Li and δ^7Li in mudrocks from the British Caledonides: Metamorphism and source influences

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Abstract

Mudrocks from three lower Paleozoic basins in the British Caledonides (southern Lake District, northern Lake District and Southern Uplands) were investigated to determine the influence of sub-greenschist facies metamorphism on Li and the factors that control Li in fine-grained terrigenous sedimentary rocks. Metamorphic grade, as determined by KI (Kübler index) does not correlate with Li content ([Li]) and δ^7Li, indicating that sub-greenschist facies metamorphism has negligible effect on Li in these rocks. Collectively, the data for all three basins show a negative correlation between [Li] and δ^7Li and a positive correlation between [Li] and the Chemical Index of Alteration (CIA), suggesting that provenance exerts the greatest control on Li in mudrocks. Samples from the northern Lake District, which were deposited in an extensional basin, have homogeneous REE patterns, similar to shale composites (PAAS), the highest CIA, Th/U and [Li] and the lowest δ^7Li and ε_{Nd}, consistent with their derivation from a highly weathered, ancient continental source. By contrast, mudrocks from the Southern Uplands range to the lowest CIA, Th/U and [Li] and have the highest δ^7Li and ε_{Nd}. These samples were deposited in a forearc basin on the southern margin of the Laurentian craton and contain volcanic detritus. Their REE patterns are the most variable, ranging from average shale-like patterns to less LREE-enriched patterns. The compositional heterogeneity within the Southern Uplands mudrocks is consistent with a mixed provenance that includes juvenile crustal materials (lower [Li], ε_{Nd} and Th/U, higher δ^7Li), likely derived from the arc, as well as more highly weathered continental detritus. Mudrocks from the southern Lake District were deposited in a foreland basin, and exhibit geochemical characteristics intermediate between the northern Lake District and the Southern Uplands mudrocks, indicating their derivation from a mixed source. Our study shows that Li concentrations and δ^7Li can provide additional information on the degree of weathering of the provenance of mudrocks.
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1. INTRODUCTION

Lithium, a light alkali metal with its two stable isotopes, ^{6}Li and ^{7}Li, has received significant attention during the last decade due to the large isotopic fractionation that has been documented in near-surface environments (δ^7Li = $\sim-20‰$ to $\sim+40‰$) (Rudnick et al., 2004; Pogge von Strandmann et al., 2006), and its potential to trace crustal recycling into the mantle. Recent studies have demonstrated large Li isotopic fractionation during arrested diffu-

sion (Richter et al., 2003; Beck et al., 2005; Lundstrom et al., 2005; Teng et al., 2006a; Jeffcoate et al., 2007; Marks et al., 2007; Parkinson et al., 2007), terrestrial weathering (Pistiner and Henderson, 2003; Huh et al., 2004; Kisakurek et al., 2004; Rudnick et al., 2004), and seafloor alteration (Chan et al., 1992, 1993, 1994; Seyfried et al., 1998; Chan and Kastner, 2000; James et al., 2003; Bouman et al., 2004). By contrast, very limited Li isotopic fractionation occurs during igneous differentiation (Tomascak et al., 1999; Bryant et al., 2004; Teng et al., 2004, 2006b; Halama et al., 2007). Consequently, this system has been suggested to be a potentially useful tracer of crustal recycling in subduction zones (e.g., Elliott et al., 2004, 2006).

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Marine sediments are a major source of Li in subducting slabs and may therefore control the Li budget of recycled materials (Chan et al., 2006). However, the behavior of Li during metamorphic devolatilization of sedimentary rocks has only been partially explored (e.g., Teng et al., 2007), as have the factors that control the Li isotopic composition of terrigenous sediments (Teng et al., 2004; Chan et al., 2006). In particular, the effects of sub-greenschist facies metamorphism on [Li] and δ^7Li, during which significant volatiles may be lost (Merriman and Roberts, 2001), is unknown.

The degree of Li isotope fractionation caused by metamorphic devolatilization is a matter of current debate. In a study of alpine eclogites, which are considered analogs for subducted oceanic crust, Zack et al. (2003) suggested that sub-greenschist to greenschist facies metamorphic dehydration of altered basalts produced the light δ^7Li values (as low as $-12\%_0$) seen in some of these samples. By contrast, Marschall et al. (2007), using the spodumene-fluid isotopic fractionation factors of Wunder et al. (2007), suggested that dehydration cannot produce such low δ^7Li. These authors concluded that the very light δ^7Li value seen in some massif eclogites are likely the result of kinetic fractionation during diffusive influx of Li from the country rocks into the eclogite body. Similarly, in a study of the effects of contact metamorphic dehydration of chlorite to sillimanite zone metapelites, Teng et al. (2007) suggested that metamorphic dehydration had little discernible effect on the δ^7Li of the rocks, despite the fact that up to half of the Li was lost during metamorphism. They showed that the limited isotopic fractionation of up to $3\%_0$ is consistent with published fluid-mineral isotopic partitioning studies (Wunder et al., 2006). However, to date, no comprehensive study of the factors that control Li and its isotopic composition in very low temperature metasediments, i.e., sub-greenschist facies metasediments, has been carried out. Such conditions should be representative of metamorphism in the forearc of subduction zones when initial dewatering process occurs.

In a recent review, Chan et al. (2006) document the major influences on the Li abundance and δ^7Li of marine sediments. While a number of factors influence Li in marine sediments, provenance plays a major role in determining the bulk Li isotopic composition and concentration of global marine sediments, with clay-rich sediments generally having higher Li abundance and lower δ^7Li than other oceanic sediments (calcareous oozes, carbonates, sand, and hydrothermally altered sediments). Sediments derived from mature continental crust are especially light and may reflect enhanced or prolonged weathering, whereas volcanogenic sediments derived from unweathered sources have relatively heavier δ^7Li values. It has yet to be established how well these provenance differences are preserved during subduction and metamorphic dehydration and to what degree Li in terrigenous sediments may act as a proxy for weathering in the source region.

We present here the Li concentration [Li], isotopic composition, major-element and trace-element abundances and Nd and Sr isotopic composition for three suites of mudrocks from lower Paleozoic basins within the British Caledonides. These samples have experienced metamorphic conditions ranging from deep diagenetic to epizonal (lower greenschist facies) metamorphism over a range of dP/dT gradients. These rocks are used to explore the factors that control lithium concentration and its isotopic composition in sub-greenschist facies metapelites and determine whether lithium is lost during dehydration reactions that occur during sub-greenschist facies metamorphism, and if so, whether isotopic fractionation occurs.

2. GEOLOGICAL BACKGROUND AND SAMPLES

The Caledonian mudrocks examined here come from Ordovician to Silurian sedimentary basins that are juxtaposed across the Iapetus Suture, the structural trace within the British Caledonides of the early Paleozoic Iapetus Ocean (Fig. 1, Merriman et al., 2009). In the northern Lake District, the Skiddaw Group formed in a sedimentary basin that developed in an extensional setting on the southern margin of the Iapetus Ocean during the early to mid-Ordovician. Thus, these sediments were metamorphosed under relatively high heat flow conditions (35–50 °C km^{-1}, Stone and Merriman, 2004). By contrast, the other two sedimentary basins formed in relatively low heat flow regimes (<25 °C km^{-1} in the Southern Uplands and <20 °C km^{-1} in the southern Lake District, Merriman and Roberts, 2001; Soper and Woodcock, 2003). The Southern Uplands terrane formed as an accretionary thrust complex at the Laurentian continental margin and the southern Lake District evolved largely in response to flexural subsidence of the crust, in convergent plate settings. These latter two basins formed as the Iapetus Ocean closed during the late Ordovician and early Silurian (Leggett et al., 1979; Stone et al., 1987; Kneller, 1991).

In response to sedimentary burial and enhanced heat flow, minerals in sediments undergo diagenetic to very low-grade metamorphic reactions as soft clays and muds are systematically converted to lithified mudrocks (Merriman and Peacor, 1999). The Caledonian samples from the three basins consist of clays, mostly <2 μm in grain size, as well as non-clay minerals. The latter include quartz (<40%), albite (<15%) minor amounts (<5%) of calcite, dolomite, K-feldspar, hematite, pyrite, and trace amounts (1<%) of rutile or anatase (Merriman, 2006). In the northern Lake District, clay mineral assemblages include K- and Na-rich white micas, chlorite, minor pyrophyllite, rectorite (Na,Ca)Al$_4$(Si,Al)$_8$O$_{20}$(OH)$_4$·2(H$_2$O)) and corrensite (Ca,-Na,K)(Mg,Fe,Al)$_9$(Si,Al)$_8$O$_{20}$(OH)$_{10}$·n(H$_2$O). The Na-rich clays indicate relatively high heat flow conditions in the mudrocks (Merriman, 2006). By contrast, Na-micas and pyrophyllite are much less abundant or absent in clay minerals from the Southern Uplands and the southern Lake District (Merriman et al., 2009) due to relatively low heat flow (Fortey, 1989; Cooper et al., 2004). Southern Uplands mudrocks also contain volcanic detritus, including unaltered pyroxene, probably derived from a nearby eroded volcanic arc. The clay minerals in the Southern Uplands samples are rich in chlorite and other Fe, Mg-clays, likely derived from weathering of mafic volcanic detritus.

