COMPARISON OF K-Ar AGES OF DIAGENETIC ILLITE-SMECTITE TO THE AGE OF A CHEMICAL REMANENT MAGNETIZATION (CRM): AN EXAMPLE FROM THE ISLE OF SKYE, SCOTLAND

W. Crawford Elliott[1],[*], Ankan Basu[1],[†], J. Marion Wampler[2], R. Douglas Elmore[3] and Georg H. Grathoff[4]

[1] Department of Geology, Georgia State University, PO Box 4105, Atlanta, GA 30302-4105, USA
[2] School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA 30332, USA
[3] School of Geology and Geophysics, Oklahoma University, Norman, OK 73019, USA
[4] Department of Geology, Portland State University, Portland, OR 97207, USA

Abstract—The clay fractions of Jurassic marls in the Great Estuarine Group in southern Isle of Skye are composed of mixed-layered illite-smectite (I-S) with large percentages (>85%) of illite layers, kaolinite, and generally smaller amounts of chlorite. These marls have not been buried to the depths normally required to convert smectite to illite-rich I-S, so it is possible that the conversion was in response to heat and hydrothermal fluids from nearby early Tertiary igneous activity ~55 Ma ago. The large percentages of illite layers in I-S, the Środoń intensity ratios, and the Kübler index values appear to be consistent with the formation of diagenetic I-S as a result of relatively brief heating caused by igneous activity. The Jurassic rocks in southern Skye contain a secondary chemical remanent magnetization (CRM) that resides in magnetite and formed at approximately the same time as the Tertiary igneous rocks on Skye. K-Ar age values for I-S based on illite age analysis have been determined to test the hypothesis that the CRM was acquired coincidently with the smectite-to-illite conversion. However, linear extrapolation of K-Ar age *vs.* percentage of $2M_1$ polytype (detrital illite) from one marl (EL-6) yields an estimate for the age of diagenetic illite of 106 Ma, which is close to the measured age of the finest subfraction (108 Ma). These estimated and measured age values, however, could be substantially greater than the true age of the diagenetic illite in I-S because of the presence of detrital $1M_d$ illite that was recycled from early Paleozoic shales and whose abundance relative to the diagenetic I-S may have been enhanced because the diagenetic fluid had a low K/Na ratio, limiting the amount of diagenetic illite formed. Nevertheless, most of the illite in the Elgol marls (80% or more in the finest fractions) must be diagenetic and probably formed in response to the early Tertiary magmatism.

Key Words—Illite, Isle of Skye, K-Ar, Scotland, Paleomagnetism.

INTRODUCTION

Determining the causes and timing of diagenetic events is crucial in studies of basin evolution as well as for hydrocarbon exploration strategies. Diagenetic illite-smectite (I-S) has often been used as a geothermometer for the study of thermal histories of sedimentary basins, wherein the conversion of smectite to illite is largely dependent on time, temperature, and the availability of K (*e.g.* Pevear, 1999 and references therein). The type of stacking order and the percentage of illite layers in diagenetic I-S are widely recognized as indicators of the thermal maturity of possible source rocks for crude oil and natural gas (*e.g.* Hoffman and Hower, 1979; Pollastro, 1993). The waters released during the conversion of smectite to illite may help expel crude oil from source rocks (Burst, 1969).

Chemical remanent magnetization (CRM) is another feature indicative of diagenesis and CRMs are common in many Phanerozoic sedimentary rocks and, in conjunction with geochemical and petrographic data, can provide valuable information on the timing of some diagenetic events (McCabe and Elmore, 1989; Elmore *et al.*, 1993; and numerous others). Many of these events occur within the range in temperature involved in the conversion of smectite to illite. The paleomagnetic dating approach is based on isolation of the CRM carried by authigenic magnetic minerals that precipitated during diagenetic reactions and comparison of the pole positions with independently established 'Apparent Polar Wander Paths'. Field tests and geochemical and petrographic studies are used to relate the diagenetic events to the formation of authigenic magnetic phases that carry the CRMs. Recent studies have provided evidence that diagenetic events such as maturation of organic matter (*e.g.* Banerjee *et al.*, 1997; Blumstein *et al.*, 2004), migration of orogenic fluids (*e.g.* Elmore *et al.*, 2001), and clay (smectite to illite) diagenesis (Katz *et al.*, 2000; Gill *et al.*, 2002) can be dated by this approach. While geochemical and petrographic studies provide important clues for establishing the relationships

* E-mail address of corresponding author:
geowce@langate.gsu.edu
† Current address: Department of Geosciences, Virginia Polytechnic Institute and State University, Blacksburg, VA, USA

between the formation of a CRM and specific diagenetic processes, the ultimate test of the dating approach requires the application of independent dating methods to compare to the paleomagnetic ages.

During the conversion of smectite to illite, Fe is released from the smectite crystal structure (Boles and Franks, 1979). Iron can be later precipitated as magnetite in the absence of sulfide ions, and authigenic magnetite records the direction of the Earth's magnetic field. Field studies suggest a causal connection between the smectite-to-illite conversion and the formation of CRM. For example, a widespread pre-Eocene CRM residing in magnetite is found where smectite was altered to illite during burial diagenesis in the Vocontian Trough, France (Katz *et al.*, 2000). A hypothesized connection between the formation of diagenetic illite and magnetite authigenesis is also supported indirectly by the results of paleomagnetic, rock magnetic, geochemical and petrographic studies of Mesozoic sedimentary rocks in the Isle of Skye, Scotland (Woods *et al.*, 2002). In southern Skye, diagenetic illite is believed to have formed within Mesozoic sediments in response to the movement of hydrothermal fluids related to Tertiary igneous activity (Andrews, 1987), and these sediments contain a CRM in magnetite that has the same direction as the magnetization of the Tertiary igneous rocks (Woods *et al.*, 2002).

In northern Skye, detrital smectite is abundant in Mesozoic sedimentary rocks and these rocks contain a weak and unstable magnetization. The presence of a CRM in marls in the south, the timing of the acquisition of the CRM, and the presence of abundant illite in marls in the south (and its absence in the north) support a hypothesis that magnetite authigenesis and the acquisition of the CRM in these marls resulted from the smectite-to-illite conversion prompted by hydrothermal fluids due to Tertiary igneous activity (Woods *et al.*, 2002). In this study, we test the hypothesized connection between the acquisition of secondary magnetization (CRM) and the formation of diagenetic illite from smectite by comparing the timing of the acquisition of the CRM and a K-Ar age value obtained by illite age analysis (Pevear, 1999) for diagenetic illite in a Mesozoic marl of southern Skye.

