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Foreword

This report is one of the published products of a study by the British Geological Survey (BGS) into the relationships between regional geochemical patterns in bedrock and the stream sediment derived from it, a project led by Dr P Stone. It forms part of an assessment of processes active, under different heat-flow conditions, in Siluro-Ordovician sedimentary basins developed under contrasting tectonic regimes. Data is drawn from the Southern Uplands of Scotland and the Lake District of NW England.

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Summary

Changes in the abundance of ten major and trace elements in mudrock lithologies have been studied in relation to progressive low-grade metamorphism. Analysed mudrock samples represent metapelitic grades ranging from deep diagenetic to epizonal (low greenschist) found in three Lower Palaeozoic basins within the British Caledonides. Mudrocks in the Scottish Southern Uplands were deposited in a trench and deformed in an accretionary complex, and those from the southern Lake District were deposited in a foreland basin; in both basins early burial and metamorphism was characterized by low heat-flow. In contrast, mudrocks from the northern Lake District accumulated in an extensional basin setting characterised by early high heat-flow. When geochemical data from whole-rock and <2μm clay fractions are plotted against the Kübler index of illite 'crystallinity' they show patterns of element mobility generated by progressive metamorphism. Three types of mobility are identified: a) localized grain- or crystal-scale mobility related to fabric-forming reactions; b) basin-scale losses during prograde metamorphism; c) basin-scale mobility associated with hydrothermal processes. Elements Al, K, Cr, Ni and Rb show limited mobility and were conserved in reactions that generated slaty cleavage in the Southern Uplands and southern Lake District mudrocks; prograde reactions also caused 20-70% basin-scale losses of B, Cs and Li in these two terranes. These results show that the formation of slaty cleavage is an important geochemical process. In the northern Lake District the distribution of K, Ba, Rb, Sr and Ni indicate pre-cleavage mobility of these elements related to early, syn-sedimentary hydrothermal activity. Plots of Cr/Ni ratios against grade suggest that this is not a reliable provenance indicator for metapelitic rocks.

1 Introduction

Sedimentary basins represent an early stage in a series of crustal processes that recycle rocks and minerals formed at the Earth's surface, and eventually result in the formation of new crust. The deposits found in sedimentary basins are principally mud, then sand and lesser amounts of calcareous material (Potter et al., 2005). During sedimentary burial, diagenetic and low-grade metamorphic reactions transform soft mud into lithified mudstone and shale. These mudrocks represent a major near-surface repository for organic compounds and for many metals. Large volumes of fluid are trapped and incorporated into the clay minerals that constitute the main mineral component of mudrocks. These fluids are progressively expelled during the evolution of sedimentary basins, initially by compactional de-watering and subsequently by diagenetic and metamorphic reactions involving clay minerals. Such fluids are the main vehicle for the recycling of major and trace elements mobilized during basin maturation and metamorphism. The mineralogical and petrological processes that characterise diagenetic and low-grade metamorphic reactions in sedimentary basins have been widely studied and documented (e.g. Frey and Robinson, 1999; Worden and Morad, 2003, and references therein). However, there are only a very few accounts of the changes in geochemistry that accompany progressive diagenetic and low-grade metamorphic reactions in mudrocks (e.g. Hannigan and Basu, 1998; Teng et al., 2007). The work presented here focuses on the mobility of elements associated with clay mineral reactions in mudrock lithologies. We have analysed mudrock samples from three Lower Palaeozoic basins with contrasting tectono-stratigraphical histories, all within the British Caledonides, in order to compare the effects of different heat flow regimes. Two of the basins, in southern Scotland and the southern Lake District, evolved in convergent plate settings characterised by low heat flow, but with different tectonic mechanisms. The third basin, in the northern Lake District, developed in an extensional setting where heat flow was relatively high.

2 Geological Background

The Ordovician to Silurian sedimentary basins considered in this paper are now juxtaposed across the Iapetus Suture, the structural trace within the British paratectonic Caledonides of the early Palaeozoic Iapetus Ocean (Fig. 1). A range of depositional environments is represented by the superficially similar turbidite-dominated, but mudrock-rich, sequences that filled the basins. In the northern Lake District the Skiddaw Group sedimentary basin (Cooper *et al.*, 1995, 2004; Stone *et al.*, 1999) developed in an extensional setting as the Iapetus Ocean expanded during the early to mid-Ordovician. Sedimentary basins in the southern Lake District (Windermere Supergroup) and the Southern Uplands terrane evolved largely in response to flexural subsidence of the crust, in convergent plate settings, as the ocean closed during the late Ordovician and early Silurian (Leggett *et al.*, 1979; Stone *et al.*, 1987; Kneller, 1991).

2.1   SOUTHERN UPLANDS

To the south of the Southern Upland Fault, the Southern Uplands terrane formed as an accretionary thrust complex at the Laurentian continental margin during the late Ordovician to mid-Silurian by northward subduction of the Iapetus Ocean. It has been widely interpreted as a forearc, supra-subduction zone prism (Leggett *et al.*, 1979; Leggett, 1987) although the northern (Ordovician) part has also been interpreted as a subsiding-shelf sequence rather than trench deposits (Armstrong *et al.*, 1996). An alternative proposal envisaged the terrane developing from an Ordovician back-arc setting into a mid-Silurian foreland basin that migrated onto the Avalonian continent following closure of the Iapetus Ocean (Stone *et al.*, 1987; Kneller, 1991: Kneller *et al.*, 1993). A recent evaluation of the Southern Uplands' basin thermal history rules out the back-arc component of this model (Stone and Merriman, 2004), but the eventual evolution into a foreland basin remains likely and has been linked with basin development in the southern Lake District as discussed below.

The structural configuration of the Southern Uplands accretionary complex is dominated by a sequence of southward propagating imbricate thrusts separating tracts of steeply inclined and northeast-striking turbidite-facies strata. Internally the tracts have an overall sense of younging towards the north whereas the minimum age of each tract decreases southwards. This diachronous tectonostratigraphic pattern (summarised by Floyd, 2001) was produced by the sequential incorporation of progressively younger turbidites into the thrust front; for detailed discussions of the phenomenon see Rushton *et al.* (1996) and Barnes and Stone (1999). Regional metamorphism in the Southern Uplands is the result of tectonic burial in the thrust stack. Metamorphic grade ranges from late diagenetic to epizonal (low greenschist facies) and was generated under a low geothermal gradient of probably less than 25°C km^{-1} (Merriman and Roberts, 2001). Following regional metamorphism, early Devonian granitic intrusions were emplaced within the thrust stack and represent the only major thermal event to affect the Southern Uplands.

2.2   LAKE DISTRICT

On the south side of the Iapetus Suture, part of the Avalonian continental margin crops out within the Lake District Lower Palaeozoic inlier of the Leinster-Lakesman Terrane (Fig. 1). The oldest stratigraphical component, the Tremadoc to Llanvirn Skiddaw Group (and its equivalent in the Isle of man, the Manx Group), seems likely to have been deposited in an ensialic extensional basin on the southern side of the Iapetus Ocean as the Avalonian microcontinental block rifted from Gondwana (Stone *et al.*, 1999, and references therein). The initiation (or resumption) of subduction at the northern Avalonian margin then caused uplift of the Skiddaw Group basin prior to the mainly Caradoc eruption of the calc-alkaline, supra-subduction zone Borrowdale Volcanic Group.

Cessation of volcanicity and slow thermal subsidence of the volcanic belt during the early Silurian was followed by abruptly accelerating subsidence, initiated during the late Wenlock, as the Iapetus Ocean closed and the Laurentian margin over-rode the Avalonian continent. The overall effect was for the foreland basin originating in the southern sector of the Southern Uplands (Stone *et al.*, 1987) to migrate southwards across the Iapetus Suture and into the

Avalonian hinterland (Kneller, 1991; Kneller *et al.*, 1993); hence the rapid acceleration of deposition rate in the Ludlow part of the Windermere Supergroup. However, the foreland thrust belt did not progress further south and during its later history the by-then static Windermere Supergroup basin filled. A period of regional transtension followed before the basin fill was deformed during the mid-Devonian Acadian Orogeny (Soper and Woodcock, 2003).

Its varied geological history allows two contrasting settings of low-grade metamorphism to be juxtaposed in the Lake District. In the north, early burial metamorphism of the Skiddaw Group took place at a higher than normal geothermal gradient, perhaps in the range 35-50°Ckm^{-1} by analogy with the similarly extensional Welsh Basin (Bevins and Merriman, 1988; Bottrell *et al.*, 1990). The elevated gradient was related primarily to high heat flow in the extensional regime that culminated in volcanism and granitic batholith emplacement (Fortey *et al.*, 1993). Subsequent anchizonal to epizonal metamorphism occurred as the extensional basin was inverted and compressed in the Acadian Orogeny. In the southern Lake District, the Windermere Supergroup was metamorphosed under low heat flow conditions of <20°Ckm^{-1} (Soper and Woodcock, 2003). Here, Silurian strata were deeply buried at high sedimentation rates with differences in grade reflecting variations in strain arising from closure and uplift of the foreland basin during the Acadian Orogeny (Merriman and Frey, 1999).

2.3   SAMPLES AND ANALYTICAL TECHNIQUES

Samples from the three Caledonian basins were selected for geochemical analysis from extensive collections of mudrocks previously analysed by X-ray diffraction (XRD) techniques (Table 1). The selection of samples was guided by several criteria. The widest possible range of grades, from deep diagenetic to epizonal (low greenschist facies), was central to the sampling strategy. Ideally such a range would have been sampled from the same stratigraphical horizon, but in all three basins the pattern of regional metamorphism did not allow this. In fact the only setting where this would have been possible is in thermal aureoles but, as noted below, these were avoided. Mudrock homogeneity was a major aim of the sampling. Originally only typical mudrock lithologies were used for the illite 'crystallinity' surveys of metamorphic grade. Such lithologies included mudstone, shale and slate, but excluded siltstones and fine sandstones. For the present study samples were further selected on the basis of the clay mineral assemblages in the <2μm separations. Only samples with white mica and chlorite as the major clay minerals were geochemically analysed. Minor amounts of kaolinite and mixed-layer minerals (including illite-smectite and intermediate K/Na micas) were permitted; unusual clay assemblages, such as those indicative of K-bentonites or palaeosols, were excluded.

Samples from the Scottish Southern Uplands (SU) were chosen from a large collection of mudrocks used to characterise the regional metamorphic history of the terrane (Merriman and Roberts, 2001). With two exceptions (BRS 429, 710; Table 1) the SU samples are from the area surrounding the Moniaive Shear Zone (MSZ), a 5 km-wide zone of ductile deformation extensively exposed between Moniaive and New Galloway (British Geological Survey, 1996; McMillan, 2001). Three samples from within the MSZ (Fig. 1) are at epizonal grade, whereas three samples from the Ordovician rocks (Glenlee Formation) on the northern boundary of the zone represent lower grades (Table 1). Post-shearing downthrow of approximate 4 km on the Orlock Bridge Fault has juxtaposed the non-sheared very low-grade Ordovician mudrocks with the phyllitic epizonal mudrocks of the MSZ along the Orlock Bridge Fault (Merriman and Roberts, 2001). The Silurian outcrop forming the non-sheared southern boundary of the MSZ is represented by 4 samples, mostly at anchizonal grade. None of the mudrocks from the area around the MSZ are within the thermal aureole of the Cairnsmore of Fleet intrusion (Fig. 1).

Samples from the Skiddaw Group (SG) were selected from a collection of mudrocks used to study the metamorphic history of the northern Lake District (Fortey, 1989). Since the present study aims to examine the effects of regional metamorphism on element mobility, mudrocks from within the aureole of the Skiddaw granite and the Crummock Water intrusion were avoided. Another collection of mudrocks previously used to characterise regional metamorphic patterns in the southern Lake District (Johnson *et al.*, 2001), provided samples of the Windermere Supergroup (WSG).

Regional differences in clay mineralogy characterise the mudrock samples and these have been related to the contrasting geotectonic settings of the basins where the mudrocks were buried and metamorphosed (Merriman, 2002). In the extensional basin of the northern Lake District and the Isle of Man, clay mineral assemblages are characteristically diverse, and include K- and Na-rich white micas, chlorite, minor pyrophyllite, rectorite and corrensite. In contrast, clay assemblages found in the convergent basins of the Southern Uplands and the southern Lake District generally contain fewer clay mineral species, with Na-micas and pyrophyllite being notably rare or absent. The chemistry of K-white micas also shows differences that can be related to geotectonic setting. Low values of the *b*-cell dimension, indicating an aluminous K-mica with low phengite content, are characteristic of the Skiddaw Group, whereas relatively large *b*-cell dimensions, indicating more phengitic K-micas, are found in the mudrocks of the Southern Uplands and the southern Lake District (Stone and Merriman, 2004).

