maximum difference between the defined groups. Immobile elements such as Nb, Y, Yb, Zr, Ti, Ta, Th and REE may or may not serve as good discriminators depending upon their relative distribution between beds. In discriminant function analysis, variables are grouped on the basis of their combined, rather than individual, ability to separate groups and the result can be more effective separation than otherwise possible with single variables. The K-bentonite beds were biostratigraphically grouped and discriminant analysis was used to test the hypothesis that such groups also have chemical characteristics which provide an independent basis for stratigraphical identification. The analysis assumes that the variables are normally distributed within each group and that each group is a sample from a multivariate normal population (Davis 1986). Most of the major elements and some non-normally distributed trace elements were rejected as unlikely or misleading discriminators and not used in the analysis.

The remaining elements were selected for the stepwise analysis on the basis of their individual discriminating ability as expressed by the F-ratio statistic. To achieve an optimal ranking of variables we employed the Wilks' lambda method

(Huff & Kolata 1989). Table 3 is a summary listing of the discriminant function analysis of the three groups of Llandovery K-bentonites. The first and second discriminant functions are used to construct a discrimination diagram showing group centroids and the territorial boundaries that separate them (Fig. 4). Using these two functions, the model is able to separate 100% of the group members as identified by their biostratigraphical position. The distance between group centroids is a measure of the significance of the discriminant analysis.

Discussion

The identification of biostratigraphically-defined groups by means of completely independent geochemical criteria provides an additional basis for regional correlation of these groups. The chemostratigraphical identity of unknown samples may be determined by plotting them on the discrimination diagram (Fig. 4). This is accomplished by computing the first and second discriminant function scores using the unstandardized canonical correlation coefficients listed in Table 4. The underlying assumption of chemical correlation is that the discriminating elements are unique and indigenous to the original ash, and are not the product of post-depositional additions or subtractions. Thus, it is striking to see a generally mobile element like Rb emerge as a prime discriminator between the three bentonite groups.

Examination of the calculated F-ratios for the Southern Uplands–Down–Longford K-bentonites show that Rb has a much larger between-group variation than within-group variation (Table 2). If Rb had been derived from adjacent host rocks during peak metamorphism there would be no compelling reason for its selective concentration in some K-bentonites as opposed to others. The beds are relatively thin and tend to be chemically and mineralogically homogeneous throughout. Velde & Brusewitz (1982) reported in their study of Ordovician bentonites of Sweden that, in general, thin beds tend to be uniformly rich in potassium while thick beds tend to be K-rich at the edges and K-poor in the centre, due to incomplete K-metasomatism. Llandovery K-bentonites in the Southern Uplands–Down–Longford terrane contain partially altered potassium feldspar and biotite (Merriman & Roberts 1990), and are chemically and mineralogically unzoned. Both minerals could have served as the source of K and Rb, which migrated into I/S during illitization. The generally positive correlation ($R = 0.77$) between the I/S K and whole-rock Rb suggests both elements have a common history.

The Silurian Period extended from 425–435 Ma to 395–410 Ma (Odin 1986). Thus it would appear that the K-Ar ages of about 390 Ma do not record depositional or early diagenetic events associated with the devitrification of volcanic ash in sea water and the alteration to a smectitic bentonite, but instead reflect some later event during which K was mobilized in sufficient quantity to convert smectite to R3 I/S with <10% smectite. The absence of age zonation and the relatively tight clustering of ages about a mean of 390 Ma suggests that illitization was the result of a common geochemical thermodynamic history for the entire section and that cation mobilization occurred as late as early Devonian or earliest Middle Devonian time.