GEOLOGICAL SETTING OF THE STUDY AREA

The Isle of Skye, the largest of the Inner Hebrides islands, is located just northwest of the Scottish mainland within a rift zone that extended from what is now East Greenland to what is now the Scottish mainland before their separation by seafloor spreading (Hallam, 1991). This island is marked by two main Tertiary igneous centers, the Cuillin Hills and the Red Hills (Figure 1). The
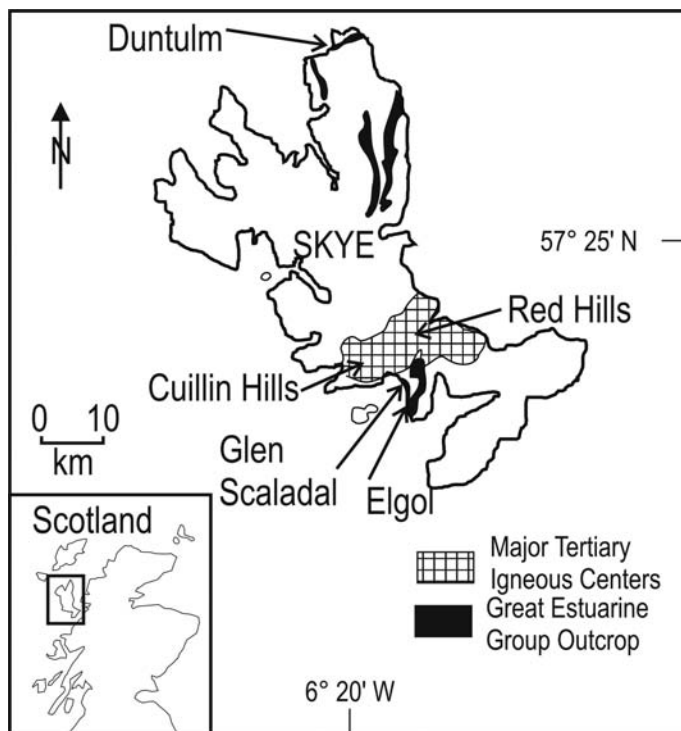

Figure 1. Map of the Isle of Skye showing the Tertiary igneous centers and the area where the Elgol marl samples were collected. The Great Estuarine Group rocks near Duntulm are dominated by smectite whereas illite is predominant in the rocks near Elgol (Andrews, 1987). Further information about the Elgol samples was provided by Woods *et al.* (2002). This figure is modified after Hudson and Andrews (1987).

Cuillin Hills are serrated peaks composed of gabbro while the Red Hills are smoothly contoured mountains composed of granite, granophyre and basalt (Richey, 1961). The igneous activity of these centers occurred between 54 and 61 Ma ago and spanned at least five magnetic polarity intervals (Dagley *et al.*, 1990). Basalts also extend over a large area of Skye. Regional dike swarms extend in a NW−SE linear trend from northwestern Scotland and the north of Ireland into southern Scotland, northern England, Wales and the Midlands (Emeleus, 1991).

Marls and mudstones for the study by Woods *et al.* (2002) were collected from multiple units within the Middle Jurassic Great Estuarine Group having ages between 157 and 165 Ma. These Mesozoic sedimentary rocks in northern Skye (near Duntulm, Figure 1) are unaltered, flat-lying or dipping at <5°, and marked by the presence of smectite as the predominant clay mineral. These sediments have not been buried deeply enough to form significant amounts of diagenetic illite by burial. The Mesozoic sedimentary rocks in southern Skye (at Elgol and Glen Scaladal) contain illitic clays and are in proximity to the Tertiary igneous rocks (Figure 1). The illitic clays in the Mesozoic rocks are believed to have formed in response to elevated geothermal gradients and hydrothermal fluids associated with Tertiary igneous activity (Andrews, 1987; Woods *et al.*, 2002). Isotopic ($^{87}Sr/^{86}Sr$, $\delta^{13}C$, $\delta^{18}O$) studies confirm that these rocks have been altered (Woods *et al.*, 2002). Maximum burial depths for the Great Estuarine Group are <1500 m except in the vicinity of the igneous complexes where thick lava sequences may have produced a maximum cover of ~2500 m (Andrews, 1987).

The rocks in southern Skye contain multi-component magnetizations. At intermediate temperatures (225−450°C), a magnetization directed southward and upward or its antipodal equivalent was removed from many samples. At higher temperatures (450−580°C), a magnetization directed northward and downward or its antipodal equivalent was removed. Both of these components have directions similar to magnetization directions of Tertiary igneous rocks on Skye. Rock magnetic studies indicate the presence of pyrrhotite and magnetite. The intermediate temperature component resides in pyrrhotite and magnetite and is interpreted as a thermoviscous remanent magnetization or a thermochemical remanent magnetization related to heat and/or hydrothermal activity. The high-temperature component resides in magnetite, and smectite is thought to have converted to illite during the formation of the CRM in these marls (Woods *et al.*, 2002).

METHODS

Marls were collected from the Kilmaluag and Duntulm formations at Elgol for combined clay mineral and K-Ar determinations (Figure 1). The marls were crushed by hand to small (<2.5 cm) pieces which were soaked in deionized water for several days before gentle crushing with a ceramic mortar and pestle. The crushed marls were treated, following the methods of Jackson (1979), to remove carbonate cements, gross organic matter, and Fe oxides to permit better sub-micrometer size separation. Reaction temperature was limited to 50°C to minimize the possibility of Ar loss from illite during pre-treatments. Some calcite remained, as evident from slow-scan X-ray diffraction (XRD) analyses of random mounts for illite polytype analyses. The pre-treated samples were separated into coarse silt- (>20 μm), medium and fine silt- (2−20 μm), and clay-sized (<2 μm) fractions by timed settling. The <2 μm fractions were further separated into 1−2 μm, 0.25−1 μm and <0.25 μm size fractions by repetitive centrifugation. The clay subfractions were dialyzed in deionized water for ~3 days to remove dissolved salts. After dialysis, the clay subfractions were dried in an oven at 50°C.

Clay minerals were identified by XRD using Georgia State University's Philips Model 12045 X-ray diffractometer equipped with the MDI Databox® for computer control of the diffractometer and the acquisition of diffraction data as a function of 2θ. Air-dried, ethylene glycol-solvated, and heated (550°C) oriented mounts were scanned from 2 to 32°2θ at 0.02°2θ s^{-1} using CuKα radiation produced at 35 kV and 15 mA and filtered with a graphite monochromator. The type of stacking order of illite-smectite (I-S) was identified following the procedures of Hower (1981). The percentage of illite layers in I-S was detected from the $002_{10}/003_{17}$ peak position measured on ethylene glycol-solvated oriented mounts (Moore and Reynolds, 1997). Since I-S in the Elgol marls contains large percentages of illite layers, the Środoń intensity ratio (IR) was measured to detect the presence of expandable layers (smectite layers) in I-S (Środoń, 1984). The IR is calculated from the intensity ratio of the 001 and 003 peaks from air-dried samples divided by the same intensity ratio of peaks from gycol-solvated samples (*e.g.* Moore and Reynolds, 1997). In samples composed of I-S only, this ratio is useful to determine more precisely the small percentages of swelling (smectite) layers in illite. In addition to IR, the Kübler index was measured from the width at half height of the 001 illite reflection using the peak area tool in the MDI Program Jade® on the raw pattern without correction to a constant baseline. The Kübler index (also known as 'the crystallinity index') has proved to be useful for determining the degree of metamorphism (diagenetic, anchizonal, or epizonal) in very low-grade pelitic rocks (Kübler, 1964, 1967, 1968). The Kübler index plotted against Środoń's IR is used to identify a small percentage of expandable layers in I-S and to derive the average scattering domain size of illite crystallites (*e.g.* Eberl and Velde, 1989).