The whole rock mineralogy of the samples consists of the regionally characteristic clay assemblages noted above, forming the <2μm fractions, with the addition of 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. Chlorite-mica stacks, up to 0.5mm across, are a significant component of some Skiddaw Group samples (Cooper *et al.*, 2004).

All of the analysed samples have been previously characterized by X-ray diffraction (XRD) analysis to determine their clay mineralogy and the Kübler index of illite "crystallinity". Details of the sample preparation and XRD techniques are given in Roberts *et al* (1991) and a review of these techniques is also provided by Merriman and Peacor (1999). The Kübler index (KI in $\Delta°2\theta$) measures small changes in the width at half-height of the illite-muscovite (white-mica) ~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. The reaction leads to a progressive increase in crystal thickness and a decrease in defects, lattice strain and compositional variability as the white micas become crystallographically more ordered (Peacor, 1992). As a result of these changes in crystallography, the half-height width of the 10 Å peak is reduced and the Kübler index decreases as grade increases. The increases in crystal thickness produced by deep burial and metamorphism are generally irreversible, and their preservation in uplifted basinal strata can be used to characterise metamorphic patterns. Changes in the Kübler index are used to define a series of metapelitic zones of diagenesis and very low-grade metamorphism (Merriman and Frey, 1999). With increasing grade these are: deep (or late) diagenetic zone KI>0.42, anchizone KI 0.42-0.25, and epizone KI<0.25.

Whole-rock and clay fraction (<2 μm) samples were analysed in order to identify geochemical mobility associated with clay mineral reactions, but at the same time explore any bulk rock changes that occurred with progressive metamorphism. Ten major and trace elements were determined. These were chosen to study the different scales of mobility (nanometre to kilometre?) that could be expected from clay mineral reactions at deep diagenetic to low-grade metamorphic conditions, spanning a temperature range of approximately 150-300°C (Merriman

and Frey, 1999). Aluminium was expected to show very limited mobility since it is one of the key linking cations that maintains the stability of the 2:1 sheet silicate structure typical of dioctahedral white mica. Potassium is the principal interlayer cation maintaining the charge balance in white mica but is potentially a highly mobile element. Rubidium generally follows K as an interlayer cation in white mica and was expected to show the same pattern of mobility. Uptake of caesium, lithium and boron by clay-rich sediments during early (shallow) diagenesis is regarded as an important sink in the oceanic mass balance of these elements (e.g. James and Palmer, 2000). However since Cs and Li mainly reside in interlayer sites in dioctahedral white mica they are likely to be displaced by K and Rb during prograde metamorphism. Boron is also a potentially highly mobile trace element in clay minerals because of its small ionic radius. In this case B^{3+}, which is generally considered to reside in the tetrahedral sheet of dioctahedral white mica, is likely to be displaced by Al^{3+} (Grew, 1996). Both barium and strontium are likely to be mobilized during clay mineral reactions because their large ionic radii and bivalent state make them unsuitable interlayer cations in mature white mica. While the above elements are mostly associated with typical 2:1 dioctahedral white mica, chromium and nickel are mostly located within the 2:1 trioctahedral sheet silicate structure of chlorite. Both Cr and Ni substitute for Fe in the octahedral sheet of the chlorite structure, but their mobility during reaction progress has not been previously recorded.

2.3.1   Chemical Analysis

Prior to chemical analysis, clay minerals were liberated from jaw-crushed mudrocks by shaking and treatment with ultrasound before sieving on 63 µm to remove 'sand' sized material. Nominal <2 µm fractions were then separated by gravity separation from <63 µm suspensions.

Aluminium, barium, chromium, potassium, lithium, nickel and strontium were determined by ICP-AES following dissolution by mixed acids. Rubidium and caesium were determined by ICP-MS on the same dissolution.

To digest the samples, aliquots of rock powder or clay fraction were accurately weighed into PTFE test tubes and soaked in hydrofluoric acid for a minimum of 48 hours. Subsequently, nitric and perchloric acids were added and the mixture step-heated to 190°C for several hours until dry, thus driving off fluoride and silica. Since this procedure also removed boron as a volatile fluoride, a separate preparation was required for this element. The samples were then reconstituted in dilute nitric acid for analysis. Reference materials and blank samples were similarly prepared for quality control purposes.

The prepared solutions were analysed using an ARL3580 inductively coupled – atomic emission spectrometer (ICP-AES) and a Thermo Excell inductively coupled – plasma mass spectrometer (ICP-MS). The instruments were calibrated with a series of synthetic multi-element solutions and all samples diluted to within this validated calibration range. All samples were analysed under a comprehensive quality control scheme. Values obtained for reference materials dissolved and analysed with the samples were within 15% of the reference values for all elements except chromium. As is characteristic with this method, chromium values were consistently 20% too low, and corrected values are shown in Table 3.

Boron was determined by ICP-MS following solublisation of sodium peroxide fusion.

The sample aliquots of rock powder or clay fraction and the sodium peroxide flux were accurately weighed into carbon crucibles and fused at 480°C for 1 hour to ensure boron was not lost. The fused material was soublised in dilute hydrochloric acid and stored prior to analysis. All preparation equipment was metal- and silicate-free to avoid contamination issues.

Solutions were analysed after dilution using a Thermo Excell inductively coupled – plasma mass spectrometer (ICP-MS). The instrument was calibrated with a series of synthetic multi-element solutions containing sodium peroxide for matrix matching and all samples diluted to within this validated calibration range. All samples were analysed under a comprehensive quality control scheme. The mean values for two reference materials prepared and analysed with the samples were within 12% of the reference value for boron.

3 Geochemistry and metapelitic grade

Comparison between the concentrations found in the whole-rock (WR) samples with those in the <2μm clay fractions (CF) shows that, with the exception of Sr, the analysed elements are generally increased in the clays (Table 2). Al, K and Rb typically show CF/WR ratios of 1.2-2.0, and while Ba also shows similar ratios, a few samples have ratios <1.0. Although B, Cs and Li also show CF/WR ratios typically in the range 1.2-2.0, all three elements show an overall decrease in ratios as metamorphic grade increases; this is discussed and illustrated below. Cr and Ni also generally show increased concentrations in the CFs, although in 4 samples the CF/WR ratios for Ni are <1.0. In contrast, the majority of the Sr data have CF/WR ratios of < 1.0. Overall, the results suggest that, with the exception of Sr, the analysed elements are significantly more abundant in clay minerals forming the <2μm fractions than they are in the silt and fine-sand components of the mudrock samples.

3.1   ALUMINIUM

The homogeneity of the mudrocks was examined by plotting CF/WR Al ratios for all samples against grade (Fig. 2a). The ratios show that aluminium is concentrated by separation of the <2μm fractions, typically by factors of 1.1 to 2.0, and confirm that clay minerals are the main host for Al in the mudrocks. Despite the scatter of data points in Fig 2a there is no systematic variation in the ratios with change in metapelitic grade, as indicated by the Kübler index. This suggests that Al was not significantly enriched or depleted by the changes in grade recorded in these rocks. The main cause of the scatter in Fig. 2a can be largely attributed to variations in the proportions of the dominant minerals in the CFs, Al-rich white mica and Al-poor chlorite.

Plots of CF/WR Al ratios for each of the three basins sampled are also shown in Fig. 2. Al ratios for the SU mudrocks show scatter but no significant variation in relation to metapelitic grade (Fig. 2b). One chlorite-rich sample (BRS 429) shows barely any increase in Al in the CF. In the WSG mudrocks a trend of decreasing CF/WR Al ratios with increasing grade is displayed (Fig. 2c). However, this is largely caused by two very low grade samples (LC 1570 and LC 1618) that have a much greater proportion of white mica to chlorite in their CFs. Al ratios in the SG mudrocks show the least scatter of the three groups of samples, but again no significant variation

with grade (Fig. 2d). These samples generally show the highest CF/WR Al ratios, reflecting the aluminous character of the white mica in the SG mudrocks (Merriman, 2006)

The problem of obtaining a homogeneous suite of mudrock samples is illustrated by the Al data. In spite of careful field sampling of typical mudrock lithologies, it is clear that some samples have significantly higher silt contents with low Al in the WR analyses, whereas others have higher clay contents and show more Al in the WR analyses. The three groups of mudrocks also show regional differences in silt content, with the WSG samples the most silty and the SG samples the most clay-rich (Table 2). Once separated from its WR sample the Al content of the CF no longer reflects silt content but is largely controlled by the proportion of white mica to chlorite. Nevertheless, the Al content appears to be little affected by changes in metapelitic grade and for this reason, in common with some other geochemical studies of metapelites (e.g. Teng et al., 2007), element variations have been considered as ratios against Al.

Element/Al ratios for the <2μm clay fractions (CF) are shown plotted against their Kübler index (KI) in Figures 3-7. Computer drawn retrogressions have been added to illustrate trends in the data distribution. Samples from each of the three basins have been plotted separately to explore element mobility trends in the different geotectonic setting described above. Note that metapelitic grade increases inversely with KI hence the degree of metamorphism increases from right to left in Figs. 3-7.

3.2   POTASSIUM AND RUBIDIUM

Variation in the clay contents of potassium and rubidium in relation to Al are shown in Figure 3. The SU clay fractions show a slight but barely significant trend of increasing K content as grade increases (Fig. 3a). A similar trend is shown by K in the WSG clay fractions (Fig. 3b). Both groups of mudrocks show considerable scatter of data points related to variable proportions of white mica and chlorite in the clay fractions. A much clearer trend of K increasing with grade is shown by the SG clay fractions (Fig. 3c). In the SU clays Rb shows no significant trend in relation to grade (Fig. 3d), with considerable scatter of data points. A similar pattern is displayed by WSG clay fractions (Fig. 3e). In contrast, the SG clays show a strong trend of Rb increasing as grade increases (Fig. 3f). There is clearly a contrast in the behaviour of K and Rb in the SU and WSG, where there is a little or no increase in contents as grade increases, and the SG where both elements increase as grade increases.

3.3   BORON AND CAESIUM

Boron/Al ratios in clay fractions from the SU mudrocks generally decrease as grade increases (Fig. 4a). A similar trend is shown by the WSG clays (Fig. 4b). Boron ratios for the SG clays also shows a slight decrease with increasing grade but the scatter of data points in more evident and the trend less secure (Fig. 4c). Relative to grade the caesium ratios generally show similar patterns to those for B. In both the SU (Fig. 4d) and WSG (Fig. 4e) Cs in the clay fractions show a general decrease with increasing grade, although the data is scattered and both trends have weak correlation coefficients. The decrease in Cs in the SG clays is more marked and the trend is more secure (Fig. 4f). Thus all three groups of mudrocks show trends of B and Cs generally decreasing in clay minerals as metamorphic grade increases.

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3.4   LITHIUM

The SU mudrocks show a general trend of Li/Al ratios decreasing as grade increases (Fig. 5a). In contrast the WSG mudrocks show no significant change in Li ratios as grade changes (Fig. 5b). A clear trend of Li decreasing is displayed by the SG mudrocks, although here the scatter of data is more pronounced (Fig. 5c). Thus Li in clay minerals decreases with increasing grade in two groups of mudrocks (SU and SG), but shows no change in the third group (WSG).

3.5   STRONTIUM AND BARIUM

Strontium ratios decrease very slightly with increasing grade in the SU mudrocks, although the trend is barely significant (Fig. 6a). A similar but more secure trend is displayed by the WSG mudrocks (Fig. 6b), whereas the SG mudrocks shows a weak trend of Sr decreasing with increasing grade (Fig. 6c). Barium ratios show opposing trends, i.e., they increase with increasing metapelitic grade. However, the data shows considerable scatter for the SU samples (Fig. 6d), and the trend for the WSG samples (Fig. 6e) is not significant. In contrast the Ba ratios are well grouped with a good correlation coefficient in the case of the SG samples (Fig. 6f). Thus the clay mineral content of these two elements show opposite trends as metapelitic grade increases, with Sr generally decreasing and Ba generally increasing.