The metamorphic grade of the samples was determined using the Kübler index (KI), which is a measure of small
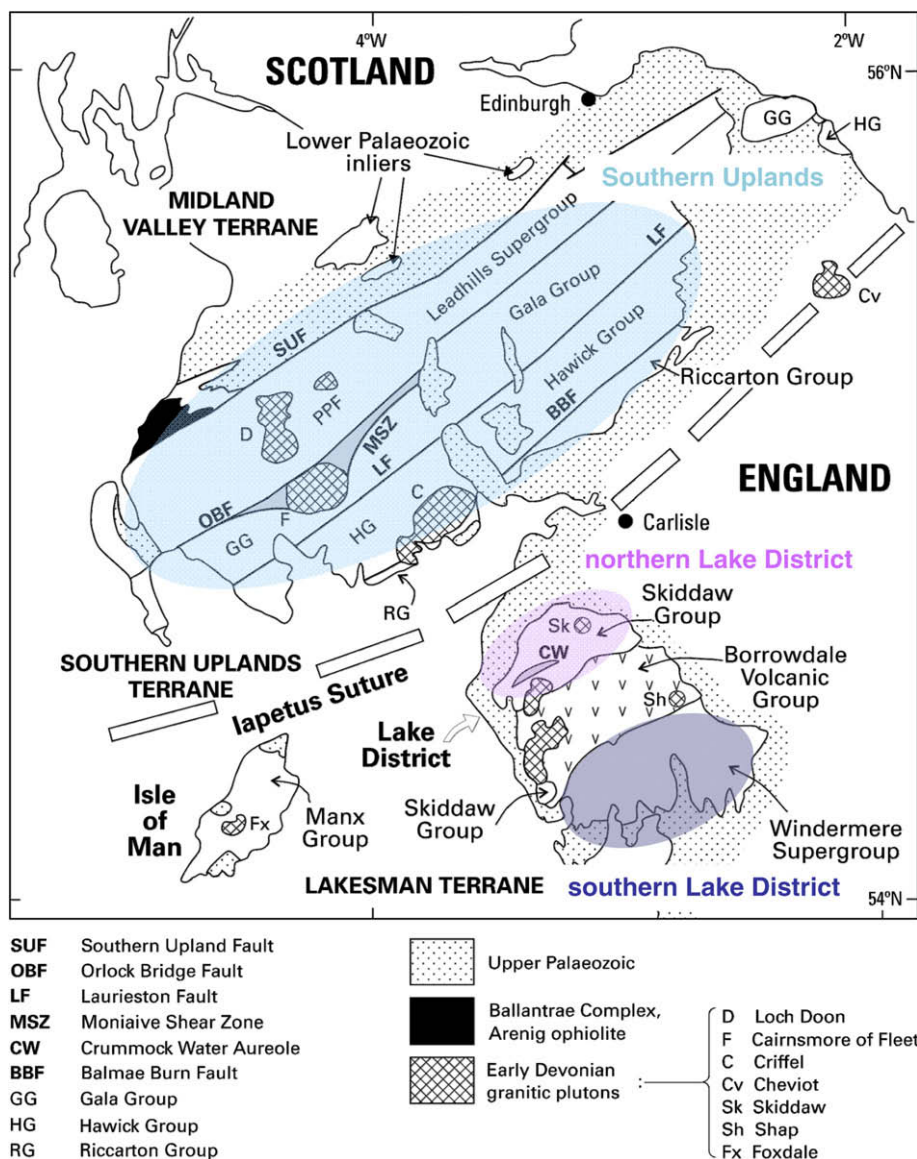
Fig. 1. Sketch map showing the location of Caledonian terranes and the sedimentary basins sampled for this study (after Merriman et al., 2009).

changes in the width at half-height of the illite-muscovite $\sim$10 Å XRD peak. These changes occur when illite reacts to form muscovite in response to deep diagenesis and low-grade metamorphism in sedimentary basins. With increasing metamorphic grade, the half-height of the illite-muscovite $\sim$10 Å XRD peak value is reduced and the Kübler index decreases (Peacor, 1992). With increasing grade, the KI value is: deep (or late) diagenetic zone KI > 0.42, anchizone KI = 0.42–0.25, and epizone/lower greenschist facies KI < 0.25 (Merriman and Frey, 1999). Typical uncertainty of the KI value determined in this way is less than <10% (2σ, Merriman and Peacor, 1999). Samples from all three basins show a range of KI values of 0.20–0.66, thus metamorphic grade of the mudrocks varies from diagenesis to lower greenschist facies in each basin.

3. ANALYTICAL METHODS

Samples for chemical analysis were selected to span a range of KI values, which were previously determined by X-ray diffraction (XRD) in order to define the metamorphic grade (Merriman and Peacor, 1999). Whole rock major-elements compositions were determined by X-Ray Fluorescence (XRF) on fused glass disks at Franklin and Marshall College. Accuracy of the XRF data from this lab can be evaluated from results obtained for the BHVO-1 and QLO-1 standards, which are published on the lab website (http://www.fandm.edu/x7992.xml). The accuracy is better than 4% for most major elements except Na_2O for BHVO-1 (2σ = 6.6%) and TiO_2 and MnO for QLO-1 (2σ = 4.8% and 11.1%, respectively).

Lithium concentrations and isotopic compositions were determined at the Geochemistry Laboratory of the University of Maryland, College Park. Most of the whole rock powders measured for Li isotopes were the same as those previously analyzed by one of us (Merriman) for selected major and trace elements, as well as KI. However, some original sample powders were fully consumed in that study, necessitating re-sampling and creation of a second batch of whole rock powders for a subset of samples. The new samples were collected at the same outcrop within a few meters from the original site and, thus, should have the same metamorphic grade (KI value) as the original samples. These samples are marked by an "r" in Tables 1 and 2.

Procedures for sample dissolution, column chemistry and instrumental analysis are the same as those reported in Teng et al. (2006b). The sample dissolution procedure does not include the high-P teflon bomb process, however, for the samples that contained organic carbon (labeled "o" in Tables 1 and 2), we used $HClO_4$ in a 1:1 mixture with HF in the first step of sample dissolution. The presence of organic carbon in the samples does not correlate with lithium concentration or isotopic composition, suggesting that there is no organic matter influence on lithium behavior in our samples. The long-term external precision of Li isotopic analyses, based on repeat analyses of pure Li standards in this laboratory over the past eight years is $\leqslant 1.0‰$ (2σ) (Teng et al., 2006b). Precision on pure Li standards analyzed during the course of our analyses is as follows: UMD-1 (50 ppb, $n = 40$ runs) $\delta^7Li = 54.2 \pm 0.6$, IRMM-016 (100 ppb, $n = 38$ runs) $\delta^7Li = -0.2 \pm 0.5$ and the rock reference material BCR-1 gives $\delta^7Li = 2.0 \pm 0.3$ $(n = 2$ runs). As a benchmark, Teng et al. (2006b) reported BCR-1 $\delta^7Li = 2.0 \pm 0.7$ in 10 runs and Rudnick et al. (2004) reported BCR-1 $\delta^7Li = 2.7 \pm 1‰$. The total procedural blank measured during the course of this study is $Li = 0.11 \pm 0.12$ ng and $\delta^7Li = -25.3 \pm 40$. Given the amount of Li processed in any one sample (minimum $Li = 30$ ng), this blank has negligible effect on both concentration and isotopic composition and thus no blank correction was applied.

Li concentration measurements were determined by voltage comparisons between sample solutions and measurements for a 50 ppb L-SVEC bracketing standard solution and then adjusting for sample weight. The rock reference material BCR-1 gives $[Li] = 12.6 \pm 0.6$ ppm $(n = 2$ runs) and GEOREM preferred value is $[Li] = 13 \pm 1$ ppm. Typical uncertainty of concentration determined in this way was previously established to be $\pm 10\%$ $(1\sigma,$ Teng et al., 2006b).

Trace-element abundances were measured using an Element 2 ICP-MS in the Geochemistry Lab, University of Maryland. The digestion procedures were the same as for Li measurements. Final sample solutions were diluted 2000 times in 2% HNO_3. An indium spike (3 ppb) was introduced to the solutions in order to monitor and correct for signal drift. BHVO-1 served as our calibration standard after applying a blank correction. BHVO-1 analyzed as unknowns during our analyses return concentration within 10% uncertainty of preferred values (Table 1).

Strontium and Nd were separated from sample solutions prepared for Li chemistry. Cation exchange column separation was performed in three steps. Strontium and REE cuts were collected by eluting with 2.5 N HCl and 6.0 N HCl through the column filled with AG 50W-X12 (200–400) mesh resin. Separation of Nd from other REE was done in another column filled with the same resins. The column was eluted with 0.15 N HCl and 0.25 N HCl first, followed by 0.34 N HCl for Nd cuts. The Sr cut purification was performed using Eichrom Sr-Spec resin in order to remove any remaining Rb (Rb in Sr cut $\leqslant 0.2\%$, Aulbach et al., 2008). Strontium was measured at the University of Maryland by VG Sector 54 TIMS in dynamic collection mode after loading cuts onto Re filaments, and using $^{87}Sr/^{86}Sr$ of 0.1194 for mass fractionation correction. The average value of multiple analyses of SRM987 determined during the course of this study is 0.710258 ± 32 $(2\sigma, n = 4)$ relative to the recommended value of 0.71025. Neodymium isotopes were measured using a Nu plasma MC-ICP-MS with an Apex nebulizer in the Geochemistry Laboratory, University of Maryland, following the method described by Aulbach et al. (2008). Multiple $^{143}Nd/^{144}Nd$ analyses of AMES Nd standard averaged 0.512175 ± 18 $(2\sigma, n = 5)$; rock standards and samples were normalized to a $^{143}Nd/^{144}Nd$ for AMES of 0.512138 (Aulbach et al., 2008). Using this method, a single analysis of BHVO-1 yielded 0.513048 ± 28 (2σ).