The percentage of the $2M_1$ illite polytype relative to the total amount of the $1M_d$, $1M$ and $2M_1$ polytypes was

determined from diffraction scans of randomly oriented clay subfractions from two Elgol marls samples. Only from EL-6 did enough sample material from each clay subfraction remain for this purpose after K-Ar measurements, and the amounts remaining were small (5–100 mg). For EL-13/14, there was sufficient material to determine the percentage of $2M_1$ illite for only the two coarser clay subfractions. Prior to polytype analyses, we heated these samples to 550°C to destroy kaolinite, from which a low-intensity *hkl* peak at 2.558 Å may interfere with quantification of illite polytypes (Brindley, 1961). Given the small masses of the size fractions remaining after K-Ar analyses, the samples were top-loaded into a quartz crystal sample holder with a circular cavity 1 cm in diameter and 0.2 mm deep. This quartz crystal is oriented in a way to minimize the background signals over the range of 2θ scanned. Surprisingly, there was not as much preferred orientation as we had expected. These XRD data were obtained with a Philips® X-pert MPD theta-theta diffractometer at Portland State University using CoKα radiation (1.78897 Å) produced at 40 kV and 30 mA. One-degree divergence and antiscatter slits and a 0.1 mm receiving slit were used.

The polytype determinations were obtained from scans performed with 0.025°2θ step size and a count time of 45 s per step. Measurements of XRD peak heights, areas, and widths of tracings were made using software provided with the Philips® machine. The percentage of the $2M_1$ polytype was determined from the area and intensity of $2M_1$ polytype specific reflections, including the 3.74 Å, 3.00 Å and 2.80 Å reflections, divided by the area of the 2.58 Å peak (Grathoff and Moore, 1996). The error is based on the standard deviation of the counts measured for a given sample. For EL-13/14, we compared experimental XRD patterns with patterns generated from mixtures of pure illite polytypes, such as those described by Grathoff and Moore (2002), to derive the percentage of the $2M_1$ polytype as an independent check of the accuracy of the quantification. The diffraction data of the standard minerals were determined with Cu radiation. The intensity *vs.* 2θ data of the Elgol clay subfractions were replotted in terms of Cu radiation and compared to the diffraction data of the mineral standard mixtures. The error is calculated from the standard deviation of the quantification results from the different polytype-specific reflections within each sample.

K-Ar measurements were done on samples of all of the size-fractionated clays except the finest subfraction of EL-5. For K determination, a portion (usually ~10 mg) of each sample was digested overnight in 1 mL of a 10:1 HF-HClO$_4$ mixture in a fluorocarbon (FEP) container. The perchlorate salts left upon evaporation of the digestion acid were dissolved in a diluting nitric acid (0.10 M) solution containing 0.0100 mol kg^{-1} of Cs. When necessary, more of the Cs-bearing diluting solution was added in gravimetri-

cally determined proportion to dilute the original sample solution. The mass fraction of K in each sample solution was determined by flame atomic absorption spectrophotometry against reference solutions prepared from a KCl standard (NIST SRM-999). Four independent comparisons of flame absorbance for each solution relative to that for reference solutions were sufficient that the relative standard error of the mean value for K content of each solution was <0.5%.

For Ar isotopic analysis, a portion (usually ~25 mg) of each sample was weighed into a Cu-foil capsule immediately after a sample of the same material had been weighed for K determination. The materials in the capsules were dried overnight under vacuum at room temperature. After reweighing (so that dry-sample masses could be calculated for reporting Ar and K contents) the capsules were placed in the Ar extraction line in a recorded sequence. A calibrated amount of ^{38}Ar was released into the extraction line during fusion of each sample. H$_2$O, CO$_2$ and some other products of thermal decomposition of the sample were condensed as ices on a cold finger cooled at its base with liquid nitrogen. Most of the remaining reactive gases were removed by reaction with Ti (initially hot, then cooling), in two stages. After adsorption of most of the Ar on liquid nitrogen-cooled charcoal, the condensed ices were allowed to evaporate and move to a second cold finger, releasing any Ar trapped with the ices initially so that it could go onto the charcoal. After its release from the charcoal, the Ar expanded into an on-line AEI MS-10 mass spectrometer, where a final reaction with Ti reduced interference by reactive gases to a low level for static isotopic analysis. Recorded peak heights representing the ion currents at *m/e* (mass/charge, in atomic units) values of 36, 38 and 40 were measured manually and used for calculation of Ar isotope ratios after correction for mass discrimination (determined from isotopic measurements of atmospheric argon) and correction for small background signals from hydrocarbons based on measurement of the signal corresponding to *m/e* 37. The *m/e* 37 signal was measurable for only the first sample, EL12 < 0.25 μm. The hydrocarbon background in that case is attributed to organic matter from the sample, because only one stage of Ti gettering was used before the Ar from the first sample was admitted to the mass spectrometer. In all subsequent argon runs, an additional gettering stage was used. The Ar isotope ratios were used to calculate the amount of radiogenic argon (^{40}Ar*) in each sample, which is reported in nmol kg^{-1} of vacuum dried sample. Three samples of the interlaboratory reference biotite, 'LP-6 Bio', were run to check the calibration of the ^{38}Ar spike and accuracy of the corrections to the raw mass spectrometric data. The measured values of ^{40}Ar$_{rad}$ for LP-6 Bio, 1915, 1929 and 1933 nmol kg^{-1}, compare well with the accepted value of 1930 nmol kg^{-1} (Odin *et al.*, 1982). The K content is reported as the mass of the

Table 1. Clay mineralogy, Kübler index, Środoń intensity ratio, and K-Ar data for Elgol marls.