3.6   NICKEL AND CHROMIUM

Nickel ratios in the SU mudrocks show a slight but non-significant increase with increasing grade (Fig. 7a), whereas those in the WSG samples show a clear and significant increase with increasing grade (Fig. 7b). In contrast, Ni ratios display a well-defined decrease with increasing grade in the SG mudrocks (Fig. 7c). Chromium ratios show a barely significant increase with increasing grade in the SU mudrocks (Fig. 7d), but a much more pronounced increase with increasing grade in the WSG samples (Fig. 7e). In contrast Cr ratios show no significant change with grade in the SG samples (Fig. 7f). It is clear that changes in these two metals in clay minerals in response to progressive metamorphism is highly characteristic of basin setting.

Grade-related changes in the nickel and chromium content of the mudrocks vary from basin to basin. Both Ni and Cr in the SU mudrocks show enrichment in the CF samples as grade increases (Fig 2i, 2j). However, the WR values show a small but barely significant decrease with grade, suggesting that Ni and Cr were locally mobilized into clay minerals, most likely into chlorite generated by metamorphic reactions in these mudrocks. In the SG mudrocks Ni and Cr behave differently as grade increases (Fig. 3i, 3j). Nickel shows significant prograde decreases in both the WR and CF samples, but no consistent pattern of distribution between clay and non-clay minerals. Chromium, in contrast, shows no significant change with grade in either the WR or CF samples, but all samples show higher values in the clays. In the WSG mudrocks, both Ni and Cr show pronounced patterns of enrichment at higher grades (Figs 4i, 4j). Here again, prograde chlorite in the clay assemblages is the most likely host.

4 Regional Trends in Element Mobility

Element mobility in mudrocks from the three basins is summarized in Table 4, where trends in relation to increasing metapelitic grade are grouped under three headings.

Little or no systematic change as grade increases.

Although four elements, Al, K, Rb and Cr, show little or no systematic increase or decrease in relation to reaction progress in mudrocks, their behaviour is not the same in all three basins. Thus Al appears to have been immobile in the SU and SG samples, and here its behaviour is consistent with the stabilizing role of Al^{3+} in the 2:1 layers of dioctahedral white mica. Moreover, it confirms that in these two basins the substitution of Al^{3+} for one-in-four Si^{4+} cations in the tetrahedral sheet of mature white mica was fundamentally a conservative process, and probably achieved by micrometric or nanometric mobility during reaction progress. The absence of the same trend in the WSG samples is suspicious (Fig. 4a), given that Al is a major element in mudrock lithologies, and considering its role in white mica reactions. This suggests that the cause of the convergent trends in the CF and WR samples is more likely to be WSG sample inhomogeneity, and not Al mobility. As pointed out above, some samples contain a relatively high proportion of silt and fine-sand compared with samples of similar grade from the other two basins. The positive trend of the CF data appears to be largely the result of two very low-grade mudstones ($KI \geq 0.4$) that are more Al-rich than samples from the other basins (Fig. 4a). Kaolinite was not recorded from these two samples but they may contain mixed-layer minerals (Hirons and Roberts, 1999).

In the SU mudrocks K and Rb appear to have been largely immobile during metamorphism (Figs 2b, 2c) and show similar trends to that of Al (Fig. 2a). This suggests that, during progressive thickening of the white micas in these accreted mudrocks, the migration of K and Rb from interlayer sites in metastable illite to similar sites within mature phengitic muscovite was a conservative process involving micrometric or nanometric mobility. The conservative role of K and Rb in mudrock reaction progress may reflect the low heat flow conditions that prevailed during the evolution of the Southern Uplands terrane, for which Merriman and Roberts (2001) estimated a palaeo-geothermal gradient of <26℃/km. These low heat flow conditions are consistent with the phengitic composition of mature K-white micas in SU mudrocks, with *b* cell dimensions indicating intermediate to high pressure facies conditions (Stone and Merriman, 2004). Because of the low heat budget, mechanical strain probably made an important contribution to activation energies, enabling white mica to recrystallise and thicken in tectonic fabrics by pressure solution and dislocation creep (Merriman *et al.*, 1995; van de Pluijm et al., 1998).

The inhomogeneities in the WSG samples, noted above, appear to be the main influence on the K and Rb trends in the mudrocks. While the data for K in the CFs shows a barely significant decrease as grade increases, the WR data show an increase in K as grade increases (Fig. 4b). The most likely explanation for this trend is a greater clay content in the higher grade rocks, as indicated also by the Al content in the WR samples (Fig. 4a). The Rb data for WR samples show a similar trend, but the CF data show a significant decrease in Rb as grade increases. The difference between K and Rb trends in the CFs is not explainable in terms of the data currently available. In the CFs the behaviour of K in response to metamorphism of the WSG is similar to that found in the SU mudrocks, i.e. its migration from interlayer sites in metastable illite to similar sites within mature phengitic muscovite was essentially a conservative process.

Metamorphic conditions in the southern Lake District were characterised by palaeo-geothermal gradients of <20˚C/km for the initial burial of the WSG (Soper and Woodcock, 2003). The low heat flow generated phengitic K-white mica compositions with *b* cell dimensions indicating intermediate to high pressure facies conditions, similar to those found in the Southern Uplands (Stone and Merriman, 2004).

In the SG of the northern Lake District, Cr appears to be immobile during prograde metamorphism. Although Cr is mostly enriched in the clays, in some cases differences between the WR and CF samples is minimal (Fig. 3j). In the clay assemblages chlorite is the most likely host for Cr where it can substitute for Fe^{2+} (or Fe^{3+}) and Mg^{2+} in the (tri)octahedral sheets of the chlorite structure. Unlike Cr in mudrocks of the other basins considered here, there is no evidence of localized mobility in response to fabric formation (see below). However, the distribution pattern suggests that Cr in some mudrocks may be hosted by highly stable detrital minerals, such as spinels, with subsidiary amounts of less stable oxides, such as ilmenite and magnetite, contributing Cr to chlorite formation across a range of metapelitic conditions.

Decreases with increasing grade.

Three elements, B, Cs and Li, systematically decrease with increased metamorphic grade in all three basins. Losses of B and Cs are highest (50-70%) in the low heat flow basins of the Southern Uplands and the southern Lake District, whereas the highest Li loss (60%) is found in the SG of the northern Lake District. The reduction of B in prograde metamorphic rocks is well documented (Leeman and Sissons, 1996 and references therein). In white mica, B^{3+} in tetrahedral sites is replaced by Al^{3+} as illite reacts to form mature phengite or muscovite. Loss of B resulting from this reaction appears to be greater in low heat flow convergent settings, possibly because temperatures were too low for borosilicate minerals to form. In the higher heat flow setting of the northern Lake District, up to 40% of B was lost as the SG mudrocks were metamorphosed to epizonal conditions. However, the flat trend of the B data in the WR samples (Fig. 3d) suggest that some of this element was captured by borosilicate minerals as it migrated out of clay minerals during prograde reactions. This is consistent with the generally higher content of B in the SG mudrocks compared with the SU and WSG mudrocks (Figs. 2d, 4d).

Losses of Cs from prograded clay minerals show the same general pattern as those found for B. Highest losses (50-60%) occur in the Southern Uplands and the southern Lake District, but less Cs (40%) appears to be lost in the SG mudrocks in the northern Lake District. The most likely cause of these reductions in the CFs is loss of the relatively large Cs cation from interlayer sites as metamorphic reactions progressed in white micas (e.g. Mezler and Wunder, 2000). Sites vacated by Cs would be filled mainly by K, with possibly some Rb also, as indicated by trends for the SU and SG mudrocks (Figs 2c, 3c). In the WSG mudrocks Cs also decreases in the CFs with increasing grade whereas the WR samples show little or no significant change (Fig. 4e). Here Cs appears to be stabilized in a non-clay mineral as grade increased, unlike the SU and SG samples where Cs appears to have migrated out of the mudrocks.

The regional patterns of Li losses differ from those of B and Cs. Greater losses of Li are found in the SG mudrocks in the northern Lake District than those in the Southern Uplands and the southern Lake District. Prograde reduction of Li in the CFs is mostly the result of replacement of Li^+ by Al^{3+} in the octahedral sheets of white mica. Because of the more aluminous white mica found in the SG mudrocks (Merriman, 2006), the loss of Li would be expected to be greater when compared with the phengitic white mica found in SU and WSG mudrocks. However, there are differences in the Li trends of the three basins that are less easily explained. In both the SG

(Fig. 3f) and WSG (Fig. 4f), Li appears to have migrated out of the mudrocks as the metamorphic grade increased. This pattern is not evident in the SU samples (Fig. 2f) where the data is more scattered but Li losses with increasing grade are much less significant.

Although Sr generally decreases with increasing grade in the two Lake District basins, the location of Sr in the SG and WSG mudrocks differs. Clays appear to be the host in the SG where both CF and WR samples show prograde decreases in Sr (Fig. 3g). This pattern suggests that Sr^{2+} was located in interlayer sites, possibly in mixed-layer smectite/illite minerals, and was replaced by K, Rb, or even Na (e.g. Fortey, 1989) as reactions progressed. In the WSG most of the mudrock samples show little difference in Sr content between the CF and WR (Fig. 4g). The data is very scattered with just two low-grade samples showing higher Sr contents and there is barely any change from mid-anchizonal to epizonal mudrocks (KI<0.35). This pattern indicates that most of the Sr is probably hosted by non-clay minerals that are stable up to epizonal (low greenschist facies) conditions.

In contrast to Cr, the content of Ni in the SG mudrocks shows a significant reduction as grade increases (Fig. 3i). The pattern of Ni distribution between WR and CF samples is not consistent, with equal numbers of samples showing enrichment either in the WR or in the CF, and two samples showing no significant difference. The pattern indicates that likely detrital hosts for Ni, including ferromagnesian minerals and the oxides ilmenite and magnetite, became increasingly unstable under prograde conditions. However, unlike the Ni distribution patterns found in the other basins, chlorite did not provide stable sites for Ni migrating out of detrital hosts in the SG. As a result the Ni contents of the highest grade mudrocks in the SG are approximately 85% lower than those in mudrocks of similar grade in the Southern Upland and southern Lake District basins.

Increases with increasing grade.

Elements that show increased concentration in mudrocks as metamorphic grade increases can be characterised in terms of basin type. In the low heat flow convergent basins of the Southern Uplands and the southern Lake District, Ba, Cr and Ni increase with grade, whereas in the relatively high heat flow basin of the northern Lake District the SG mudrocks show Ba, K and Rb increasing with grade (Table 4). Although Ba generally increases in all three basins, the patterns of enrichment differ. In the SU and SG mudrocks both the WR and CF samples show Ba increasing as grade increases. However, Ba is consistently enriched in the CF samples of the SG (Fig. 3h). The most likely host in the clay assemblages is white mica, where Ba can substitute for interlayer cations such as K and Rb; in addition the increased Ba may have balanced the prograde loss of Cs and Sr from the SG mudrocks. In the SU mudrocks three samples show Ba more enriched in the WR (Fig. 2h). Hence Ba also appears to be hosted by non-clay minerals, such as baryte, that were generated by prograde conditions in the SU mudrocks. In the WSG non-clay minerals produced by prograde metamorphic reactions appear to be the dominant host for Ba in the mudrocks (Fig. 4h). It should be emphasized that Ba-rich non-clay minerals, such as baryte, have not been detected by XRD analysis in any of the samples described here. Hence they probably form less than 0.5 % of the WR mineralogy.

Although Sr generally appears to increase with prograde conditions in the SU mudrocks (Fig. 2g), the data is scattered. This appears to be largely due to its removal from clay minerals and growth of non-clay minerals.

Increases in Cr and Ni with increasing grade characterise the low heat-flow basins of the Southern Uplands and the southern Lake District. Patterns of distribution between WR and CF samples indicate that the Cr and Ni are mostly contained in clay minerals, with chlorite the most likely host. Both elements can substitute for Fe^{2+} (or Fe^{3+}) and Mg^{2+} in the (tri)octahedral sheets of the Fe-chlorites typically found in these basins (e.g. Merriman *et al.*, 1995). A significant increase in the CF content of both Cr and Ni is observed for KI<0.35, i.e. for mid-anchizonal to epizonal mudrocks (Figs. 2j, 4i, 4j). At these grades a penetrative slaty cleavage fabric is widely developed in regionally metamorphosed mudrocks (Merriman and Peacor, 1999, fig. 2.1), as is the case for the SU and WSG mudrocks. Thus these grade-related patterns of enrichment suggest that Cr and Ni were incorporated into fabric forming chlorite. In the SU mudrocks the lack of any significant change in the WR content of Cr and Ni at higher grades indicates that unstable detrital or diagenetic minerals were the most likely source of these elements, and hence mobility may have been limited to the micrometric or nanometric scale. In contrast, both WR and CF samples of the WSG mudrocks show increases in Cr and Ni for KI<0.35, indicating perhaps more extensive mobility of these elements during deformation and fabric development in the southern Lake District. However, the lack of evidence for regional mineralization involving these elements (British Geological Survey, 1992), suggests that unstable Cr- and Ni-bearing detrital minerals in associated sandstone beds may have provided the source. In turn this implies Cr and Ni mobility on the scale of metres in the WSG.