4. RESULTS

Major- and trace-element concentrations of all samples are reported in Table 1. Lithium concentrations and isotopic compositions are reported in Table 2, along with the KI values and Nd and Sr isotopic compositions.

4.1. Lithium concentration and its isotopic composition

The concentrations of Li determined in this study are generally within 2σ analytical uncertainties of those determined by Merriman et al. (2009) via solution ICP-MS (Table 2). The exceptions are the samples for which new powders were prepared (16, in total). For three of these samples, LC1618, BRS822 and BRS879, our Li concentrations are about 20–40% higher (i.e., just beyond 2σ uncertainty) than those determined by Merriman et al. (2009). By contrast, for three other samples, LC495, BRS710 and BRS829, our Li concentrations are about 20–50% lower than those determined by Merriman et al. (2009). For the remaining 10 new powders, [Li] determined here is within error of that previously determined by Merriman et al. (2009) on the original powders. Because these discrepancies exist only for separate powders of re-sampled outcrops, they likely reflect heterogeneity of Li concentration at the outcrop scale. Although KI was not determined on the new samples, we assume that metamorphic grade will not vary significantly on the outcrop scale, and therefore the KI for the original rock samples also applies to the new powders prepared for samples from the same outcrop.

Lithium concentrations of the mudrocks vary widely, from 29 to 139 ppm, with samples from the northern Lake District generally having higher concentrations (56–

Table 1
Geographical, major (%) and trace (ppm) element data for mudrock samples from the three basins.

Sample	Grid reference[M]	SiO$_2$	TiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MnO	MgO	CaO	Na$_2$O	K$_2$O	P$_2$O$_5$	Total	LOI	LOI[*]	CIA	Li	Sc	V	Cr	Co
Southern Lake District																				
SH19	SD 4085 9840	60.35	0.90	18.4	8.4	0.10	4.94	0.83	1.15	4.27	0.18	99.52	5.3	5.3	71	52	24	160	194	28
SH22	SD 4320 9921	60.86	0.91	18.0	8.3	0.13	4.89	0.57	1.43	4.19	0.21	99.46	4.8	4.8	71	50	19	137	188	22
SH24[o]	NY 4145 0115	59.65	0.88	19.1	8.4	0.08	5.18	0.31	1.30	4.47	0.17	99.58	4.7	4.7	73	40	21	153	183	24
SH59	SD 6219 9093	60.47	0.84	17.4	8.0	0.34	4.53	2.73	1.39	3.83	0.18	99.69	6.2	5.0	67	51	18	126	174	24
LC940	SD 4060 8437	64.88	0.83	14.8	6.7	0.17	3.90	3.14	1.81	3.07	0.23	99.52	5.2	4.0	61	41	14	105	158	16
LC1617[o]	SD 6924 9318	60.73	0.79	15.2	7.0	0.10	4.98	5.99	0.95	3.48	0.14	99.43	8.9	4.9	69	51	14	112	132	19
LC1606[r,o]	SD 5528 8712	62.28	0.90	17.6	8.0	0.08	4.72	0.24	1.66	3.90	0.18	99.52	4.5	4.5	72	53	19	130	215	22
LC1570[r,o]	SD 6860 8770	46.37	0.62	14.1	7.1	0.55	1.89	26.5	0.72	2.24	0.18	100.14	19.3	N/A	75	55	12	102	106	16
LC1618[r,o]	SD 7051 9580	60.15	0.93	18.8	8.8	0.17	2.14	4.46	0.95	3.09	0.13	99.65	8.0	5.2	74	93	19	54	149	10
Northern Lake District																				
LC142	NY 1560 1825	65.60	1.06	17.8	9.1	0.10	2.20	0.27	0.75	2.86	0.14	99.92	3.6	3.6	80	80	23	149	209	20
LC199[o]	NY 1649 2111	58.28	1.21	24.0	8.5	0.07	1.98	0.29	0.81	4.14	0.19	99.44	9.6	9.6	80	137	22	144	108	5
LC348	SD 1476 8617	56.83	1.15	25.0	8.8	0.21	1.79	0.35	0.33	5.12	0.26	99.79	4.2	4.2	79	56	22	130	121	9
LC434	NY 3827 2586	57.05	1.24	23.3	11.0	0.29	2.10	0.24	0.97	3.28	0.13	99.63	6.4	6.4	82	108	23	140	134	26
LC507	NY 2956 2520	66.05	1.02	18.8	8.5	0.10	1.87	0.26	0.71	2.36	0.17	99.86	4.6	4.6	83	90	17	118	124	25
LC521[r]	NY 2565 2634	57.88	1.25	24.2	9.4	0.14	1.92	0.34	0.99	3.48	0.13	99.70	4.9	4.9	81	139	23	155	171	15
LC495[r]	NY 4732 2201	56.17	1.09	25.9	9.5	0.18	1.49	0.28	1.00	3.93	0.16	99.70	8.0	8.0	81	69	21	158	149	26
LC482[r]	NY 5506 1311	52.36	1.12	28.9	10.2	0.24	2.05	0.12	0.58	3.85	0.11	99.53	6.3	6.3	85	139	23	154	148	22
Southern Uplands																				
BRS882	NX 830 884	56.07	1.07	20.1	9.0	0.09	5.32	0.45	1.65	5.51	0.25	99.50	4.7	4.7	69	54	22	143	167	32
BRS1028	NX 859 728	58.45	1.02	19.8	7.3	0.06	3.93	3.52	0.41	4.98	0.21	99.67	9.0	6.6	75	68	23	176	167	21
BRS822[r]	NX 733 754	55.90	0.93	20.9	9.5	0.07	4.89	0.26	1.13	5.74	0.20	99.48	4.2	4.2	72	74	22	147	146	24
BRS781[r]	NX 7115 8385	58.08	1.04	19.8	8.1	0.07	5.92	0.30	1.11	5.21	0.20	99.88	5.0	5.0	72	55	20	159	206	20
BRS879[r]	NX 824 908	55.25	1.09	22.0	7.7	0.06	5.47	0.78	1.00	6.12	0.23	99.69	5.2	5.2	71	47	24	162	184	9
BRS753[r]	NX 6358 8363	65.67	0.81	16.4	7.5	0.06	3.64	0.26	1.39	3.51	0.17	99.44	4.2	4.2	73	49	17	123	369	18
BRS742[r,o]	NX 657 823	58.08	1.01	22.9	7.4	0.06	3.30	0.23	1.67	5.34	0.23	100.20	5.3	5.3	73	46	26	170	183	25
BRS710[r, o]	NX 717 488	69.58	0.67	11.9	5.7	0.15	4.09	3.49	2.07	2.07	0.17	99.86	6.9	5.7	57	29	12	94	310	14
BRS807[r]	NX6590 7895	56.98	1.02	19.6	8.8	0.09	5.48	0.65	1.72	4.96	0.21	99.49	4.1	4.1	69	55	23	162	317	20
BRS824[r]	NX 6945 7616	60.34	0.86	19.4	8.2	0.07	4.44	0.42	1.33	4.39	0.26	99.71	4.3	4.3	73	56	18	117	170	17
BRS829[r,o]	NX 688 857	61.40	0.97	21.1	6.0	0.09	3.37	0.12	1.12	5.39	0.17	99.74	5.1	5.1	73	31	22	147	183	17
BRS790[r]	NX 7051 8024	59.90	0.82	16.9	6.9	0.11	4.74	3.85	1.67	3.92	0.78	99.58	5.8	4.1	63	40	18	127	218	15
BHVO-1																				
BHVO-1																34	337	301	45	
BHVO-1[P]																31	318	287	45	

Li and δ[7]Li in mudrocks from the British Caledonides

Table 1 (*continued*)