Sample, size fraction	Clay mineralogy	Kübler index	Intensity ratio	K (wt. %)	^{40}Ar* (%)	^{40}Ar* (nmol kg^{-1})	Apparent age (Ma)
EL-5, 1−2 μm	K, I-S (90%I), C	0.81	1.31	1.83			
EL-5, 0.25−1.0 μm	I-S (85%I), K	0.89	1.63	3.05	18	716	131±14
					17	735	134±16
EL-5, <0.25 μm	I-S (85%I), K. tr. C	1.20	1.33				
EL-6, 1−2 μm	K, I-S (90%I), C	0.50	1.20	1.93	55	559	160±4
EL-6, 0.25−1 μm	K, I-S (90%I), C	0.77	1.42	2.73	28	661	135±9
					24	683	139±11
EL-6, <0.25 μm	I-S (90%I), K, tr. C	0.90	1.30	3.12	39	604	108±5
EL-12, 1−2 μm	K, I-S (90%I), C	0.75	2.04	2.40	67	955	216±4
EL-12, 0.25−1 μm	I-S (90% I), K. tr. C	0.68	1.40	1.99	10	591	164±34
EL-12, <0.25 μm	I-S (90% I), K	1.00	1.18	2.02	13	384	106±17
EL-13/14, 1−2 μm	I-S (90%I), K, tr. C	0.80	1.26	3.55	89	1238	191±3
EL-13/14, 0.25−1 μm	I-S (90%I), K, tr. C	0.90	1.76	4.08	87	1105	150±2
EL-13/14, <0.25 μm	I-S (90% I), K.	1.20	1.89	4.64	89	850	103±2

Notes: K − kaolinite, I-S − illite-smectite; C − chlorite; tr. − trace; ^{40}Ar* − radiogenic argon. Repeat measurements for ^{40}Ar* are given for the 0.25−1.0 μm fractions of EL-5 and EL-6. Uncertainties in age values are based on estimates of the effect of analytical errors at the 95% confidence level (2σ).

element K, expressed as a percentage of the mass of material sampled, had that material been vacuum-dried. The K content of LP-6 Bio measured in this study (8.34% K, by mass) also compares well with the accepted value of 8.29% K (Odin *et al.*, 1982). See Basu (2004) for additional details of clay mineralogy and K-Ar procedures used for this study.

Lastly, given the K-Ar ages of the clay fractions and the percentages of $2M_1$ illite polytype in some of these fractions, illite age analysis was applied to these data to estimate the age of diagenetic illite (Pevear, 1999). Linear regressions of K-Ar age *vs.* the percentages of the $2M_1$ illite polytype were accomplished using an Excel spreadsheet to provide estimates of the age of diagenetic illite in EL-6 and EL-13/14 (Grathoff and Moore, 1996; Pevear, 1999).

RESULTS

The clay mineralogy results and the K-Ar dates of clay fractions are given in Table 1. In terms of the mineralogy of the clay fractions from oriented mounts of the clay fractions, kaolinite and I-S are present in all samples of the Elgol marls. The percentages of illite layers in I-S range from 85 to 90%, and the Kalkberg stacking order (R = 3) of I-S is observed in all clay fractions. Chlorite is also present in most clay fractions. Small amounts of calcite are noted in EL-6 and in EL-13/14 as seen from the slow-scan XRD data measured to quantify the percentage of the $2M_1$ polytypes. Albite was observed in the two coarser clay fractions of EL-13/14.

The presence of smectite layers in I-S is seen also by IR and Kübler index measurements. The Kübler index values range from 0.50 to 1.20 and these values generally decrease with increased grain size. The IR

values vary from 1.18 to 2.04 for EL-12 (1−2 μm). From the cross plot of IR *vs.* Kübler index (Figure 2), it appears that 10 of 12 Elgol I-S have 3−6% of expandable (smectite) layers. The <0.25 μm subfraction of EL-13/14 has ~7% expandable layers and the 1−2 μm subfraction of EL-6 has ~2% expandable layers. The EL-12 samples had relatively small peak to saddle ratios for the 001 peaks, so the Kübler index and IR measurements for EL-12 are less precise than those for other samples.

The percentages of the $2M_1$ illite polytype are given in Table 2. As mentioned in the Methods section above, the percentage of $2M_1$ polytype was measured only for EL-6 and for two clay fractions of EL-13/14. These percentages vary from ~5% to 28% and they increase
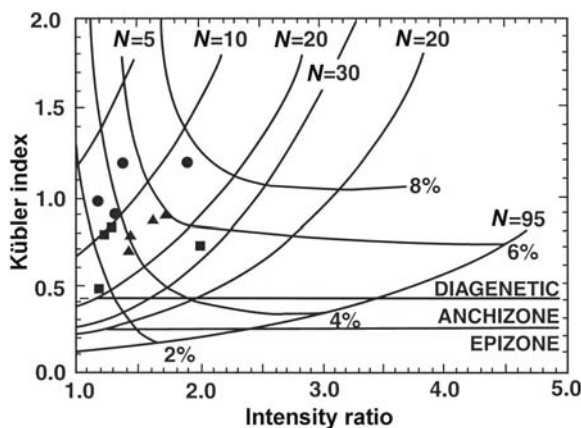

Figure 2. A plot of Kübler index *vs.* the Środoń intensity ratio for Elgol I-S. Isopleths (from Eberl and Velde, 1989) are of the XRD scattering domain size (*N*) of I-S crystallites and of the percentage of swelling (smectite) layers in I-S. Circles denote <0.25 μm fractions, triangles denote 0.25−1.0 μm fractions, and squares denote 1−2 μm fractions.

Table 2. Percentages of the $2M_1$ polytype for the Elgol marls.

Sample	Size fraction (μm)	$2M_1$ polytype (peak area) (%)	K-Ar age value (Ma)
EL-6	<0.25	<5±5[#]	108
EL-6	0.25−1	12±3	135, 139
EL-6	1−2	26±6	160
EL-13/14	<0.25	n.d.	103
EL-13/14	0.25−1	12±4	150
EL-13/14	1−2	28±6	191

Notes: # denotes estimated percentage of $2M_1$ polytype. n.d. is not determined. K-Ar ages are from Table 1.

with increasing particle size. In EL-6, the percentages of the $2M_1$ illite polytype increase from just detected (<5%) in the <0.25 μm fraction, to 12% for the 0.25−1.0 μm fraction and to 26% in the 1−2 μm fraction (Table 2, Figure 3). In EL-13/14, the percentages of the $2M_1$ polytype are 12% in the 0.25−1.0 μm fraction and 28% in the 1−2 μm fraction (Figure 4). Of note, the measured percentages of the $2M_1$ polytype in EL-13/14 agree well with the percentages of the $2M_1$ illite determined from measurement of mixtures of $2M_1$ and $1M_d$ illite polytypes (Table 2, Figure 4).