An increase in K and Rb with increasing grade is a distinctive feature of element mobility in the SG mudrocks of the northern Lake District (Figs. 3b, 3c). When compared with K distribution in the SU mudrocks (Fig. 2b), lowest grade, late diagenetic mudrocks (KI>0.42) in the SG have 15-40% less K in the CF samples, whereas differences at highest grades are not significant. Similar or greater differences in the K content of CF samples are also found between the lowest grade WSG mudrocks (Fig. 4b) and those of the SG. These disparities in K content are consistent with the Na-rich composition of white micas reported by Fortey (1989) and Fortey *et al.* (1993). Both intermediate K/Na mica and paragonite occur widely in the SG mudrocks, with Na replacing K as the dominant interlayer cation in the white mica of some clay assemblages. The effect of such replacement appears to be greatest at lower grades and K becomes increasingly dominant as metamorphic reactions progressed. The patterns of K, Na and Rb distribution indicates significantly greater alkali mobility in the northern Lake District basin than in the other basins considered here. In other extensional basins in the British Caledonides, Na-white micas are typical of clay assemblages in mudrocks, and probably formed by migration of alkali-enriched fluids generated by mixing hydrothermal fluids with seawater (Merriman, 2002, 2006). Such fluids are the main cause of paragonitic alteration in modern sea-floor hydrothermal systems (Alt and Teagle, 1998).

5 Discussion

Data from the suite of elements analysed for this study suggest that three types of geochemical mobility characterise metamorphic reaction in clay minerals at low-grades. These are: (a) localized, generally grain- or crystal-scale mobility related to fabric-forming clay mineral reactions; (b) basin-scale losses during prograde metamorphism; (c) basin-scale mobility associated with hydrothermal processes.

5.1   MOBILITY RELATED TO FABRIC-FORMING CLAY MINERAL REACTIONS

In the sedimentary basins of the Southern Uplands and southern Lake District the major elements Al and K, and trace elements Cr, Ni and Rb show limited mobility and are essentially conserved

in mudrocks during reaction progress. Sediments deposited in both basins were buried and metamorphosed in low heat-flow settings typically found in plate-convergent tectonic settings. Clay mineral reactions in both basins were closely associated with the development of slaty cleavage fabric in mudrocks. In the Southern Uplands, the tectonic fabric is associated with imbrication and developed synchronously with the assemblage of an accretionary prism from the early Caradoc to the early Wenlock (Merriman and Roberts, 2001). Although earlier tectonic fabrics in clay minerals were overprinted and intensified during D3 strike-slip movement in the Moniaive Shear Zone (Philips *et al.*, 1995), there is no evidence of increased mobility of Al, K, Rb, Cr or Ni resulting from this event. Slaty cleavage developed later in the southern Lake District in response to the Acadian (Early Devonian) deformation of England and Wales (Soper and Woodcock, 2003). The conservative behaviour of Al, K and Rb in both these plate-convergent basins suggests that pre-existing clay minerals provided most of the cations needed for the crystal growth of white mica in cleavage fabrics. Some growth was probably by solid-state replacement and thickening of illite and illite/smectite mixed-layer (I/S) minerals of diagenetic origin. Such growth involved the elimination of layer terminations and other stacking defects (e.g. Warr and Nieto, 1998), and needed no addition of Al or K. Mechanically deformed and broken crystals created pathways for pressure-solution processes (e.g. Merriman *et al.*, 1995), and these allowed grain-scale migration of Al, K and Rb. Thus a high proportion of the mature white mica developed in cleavage fabrics probably sourced its Al, K and Rb from metastable I/S and illite as reactions progressed in the low heat-flow basins of the Southern Uplands and southern Lake District.

Chlorite is also an important fabric-forming mineral in both low heat-flow basins. It probably derived most of the cations necessary for reaction progress from pre-existing Fe, Mg-rich clay minerals, e.g. saponite, which may have contained trace amounts of Cr and Ni. Unstable detrital oxides, such as magnetite and ilmenite, may have been additional sources of these two trace metals. While the patterns of geochemical and KI data suggest grain-scale mobility of Cr and Ni into fabric-forming chlorite in the Southern Uplands, the patterns derived from the southern Lake District indicate a greater scale of Cr and Ni mobility, possibly between adjacent beds of different lithologies.

5.2   BASIN-SCALE LOSSES

Losses of B, Cs and Li characterise the prograde sequences of mudrocks in the low heat-flow basins of the Southern Uplands and the southern Lake District. B and Cs losses in the range 50-70% are typical of the transformation from deep diagenetic mudstones and shales to epizonal (low greenschist facies) slates. Losses of Li are lower in these basins, at around 20%. The loss of B from metasediments is well documented (Leeman and Sissons, 1996). In present day accretionary settings B and Li are expelled in fluids and sediment pore water in the vicinity of décollement zones (You *et al.*, 1995). Further release of B occurs during subduction related metamorphism, and the migration of B-rich fluids into the overlying mantle wedge can be linked with arc magma generation (e.g. Bebout and Nakamura, 2003). It seems likely that the same processes were responsible for the expulsion of B, Cs and Li during assemblage of the Southern Uplands accretionary complex. Early release was probably in fluids channelled along zones of décollement in the initial stages of imbrication, with further release of these elements along major faults and shears during underplating and cleavage formation (Merriman and Roberts, 2001).

In the southern Lake District, expulsion of B and Li most likely occurred during Acadian deformation and uplift of the WSG. Although Cs also appears to have been released from clay

minerals during this event, it was not expelled from mudrock lithologies. This suggests it migrated into a stable site(s) in a non-clay mineral generated during low-grade metamorphism. Rapid accumulation of the WSG under low heat-flow conditions, together with possible overpressuring of the mudrocks, probably inhibited diagenetic clay reactions and early release of mobile elements. However, the transtensional model of Early Devonian deformation in the southern Lake District proposed by Soper and Woodcock (2003), suggests that uplift was accompanied by higher heat flow and generation of a northerly-trending fault pattern. Cleavage formation, increased heat-flow and faulting of the inverted WSG may well have driven fluid release and loss of B and Li.

5.3   BASIN-SCALE MOBILITY AND HYDROTHERMAL PROCESSES

Patterns of element mobility in the SG of the northern Lake District are distinctly different from those found in the other basins considered here. In particular, K, Rb, and Ni appear to have been significantly more mobile, in contrast to their conservative behaviour during prograde metamorphism in the Southern Uplands and southern Lake District basins. The characteristics of the clay mineral assemblages, including Na-rich micas and pyrophyllite, and the aluminous composition of the white mica suggest that high-heat flow and hydrothermal activity played an important part in the evolution of the mudrocks in the northern Lake District basin (Fortey, 1989; Merriman, 2002). Two lines of evidence suggest that patterns of K and Rb distribution in the SG predated cleavage formation. Firstly, Fortey *et al.* (1993) record that closure of the basin, with associated slaty cleavage development, post-dated deep diagenetic burial of the SG and associated volcanism, granite emplacement and high heat flow. Secondly, in the SU and WSG mudrocks where slaty cleavage formed early, K and Rb mobility was limited to a very local, crystal- and grain- scale migration, and no significant change in these elements occurred as grade increased and the fabric developed. Since pre-existing clays provided most of the cations needed for fabric-forming minerals in both the SU and WSG mudrocks, any cation enrichment or depletion in pre-cleavage clay assemblages were probably inherited by the metamorphic phyllosilicates forming the cleavage in the SG. The migration of mobile alkalis, such as K and Rb, was more likely to have been generated by syn-sedimentary volcanic activity and high heat-flow in the early stages of the SG basin development. In such a setting low-temperature hydrothermal activity associated with sea-floor volcanism would have been a potential source of Na-rich micas (Merriman, 2006), whereas K-rich micas, containing Rb and Ba, may have developed by higher temperature incipient 'sericitic' alteration or greisenization associated with the outermost zone of hydrothermal activity from sub-surface plutons. The loss of Ni in the SG may reflect scavenging by hydrothermal circulation associated with cooling plutons, as described by Stone *et al.* (2003) from the aureole of the Loch Doon Pluton in the Southern Uplands. It may also result from a lack of chlorite in zones of intense 'sericitic' alteration. The presence of fine-grained tourmaline in the SG mudrocks (Fortey and Cooper, 1986; British Geological Survey, 1992) is also evidence of hydrothermal alteration. Early tourmaline formation probably provided sites for B sequestration during Acadian cleavage development and prevented significant loss of B from the SG mudrocks overall.

The results of our study show that the formation of slaty cleavage is an important geochemical process in terms of the major and trace elements found in mudrocks. Those elements that are necessary for the development of metamorphic white mica and chlorite, the principal phyllosilicates present in slate, were largely inherited from pre-existing diagenetic clay minerals, and their concentrations were essentially conserved during metamorphic reactions. Significant amounts of other trace elements inherited from diagenetic clays, specifically B, Cs and Li from this study, were not accommodated in metamorphic white mica or chlorite, and were expelled. Studies of a modern subduction zone indicate that loss of these elements may begin early, during the initial imbrication and décollement of sedimentary sequences (You *et al.*, 1995). We would

also expect some loss of these elements during deep diagenesis where fluids are expelled, such as from shale or mudstone diapirs. However, the most significant losses of B, Cs and Li appear to occur once mudrocks prograde to the anchizone (KI<0.42) and acquire a slaty cleavage. This is consistent with the numerous conduits created for fluid movement during deformation processes, by bedding-plane slip, crenulation of bedding lamination, fracture cleavage formation and faulting at various scales.

Our results provide clear evidence of element mobility during low-grade metamorphism, both within clay fractions of mudrocks and between clays and the non-clay minerals. Although the evidence has been drawn from mudrocks, similar patterns of element mobility are likely to be found in the matrix mineralogy of coarser grained sandstones, particularly in matrix-rich wackes (e.g. Abad *et al.*, 2002). This has implications for provenance interpretations based on modern sand geochemistry as an analogue for ancient sandstones.

The sedimentary analogue approach takes modern marine sands derived from known tectonic settings (island arc, passive margin etc.) and uses their geochemistry as a guide to the tectonic characteristics of the provenance area of ancient sandstones, themselves originally deposited as marine sands. The technique was pioneered by Bhatia (1983; see also Bhatia and Crook, 1986) and has been applied in the Southern Uplands by Duller and Floyd (1995) and in the Lake District by Cooper *et al.* (1995) for the Skiddaw Group and by McCaffrey and Kneller (1996) for the Windermere Supergroup. The difficulty that now arises with such a technique is that most modern sediments are shallow to deep diagenetic in terms of their maturity, whereas the ancient examples with which they are compared will inevitably have experienced some degree of low-grade metamorphism. We have not examined the behaviour of all of the supposedly immobile elements that are commonly used in these comparisons but some suspicion must be cast on the use of trace elements Cr and Ni, whereas the use of the major oxide Al seems secure. The Cr/Ni ratio has been employed as an indicator of igneous rock types contributed as detritus to sedimentary basins. Garver *et al.* (1996) showed that an ultramafic provenance produces Cr/Ni ratios of about 1.5 in derived sedimentary rocks, whilst higher ratios of about 2 or more are indicative of a mafic-volcanic source. Plots of Cr/Ni ratios against metapelitic grade for the basins considered here suggest that this approach is unreliable if applied to meta-sedimentary rocks (Fig. 5). In the SU mudrocks no significant change in the Cr/Ni ratio occurs in WR or CF samples as grade increases (Fig. 5a). Here the limited mobility of Cr and Ni under prograde conditions suggests that the Cr/Ni ratio could be used as a provenance indicator, and in this case indicates a dominantly ultramafic source. In contrast, the SG and WSG mudrocks show significant changes in Cr/Ni with grade. Cr/Ni ratios in the SG mudrocks increase with grade (Fig. 5b), falsely indicating a change from an ultramafic source in diagenetic mudstones to a mafic-volcanic source in epizonal slates. The opposite effect is found in the WSG mudrocks (Fig. 5c), with an apparent but probably erroneous change indicated, from mafic-volcanic rocks to an ultramafic source as grade increases.