The interpretation of K-Ar ages is not a straightforward matter, since other studies have shown that Ar can remain

Table 2. Analyses of Llandovery K-bentonites and selected ANOVA results

Sample	SiO$_2$	Al$_2$O$_3$	TiO$_2$	Fe$_2$O$_3$	MgO	CaO	Na$_2$O	K$_2$O	P$_2$O$_5$	As	B	Ba	Br	Co	Cr	Cs	Cu	Hf	Nb	Ni	Pb
NI-1	54.20	23.20	0.83	4.19	3.74	0.46	0.36	7.27	0.25	2.00	110	550	2.60	4.90	10	5.70	9	14	35	12.00	6.00
NI-2	51.80	24.20	0.54	3.23	3.78	0.98	0.94	7.03	0.11	3.00	190	610	4.90	20.00	20	8.70	7.5	13	30	26.00	8.00
NI-3	61.50	20.60	0.35	2.01	3.04	0.08	0.39	7.13	0.08	3.00	120	500	4.10	2.90	10	4.80	3	16	48	8.00	10.00
NI-4	51.20	27.00	0.86	2.56	2.24	0.34	0.91	8.12	0.43	42.00	190	1400	18.00	3.40	10	3.90	19	21	39	11.00	12.00
NI-5	50.40	23.30	0.82	3.01	3.17	2.66	0.50	8.24	0.18	6.00	190	310	4.40	5.30	10	15.90	47	18	40	13.00	14.00
CB-2	51.70	27.10	0.55	1.42	3.13	0.21	0.44	8.14	0.08	5.00	250	730	4.80	23.00	NA	11.90	140	18	40	22.00	6.00
CB-4	50.60	25.20	1.50	3.73	2.24	0.28	2.37	6.56	0.23	10.00	200	780	15.00	44.00	30	7.10	56	15	30	23.00	30.00
CB-5	51.30	25.20	1.43	2.57	2.30	0.51	2.52	6.42	0.38	4.00	180	750	7.70	34.00	30	5.80	37	14	20	18.00	18.00
CB-6	51.40	26.40	1.10	2.26	3.18	0.21	0.51	8.06	0.10	2.00	220	750	6.90	17.00	30	13.40	9.5	15	40	11.00	10.00
CB-7	51.20	26.70	1.11	1.74	3.24	0.19	0.52	8.13	0.11	1.00	230	740	5.50	22.00	20	13.80	170	17	40	12.00	8.00
CB-8	51.40	25.80	0.52	2.85	3.51	0.43	1.00	7.42	0.12	1.00	190	620	10.00	26.00	30	8.70	33	13	30	21.00	8.00
CB-9	49.90	26.50	1.19	2.72	2.90	0.20	0.58	8.18	0.12	1.00	NA	710	15.00	32.00	20	17.80	NA	17	40	NA	NA
B17	56.70	21.80	0.47	2.75	2.47	0.03	0.47	5.19	0.08	16.00	160	640	3.10	11.00	20	15.60	36	13	30	13.00	24.00
B17-0	49.10	28.10	1.16	1.25	2.26	0.02	0.54	6.43	0.08	5.00	230	730	2.80	6.30	10	19.90	62	15	40	9.00	24.00
B17-1	51.50	25.90	0.97	1.46	2.40	0.06	0.62	6.51	0.07	6.00	230	770	2.20	15.00	20	19.00	32	18	40	11.00	12.00
B17-2	45.20	23.10	0.73	6.60	2.34	0.02	0.28	5.76	0.06	58.00	210	630	26.00	6.70	20	23.90	29	13	30	8.00	24.00
B17-3	48.60	26.30	0.98	1.96	2.48	0.02	0.33	6.55	0.04	31.00	290	690	8.90	4.60	30	27.80	11	16	20	6.00	2.00
B17-4	48.90	28.60	1.18	1.21	1.91	0.46	0.49	6.50	0.14	1.00	290	900	1.60	8.40	10	13.60	15	19	70	21.00	4.00
B17-5	50.10	26.20	0.94	2.21	2.28	1.18	0.20	6.20	0.09	1.00	240	770	1.90	18.00	30	18.70	39	16	30	37.00	4.00
B17-6	53.20	27.00	0.97	1.15	1.84	0.34	0.54	6.33	0.15	1.00	250	920	2.10	8.00	10	10.50	19	14	40	8.00	2.00
Wilks' L			0.87												0.75	0.59	0.93	0.86	0.94	0.54	
F-Ratio			1.81												2.70	5.56	0.58	1.32	0.50	6.88	