The K-Ar age values of the clay subfractions vary from 103 Ma to 216 Ma. There was no measurement of the finest fraction of EL-5, and no Ar data are reported for the coarsest fraction of that sample because, in each of two Ar measurements, the amount of radiogenic Ar could not be determined owing to an overwhelming amount of atmospheric Ar. Otherwise, the age values increase with increasing particle size. The K mass fractions of the size fractions vary significantly. The

coarsest size fraction has the smallest K content in three of the four marls. The overall low K values relative to ideal K contents for illite (~7%) reflect the presence of significant amounts of kaolinite and chlorite in the clay fractions. Kaolinite and chlorite are dilutants with respect to K and Ar measurements; their presence should have had no appreciable effect on the K-Ar age values.

The increase in both the K-Ar age values and the percentages of the $2M_1$ polytype with increasing grain size is shown for EL-6 and EL-13/14 in Figure 5. The estimated ages for diagenetic illite (I-S) in samples EL-6, and EL-13/14 are 106 and 100 Ma, respectively, based on extrapolation of the linear regression of K-Ar age to 0% of $2M_1$ illite and using 2.5% as the amount of the $2M_1$ polytype in the finest fraction in each case.

INTERPRETATION AND DISCUSSION

The primary goal of this study has been to determine the age of the diagenetic I-S in the Elgol marls for comparison with the previously determined early Tertiary age of the CRM of these and other rocks of the Great Estuarine Group in southern Skye.

The large percentages of illite layers (>85%), the Kalkberg stacking order, and the Kübler Index values (0.50−1.20) observed in the Elgol marl I-S indicate that the I-S was formed in these marls by processes the temperatures of which were greater than could be explained by 2.5 km of burial. A more precise determination of the percentages is not possible by use of the $002_{10}/003_{17}$ peak positions because the positions of those peaks corresponding to 90% and 100% illite layers in I-S differ only by approximately 0.3°2θ (Moore and Reynolds, 1997). In addition, the 001 and 003 reflections of the $2M_1$ polytype, interpreted to be a detrital phase,
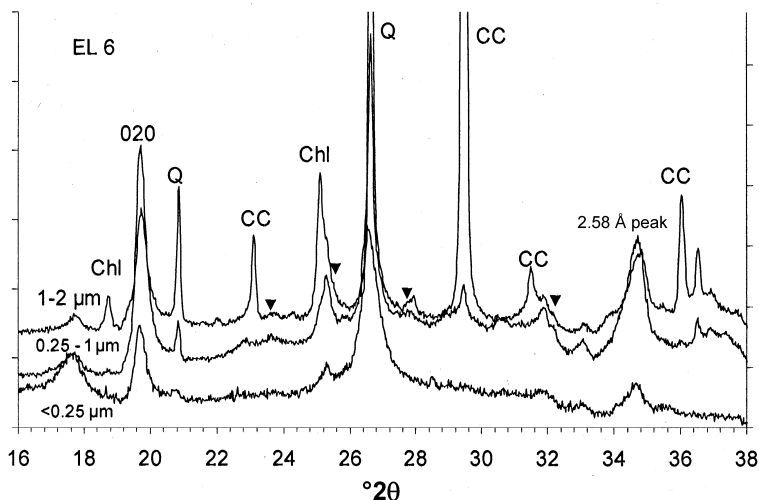

Figure 3. Stacked XRD patterns of the subfractions of EL-6. The uppermost pattern is of the 1−2 μm subfraction, which contains 26% $2M_1$ polytype. The middle pattern is of the 0.25−1.0 μm subfraction, which contains 12% $2M_1$ polytype. The lowermost pattern is of the 0.25 μm subfraction, which contains <5% $2M_1$ polytype. CC is calcite; Q is quartz; Chl is chlorite. The inverted triangles point to $2M_1$ polytype-specific peaks.
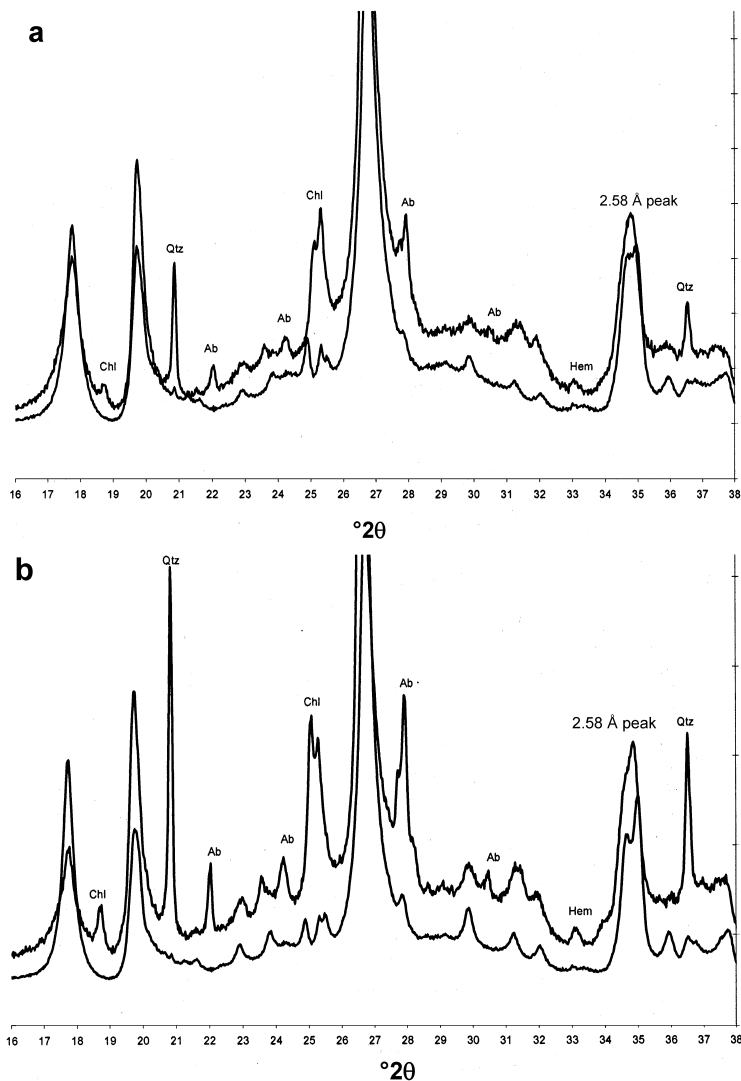
Figure 4. (a) The upper pattern is the XRD pattern of the 0.25−1 μm subfraction of EL-13/14. The lower pattern is a calculated pattern of a mixture containing 12% of the <2 μm SG4 ($2M_1$ illite) (Eberl *et al.*, 1987) with 88% of the <2 μm Silver Hill ($1M_d$ illite) (Hower and Mowatt, 1966). (b) The upper XRD pattern is of the 1−2 μm subfraction of EL-13/14. The lower pattern is a calculated diffraction pattern for a mixture of 28% <2 μm SG4 ($2M_1$) and 72% Silver Hill illite ($1M_d$). Ab is low albite; Hem is hematite; Qtz is quartz; Chl is chlorite.

overlap with the strong basal reflections of I-S, which decreases the precision of both illite crystallinity (Kübler index) values and illite intensity ratio values as applied to this work. Consequently, the combined use of IR and Kübler index values, which is normally thought to provide a more precise estimate of the percentage of smectite layers in illitic I-S, is considered in this work to provide estimates for the percentages of illite layers in I-S that are consistent with the percentages of illite layers in I-S from the $002_{10}/003_{17}$ peak positions. The presence of illitic I-S is consistent with temperature conditions that are greater than temperatures expected from burial alone in this area.