6 Conclusions

During low-grade metamorphism the mobility of the group of elements considered in this study ranged from crystal- or grain-scale (nm or mm), to basin-scale (km). Mobility characteristics can be linked with basin tectonics and thermal history. In the low heat-flow basins of the Southern Uplands and southern Lake District the mobility of Al, K, Cr, Ni and Rb was limited to crystal- or grain-scale reactions associated with slaty cleavage formation. The white mica developed in

cleavage fabrics derived Al, K and Rb from metastable I/S and illite, whereas chlorite developed mainly from pre-existing Fe- and Mg-rich clay minerals that contained trace amounts of Cr and Ni. A greater scale of Cr and Ni mobility, possibly between adjacent beds, appears to characterise chlorite formation in the southern Lake District. Losses of B, Cs and Li occurred on a basin-wide scale during low-grade metamorphism in the Southern Uplands and the southern Lake District. Here, B and Cs concentrations were reduced by 50-70%, and Li concentration by 20%, when mudstones and shales were converted to slates. These results show that the formation of slaty cleavage is an important geochemical process contributing to the evolution of low-grade metamorphic terranes.

In the northern Lake District basin, K, Rb, and Ni appear to have been significantly more mobile during low-grade metamorphism, in contrast to their conservative behaviour in the Southern Uplands and southern Lake District. The distribution of K and Rb appears to predated cleavage formation in the northern Lake District, and probably reflects hydrothermal distribution associated with high heat-flow in the early stages of basin development.

The use of Cr/Ni ratios as a provenance indicator proved unreliable when applied to most of the mudrocks considered here.

7 References

British Geological Survey holds most of the references listed below, and copies may be obtained via the library service subject to copyright legislation (contact libuser@bgs.ac.uk for details). The library catalogue is available at: http://geolib.bgs.ac.uk.

Abad, I., Nieto, F. and Velilla, N. 2002. Chemical and textural characterisation of diagenetic to low-grade metamorphic phyllosilicates in turbidite sandstones of the South Portuguese Zone: A comparison between metapelites and sandstones. *Schweizerische Mineralogische und Petrographische Mitteilungen*, **82,** 303-324.

Alt, J.C. and Teagle, D.A.H. 1998. Probing the TAG hydrothermal mound and stockwork: oxygen-isotope profiles from deep ocean drilling. In: Proceedings of the Ocean Drilling Program, Scientific Results 158, (eds P.M. Herzig, S.A. Humphris, D.J. Miller, R.A. Zierenberg), 285-295.

Armstrong, H.A., Owen, A.W., Scrutton, C.T., Clarkson, E.N.K. and Taylor, M. 1996. Evolution of the Northern Belt, Southern Uplands: implications for the Southern Uplands controversy. Journal of the Geological Society, London, 153, 197-205.

Barnes, R.P. and Stone, P. 1999. Trans-Iapetus contrasts in the geological development of southern Scotland (Laurentia) and the Lakesman Terrane (Avalonia). In: In sight of the suture: the geology of the Isle of Man in its Iapetus Ocean context (eds Woodcock, N.H., Fitches, W.R., Quirk D.G., Barnes R.P.), Geological Society, London, Special Publication 160, 307-323.

Bebout, G.E. and Nakamura, E. 2003. Record in metamorphic tourmaline of subduction-zone devolatization and boron recycling. Geology, 31, 407-410.

Bevins, R.E. and Merriman, R.J. 1988. Co-existing prehnite-actinolite and prehnite-pumpellyite facies assemblages in the Tal y Fan Metabasite Intrusion, North Wales: Implications for Caledonian metamorphism. Journal of Metamorphic Geology, 6, 17-39.

Bhatia, M.R. 1983. Plate tectonics and geochemical composition of sandstones. Geological Journal, 91, 611-643.

Bhatia, M.R. and Crook, A.W. 1986. Trace element characteristics of greywackes and tectonic setting discrimination of sedimentary basins. Contributions to Mineralogy and Petrology, 92, 181-193.

Bottrell, S.H., Greenwood, P.B., Yardley, B.W.D., Shepherd, T.J. and Spiro, B. 1990. Metamorphic and post-metamorphic fluid flow in the low-grade rocks of the Harlech Dome, north Wales. Journal of Metamorphic Geology, 8, 131-143.

British Geological Survey. 1992. Regional geochemistry of the Lake District and adjacent areas. (Keyworth, Nottingham: British Geological Survey).

British Geological Survey. 1996. Thornhill, Scotland. Sheet 9E. Solid Geology 1:50,000 (Keyworth, Nottingham).

Cooper, A.H., Rushton, A.W.A., Molyneux, S.G., Hughes, R.A., Moore, R.M. and Webb, B.C. 1995. The stratigraphy, correlation, provenance and palaeogeography of the Skiddaw Group (Ordovician) in the English Lake District. Geological Magazine, 132, 185-211.

Cooper, A.H., Fortey, N.J., Hughes, R.A., Molyneux, S.G., Moore, R.M., Rushton, A.W.A. and Stone, P. 2004. The Skiddaw Group of the English Lake District. Memoir of the British Geological Survey. British Geological Survey, Keyworth, Nottingham.

Duller, P.R. and Floyd, J.D. 1995. Turbidite geochemistry and provenance studies in the Southern Uplands of Scotland. Geological Magazine, 132, 557-569.

Floyd, J.D. 2001. The Southern Uplands Terrane: a stratigraphical review. Transactions of the Royal Society of Edinburgh: Earth Sciences, 91 (for 2000), 349-362.

Fortey, N.J. 1989. Low grade metamorphism in the Lower Ordovician Skiddaw Group of the Lake District, England. Proceedings of the Yorkshire Geological Society, 47, 325-337.

Fortey, N.J. and Coper, D.C. 1986. Tourmalinization in the Skiddaw Group around Crummock Water, English Lake District. Mineralogical Magazine, 50, 17-26.

Fortey, N.J., Roberts, B. and Hirons, S.R. 1993. Relationship between metamorphism and structure in the Skiddaw Group, English Lake District. Geological Magazine, 130, 631-638.

Frey, M and Robinson, D. 1999. Low-Grade Metamorphism. Blackwell Sciences Ltd., Oxford. 313 pp.

Garver, J.I., Royce, P.R. and Smick, T.A. 1996. Chromium and nickel in shale of the Taconic foreland: a case study for the provenance of fine-grained sediments with an ultramafic source. Journal of Sedimentary Research, 66, 100-106.

Grew, E.S. 1996. Borosilicates (exclusive of tourmaline) and boron in rock-forming minerals in metamorphic environments. In: Boron: Mineralogy, Petrology and Geochemistry (eds Grew, E.S., Anovitz, L.M.), Mineralogical Society of America, Reviews in Mineralogy, 33. 387-502.

Hannigan, R. and Basu, A.R. 1998. Late diagenetic trace element remobilization in organic black shales of the Taconic Foreland Basin of Quebec, Ontario and New York. In: *Shales and Mudstone II* (eds Schieber, J., Zimmerle, W., Sethi, P.S.), 209-234. E. Schweizerbart'sche Verlagsbuchhandlung, Stuttgart.

Hirons, S.R. and Roberts, B., 1999. Metamorphic survey of the 1:50 000 Kendal and Kirkby Lonsdale geological sheets 39 and 49. British Geological Survey Technical Report WA/99/51.

James, R.H. and Palmer, M.R. 2000. Marine geochemical cycles of the alkali elements and boron: The role of sediments. Geochimica et Cosmochimica Acta, 64, 3111-3122.

Johnson, E.W., Soper, N.J., Burgess, I.C., Beddoe-Stephens, B., Carruthers, R.M., Fortey, N.J., Hirrons, S.R., Merritt, J.W., Millward, D., Molyneux, S.G., Roberts, B., Rushton, A.W.A., Walker, A.B. and Young, B. 2001. Geology of the country around Ulverston. Memoir of the British Geological Survey, Sheet 48 (England and Wales).

Kneller, B.C. 1991. A foreland basin on the southern margin of Iapetus. Journal of the Geological Society, London, 148, 207-210.

Kneller, B.C., King, L.M. and Bell, A.M. 1993. Foreland basin development and tectonics on the northwest margin of eastern Avalonia. Geological Magazine, 130, 691-697.

Leeman, W.P. and Sisson, V.B. 1996. Geochemistry of boron and its implications for crustal and mantle processes. In: Boron: Mineralogy, Petrology and Geochemistry (eds Grew, E.S., Anovitz, L.M.), Mineralogical Society of America, Reviews in Mineralogy, 33. 645-708.

Leggett, J.K. 1987. The Southern Uplands as an accretionary prism: the importance of analogues in reconstructing palaeogeography. Journal of the Geological Society, London, 144, 737-752.

Leggett, J.K., McKerrow, W.S. and Eales, M.H. 1979. The Southern Uplands of Scotland: a Lower Palaeozoic accretionary prism. Journal of the Geological Society, London, 136, 755-770.

McCaffrey, W.D. and Kneller, B.C. 1996. Silurian turbidite provenance on the northern Avalonian margin. Journal of the Geological Society, London, 153, 437-450.

McMillan, A.A. 2001. A concise account of the geology around New Galloway and Thornhill. Memoir of the British Geological Survey, sheets 9W and 9E (Scotland).

Merriman, R.J. 2002. Contrasting clay mineral assemblages in British Lower Palaeozoic slate belts: the influence of geotectonic setting. Clay Minerals, 37, 207-219.

Merriman, R.J. 2006. Clay mineral assemblages in British Lower Palaeozoic mudrocks. Clay Minerals, 41, 473-512.

Merriman, R.J. and Frey, M. 1999. Patterns of very low-grade metamorphism in metapelitic rocks. In: Low-Grade Metamorphism (eds Frey, M., Robinson, D.), 61-107. Blackwell Sciences Ltd., Oxford.

Merriman, R.J. and Peacor, D.R. 1999. Very low-grade metapelites; mineralogy, microfabrics and measuring reaction progress. In: Low-Grade Metamorphism (eds Frey, M., Robinson, D.), 10-60. Blackwell Sciences Ltd., Oxford.

Merriman, R.J. and Roberts, B. 2001. Low-grade metamorphism in the Scottish Southern Uplands terrane: deciphering the patterns of accretionary burial, shearing and cryptic aureoles. Transactions of the Royal Society of Edinburgh: Earth Sciences, 91, 521-537.

Merriman, R.J., Roberts, B., Peacor, D.R. and Hirons, S.R. 1995. Strain-related differences in the crystal growth of white mica and chlorite: a TEM and XRD study of the development of metapelite microfabrics in the Southern Uplands thrust terrane, Scotland. *Journal of Metamorphic Geology*, **13**, 559-576.

Mezler, S. and Wunder, B. 2000. Island-arc basalt alkali ratios: Constraints from phengite-fluid partitioning experiments. *Geology*, **28**, 583-586.

Peacor, D.R. 1992. Diagenesis and low-grade metamorphism of shales and slates. In: *Minerals and Reactions at the Atomic Scale: Transmission Electron Microscopy* (ed P.R.Buseck), Mineralogical Society of America, Reviews in Mineralogy, **27**. 335-380.

Phillips, E.R., Barnes, R.P., Boland, M.P., Fortey, N.J. and McMillan, A.A. 1995 The Moniaive Shear Zone: a major zone of sinistral strike-slip deformation in the Southern Uplands of Scotland. *Scottish Journal of Geology*, **31**, 139-149.

Potter, P.E., Maynard, J.B. and Depetris, P.J. 2005. *Mud and Mudstones*. Springer. Berlin, Heidelberg, New York, 297 pp.

Roberts, B., Merriman, R.J. and Pratt, W. 1991. The relative influences of strain, lithology and stratigraphical depth on white mica (illite) crystallinity in mudrocks from the district centred on the Corris Slate Belt, Gwynedd-Powys. *Geological Magazine*, **128**, 633-645.

Rushton, A.W.A., Stone, P. and Hughes, R.A. 1996. Biostratigraphical control of thrust models for the Southern Uplands of Scotland. *Transactions of the Royal Society of Edinburgh: Earth Sciences*, **86**, 137-152.