Ni	Cu	Y	Zr	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Pb	Th	U	Th/U	Th/La	Th/Sc	(La/Yb)$_n$
101	38	25	159	49	101	12	44	8.1	1.7	7.2	1.1	5.0	1.0	3.0	0.42	2.9	0.42	49	14	3.2	4.5	0.29	0.61	11.7
80	31	27	157	42	83	10	38	7.1	1.5	6.2	1.0	5.0	1.0	3.0	0.41	2.7	0.38	12	11	2.7	4.2	0.28	0.61	10.6
96	50	17	142	12	25	4	14	3.1	0.8	3.1	0.5	3.2	0.7	2.2	0.36	2.5	0.38	23	12	2.9	4.2	1.0	0.58	3.2
77	37	26	157	37	77	9	34	6.5	1.4	6.3	0.9	4.8	0.9	2.9	0.41	2.7	0.38	21	11	2.5	4.3	0.29	0.59	9.4
62	30	30	173	42	87	10	39	7.4	1.6	6.8	1.0	5.5	1.1	3.1	0.43	2.8	0.40	23	11	2.6	4.4	0.27	0.77	10.2
56	44	24	133	35	75	9	33	6.2	1.3	5.8	0.9	4.5	0.9	2.7	0.38	2.5	0.36	50	10	2.9	3.4	0.29	0.71	9.5
90	48	24	158	40	86	10	35	6.3	1.2	5.9	0.8	4.6	0.9	2.7	0.42	2.7	0.40	11	13	3.4	3.7	0.31	0.68	10.2
82	14	25	73	39	73	9	34	6.7	1.3	6.6	0.9	4.7	0.9	2.6	0.34	2.2	0.31	19	9	1.7	5.4	0.23	0.74	11.8
64	74	26	129	43	84	10	38	6.4	1.2	6.0	0.9	4.3	0.9	2.7	0.37	2.5	0.36	89	13	2.2	5.8	0.30	0.67	11.7
48	55	26	88	47	102	12	44	8.7	1.9	9.5	1.1	5.7	1.1	3.2	0.47	3.2	0.48	157	15	2.8	5.2	0.31	0.64	9.9
21	11	26	142	49	100	12	44	8.3	1.7	6.8	1.1	5.4	1.0	3.0	0.41	2.7	0.40	57	16	2.8	5.7	0.33	0.73	12.2
40	6	33	134	57	108	13	47	8.9	1.9	9.0	1.3	6.3	1.2	3.6	0.48	3.1	0.44	5	18	2.8	6.4	0.31	0.80	12.2
51	38	27	154	49	97	11	39	6.9	1.5	5.7	0.9	4.9	1.0	3.1	0.44	2.9	0.42	14	14	2.4	5.9	0.29	0.63	11.5
48	28	22	165	43	88	10	35	6.2	1.4	5.7	0.8	4.2	0.8	2.5	0.35	2.4	0.35	14	14	2.3	5.9	0.32	0.80	12.2
40	21	26	134	46	97	11	41	7.8	1.7	7.4	1.1	5.1	1.0	3.0	0.41	2.7	0.40	27	15	2.5	6.2	0.33	0.66	11.5
50	4	33	133	67	136	15	53	9.8	2.1	9.1	1.2	6.3	1.2	3.6	0.50	3.2	0.45	9	20	2.8	7.0	0.29	0.92	14.3
51	22	29	117	67	132	14	51	8.7	1.8	7.3	1.1	5.6	1.1	3.2	0.45	2.9	0.41	23	20	3.0	6.7	0.29	0.86	15.9
83	9	43	223	44	94	11	40	7.6	1.9	7.6	1.2	7.4	1.5	4.3	0.62	3.9	0.57	11	15	3.1	4.9	0.34	0.67	7.6
77	54	29	165	40	83	10	35	6.6	1.4	6.1	1.0	5.3	1.1	3.2	0.47	3.1	0.45	17	14	3.1	4.3	0.34	0.58	9.0
100	35	40	216	92	153	18	64	11.4	2.6	11.3	1.6	7.8	1.5	4.3	0.59	3.7	0.53	29	14	3.1	4.7	0.16	0.64	16.8
92	33	33	287	53	105	13	46	7.5	1.7	6.8	1.1	5.7	1.2	3.8	0.56	3.8	0.56	6	11	3.5	3.3	0.22	0.58	9.6
50	27	29	201	5	16	2	11	3.7	1.1	4.0	0.7	5.1	1.1	3.1	0.50	3.2	0.48	11	14	3.5	3.9	2.7	0.55	1.1
124	36	23	146	36	76	9	32	5.9	1.3	6.0	0.8	4.4	0.9	2.5	0.35	2.3	0.34	29	10	2.9	3.4	0.28	0.57	10.5
96	91	25	193	43	87	10	36	6.5	1.6	5.9	0.9	4.6	0.9	2.9	0.41	2.7	0.40	20	12	3.2	3.9	0.29	0.48	10.8
107	11	20	53	32	62	7	27	5.2	1.2	5.2	0.7	3.8	0.7	2.2	0.30	1.9	0.28	11	7	1.7	4.3	0.22	0.62	11.4
120	241	18	159	18	40	5	19	3.7	1.0	3.7	0.6	3.2	0.7	2.2	0.35	2.4	0.36	11	12	3.1	3.9	0.65	0.53	5.1
77	4	28	164	49	104	12	47	9.2	1.8	7.9	1.1	5.5	1.0	3.0	0.41	2.7	0.40	6	12	2.7	4.5	0.25	0.68	12.3
66	130	32	166	47	88	11	41	7.6	1.7	7.7	1.1	5.7	1.1	3.2	0.45	2.9	0.41	5	12	2.4	5.1	0.26	0.55	11.1
125	46	28	165	48	80	11	41	7.3	1.7	7.3	1.0	5.0	1.0	3.1	0.44	2.9	0.43	723	10	2.5	4.1	0.21	0.56	11.2
126	152	27	184	16	39	5.6	26	6.4	2.2	6.8	1.0	5.6	1.0	2.7	0.3	2.1	0.29	2.6	1.1	0.4				
118	137	26	174	16	38	5.4	25	6.1	2.1	6.3	1.0	5.3	1.0	2.6	0.3	2.0	0.27	2.4	1.2	0.4				

n: chondrite normalized (Sun and McDonough, 1989).
[M] Merriman et al. (2009).
[*] Corrected by removing CO_2 content, see text for details.
[r] Re-sample from the original sample of Merriman et al. (2009).
[o] Sample with organic carbon.
[P] Preferred values from GEOREM; URL: http://georem.mpch-mainz.gwdg.de/.

Table 2
Lithium concentrations and Li, Sr and Nd isotopic compositions for whole rock samples from the three basins.

Sample	KI[M]	Li	Li[M]	δ^7Li	Sr	Rb	$^{87}Rb/^{86}Sr$	$^{87}Sr/^{86}Sr$	$^{87}Sr/^{86}Sr_{(i)}$	Sm	Nd	$^{147}Sm/^{144}Nd$	$^{143}Nd/^{144}Nd$	$\varepsilon_{Nd(i)}$
Southern Lake District														
SH19	0.29	52	46	−1.4										
SH22	0.29	50	45	−0.5	47	162	10.1	0.77792	0.71311	7.13	38.3	0.114	0.51195	−8.6
SH24[o]	0.27	40	41	0.0	41	177	12.6	0.79914	0.71830	3.15	13.6	0.141	0.51203	−8.6
SH59	0.33	51	48	−0.6										
LC940	0.26	41	38	−0.4	135	104	2.2	0.72899	0.71468	7.44	39.1	0.116	0.51201	−7.6
LC1617[o]	0.45	51	46	−0.6										
LC1606[r,o]	0.34	53	56	−0.4										
LC1570[r,o]	0.40	55	43	−1.4	1179	85	0.2	0.70914	0.70780	6.87	34.0	0.124	0.51202	−8.0
LC1618[r,o]	0.66	93	65	−3.4	565	131	0.7	0.71225	0.70795	6.58	38.6	0.104	0.51199	−7.4
Northern Lake District														
LC142	0.32	80	67	−3.5										
LC199[o]	0.22	137	129	−1.8	136	189	4.0	0.74046	0.71459	8.26	43.8	0.114	0.51193	−9.2
LC348	0.20	56	50	−3.2	55	237	12.5	0.79018	0.71037	9.11	48.2	0.116	0.51195	−8.8
LC434	0.51	108	116	−3.8										
LC507	0.46	90	86	−3.7	81	114	4.1	0.73956	0.71355	6.28	34.3	0.112	0.51196	−8.3
LC521[r]	0.39	139	118	−4.0	134	161	3.5	0.73553	0.71318	7.89	42.5	0.117	0.51194	−9.1
LC495[r]	0.63	69	138	−3.7										
LC482[r]	0.40	139	130	−2.2										
Southern Uplands														
BRS882	0.28	54	46	1.0	135	165	3.5	0.73675	0.71413	7.64	39.8	0.121	0.51207	−6.6
BRS1028	0.44	68	70	−2.4	101	175	5.0	0.74419	0.71212	6.61	34.9	0.116	0.51207	−6.5
BRS822[r]	0.37	74	60	−4.4	66	213	9.3	0.76776	0.70811	11.43	63.7	0.109	0.51199	−7.6
BRS781[r]	0.20	55	42	1.6										
BRS879[r]	0.29	47	37	2.1	55	227	12.0	0.78527	0.70831	3.75	10.7	0.213	0.51235	−6.7
BRS753[r]	0.32	49	45	2.2										
BRS742[r,o]	0.45	46	45	0.3	100	121	3.5	0.74172	0.71918	6.76	36.2	0.116	0.51204	−7.0
BRS710[r,o]	0.50	29	43	0.7	74	80	4.9	0.72714	0.69570	5.32	26.8	0.121	0.51211	−6.0
BRS807[r]	0.22	55	52	−1.3	148	109	3.4	0.72812	0.70628	3.86	19.1	0.126	0.51201	−8.2
BRS824[r]	0.23	56	50	0.6										
BRS829[r,o]	0.48	31	43	3.7	41	184	13.1	0.79284	0.70875	7.61	40.2	0.116	0.51198	−8.2
BRS790[r]	0.20	40	43	1.3	224	133	1.7	0.72085	0.70983	7.52	40.9	0.112	0.51203	−7.0
BHVO-1 and BCR-1														
BHVO-1													0.51305	
BHVO-1[P]													0.51298	
BCR-1		12.6 ± 0.6	2.0 ± 0.3											
BCR-1[P]		13	1.8											

KI: Kübler index.

i: initial value, assuming depositional age of sediments are 450 Ma; $^{143}Nd/^{144}Nd_{chur(0)} = 0.512638$.

[M] Merriman et al. (2009).

[r] Re-sample from the original sample of Merriman et al. (2009).

[o] Sample with organic carbon.

[P] Preferred values from GEOREM; URL: http://georem.mpch-mainz.gwdg.de/.