The measured K-Ar ages range from 103−216 Ma and the ages increase with increased grain size

(Table 1). The measured K-Ar ages from even the smallest size fractions are >40 Ma greater than the age of early Tertiary magmatic activity in southern Skye and are thus substantially greater than the age of CRM inferred by Woods *et al.* (2002). In-so-far as it was determined, the amount of the $2M_1$ polytype also increases with increasing grain size as shown in Figures 3 and 4 and Table 2. Similar increases in both the K-Ar age value and the percentage of the $2M_1$ polytype with increasing grain size have also been observed in many previous studies of argillaceous rocks (*e.g.* Hower *et al.*, 1963; Grathoff, 1996; Grathoff and Moore, 1996; Bechtel *et al.*, 1999). In these and other studies, the measured K-Ar age of the illitic clay in shales and marls is conventionally viewed as a weighted
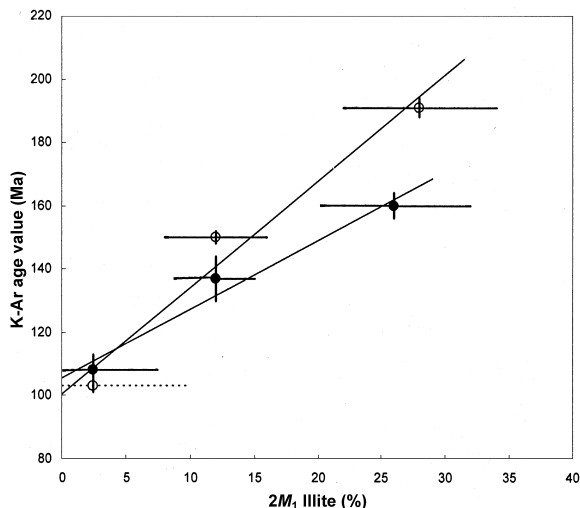
Figure 5. K-Ar age values *vs.* percentages of $2M_1$ polytype for clay subfractions of EL-6 (filled symbols) and EL-13/14 (open symbols) showing regression lines for illite age analysis. The value used in the regressions for the $2M_1$ illite polytype in the finest clay subfraction (<0.25 μm) of each marl is 2.5%, but the dashed line indicates that the value for that subfraction of EL-13/14 was not measured and might be considerably larger than 2.5% or even 5%.

average of the ages of diagenetic and detrital illites. Consequently, small amounts of detrital illite make it difficult to find the age of diagenetic illite directly even by way of separating finer submicrometer size fractions of marls and shales (*e.g.* Clauer *et al.*, 1997).

Illite age analysis is one approach used to estimate the age of diagenetic illite in the presence of detrital illite for time-temperature burial history analyses (Pevear, 1999). As applied to this study, illite age analysis (*i.e.* a linear extrapolation of the K-Ar age as a function of the percentage of the $2M_1$ polytype to 0% $2M_1$ polytype) yields 106 Ma as the age of diagenetic illite for EL-6 (Figure 5), a value still >40 Ma greater than the age of Tertiary magmatic rocks of southern Skye and the CRM associated with these marls (Woods *et al.*, 2002). If it were to be assumed that the $2M_1$ polytype in the finest fraction of EL-13/14 is virtually undetectable (<5%), as it was in the finest subfraction of EL-6, illite age analysis would yield an age of diagenetic illite of ~100 Ma, not significantly different from the result for EL-6. We also note that additional data points would aid in curve fitting and help to define the age estimates for detrital and diagenetic illite.

Derivation of the age of diagenetic illite from linear illite age analysis plots was questioned by Środoń (1999). The use and derivation of illite age analysis were discussed and clarified by Ylagan *et al.* (2000) and further discussed by Środoń (2000). Strictly, a linear relationship of the kind used in illite age analysis is not to be expected from a binary mixture of detrital and diagenetic illite (or I-S) if either the ages or the K contents of the two components differ. However, the

departure from linearity is minor if the K contents of detrital and diagenetic illites differ by only a small factor (<1.5) and if the ages of the two components differ by less than the half-life of ^{40}K (1250 Ma) (Bechtel *et al.*, 1999; Środoń, 1999; Ylagan *et al.*, 2000). Pevear (1999) considered hypothetical situations in which illite age analysis might not work and recognized the intrinsic non-linearity of the function that is extrapolated in the technique. He noted, however, that most of many data sets fit a straight line rather well and pointed out that the method has worked in cases where there is an independent test of the age of a component, as for example when the age of diagenetic I-S is supported by the K-Ar age of I-S from a bentonite.

The most accurate extrapolation to derive the age of a diagenetic end-member requires knowledge of the K content of the diagenetic illite phase relative to that of the detrital illite, which is difficult to determine (Ylagan *et al.*, 2000; Środoń, 2000). The presence of dilutants (chlorite and kaolinite, as well as some organic matter), in amounts that are not known quantitatively, in the clay fractions of the Elgol marls (Table 1) makes it difficult to determine precisely the K content of the diagenetic illite from the measured K content of any size fraction. Although K content increases with decreasing particle size in these samples, both dilutants are present in even the finest fraction of the EL-6 and EL-13/14 marls.

In the case of the EL-6 marl and possibly EL-13/14, the virtual undetectability of the $2M_1$ polytype in the finest subfraction results in there being no significant difference between the K-Ar age of that subfraction and the age of diagenetic I-S therein estimated by illite age analysis. This fortunate consequence makes it unimportant whether or not a linear regression should be used in illite age analysis for EL-6. The same would be true for EL-13/14 if <5% of the illite in its finest subfraction were $2M_1$.