| Sample	Rb	Sb	Sc	Sr	Ta	Th	U	V	Y	Zn	Zr	La	Ca	Nd	Sm	Eu	Tb	Dy	Yb	Lu	Mn
NI-1	280	0.60	9.59	10	1.7	32	9.0	54	80	58	580	99.7	176	74	11.10	3.14	1.50	8.6	3.93	0.69	250
NI-2	210	0.70	7.47	20	2.2	40	4.3	38	70	40	450	85.9	177	71	11.20	2.07	1.60	8.0	4.81	0.68	2400
NI-3	280	2.20	5.19	10	2.8	56	12.6	20	50	54	430	128.0	196	64	9.13	1.79	1.20	5.5	6.06	1.06	50
NI-4	260	1.10	9.30	40	2.9	37	8.5	54	130	33	840	142.0	259	105	15.70	2.74	2.60	14.4	7.09	1.03	220
NI-5	320	3.60	13.30	80	2.1	29	6.0	82	80	35	630	134.0	259	102	17.20	4.26	2.20	11.6	7.01	1.05	190
CB-2	210	1.00	8.03	20	2.5	34	8.1	22	160	23	810	96.6	203	87	15.80	3.97	2.90	22.8	7.28	1.07	490
CB-4	170	2.20	17.40	90	2.3	14	8.5	130	140	18	730	111.0	229	98	17.90	5.45	2.20	17.1	6.90	1.03	220
CB-5	170	0.80	17.30	90	1.3	13	6.0	120	110	19	610	65.4	136	66	13.70	4.37	2.00	16.2	6.73	0.99	230
CB-6	230	1.60	11.00	10	1.2	23	13.9	50	90	29	650	96.6	205	82	13.70	3.48	1.90	12.7	4.23	0.80	460
CB-7	230	1.20	11.20	20	2.1	23	3.7	64	80	28	680	106.0	219	85	14.30	3.65	2.40	12.5	4.63	0.61	450
CB-8	210	0.70	6.14	10	2.4	36	2.5	48	70	42	420	83.4	169	64	10.50	2.00	1.60	8.8	4.42	0.63	1300
CB-9	230	3.20	12.50	20	2.3	24	3.3	NA	100	NA	730	100.0	228	102	14.60	3.30	3.00	16.0	6.00	1.00	NA
B17	190	1.10	7.30	10	2.3	30	12.7	26	60	45	560	79.2	160	62	11.90	2.69	2.10	9.9	4.21	0.67	150
B17-0	220	0.70	16.50	40	2.4	28	13.9	62	100	37	700	86.3	204	98	18.60	4.94	3.00	16.7	6.74	1.01	50
B17-1	250	0.70	7.72	30	3.7	26	11.9	56	100	65	900	93.3	186	81	14.40	5.57	2.50	14.0	4.91	0.71	510
B17-2	210	13.00	9.11	20	2.1	36	25.3	36	20	31	440	69.9	145	68	13.40	3.10	1.90	9.1	2.38	0.46	60
B17-3	220	3.20	13.40	20	2.1	26	12.5	52	120	22	710	83.4	198	91	18.20	3.77	2.90	18.7	7.07	1.08	92
B17-4	190	0.40	15.10	90	4.0	19	4.6	38	130	110	950	114.0	273	117	21.90	5.50	3.20	20.2	8.48	1.17	520
B17-5	190	0.60	7.94	60	2.1	28	1.4	20	80	100	760	85.2	170	70	11.70	2.59	1.70	10.2	4.18	0.63	2100
B17-6	190	0.50	9.65	50	2.0	21	9.2	44	70	100	580	87.6	173	74	13.30	3.39	1.80	10.7	4.61	0.76	300
Wilks' l	0.20	0.91	0.93		0.99	0.70		0.98	0.85	0.88	0.95	0.46	0.86	0.97	0.96	0.91	0.92	0.83	0.83	0.81	
F-Ratio	32.38	0.81	0.59		0.02	3.36		0.18	1.47	1.07	0.42	9.57	1.31	0.29	0.35	0.77	0.71	1.62	1.60	1.83	
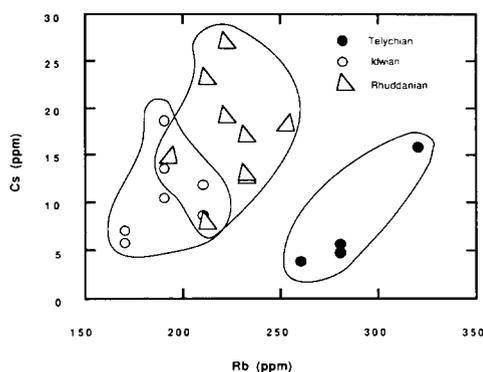
Fig. 3. Cs-Rb covariance plot of Telychian, Idwian and Rhuddanian K-bentonite samples using elements shown by analysis of variance to be good discriminators. Beds grouped by graptolite biozone membership form distinct groups with some overlap between Idwian and Rhuddanian samples.