Soper, N.J. and Woodcock, N.H. 2003. The lost Old Red Sandstone of England and Wales: a record of post-Iapetan flexure of Early Devonian transtension*? Geological Magazine*, **140,** 627-647.

Stone, P. and Merriman, R.J. 2004. Basin thermal history favours an accretionary origin for the Southern Uplands terrane, Scottish Caledonides. *Journal of the Geological Society, London*, **161**, 829-836.

Stone, P., Floyd, J.D., Barnes, R.P. and Lintern, B.C. 1987. A sequential back-arc and foreland basin thrust duplex model for the Southern Uplands of Scotland. *Journal of the Geological Society, London*, **144**, 753-764.

Stone, P., Cooper, A.H. and Evans, J.A. 1999. The Skiddaw Group (English Lake District) reviewed: early Palaeozoic sedimentation and tectonism at the northern margin of Avalonia. In: *In sight of the suture: the geology of the Isle of Man in its Iapetus Ocean context* (eds Woodcock, N.H., Fitches, W.R., Quirk D.G., Barnes R.P.), pp 325-336. Geological Society, London, Special Publication **160**.

Stone, P., Breward, N. and Merriman, R.J. 2003. Mineralogical controls on metal distribution in stream sediment derived from the Caledonides of the Scottish Southern Uplands and English Lake District. Mineralogical Magazine, 67, 325-338.

Teng, F.-Z, McDonough, W.F., Rudnick, R.L. and Wing, B.A. 2007. Limited lithium isotopic fractionation during progressive metamorphic dehydration in metapelites: A case study from the Onawa contact aureole, Maine. *Chemical Geology*, **239**, 1-12.

van de Pluijm, B.A., Ho, N.-C., Peacor, D.R. and Merriman, R.J. 1998. Contradictions of slate formation resolved. *Nature*, **392**, 348.

Warr, L.N. and Nieto, F. 1998. Crystallite thickness and defect density of phyllosilicates in low-temperature metamorphic pelites: A TEM and XRD study of clay-mineral crystallinity-index standards. *The Canadian Mineralogist,* **36**, 1453-1474.

Worden R.H. and Morad, S (eds). 2003. *Clay Mineral Cements in Sandstones*. Special Publication of the International Association of Sedimentologists, No. 34. Blackwell Science. 509 pp.

You, C.-F., Chan, L.H., Spivack, A.J. and Gieskes, J.M. 1995. Lithium, boron, and their isotopes in sediments and pore waters of Ocean Drilling Program Site 808, Nankai Trough: Implications for fluid expulsion in accretionary prisms. *Geology*, **23**, 37-40.
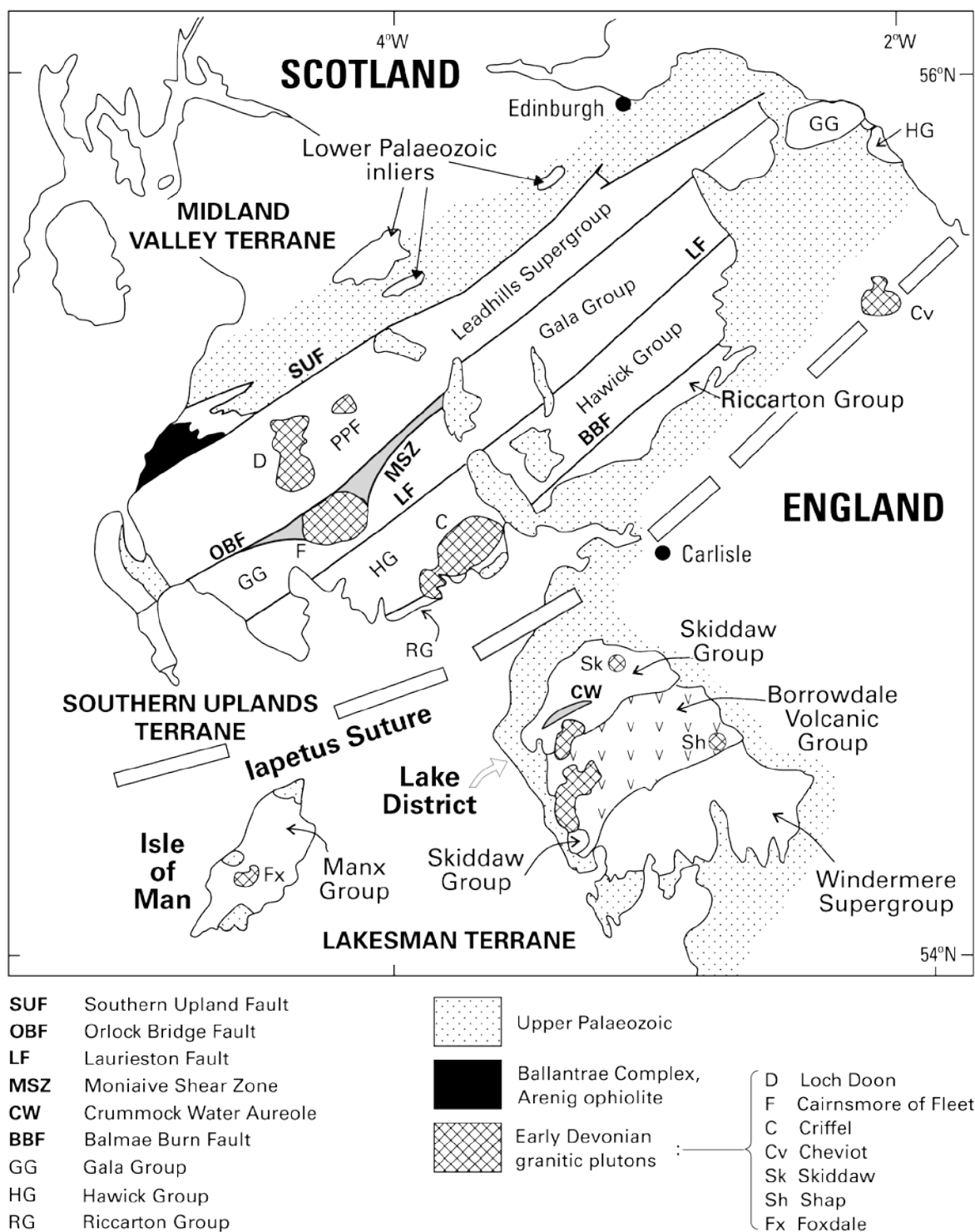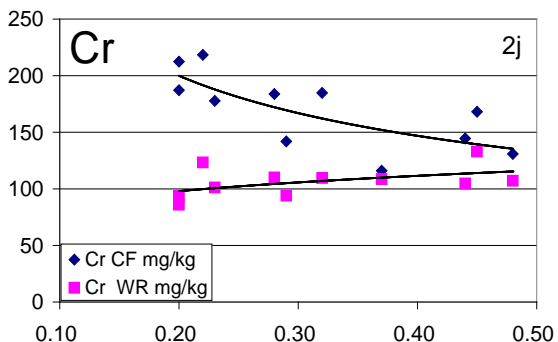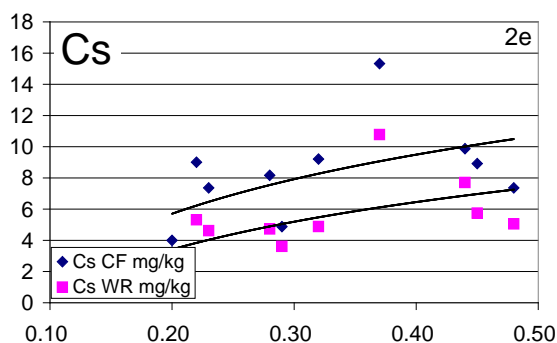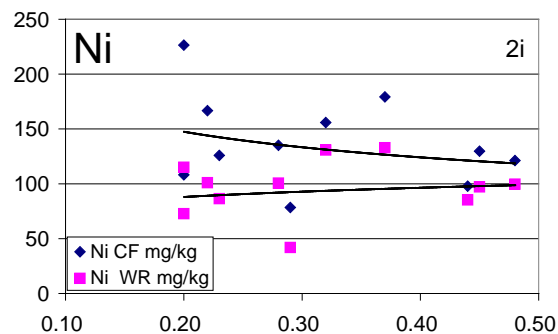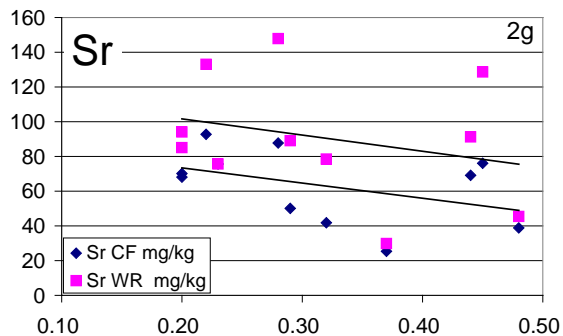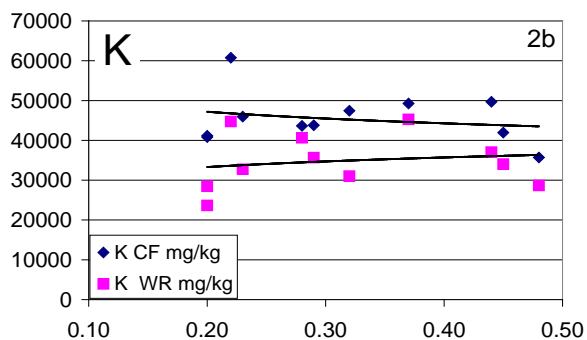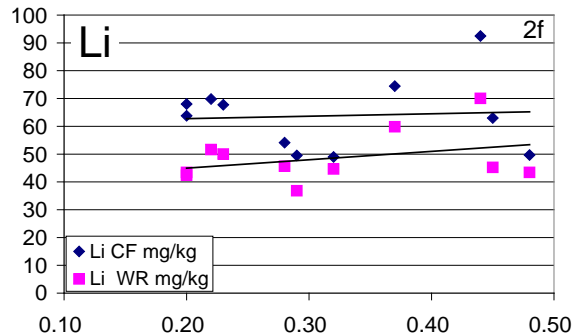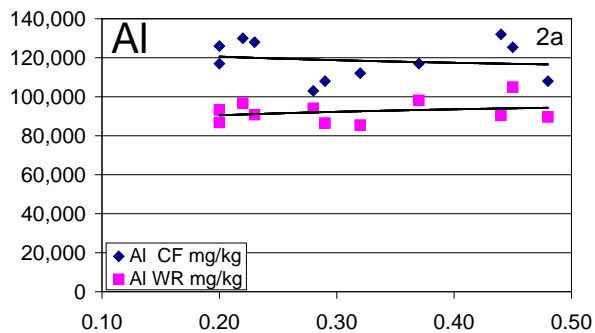
Figure 1. Sketch map showing the location of Caledonian terranes and the sedimentary basins sampled for the study.
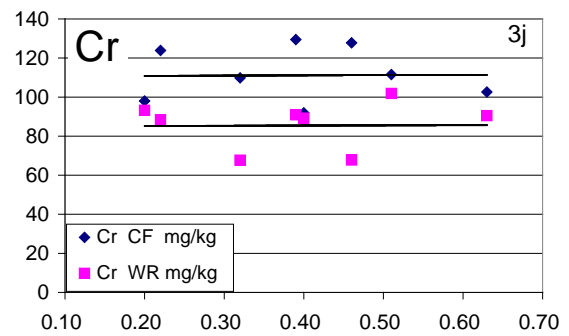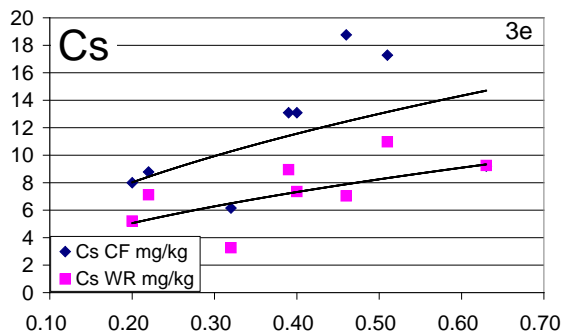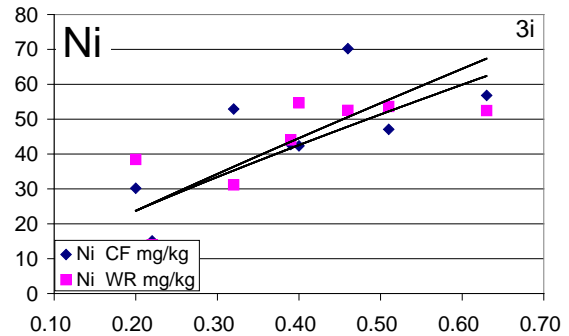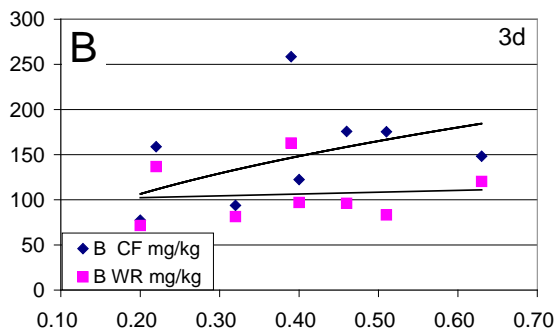
Figure 2.

