

## K-AR DATING OF ILLITIC FRACTIONS OF ESTONIAN “BLUE CLAY” TREATED WITH ALKYLAMMONIUM CATIONS

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**Abstract**—Two clay fractions of a Cambrian claystone from Estonia, consisting essentially of illite and 20% expandable illite–smectite, (I–S) were treated with C<sub>12</sub> and C<sub>18</sub> alkylammonium cations for K-exchange. Both the untreated and treated samples were dated by the K-Ar method. The treated clays lost several percent of their original K<sub>2</sub>O, with greater losses for longer-chain cations and for longer reaction time, in accordance with previously published studies. The dates of the treated clay fractions were 20–30 Ma lower than those of the untreated clays. The decrease in the dates suggests preferential opening of older, detrital clays. The K-Ar dates of the illite layers susceptible to K extraction by the various treatments were calculated by subtracting K<sub>2</sub>O and radiogenic <sup>40</sup>Ar values of the consecutive step products, and they were plotted against the total % K<sub>2</sub>O removed, used as an indicator of the reaction progress. Extrapolation of the plot revealed a detrital (1550 Ma) and a diagenetic (380 Ma) age for the 2 illitic minerals present in the investigated shale sample. The inferred Devonian age of diagenesis of the Estonian clay corresponds to the period of massive dolomitization in the area. Both alteration processes can be related to a Devonian incursion of hot or alkaline fluids, which helps to explain the occurrence of 20% expandable I–S in claystones that have never been buried more than 1000 m.

Extrapolated K-Ar ages and K<sub>2</sub>O contents of the illitic minerals, estimated from the X-ray diffraction (XRD) data, were used to model the experimental data. A good agreement was reached when dilution effects (chlorite and expanded illite) were taken into account.

**Key Words**—Alkylammonium Cations, Estonian “Blue Clay”, Illite, K-Ar, Shale Diagenetic Age.

### INTRODUCTION

Defining reliable diagenetic ages of illitization in shales, where almost invariably diagenetic clay minerals are intimately mixed with detrital clay minerals, still remains a formidable challenge in isotope geochemistry of sedimentary rocks, even if radiogenic <sup>40</sup>Ar is not preferentially lost by small illite crystals, either in nature or during treatment (Clauer et al. 1997, and references therein). In most sedimentary basins, the detrital material of shales contains not only first-cycle coarse mica from crystalline rocks, but also eroded diagenetic illite and I–S. In such situations, separation of the postsedimentary diagenetic component is impossible, even if it is carried out down to grain sizes as small as <0.02 μm (Clauer et al. 1997). Different aspects of this problem have been covered in several publications (Burley and Flisch 1989; Ehrenberg and Nadeau 1989; Glasmann, Larter et al. 1989; Glasmann, Lundegard et al. 1989; Mossman 1991; Pevear 1992; Clauer and Chaudhuri 1996; Clauer et al. 1996).

An approach tried in this study explores the effect of opening the interlayer sites by alkylammonium cations on K-Ar systematics of illite. Alkylammonium cations are known to replace K cations in mica and illite stoichiometrically. In general, trioctahedral mica is more susceptible to K depletion, and longer-chain alkylammonium cations displace more K than the short ones (Weiss 1963; Mackintosh and Lewis 1968;

Galaly and Weiss 1969; Mackintosh et al. 1971, 1972; Ruhlicke and Niederbudde 1985; Laird et al. 1987). Additionally, unpublished HRTEM observations of Środoń and Vali indicate that the process is very selective: even in apparently homogenous illite or I–S, some crystals undergo opening and some remain untouched. Moreover, they observed that the replacement of K by alkylammonium cations is not restricted to crystal edges, but extends to the entire interlayer, implying favorable conditions for removal of K and its daughter <sup>40</sup>Ar from these sites. Alkylammonium treatment followed by K-Ar dating was then tried on size fractions from a claystone known to consist of detrital and authigenic illite. It was hoped that one of the components will be more susceptible than the other to opening by alkylammonium cations.

### MATERIAL AND ANALYTICAL PROCEDURES

The clay sample selected for the alkylammonium ion-exchange study was separated from a claystone of the Lower Cambrian Lontova unit that is exposed in a quarry near Kolgakula town in northern Estonia. The location of the quarry and the general geologic setting of this stratigraphic unit were given in Gorokhov et al. (1994). Following disaggregation of the claystone sample by shaking it in distilled water, the initial extraction of the <2 μm fraction was done by sedimentation and finer size fractions were collected by ultracentrifugation. Portions of the <0.1 and 0.1–0.4 μm