mobile in some minerals at temperatures within the range of low-grade metamorphism reactions (Dodson 1973). Further documentation for this comes from studies of micas in the Glarus Alps (Hunziker 1979) and the Scottish Caledonides (Harper 1967) which provided evidence for closure of the K-Ar system during post-tectonic and post-metamorphic uplift and cooling rather than during peak metamorphism. The closure or blocking temperature is that point below

Table 3. *Summary table and statistics for discriminant analysis**

Step	Entered	Removed	Wilks' Lambda
1	Rb		0.198
2	Cs		0.101
3	Ni		0.070
4	Cr		0.051
5	Lu		0.041
6	Fe		0.029
7	Zn		0.018
8		Cr	0.021
9	Nb		0.013
10	Cr		0.007
11	La		0.005
12	Ta		0.003
Function	Eigenvalue	Percent of variance	Canonical correlation
1	47.02	90.1	0.99
2	5.18	9.9	0.92

* Ten elements combined in 12 steps to produce the optimal discrimination between the groups at the 95% level of confidence. The contribution of each element toward reducing the unexplained variance between beds is expressed by Wilks' Lambda, the ratio of unexplained variance to total variance. Thus, after Rb was considered alone, 20% of the between-bed variance remained to be accounted for by other elements. The addition of Cs reduced that to 10%. Chrome was entered in step 4, removed in step 8, and re-entered in step 10. The first discriminant function alone accounts for 90% of the total variance in the discriminant model, and the second, operating on the residual variance, adds an additional 10%. Thus, using the first and second functions, the model is able to separate 100% of the group members as defined by their biostratigraphic position.

which no significant loss of daughter product occurs, and is a function of several variables including cooling rate, particle size and degree of crystal perfection. Although not determined precisely for illite, the closure temperatures reported for some low-grade metamorphic micas range between 225 °C for biotite (Dodson 1979) to 350°C for phengitic mica (Hunziker 1979).

The significance of measured ages diminishes in systems in which Ar diffusion has continued for very long time intervals, such as those approaching the half-life of the parent. Metamorphism in the Southern Uplands accretionary prism was discussed by Oliver & Leggett (1980). They suggested that, based on the comparative distribution of metamorphic facies from other localities, P–T conditions accompanying prehnite–pumpellyite metamorphism were minimally 2.5 kbar and 300 °C. Their cross-section predicts that greenschist facies rocks are probably just below the present day surface in the Southern Uplands and, by association, in the Down–Longford terrane. The question arises whether burial in a trench environment or tectonic burial during accretion provides the best explanation for the metamorphism. Burial metamorphism would have occurred with an overburden of up to 3 km, but the 300 °C necessary for prehnite–pumpellyite metamorphism would not have occurred at that depth (Bevins *et al.* 1985). Tectonic burial on an emergent trench-slope could have generated 300 °C, if metamorphism occurred while earlier accreted slices were rotating through the accretionary prism (Bevins *et al.* 1985). Previous studies have shown that neoformed illitic clay minerals are excellent K-Ar clocks under sedimentary and diagenetic environmental conditions (Aronson & Lee 1986). At higher temperatures, Ar diffusion may cause resetting of the ages to coincide with the blocking temperature during post-metamorphic cooling (Hunziker 1986). The application of K-Ar ages in geothermometry and illitization studies is therefore constrained by temperatures characteristic of low-grade metamorphic environments. At higher temperatures the reliability of the age measurements will be strengthened by thermal history data and measurement in a second radiometric system, such as Rb-Sr (Hunziker 1986).