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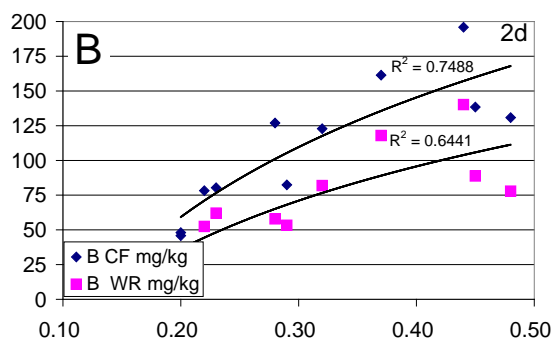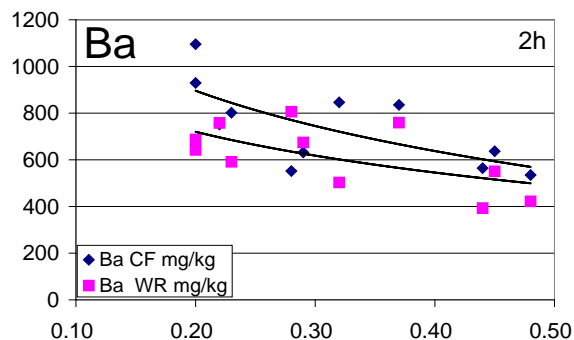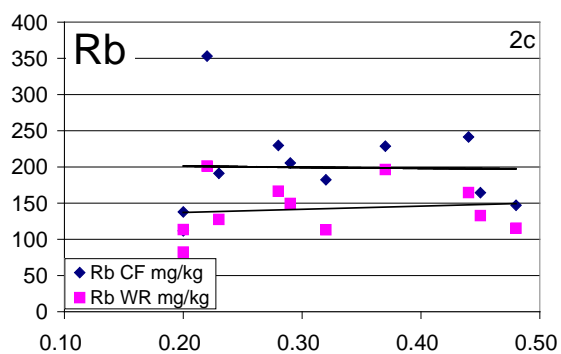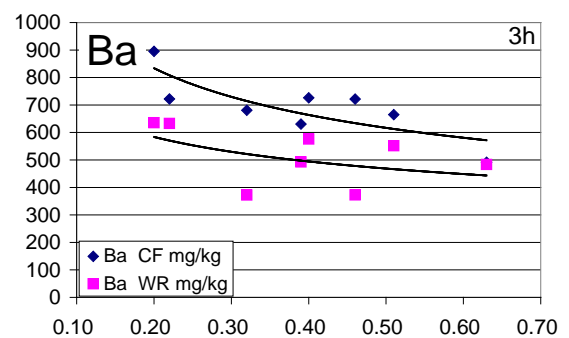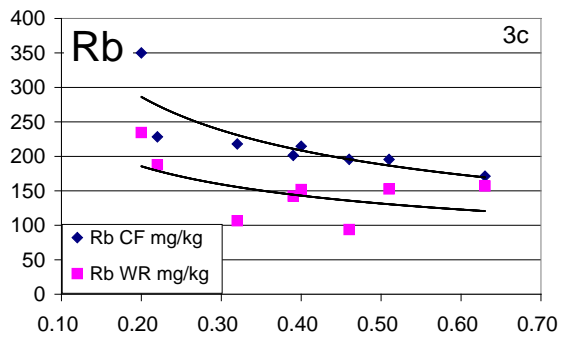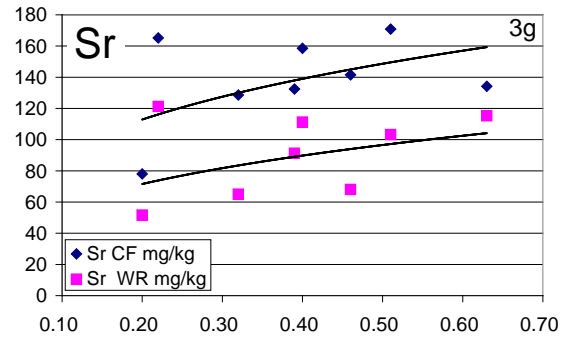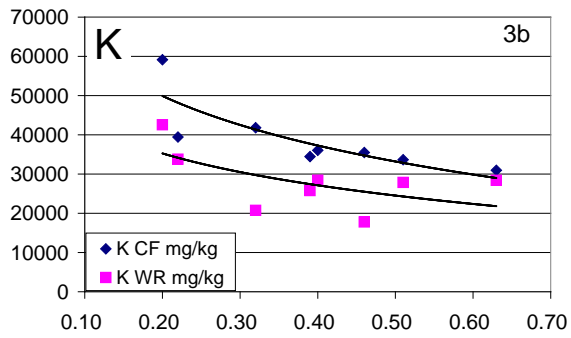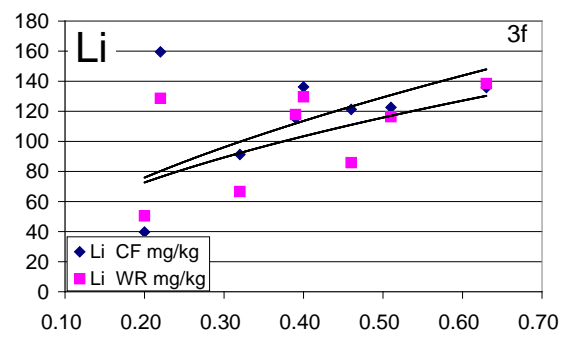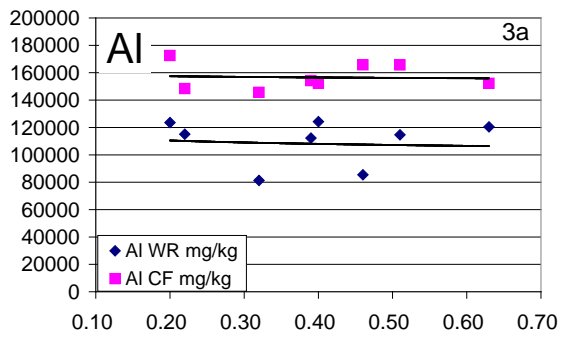
Figure 3

Figure 4.