139 ppm, average 102 ppm) than those from the Southern Uplands (28–74 ppm, average 50 ppm) or southern Lake District (40–93 ppm, average 52 ppm) basins. There is no correlation between [Li] and metamorphic grade within a given basin, as indicated by KI (Fig. 2a). The only possible exception to this is for the mudrocks from the southern Lake District basin (Fig. 2a), but the trend in these data is defined by a single sample with a high [Li].

Lithium isotopic compositions (Fig. 2b) of mudrocks from the northern Lake District (average $\delta^7Li = -3.2 \pm 1.1$, 1σ) are relatively constant and low compared to those of the mudrocks from the southern Lake District (−3.4 to 0, average = -1 ± 1, 1σ) and the Southern Uplands (−4.4 to +3.7, average = $+0.5 \pm 2.2$, 1σ), the latter of which contain the volcanic arc detritus and show the greatest variation in δ^7Li of all basins. There is no correlation between δ^7Li and metamorphic grade (Fig. 2b).

4.2. Chemical Index of Alteration (CIA) and Loss on Ignition (LOI)

The Chemical Index of Alteration (CIA) is a useful means by which to quantify the intensity of weathering (Nesbitt and Young, 1982). The index is calculated using molar proportions of major oxides: $CIA = Al_2O_3/(Al_2O_3 + CaO^* + Na_2O + K_2O)$, where CaO^* is the amount of Ca incorpo-

rated in the silicate fraction of the rock. Correction for Ca in apatite is done on the basis of the P_2O_5 concentration. Correction for Ca in carbonate is generally done on the basis of CO_2 concentrations. Due to the lack of CO_2 concentration data for our samples, only Ca in apatite corrections were carried out for samples that have $CaO/Na_2O < 1$. If $CaO/Na_2O > 1$, it was assumed that the concentration of silicate CaO equals that of Na_2O and that the other CaO is from $CaCO_3$ (Bock et al., 1998). In general, the higher the CIA, the more intense the weathering; a value of 40–60 is defined as "low weathering"; 60–80 as "intermediate weathering", and 80–100 as "heavy weathering" (Nesbitt and Young, 1982).

The CIA of most samples from the Southern Uplands and southern Lake District is between 61 and 75 (Fig. 3), indicating an intermediate degree of weathering in the source region. A single sample from the Southern Uplands has a low CIA (57), indicating a low degree of weathering. Northern Lake District mudrocks have the highest CIA values of 79–85, indicating a high degree of weathering of their source rocks. Lithium concentrations generally increase with CIA value (Fig. 3a). The correlation between
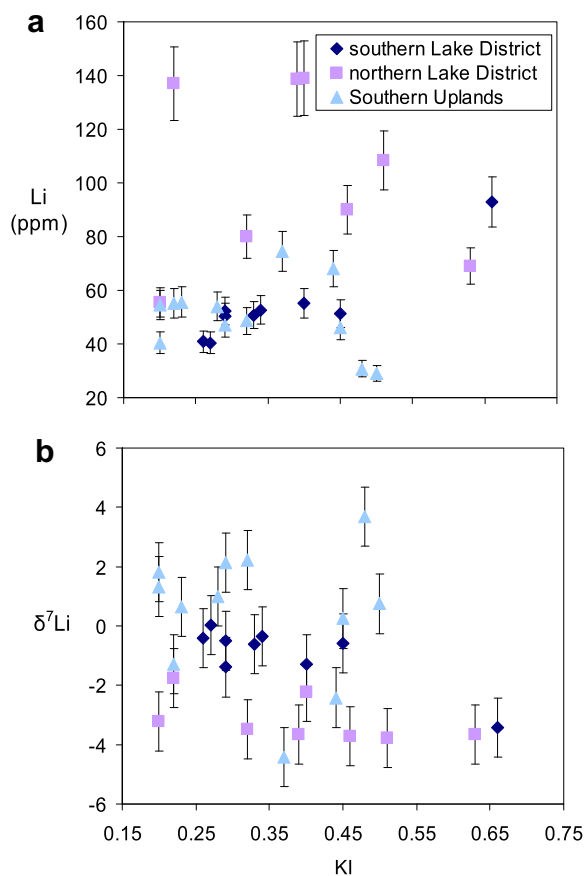
Fig. 2. Plots of Li concentration (a) and δ^7Li (b) versus KI value (Kübler index) for mudrocks from the three Caledonian basins.
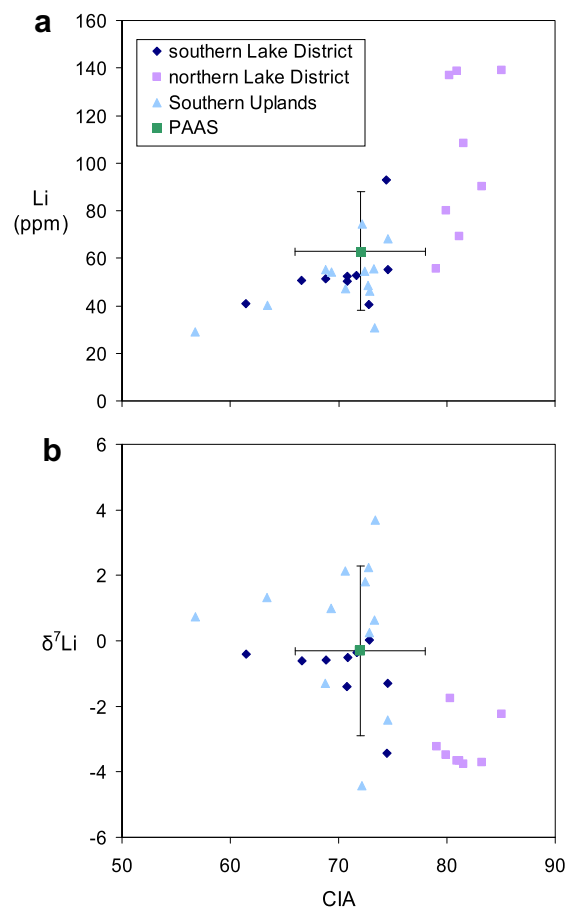
Fig. 3. Plots of Li concentration [Li] (a) and δ^7Li (b) versus CIA (Chemical Index of Alteration) for mudrocks from the three Caledonian basins. PAAS: Post Archean Australian Shales. Average [Li] and δ^7Li of PAAS is from Teng et al. (2004), showing 1σ of the average.

δ7Li and CIA is not strong, though mudrocks with the highest CIA values generally have the lowest δ7Li (Fig. 3b).

Relative H_2O loss by metamorphic dehydration can be estimated by comparing LOI (loss on ignition, which approximates rock volatile content, mainly $H_2O + CO_2$) contents in the samples (Teng et al., 2007). In order to estimate the H_2O component of the LOI, CO_2 values are subtracted using the same method applied to the CIA correction by calculating $CaCO_3$ based on CaO/NaO. One exception is sample LC1570, which has the highest volatile content, abnormally low SiO_2 and high CaO (Table 1). Because these compositional characteristics indicate that this sample has a large carbonate content, it was not included in the LOI study. Generally speaking, LOI* (Table 1) shows a positive trend with KI value (Fig. 4, except for the sample with the highest LOI*); LOI* changes by a factor of ~3 in northern Lake District samples and by a factor of 1.3–1.6 in samples from the other two basins. Thus, with increasing metamorphic grade, the H_2O content in the samples decreases.

4.3. Trace elements

REE, Th, Sc are useful elements for determining the proportion of mafic to felsic igneous rocks in the provenance of clastic sedimentary rocks (McLennan et al., 1993a; Asiedu et al., 2000), since they include both incompatible elements (LREE, Th) and compatible elements (Sc), whose concentrations are not significantly affected by weathering, transport and diagenesis. Concentrations of these elements in clastic sedimentary rocks are, thus, also useful for determining the average composition of the upper continental crust (Taylor and McLennan, 1985; Rudnick and Gao, 2003).

On chondrite-normalized REE diagrams (Fig. 5), all of the samples from the northern Lake District and most of the samples from the southern Lake District exhibit LREE

enrichment and a relatively narrow range of $(La/Yb)_n$: 9.9–15.9, which is similar to post-Archean Australian shale (9.3 for PAAS; Taylor and McLennan, 1985). One sample from the southern Lake District (SH24) has a low $(La/Yb)_n$ of 3.2. In contrast, the REE patterns of Southern Uplands mudrocks are more variable $((La/Yb)_n = 1.1–16.8)$, including one sample that has a LREE depleted pattern.

Mudrocks from the northern Lake District have consistent Th/La of 0.29–0.33 relative to the other two basins, and an average value of 0.31 ± 0.01 (1σ) that is slightly lower than that of PAAS (Th/La = 0.35). Southern Lake District mudrocks have Th/La mostly between 0.23 and 0.31, with one sample (the same one that had a different REE pattern, SH24) having a distinctly higher Th/La of 1.0. As with their REE patterns, the Southern Uplands mudrocks have highly variable Th/La of 0.16–2.7.