By illite age analysis, the diagenetic I-S in the EL-6 marl is estimated to be >40 Ma older than the nearby Tertiary igneous rocks. In the presence of independent evidence that these marls were altered in response to the Tertiary igneous activity (Woods *et al.*, 2002) and in the absence of evidence for alteration of these rocks ~100 Ma ago, it is necessary to consider that the assumptions of illite age analysis do not apply in this case. Hurley *et al.* (1963) noted that recycled $1M_d$ illite is present in relatively young (post-Paleozoic) shales. Much more recently, Środoń (1999) suggested for a particular case (the Kupferschiefer) that part of the $1M_d$ illite in sedimentary rocks may be detrital. The presence of a modest amount of $1M_d$ illite recycled from early Paleozoic shales may well account for the greater than expected result of illite age analysis for the EL-6 clay. For example, the observed K-Ar age of the finest size fraction of the EL-6 marl can be explained as the weighted average of a small amount (~20%) of detrital Caledonian illite (325 Ma) and 80% diagenetic illite of early Tertiary age (55 Ma).

If no diagenetic illite had formed in the Elgol marls, there presumably would be small amounts of illite in the marls that came largely from shales and slates of the Scottish Caledonides and that would have K-Ar ages of 325 Ma or more. Assuming that, the measured K-Ar ages can be interpreted as showing that a large percentage of the illite in the Elgol marls must be substantially younger than 100 Ma. That would support the inference by Andrews (1987) and by Woods *et al.* (2002) that there was extensive illitization in the early Tertiary. Although the date of the illitization has not been pinned down to the early Tertiary by illite age analysis in this work, there is no known event other than the early Tertiary hydrothermal activity that might have caused extensive illitization in these marls.

The presence in EL-13/14 of albite interpreted to be diagenetic permits speculation that the fluids released during Early Tertiary volcanism had a low K/Na ratio. The amount of diagenetic illite that can be formed increases with increasing K/Na in solution (Pytte, 1982; Altaner, 1989; Elliott and Matisoff, 1996). The presence of albite-forming diagenetic fluids having low K/Na ratios during illitization of the Elgol marls may have limited the amount of diagenetic illite formed, thus enhancing the abundance of detrital $1M_d$ illite relative to diagenetic illite in this case.

The smectite-to-illite conversion is a prevalent process in argillaceous rocks, and continued work on refining techniques for finding the age of diagenetic illite should be helpful in understanding thermal histories of sedimentary basins and timing of thermal maturation of reservoir rocks (*e.g.* Pevear, 1999). Further work on approaches to derive an estimate of the age of diagenetic illite is clearly warranted, particularly in such cases as the Elgol marls where the thermal and chemical environments, over time, may have been quite different from those within argillaceous detrital rocks of typical sedimentary basins.

CONCLUSIONS

X-ray diffraction studies of clay separated from Jurassic marls from Elgol, Isle of Skye show the presence of I-S with >85% illite layers, as determined by measurement of I-S $002_{10}/003_{17}$ peak positions and supported by values of the Środoń intensity ratio. Kaolinite and small amounts of chlorite are also present. The presence of illite-rich I-S, and the observed crystallinity index values indicate that these rocks experienced temperatures greater than those to be expected from their relatively shallow burial. These results are consistent with proposals by others that the illite formed in response to regional heating from nearby early Tertiary igneous activity and associated hydrothermal activity.

An estimate of the age of diagenetic illite based on illite age analysis suggests that the diagenetic illite is >40 Ma older than the Tertiary intrusions in this region, but this is not consistent with a body of other evidence that associates illitization of the Elgol marls with the Tertiary igneous activity. The cause of the inconsistency may be the presence of relatively small amounts of detrital $1M_d$ illite, the ages of which are superimposed on that of illite produced diagenetically in the early Tertiary. Given the presence of albite in the two coarser clay subfractions of EL-13/14, the amounts of diagenetic illite in the Elgol marls may have been limited by small K/Na ratios in the hydrothermal fluids. The results of this study indicate that further work on illite age analysis is warranted, particularly where illite formation has occurred in environments considerably different from those deep in a typical sedimentary basin.

REFERENCES

Altaner, S.P. (1989) Calculation of K diffusional rates in bentonite beds. *Geochimica et Cosmochimica Acta*, **53**, 923−931.

Andrews, J.E. (1987) Jurassic clay mineral assemblages and their post-depositional alteration: Upper Great Estuarine Group, Scotland. *Geological Magazine*, **124**, 261−271.

Banerjee, S., Elmore, R.D. and Engel, M.H. (1997) Chemical remagnetization and burial diagenesis of organic matter: Testing the hypothesis in the Pennsylvanian Belden Formation, Colorado. *Journal of Geophysical Research*, **102**, 24825−24842.

Basu, A. (2004) A Comparison of K-Ar Ages of Illite to the Age of Chemical Remnant Magnetization. MS thesis, Georgia State University, Atlanta, USA, 107 pp.

Bechtel, A., Elliott, W.C., Wampler, J.M. and Oszczepalski, S. (1999) Clay mineralogy, crystallinity, and K-Ar ages of illites within the Polish Zechstein Basin: Implications for the age of Kupferschiefer mineralization. *Economic Geology*, **94**, 261−272.

Blumstein, A.M., Elmore, R.D. and Engel, M.H. (2004) Paleomagnetic dating of burial diagenesis in Mississippian carbonates, Utah. *Journal of Geophysical Research*, **109**, B4, B04101, 10.1029/2003JB002698

Boles, J.R. and Franks, S.G. (1979) Clay diagenesis in Wilcox sandstones of Southwest Texas: Implications of smectite diagenesis on sandstone cementation. *Journal of Sedimentary Petrology*, **49**, 55−70.

Brindley, G.W. (1961) Kaolin, serpentine, and kindred minerals. Pp. 51−131 in: *The X-ray Identification and Crystal Structures of Clay Minerals*, 2nd edition (G. Brown, editor). Mineralogical Society, London.

Burst, J.F. (1969) Diagenesis of Gulf Coast clayey sediments and its possible relation to petroleum migration. *American Association of Petroleum Geologists Bulletin*, **53**, 73−93.

Clauer, N., Środoń, J., Francǔ, J. and Šucha, V. (1997) K-Ar dating of illite fundamental particles separated from illite-smectite. *Clay Minerals*, **32**, 181−196.

Dagley, P., Musset, A.E. and Skelhorn, R.R. (1990) Magnetic polarity stratigraphy of the Tertiary igneous rocks of Skye,

Scotland. *Geophysical Journal International*, **101**, 395−409.

Eberl, D.D. and Velde, B. (1989) Beyond the Kübler Index. *Clay Minerals*, **24**, 571−577.

Eberl, D.D., Srodon, J., Lee, M., Nadeau, P.H. and Northrop, H.R. (1987) Sericite from the Silverton caldera, Colorado: Correlation among structure, composition, origin, and particle thickness. *American Mineralogist*, **72**, 914−934.

Elliott, W.C. and Matisoff, G. (1996) Evaluation of kinetic models for the smectite to illite transformation. *Clays and Clay Minerals*, **44**, 77−87.