Figure 5

Table 1. Details of mudrock samples and metapelitic grade

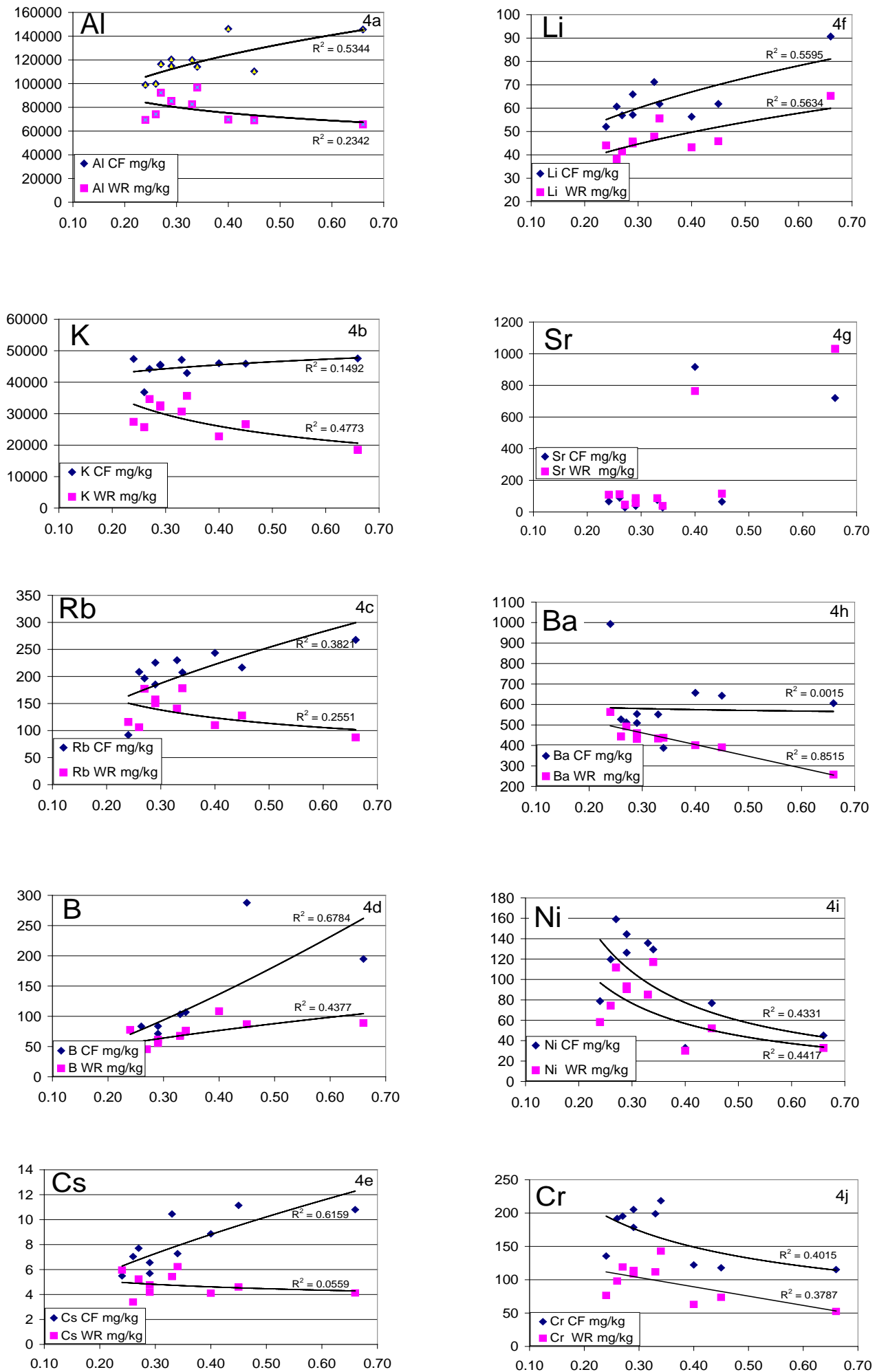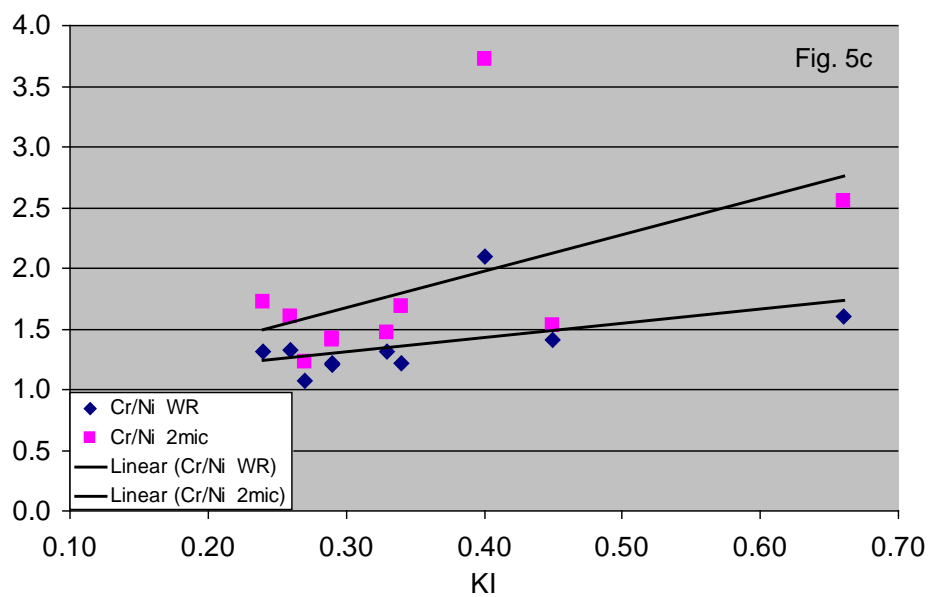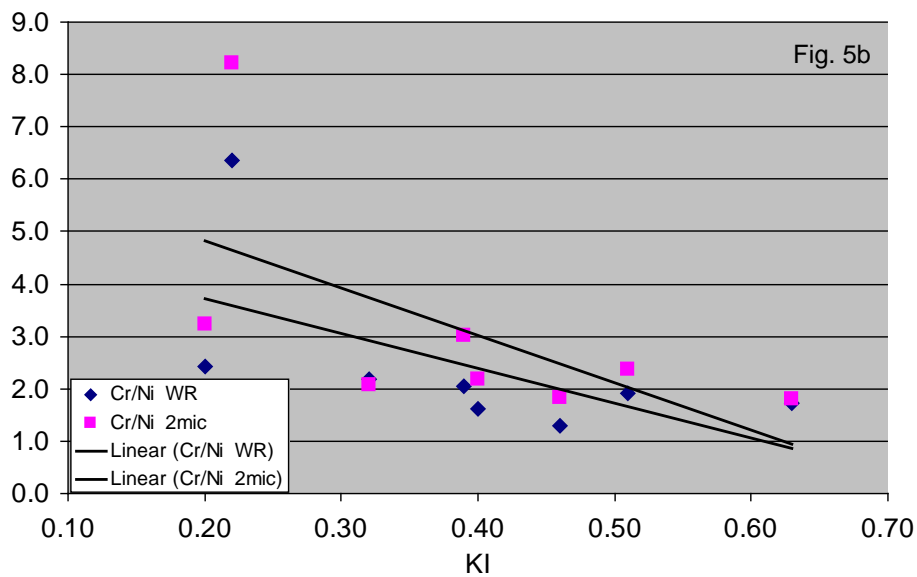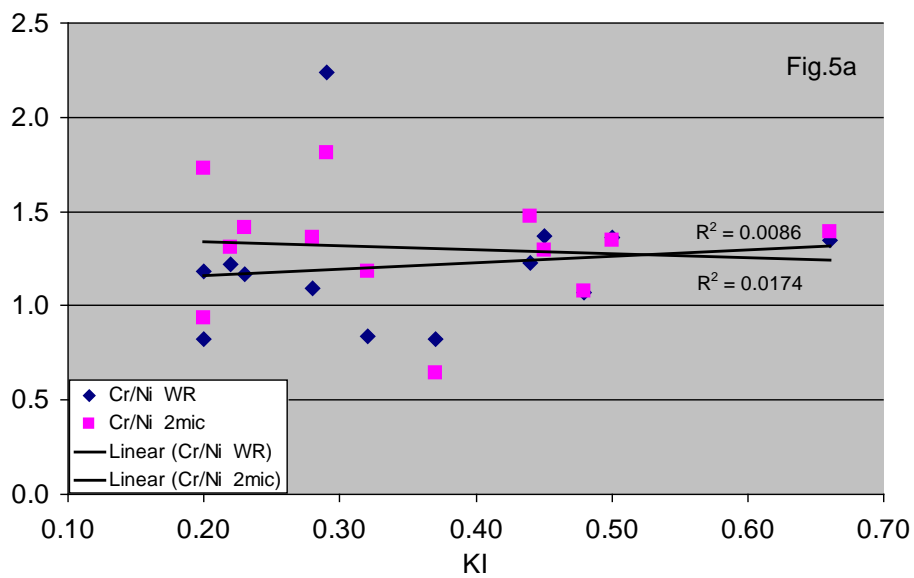| Sample No	Kubler index	Strata and Basin	Grid Reference	Metapelitic grade
SH19	0.29	Windermere SG, southern Lake District	SD 4085 9840	anchizone
SH22	0.29	Windermere SG, southern Lake District	SD 4320 9921	anchizone
SH24	0.27	Windermere SG, southern Lake District	NY 4145 0115	anchizone
SH59	0.33	Windermere SG, southern Lake District	SD 6219 9093	anchizone
LC127	0.24	Windermere SG, southern Lake District	NY 4237 0339	epizone
LC940	0.26	Windermere SG, southern Lake District	SD 4060 8437	anchizone
LC1570	0.40	Windermere SG, southern Lake District	SD 6860 8770	anchizone
LC1606	0.34	Windermere SG, southern Lake District	SD 5528 8712	anchizone
LC1617	0.45	Windermere SG, southern Lake District	SD 6924 9318	deep diagenetic zone
LC1618	0.66	Windermere SG, southern Lake District	SD 7051 9580	deep diagenetic zone
LC142	0.32	Skiddaw Group, northern Lake District	NY 1560 1825	anchizone
LC199	0.22	Skiddaw Group, northern Lake District	NY 1649 2111	epizone
LC348	0.20	Skiddaw Group, Black Combe, Lake District	SD 1476 8617	epizone
LC434	0.51	Skiddaw Group, northern Lake District	NY 3827 2586	deep diagenetic zone
LC482	0.40	Skiddaw Group, northern Lake District	NY 5506 1311	anchizone
LC495	0.63	Skiddaw Group, northern Lake District	NY 47322201	deep diagenetic zone
LC507	0.46	Skiddaw Group, northern Lake District	NY 2956 2520	deep diagenetic zone
LC521	0.39	Skiddaw Group, northern Lake District	NY 2565 2634	anchizone
BRS429	0.66	Corsewall Formation, Southern Uplands	NW 992 726	deep diagenetic zone
BRS710	0.50	Carghidown Formation, Southern Uplands	NX 717 488	deep diagenetic zone
BRS742	0.45	Glenlee Formation, Southern Uplands	NX 657 823	deep diagenetic zone
BRS753	0.32	Glenlee Formation, Southern Uplands	NX 6358 8363	anchizone
BRS781	0.20	Moniaive Shear Zone, Southern Uplands	NX 7115 8385	epizone
BRS790	0.20	Moniaive Shear Zone, Southern Uplands	NX 7051 8024	epizone
BRS807	0.22	Moniaive Shear Zone, Southern Uplands	NX 6590 7895	epizone
BRS822	0.37	Gala Group (G5), Southern Uplands	NX 733 754	anchizone
BRS824	0.23	Gala Group (G4), Southern Uplands	NX 6945 7616	epizone
BRS829	0.48	Glenlee Formation, Southern Uplands	NX 688 857	deep diagenetic zone
BRS879	0.29	Gala Group (G2), Southern Uplands	NX 824 908	anchizone
BRS882	0.28	Gala Group (G4), Southern Uplands	NX 830 884	anchizone
BRS1028	0.44	Carghidown Formation, Southern Uplands	NX 859 728	deep diagenetic zone

Table 2.

Metapelitic zones in mudrock lithologies defined by the Kübler index.

5.2.1 Metapelitic zones	Epizone/ low-greenschist	Anchizone	Deep diagenetic zone
Kübler index (KI in Δ°2θ)	< 0.25	0.25-0.42	> 0.42

Table 3. Geochemical analyses of whole mudrock samples (WR) and separated clay fractions (CF).

Sample No.	Al CF	Al WR	Ba CF	Ba WR	Cr CF	Cr WR	K CF	K WR	Li CF	Li WR	Ni CF	Ni WR	Sr CF	Sr WR	Rb CF	Rb WR	Cs CF	Cs WR	B CF	B WR
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
SH19	114835	85136	554	460	179	114	45320	32224	57	46	126	93	39	87	226	157	7	4.76	84	61
SH22	120383	85344	510	432	205	109	45586	32654	66	45	144	91	39	57	185	150	6	4.18	71	56
SH24	116418	92250	513	492	195	119	44215	34662	57	41	159	112	28	45	197	177	8	5.24		45
SH59	120030	82616	552	433	199	112	47140	30681	71	48	136	85	76	87	230	141	10	5.44	103	68
LC127	98951	69385	993	564	136	77	47403	27415	52	44	79	58	66	109	92	116	5	5.96		78
LC940	99809	74186	527	443	192	98	36839	25738	61	38	120	74	89	112	208	106	7	3.40	83	47
LC1570	146157	69608	657	401	122	63	46027	22776	56	43	33	30	917	764	244	110	9	4.10		109
LC1606	114157	96785	388	437	218	143	42911	35659	62	56	129	117	28	38	208	178	7	6.24	107	76
LC 1617	110301	69023	643	391	118	74	45876	26617	62	46	77	52	65	114	217	128	11	4.60	288	87
LC1618	145632	65570	606	258	115	52	47557	18509	91	65	45	33	720	1031	268	87.3	11	4.12	195	89
LC142	145647	81319	681	373	110	68	41811	20741	91	67	53	31	129	65	218	107	6	3.26	94	81
LC199	148435	115131	722	633	124	88	39444	33800	160	129	15	14	165	121	228	188	9	7.12	159	137
LC507	165764	85414	722	373	128	68	35496	17781	121	86	70	53	142	68	196	93.8	19	7.04	176	96
LC521	154250	112300	630	493	129	91	34445	25788	116	118	43	44	132	91	201	142	13	8.95	259	163
LC348	172574	123544	895	636	98	93	59151	42548	40	50	30	38	78	52	350	235	8	5.21	77	72
LC434	165692	114662	665	552	112	102	33661	27864	123	116	47	54	171	103	196	153	17	11.0	175	83
LC482	152372	124230	726	576	92	89	36057	28425	136	130	42	55	159	111	215	152	13	7.36	122	97
LC495	152263	120449	492	484	103	91	30950	28399	136	138	57	52	134	115	171	157	9	9.25	148	120
BRS429	82722	81695	454	1060	129	66	24275	36412	203	103	92	49	142	377	114	93.0	6	3.52	74	24
BRS753	112091	85565	846	503	185	110	47448	31009	49	45	156	131	42	78	182	113	9	4.89	123	82
BRS742	125378	105141	637	551	168	133	41945	34051	63	45	130	97	76	129	164	133	9	5.75	138	89
BRS710	125929	79217	295	259	192	102	42627	24676	72	43	143	75	32	42	167	101	10	5.29	124	68
BRS807a	130871	96730	751	758	218	123	60748	44743	70	52	167	101	93	133	353	201	9	5.32	78	52
BRS824	128112	90852	802	591	178	101	45963	32743	68	50	126	86	76	76	191	128	7	4.62	80	62
BRS829	108726	89626	535	422	131	107	35716	28666	50	43	121	100	39	45	147	115	7	5.06	131	78

Table 3 contd

Sample No.	Al CF	Al WR	Ba CF	Ba WR	Cr CF	Cr WR	K CF	K WR	Li CF	Li WR	Ni CF	Ni WR	Sr CF	Sr WR	Rb CF	Rb WR	Cs CF	Cs WR	B CF	B WR
BRS781	126713	93270	930	687	212	94	41152	28445	68	42	226	115	70	85	138	113	3	2.44	46	19
BRS790	117046	86818	1095	642	187	86	40821	23644	64	43	108	73	68	94	112	82.4	4	2.39	48	34
BRS822	117200	98237	835	759	116	109	49258	45283	74	60	179	133	25	30	229	196	15	10.8	161	118
BRS879	108293	86581	632	674	142	94	43807	35666	50	37	78	42	50	89	206	150	5	3.61	82	53
BRS882	103741	94173	552	806	184	110	43651	40647	54	46	135	101	88	148	230	166	8	4.73	127	58
BRS1028	132638	90489	564	393	145	105	49686	37057	92	70	98	85	69	91	241	165	10	7.70	196	140

Table 4.

Element mobility in Caledonian mudrocks related to increasing metapelitic grade

Strata and basin setting	Little or no systematic change as grade increases	Decreases with increasing grade	Increases with increasing grade
Ordovician-Silurian Southern Uplands Accretionary prism	Al, Rb, Cr, Ni	B, Cs, Li, Sr	K, Ba,
Windermere Supergroup Southern Lake District Foreland basin	Rb, Ba, Li	B, Cs, Sr,	K, Cr, Ni
Skiddaw Group Northern Lake District Extensional basin	Al, Cr	B, Cs, Li, Ni, Sr	Ba, K, Rb