The geological significance of the K-Ar ages hinges upon their relationship to one or more tectonomagmatic events in the history of the Southern Uplands–Longford–Down terrane. Deformation is attributed to three successive processes: (a) soft sediment downslope gravity-driven movements in a fore-arc trench context (Knipe & Needham 1986; Needham & Knipe 1986), (b) either the process of subduction and accretion of oceanic sediments (Leggett *et al.* 1979; Anderson & Cameron 1979; Stringer & Treagus 1980; Knipe & Needham 1986) or the development of a back-arc and foreland basin thrust-duplex (Stone *et al.* 1987), and (c) the end-Silurian–early-Devonian continental collision and final docking of the Laurentian and East Avalonian terranes (Anderson & Cameron 1979; Barnes *et al.* 1989). The most intense deformation and maximum low-grade metamorphism has been attributed to (b) (Oliver & Leggett 1980) and the age of the latest metamorphism is Wenlock, based on structural evidence (Barnes *et al.* 1989). The K-Ar dates would appear to be related more closely to the collision event (c), even though the collision has been interpreted to post-date the regional metamorphic peak.

Conodont alteration indices, graptolite reflectance (Bergström, 1980) and illite crystallinity (Oliver & McKerrow 1984) data all point to a thermal history for parts

Fig. 4. Discrimination diagram using the first and second discriminant functions showing the distribution of Telychian, Idwian and Rhuddanian K-bentonite samples. Asterisks mark the group centroids. Ten elements were required to define the group boundaries. The Rhuddanian and Idwian K-bentonite beds have group means which are closer together than either group to the mean of the Telychian beds. A standard test of significance of a discriminant function is to examine the distance between the centroids, or multivariate means, of the groups (Davis 1986). This distance is graphically displayed by the centroid markers and is clearly greater than the group variance at the 95% confidence level. Thus the discriminant functions reveal chemical differences between the three groups that are persistent and unique over the range of samples studied.
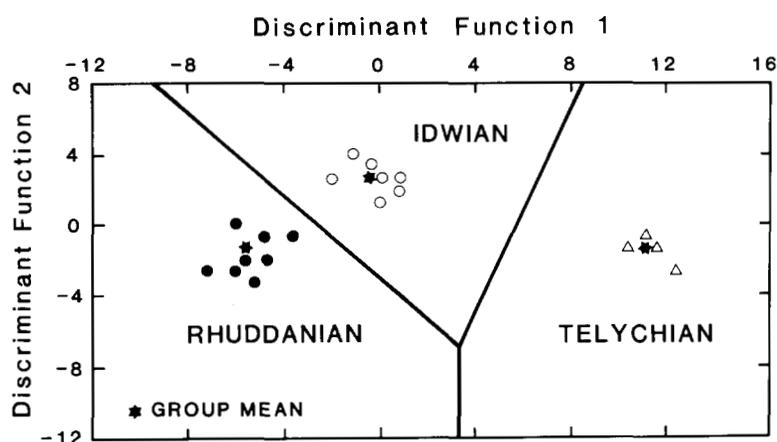
Table 4. *Unstandardized discriminant function coefficients*

Element	Function 1	Function 2
Fe	1.7937	0.1656
Nb	−0.2728	−0.0319
Ni	0.0601	0.1482
Rb	0.0726	−0.0353
Ta	−1.2185	−0.7494
Cr	−0.1766	−0.0879
Cs	−0.3615	−0.0452
Zn	0.1227	0.0284
La	0.0972	0.0019
Lu	13.5220	4.3068
(Constant)	−27.5433	5.1282

of the Southern Uplands as high as 400 °C. If the illitization is a result of low grade prehnite–pumpellyite facies regional metamorphism, then this should be reflected in the ages on the illites. However, if the K-Ar system remained open at that temperature, it is more likely the illite dates record the time of peak uplift and cooling down at approximately 390 Ma. The coincidence of this age with the collision of Laurentia and Avalonia is consistent with that interpretation.

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