Fig. 4. Plot of LOI* (loss on ignition) and KI value (Kübler index) for three Caledonian basins. LOI* reflects water content only after removing CO_2 content, see text for details. Correlation coefficients for the data from the three basins are as follows: 0.45 for southern Lake District, 0.82 for northern Lake District (excluding the sample with the highest LOI that clearly deviates from the trend) and 0.61 for Southern Uplands.
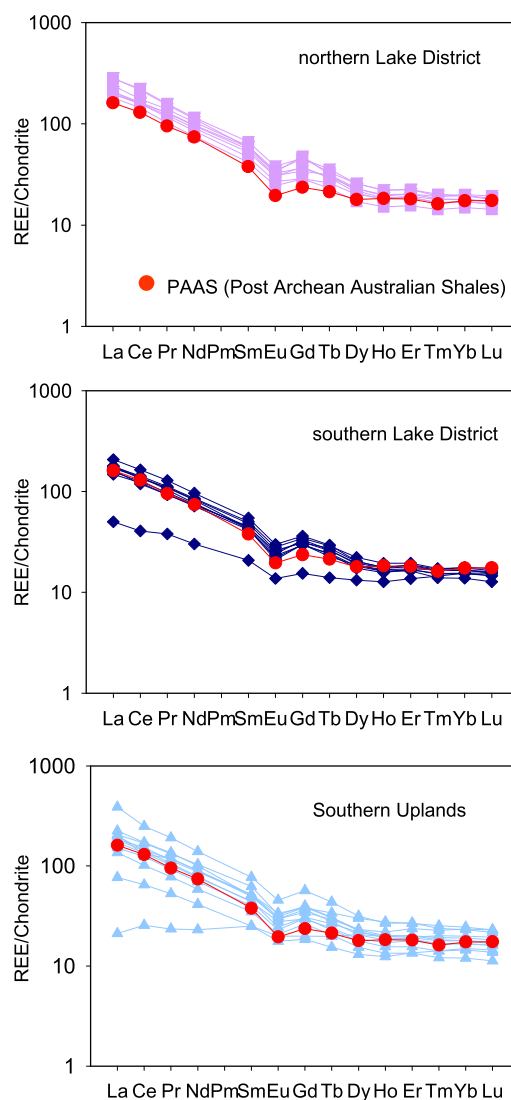

Fig. 5. Chondrite normalized rare earth element plot for mudrock samples from the three Caledonian basins. Chondrite normalization values are from Sun and McDonough (1989). PAAS value (Post Archean Australian Shales) is from Taylor and McLennan (1985).

The Th/Sc ratios of all mudrocks studied here are, in general, lower than that of PAAS. Amongst the different basins, the northern Lake District mudrocks have the highest average Th/Sc (Th/Sc = 0.76 ± 0.11, 1σ), which is closer to the value of PAAS (Th/Sc = 0.9) than the average Th/Sc of mudrocks from the other two basins (southern Lake District: Th/Sc = 0.66 ± 0.07, 1σ; Southern Uplands: Th/Sc = 0.58 ± 0.06, 1σ).

Th/U ratio can also be an indicator of weathering intensity of the sediment source (McLennan et al., 1993a). Mudrocks from the northern Lake District have higher average Th/U ratio (6.1 ± 0.6, 1σ) than those from the southern Lake District (4.4 ± 0.7, 1σ) and Southern Uplands (4.2 ± 0.5, 1σ).

The ferromagnesian trace elements, Ni and Cr, are generally abundant in mafic and ultramafic rocks relative to felsic rocks, so their abundance in sedimentary rocks may be indicative of the provenance of the sediments (McLennan et al., 1993b). In the British Caledonides mudrocks, Ni and Cr are positively correlated (Fig. 6), with the northern Lake District samples having the lowest average concentrations (average = 44 and 145 ppm, respectively) and the Southern Uplands samples having the highest average concentrations (93 and 218 ppm, respectively), with the samples from the southern Lake District falling in between (79 and 166 ppm, respectively).

4.4. Sr and Nd isotopes

Samples chosen for Nd and Sr isotope analyses are representative of the three basins and include samples with suspected mantle-derived signatures based on their trace-element abundances as well as the presence of volcanic arc detritus; the average [Li] and δ^7Li of the selected rocks are similar to the average value of all the samples within the basin. The Nd and Sr isotopic compositions of sediments reflects the average provenance age (McCulloch et al., 1987; McLennan et al., 1993b). These mudrocks are marine
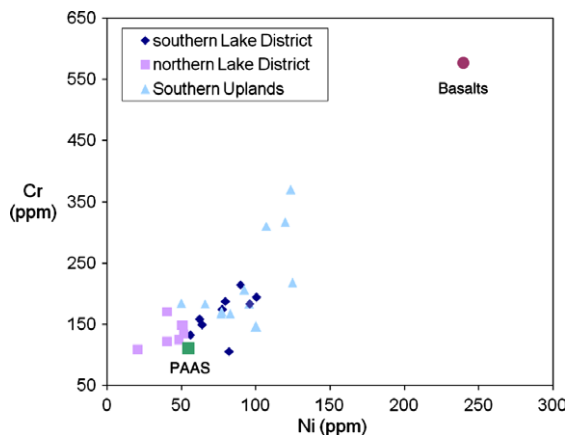
sediments deposited during the Ordovician to Silurian. Initial Sr and Nd isotope ratios are therefore calculated assuming an average depositional age of 450 Ma (Fig. 7). Although the Rb–Sr regression lines (Fig. 8) have a large variation in MSWD, the ages corresponding to the regression lines range from 423 ± 33 Ma to 494 ± 60 Ma and therefore the ∼450 Ma age is consistent with the interpreted depositional age. Initial ε_{Nd} values for the three basins (Table 2) show a general increase from the northern Lake District (average = −8.8 ± 0.4, 1σ) to southern Lake District (average = −8.0 ± 0.4, 1σ) to Southern Uplands (average = −7.0 ± 0.8, 1σ).

5. DISCUSSION

5.1. Effects of metamorphism on Li

Lithium is a fluid-mobile element whose partitioning behavior between fluid and rock ($^{fluid/rock}K_{Li}$) varies as a function of temperature; $^{fluid/rock}K_{Li}$ is always greater than 1, and increases with increasing temperature (Seyfried et al., 1998). This means that Li concentrations in mudrocks are expected to decrease with increasing metamorphic grade, since dehydration reactions dominate in metapelites from sub-greenschist through granulite-facies metamorphism. On the basis of petrologic and thermobarometric studies, Marschall et al. (2007) suggested that, depending on the initial H_2O content, between 5% and 40% of the original Li can be lost from rocks during metamorphic dehydration. Teng et al. (2007) showed that about 50% of Li was lost from regional chlorite-zone metapelites during contact metamorphism up to sillimanite zone. The correlation between LOI and KI of our samples (Fig. 4) indicates that up to 50% of the original H_2O has been lost during sub-greenschist-facies metamorphism ranging from diagenesis to epizone (90–300 °C, Hower, 1976; Kisch, 1983; Frey and Robinson, 1999). However, [Li] in the mudrocks (Fig. 2a) does not change systematically over this interval, indicating that Li is not progressively lost under conditions of sub-greenschist facies metamorphism. Lithium isotopic
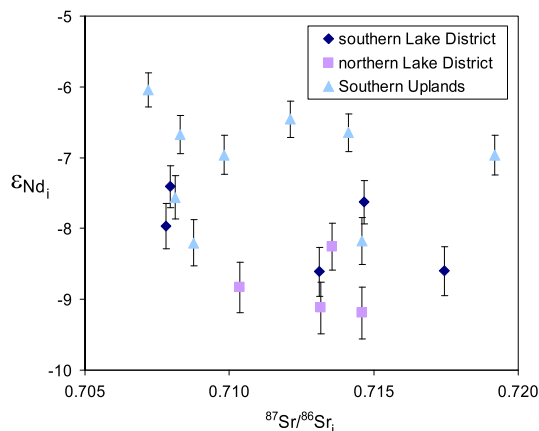

Fig. 6. Plot of Ni versus Cr concentration for mudrocks from three Caledonian basins. The Ni and Cr contents of PAAS are from Taylor and McLennan (1985) and island arc basalts are from Kelemen et al. (2003), standard deviations for these estimates are not available. The mudrock data have a correlation coefficient of 0.70.

Fig. 7. Plot of initial $^{87}Sr/^{86}Sr$ and initial ε_{Nd}, assuming that the depositional age of the sediments is 450 Ma and $^{143}Nd/^{144}Nd_{chur(0)}$ = 0.512638.
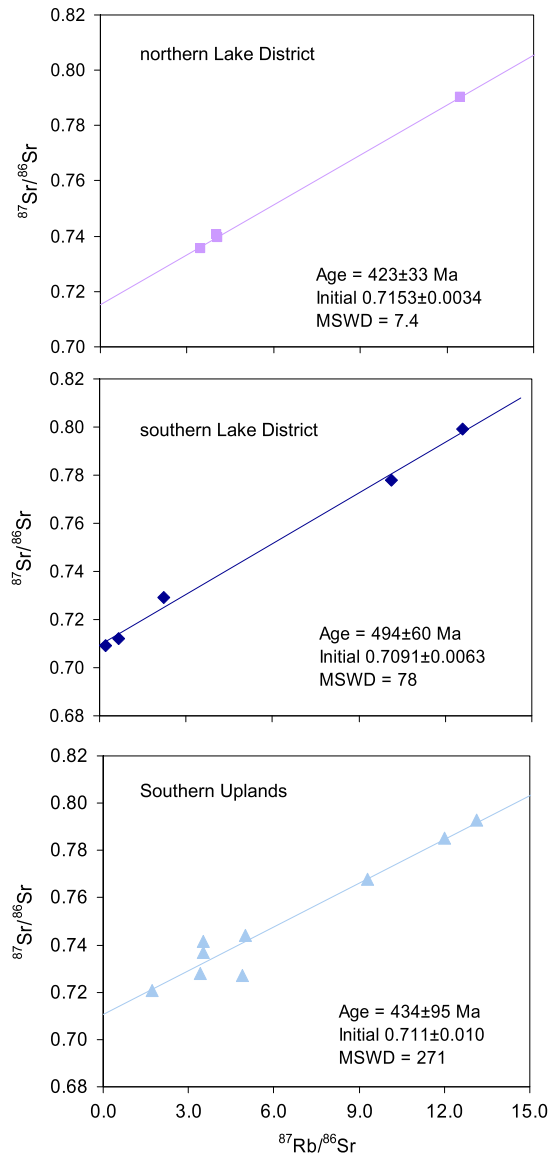
Fig. 8. Plots of Rb–Sr pseudo-isochron regression lines for mudrocks from three Caledonian basins. Note the MSWD value increases from the northern Lake District to the southern Lake District and to Southern Uplands. See text for details.

compositions also do not show a correlation with metamorphic grade in the sub-greenschist facies (Fig. 2b). This relatively stable lithium signature during prograde metamorphism probably reflects Li sorption onto clay minerals, which are relatively abundant in all of the mudrocks investigated here (Merriman, 2006).