Elmore, R.D., London, D., Bagley, D., Fruit, D. and Gao, G. (1993) Remagnetization by basinal fluids: Testing the hypothesis in the Viola Limestone, southern Oklahoma. *Journal of Geophysical Research*, **98**, 6237−6254.

Elmore, R.D., Kelley, J., Evans, M. and Lewchuk, M.T. (2001) Remagnetization and orogenic fluids: Testing the hypothesis in the central Appalachians. *Geophysical Journal International*, **144**, 568−576.

Emeleus, C.H. (1991) Tertiary igneous activity. Pp. 455−502 in: *Geology of Scotland*, 3rd edition (G.Y. Craig, editor). Geological Society, London.

Gill, J.D., Elmore, R.D. and Engel, M.H. (2002) Chemical remagnetization and clay diagenesis: Testing the hypothesis in the Cretaceous sedimentary rocks of northwestern Montana. *Physics and Chemistry of the Earth*, **27**, 1131−1139.

Grathoff, G.H. (1996) Illite in the lower Paleozoic of the Illinois basin. Origin, age, and polytype quantification. PhD dissertation, University of Illinois Urbana-Champaign, USA, 87 pp.

Grathoff, G.H. and Moore, D.M. (1996) Illite polytype quantification using WILDFIRE© calculated X-ray diffraction patterns. *Clays and Clay Minerals*, **44**, 835−842.

Grathoff, G.H. and Moore, D.M. (2002) Characterization of the Waukesha illite: A mixed-polytype illite in the Clay Mineral Society repository. *American Mineralogist*, **87**, 1557−1563.

Hallam, A. (1991) Jurassic, Cretaceous and Tertiary sediments. Pp. 439−453 in: *Geology of Scotland*, 3rd edition (G.Y. Craig, editor). Geological Society, London.

Hoffman, J. and Hower, J. (1979) Clay mineral assemblages as low grade metamorphic geothermometers: Application to the thrust faulted disturbed belt of Montana, U.S.A. Pp. 55−79 in: *Aspects of Diagenesis* (P.A. Scholle and P.R. Schluger, editors). Special Publication **26**, Society of Economic Paleontologists and Mineralogists.

Hower, J. (1981) X-ray diffraction identification of mixed-layer clay minerals. Pp. 39−59 in: *Clays and the Resource Geologist* (F.J. Longstaffe, editor). Short Course, **7**, Mineralogical Association of Canada.

Hower, J. and Mowatt, T.C. (1966) The mineralogy of illites and mixed-layer illite/montmorillonites. *American Mineralogist*, **51**, 825−854.

Hower, J., Hurley, P.M., Pinson, W.H. and Fairburn, H.W. (1963) The dependence of K-Ar age on the mineralogy of various particle size ranges in a shale. *Geochimica et Cosmochimica Acta*, **27**, 405−410.

Hudson, J.D. and Andrews, J.E. (1987) The diagenesis of the Great Estuarine Group, Middle Jurassic, Inner Hebrides, Scotland. Pp. 259−276 in: *Diagenesis of Sedimentary Sequences* (J.D. Marshall, editor). Special Publication **36**, Geological Society, London.

Hurley, P.M., Hunt, J.M., Pinson, W.H. and Fairbairn, H.W. (1963) K-Ar age values on the clay fractions in dated shales. *Geochimica et Cosmochimica Acta*, **27**, 279−284.

Jackson, M.L. (1979) *Soil Chemical Analysis − Advanced Course*. Published by the Author, Madison, Wisconsin, 895 pp.

Katz, B., Elmore, R.D., Engel, M.H., Cogoini, M. and Ferry, S. (2000) Associations between burial diagenesis of smectite, chemical remagnetization, and magnetite authigenesis in the Vocontian Trough, SE France. *Journal of Geophysical Research*, **105**, 851−868.

Kübler, B. (1964) Les argiles, indicateurs de metamorphisme. *Revue de l'Institut Francais du Petrole*, **19**, 1093−1112.

Kübler, B. (1967) La crystallinite de l'illite et les zones tout a fait superieures du metamorphisme. Pp. 105−122 in: *Etages Tectoniques*. Institute of Geology, Neuchatel University, Switzerland.

Kübler, B. (1968) Evaluation quantitative du metamorphisme par la cristallinite de l'illite: Etat des progres realises ces dernieres annees. *Centre de Recherches de Pau (Societe Nationale des Petroles d'Aquitaine) Bulletin*, **2**, 385−397.

McCabe, C. and Elmore, R.D. (1989) The occurrence and origin of late Paleozoic remagnetization in the sedimentary rocks of North America. *Review of Geophysics*, **27**, 471−494.

Moore, D.M. and Reynolds, R.C. Jr. (1997) *X-ray diffraction and the Identification and Analysis of Clay Minerals*. Oxford University Press, Oxford, UK, 378 pp.

Odin, G.S. and 35 collaborators (1982) Interlaboratory standards for dating purposes. Pp. 123−150 in: *Numerical Dating in Stratigraphy* (G.S. Odin, editor). John Wiley & Sons, New York, 1040 pp.

Pevear, D.R. (1999) Illite and hydrocarbon exploration. *Proceedings of the National Academy of Sciences*, **96**, 3440−3446.

Pollastro, R.M. (1993) Considerations and applications of the illite/smectite geothermometer in hydrocarbon-bearing rocks of Miocene to Mississippian age. *Clays and Clay Minerals* **41**, 119−133.

Pytte, A.M. (1982) The kinetics of the smectite to illite reaction in contact metamorphic shales. MA thesis, Dartmouth College, Hanover, New Hampshire, USA, 78 pp.

Richey, J.E. (1961) Tertiary igneous rocks: Introduction and plateau lavas. Pp. 41−54 in: *The Tertiary Volcanic Districts of Scotland*, 3rd edition (revised by A.G. MacGregor and F.W. Anderson). British Geological Survey, Nottingham, UK.

Środoń, J. (1984) X-ray powder diffraction identification of illitic materials. *Clays and Clay Minerals*, **32**, 337−349.

Środoń, J. (1999) Extracting K-Ar ages from shales: a theoretical test. *Clay Minerals*, **33**, 375−378.

Środoń, J. (2000) Reply to discussion of 'Extracting K-Ar ages from shales: a theoretical test'. *Clay Minerals*, **35**, 605−608.

Woods, S.D., Elmore, R.D. and Engel, M.H. (2002) Paleomagnetic dating of the smectite-to-illite conversion: Testing the hypothesis in Jurassic sedimentary rocks, Skye, Scotland. *Journal of Geophysical Research*, **107**, B5, 10.1029/2000JB000053.

Ylagan, R.F., Pevear, D.R. and Vrolijk, P.J. (2000) Discussion of 'Extracting K-Ar ages from shales: a theoretical test'. *Clay Minerals*, **35**, 599−604.