5.2. Factors controlling lithium signature in mudrocks: provenance of sediments

The above observations suggest that variations in [Li] and δ^7Li are not directly influenced by sub-greenschist facies metamorphism. In fact, the relationship between concentration and isotopic composition shows the opposite trend to what would be expected if metamorphism had

caused Li loss and lighter isotopic composition via metamorphic dehydration. More specifically, increasing [Li] is correlated with lighter isotopic compositions (Fig. 9). The correlation shows a much larger range than the PAAS composite, which has average δ^7Li = −0.3 ± 2.6‰ (1σ), and [Li] = 63 ± 25 ppm (1σ) (Teng et al., 2004). We propose that the correlation in Fig. 9 may reflect differences in the provenance of the mudrocks.

A variety of compatible and incompatible elements and their ratios, as well as Nd isotope compositions, have proven useful for deducing the nature of the provenance for fine-grained sedimentary rocks (Taylor and McLennan, 1985; McLennan et al., 1993a, and references therein). Here we use the REE patterns, Th/Sc, La/Th, Th/U, Cr and Ni concentrations and Nd isotopes to unravel the proportion of felsic to mafic crust in the source region of the mudrocks. The results are summarized in Table 3 and discussed below.

In general, mafic rocks contain low LREE/HREE ratios, whereas felsic rocks usually contain higher LREE/ HREE ratios (Taylor and McLennan, 1985). One sample from the southern Lake District and three samples from the Southern Uplands have low (La/Yb)$_n$ relative to PAAS (Fig. 5), suggesting a higher proportion of mafic rocks in their source regions. REE patterns of the other samples assessed here resemble that of PAAS, indicative of an average upper continental crustal source.

The source difference is also reflected by Th, Sc, Ni, Cr signatures. During igneous differentiation, Th is incompatible and, therefore, is expected to be abundant in felsic crust, whereas Sc, which is compatible, is expected to be abundant in mafic crust (Taylor and McLennan, 1985). The increasing average ratio of Th/Sc from Southern Uplands (0.58) to southern Lake District (0.66) and northern Lake District (0.78) indicates that the provenances of these
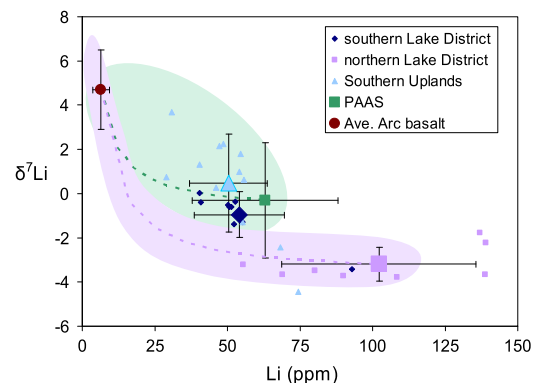

Fig. 9. Two end-member mixing trends between average basaltic arc lava and either PAAS (light green) or average northern Lake District mudrock (light purple). Basaltic arc lavas have [Li] = 6.5 ± 2.9 (1σ) ppm and δ^7Li = 4.7 ± 1.8‰ (1σ), whereas PAAS has 63 ± 25 (1σ) ppm Li and δ^7Li = −0.3 ± 2.6‰ (1σ) and northern Lake District has 102 ± 33 (1σ) ppm Li and δ^7Li = −3 ± 1‰ (1σ). Large solid symbols for each of the three basins show the average and 1σ for the samples from each basin. The dashed lines are mixing trends between the two end members, whereas the fields incorporate 1σ uncertainties in the averages. See text for further details. (For interpretation of color mentioned in this figure the reader is referred to the web version of the article.)

Table 3
Compositional characteristics used to infer provenance for the mudrocks.

Indicators	Felsic	Mafic	northern Lake District	southern Lake District	Southern Uplands
La/Yb	High	Low	High	Variable	Variable
Th/Sc	High	Low	High	Intermediate	Low
Th/La	High	Low	High	Variable	Variable
Ni, Cr (ppm)	Low	High	Low	Intermediate	High
ε_{Nd}	Low	High	Low	Intermediate	High

Felsic source indicates the provenance includes a PAAS-like component; mafic source indicates an arc volcanic rock component.

sediments change from relatively mafic to relatively felsic crust that approaches the PAAS value (0.9).

Another ratio that may discriminate mafic from felsic sources is Th/La ratio, which is high in the upper continental crust (0.25–0.35, Rudnick and Gao, 2003 and references therein), low in intraplate and mid-ocean ridge basalts (<0.1, Sun and McDonough, 1989) and highly variable in arc basalts (0.06–0.6), reflecting the variable amount of subducted sediments in their sources (Plank, 2005). Mudrocks from the northern Lake District have fairly constant Th/La at about (0.29–0.33), which is close to the value for PAAS (0.35, Taylor and McLennan, 1985) and overlaps that of the upper continental crust. This consistency in Th/La of the northern Lake District mudrocks suggests their derivation from well-homogenized upper continental crust, possibly pre-existing mudrocks. By contrast, the large variation in Th/La of Southern Uplands (0.15–2.5) and southern Lake District mudrocks (0.23–1) indicates a heterogeneous source of sediments, which likely includes arc volcanic rocks.

The compatible elements Cr and Ni are especially sensitive to the proportion of mafic to ultramafic rocks in a sedimentary source region. The northern Lake District has lower Cr and Ni contents (Fig. 6) than the other two basins, and average concentrations (Cr = 145, Ni = 44) close to those of PAAS (Cr = 110, Ni = 55, Taylor and McLennan, 1985). The Southern Uplands and southern Lake District mudrocks have a larger range of Cr and Ni contents, and the concentrations are much higher than northern Lake District (up to Cr = 369 and Ni = 124), which is close to the concentrations in island arc basalts (Cr = 576, Ni = 240, Kelemen et al., 2003). The Ni and Cr signature also indicates that the Southern Uplands and southern Lake District have a significant proportion of mafic rocks in their provenance, but the northern Lake District has a provenance similar to that of PAAS. The Southern Uplands samples contain volcanic detritus, including unaltered pyroxene, attributed to an eroded volcanic arc (Merriman et al., 2009), which is consistent with a greater proportion of mafic rocks in their source region. Recycling of this volcanic detritus into the southern Lake District basin may have occurred during the uplift and erosion of the Southern Uplands terrane (Stone et al., 1987).

Mantle versus older crustal sources can also be distinguished by their distinctive Nd isotopic ratios (Figs. 7 and 8). Old continental crust is typically characterized by $\varepsilon_{Nd} < -6$ (McCulloch and Wasserburg, 1978), and juvenile crust has $\varepsilon_{Nd} > +5$ (DePaolo et al., 1991; Kelemen et al., 2003). From the Southern Uplands, to the southern Lake

District to the northern Lake District, the average value of initial ε_{Nd} decreases slightly from ~ -7 to ~ -9, reflecting increasingly older components in their provenances.

5.3. Mixing model for lithium

As discussed above, the provenance of these three basin sediments include mafic juvenile sources, and older, more felsic, upper continental crust sources. Southern Uplands and southern Lake District samples contain both of these components, whereas the northern Lake District appears to have a more homogeneous provenance similar to upper continental crust material, like PAAS, but with higher [Li] and lower δ^7Li. Basaltic arc lavas have [Li] = 6.5 ± 2.9 ppm (1σ) and δ^7Li = 4.7 ± 1.8‰ (1σ) (based on 65 samples, Moriguti and Nakamura, 1998; Chan et al., 2002; Tomascak et al., 2002; Moriguti et al., 2004; Magna et al., 2006), whereas PAAS has [Li] = 63 ± 25 ppm (1σ) and δ^7Li = −0.3 ± 2.6‰ (1σ) (Teng et al., 2004). Mixing between average basaltic arc lava and PAAS reproduces most of the range seen in the majority of Southern Uplands and southern Lake District samples, albeit with slightly different mixing proportions (the Southern Uplands samples have a greater proportion of the arc component, Fig. 9). By contrast, the three samples in these two basins with high [Li] may be a mixture between an arc lava component and the average northern Lake District mudrocks (Fig. 9). However, the majority of the Southern Uplands and southern Lake District samples do not fall on the mixing array between arc basalt and the northern Lake District average composition. This indicates there are likely different mixing end members applying to different samples in the southern Lake District and Southern Uplands basins.

5.4. Lithium: a useful indicator of weathering

Weathering of continental crust produces light lithium isotopic compositions (Chan and Edmond, 1988; Huh et al., 2004; Rudnick et al., 2004). Based on the observation that the upper continental crust is characterized by lower δ^7Li values of 0 ± 2‰ (1σ, Teng et al., 2004) than upper mantle derived MORB (4 ± 2‰, 1σ, Chan et al., 1992; Moriguti and Nakamura, 1998; Elliott et al., 2006; Nishio et al., 2007; Tomascak et al., 2008), Teng et al. (2004) suggested that the isotopically light signature of the upper continental crust is due to weathering processes, which preferentially remove heavy lithium to water. River water and ocean water have heavy lithium isotopic compositions (ocean water: δ^7Li = 31‰, Chan and Edmond, 1988; You

and Chan, 1996), and residues of intense crustal weathering, such as saprolites, have very light isotopic composition (δ^7Li down to $-20\%_0$, Rudnick et al., 2004).

Besides the Chemical Index of Alteration (Section 4.2), the Th/U ratio also reflects the different weathering intensity of the provenances. In an oxidized environment, U is more fluid-mobile than Th, and will be preferentially removed from rocks by weathering, resulting in elevated Th/U in highly weathered domains (McLennan et al., 1993b). Estimates of the average Th/U ratio of the upper continental crust range from 3.8 to 4.3 (Taylor and McLennan, 1985; Rudnick and Gao, 2003), whereas the ratio for mantle rocks varies from 2.6 to 3.8 (Paul et al., 2003). McLennan et al. (1993a,b) suggested sedimentary rocks characterized by Th/U greater than that of PAAS (Th/U = 4.7) have been influenced by weathering processes. All of the northern Lake District samples have Th/U > 5.2, whereas only two samples from the southern Lake District and two samples from the Southern Uplands have Th/U greater than 4.7. Th/U of the mudrocks from the three basins show a positive correlation with CIA (Fig. 10), and therefore like CIA, Th/U also shows a positive correlation with [Li] and negative correlation with δ^7Li (Fig. 11). According to these signatures, the northern Lake District samples are clearly derived from a more highly weathered provenance compared to samples from the other basins.

Lithium concentrations generally increase and δ^7Li values decrease with higher CIA (Fig. 3). Although the northern Lake District mudrocks exhibit consistently low δ^7Li (down to -3.8), consistent with significant weathering, the Li abundances of these samples are actually enriched relative to PAAS, counter to what is expected from a weathered provenance. The high [Li] in these samples is likely due to an abundance and wide variety of clay minerals, including Na-bearing species in these samples (Merriman, 2006). Thus, although the northern Lake District mudrocks derived from a highly weathered source that has preferentially

Fig. 11. Plots of [Li] (a) and δ^7Li (b) versus Th/U, respectively. CIA, [Li] and [δ^7Li] of PAAS is from Teng et al. (2004). Th/U of PAAS is from Taylor and McLennan (1985).

lost ^{7}Li during weathering process, the concentration of Li is elevated by the abundance of clay minerals.

During clay mineral formation process, Li likely substitutes for Mg^{2+} in the octahedral sites in the crystal lattice (Williams and Hervig, 2005; Vigier et al., 2008). This process may be responsible for higher lithium concentration in the mudrocks of the northern Lake District. A way of evaluating the relative clay mineral proportion is through an A–CN–K ternary plot (Al_2O_3–CaO + Na_2O–K_2O); the closer to the Al_2O_3 apex, the higher the clay mineral proportions in the samples (Nesbitt and Young, 1984) (Fig. 12). The first stage of weathering on this type of diagram is represented by the lower arrow in Fig. 12, radiating away from the CaO + Na_2O apex, resulting in the depletion of CaO and Na_2O in primary minerals such as feldspars or pyroxenes. Later stages of weathering produce clays that are enriched in Al_2O_3 by removing K_2O and forming Al-rich clay minerals such as kaolinite and halloysite (upper arrow, Wollast and Chou, 1992). Southern Lake District and Southern Uplands mudrocks fall on the first stage of this weathering trend, whereas northern Lake District mudrocks fall on the second stage of the weathering trend, which indicates higher degrees of weathering, significant clay mineral formation and possibly multiple cycles of sedimentation in the northern Lake District samples. Therefore, the high lithium concentration in the northern Lake District basin likely reflects the high modal proportions of clay minerals.
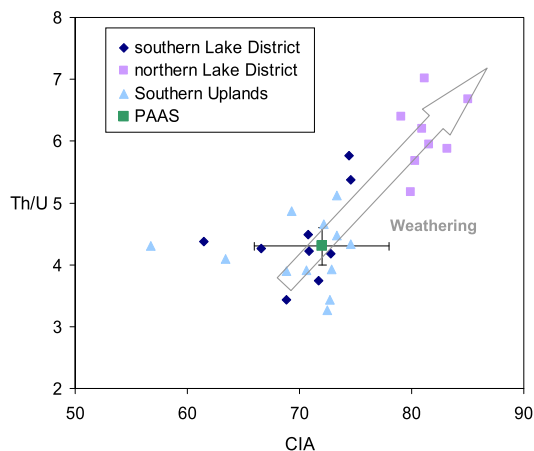
Fig. 10. Plot of Th/U versus CIA value (Chemical Index of Alteration). Open arrow indicates the direction of increased weathering. Th/U of PAAS is from Taylor and McLennan (1985). CIA of PAAS is from Teng et al. (2004). See text for discussion.
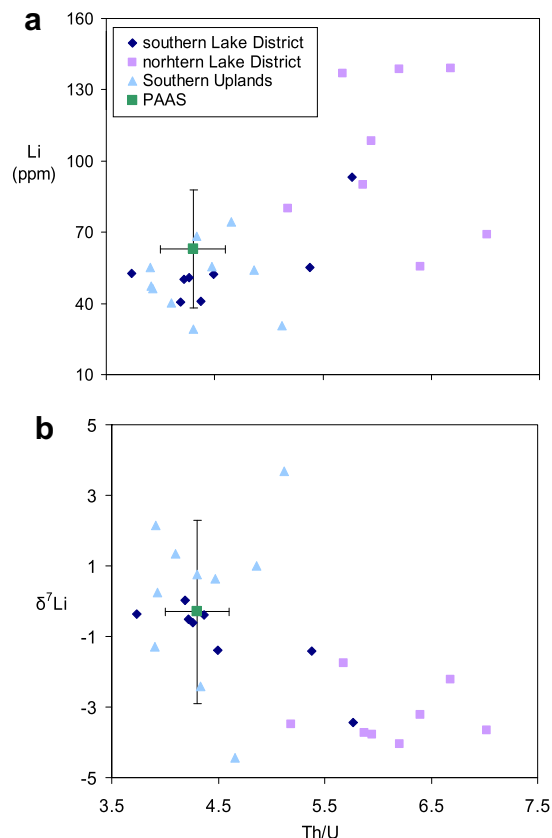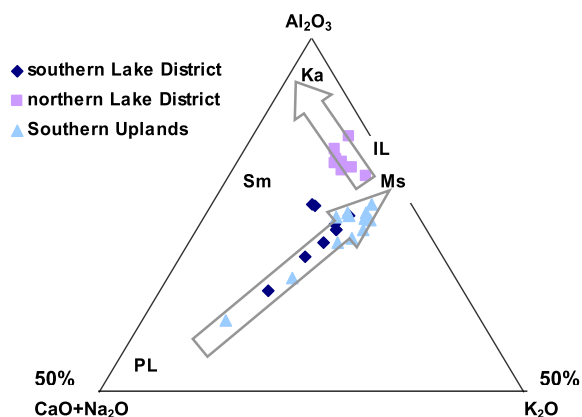
Fig. 12. The Al_2O_3–($CaO^* + Na_2O$)–K_2O (A–CN–K) ternary diagram for mudrocks from the three basins (after Nesbitt and Young, 1984). Open arrows are plotted according to Wollast and Chou (1992). See Sections 4.2 and 5.4 for details. Abbreviations mark position on plot for the following minerals: Pl – plagioclase feldspar; Sm – smectite; Ms – muscovite; IL – illite; Ka – kaolinite.

In conclusion, Li isotopic compositions, when combined with concentration data, is an indicator of weathering intensity for pelitic sediments; mudrocks with high Li concentrations (over 63 ppm, average of PAAS, Teng et al., 2004) but light isotopic compositions ($<-3\permil$) likely derive from a highly weathered provenance.

6. CONCLUSIONS

Three suites of mudrocks from three lower Paleozoic basins within the British Caledonides exhibit wide variation of lithium concentration and isotopic composition, ranging from 29 to 139 ppm and $-4.4\permil$ to $+3.7\permil$, respectively. [Li] and δ^7Li in the mudrocks do not correlate with sub-greenschist facies metamorphic grade determined by the Kübler index, suggesting little impact of low-grade metamorphism on these variables. CIA values, trace elements, and Nd and Sr isotope data indicate that the provenances of the sediments control the signature of lithium in these three basins. Mudrocks from the Southern Uplands and the southern Lake District reflect a mixed provenance of arc lavas and PAAS-like upper continental crust, whereas mudrocks from the northern Lake District are clay-rich, derived from a highly weathered, older upper continental crust source. The higher [Li] in the mudrocks of the northern Lake District reflects the higher proportions and greater variety of clay minerals in the rocks. Thus, lithium in mudrocks can be used as an indicator of weathering intensity of their source regions.

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