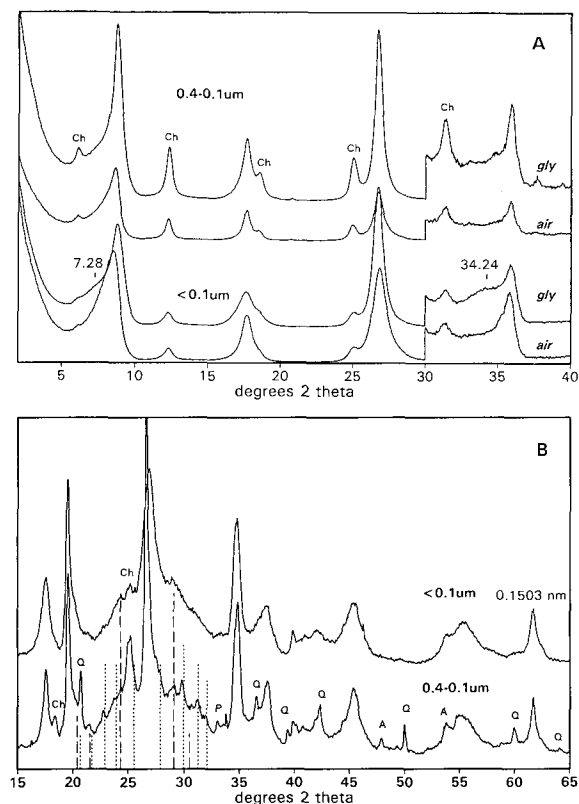


Figure 1. XRD patterns of oriented (A) and random (B) preparations of clay fractions of the Lontova shale. Peak positions are given for the reflections of I-S used for the expandability measurement. Diagnostic peaks of  $2M_1$  and  $1Md$  (predominantly *trans*-vacant) illite polytypes are marked as dot and dash lines, respectively. Ch = chlorite, Q = quartz, P = pyrite, A = anatase.

size fractions of sample 807/8, which were analyzed earlier by Gorokhov et al. (1994) for their Rb-Sr systematics, were investigated.

XRD analysis of the oriented preparations (Figure 1A) indicated that a dioctahedral, Fe-poor illitic clay is the dominant component of both fractions. It is slightly expandable, as shown by the changes of the peak shape after ethylene-glycol treatment. A weak, broad reflection at  $34.2^\circ 2\theta$ , appearing on the glycolated pattern of the  $<0.1 \mu\text{m}$  fraction, permits the identification of the swelling component of the illitic fraction as R1 ordered I-S having 19–20% S (smectitic layers, Środoń 1984, Figure 7). The shoulder appearing after glycolation on the low-angle side of the 001 illite peak at  $7.3^\circ 2\theta$ , confirms this identification. Low values of the Ir index (1.48 and 1.47 for  $<0.1$  and  $0.1\text{--}0.4 \mu\text{m}$  fractions respectively) indicate that I-S is accompanied by a large amount of discrete illite (Środoń 1984). The intensity ratio of the  $34.2^\circ 2\theta$  and  $36^\circ 2\theta$  peaks confirms this interpretation and shows clearly that illite is more abundant in the coarser fraction.

The illite and I-S are accompanied by a small amount of chlorite, identified as trioctahedral and Fe-rich, based on the relative intensities of the 00 $l$  reflections (Moore and Reynolds 1997). The chlorite is present in trace amounts in the  $<0.1 \mu\text{m}$  fraction and is more abundant in the coarser fraction. The XRD patterns of random mounts (Figure 1B) allow for identification of small admixtures of quartz, anatase and pyrite in the coarser fraction. The illitic clay is dioctahedral ( $d(060) = 0.1503 \text{ nm}$ ). The dominant variety of illite can be characterized, according to the criteria summarized by Moore and Reynolds (1997), as  $1Md$  predominantly *trans*-vacant, with a high degree of rotational disorder, including some  $n60^\circ$  disorder. Its XRD pattern resembles very closely the pattern of 20% S R1 I-S from a Paleozoic K-bentonite presented by Moore and Reynolds (1997, Figure 10.18). Less than 10% admixture of  $2M_1$  polytype (based on intensity ratio of the reflections at 30 and  $35^\circ 2\theta$ ) can be identified in the XRD pattern of the coarser sample.

The clay fractions were treated either with dodecylamine ( $C_{12}$ ) or octadecylamine ( $C_{18}$ ) hydrochloride for periods of 4 or 72 h. The alkylamine hydrochlorides and the treatment solutions were prepared by following the method of Ruhlicke and Kohler (1981). Each approximately 0.25-g clay portion was mixed with 10 mL of the appropriate 0.1 N alkylamine hydrochloride solution, and then the mixture was incubated at  $60^\circ \text{C}$  for either 2 or 36 h, after which the suspension was centrifuged and the supernatant separated from the solid and discarded. The incubation was repeated once more with the same solution for the same length of time. The samples were recovered by centrifugation, washed in 95% ethanol until the supernatant was found to be free of chloride, as determined by the  $\text{AgNO}_3$  test, and then dried in air.

All samples, both untreated and treated, were analyzed for their Ar concentration in a glass line connected to a mass spectrometer, closely following the method described by Bonhomme et al. (1975). The samples were preheated under vacuum at  $80^\circ \text{C}$  for several hours to release the atmospheric Ar added to the particles during handling. The reproducibility of the method was controlled by periodic determinations of the GLO standard, the blank in radiogenic  $^{40}\text{Ar}$  in the extraction line and mass spectrometer, and the  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio of the atmospheric Ar. The amount of radiogenic  $^{40}\text{Ar}$  in the standard averaged  $24.81 \pm 0.30$  ( $2\sigma$ )  $\cdot 10^{-6} \text{ cm}^3/\text{g}$  (STP) for 6 independent determinations during the course of the study, which is within the admitted value (Odin 1982). The amount of radiogenic  $^{40}\text{Ar}$  present as blank in the extraction line and mass spectrometer never exceeded  $1 \cdot 10^{-8} \text{ cm}^3$ . The  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio of the atmospheric Ar averaged  $287.0 \pm 2.0$  ( $2\sigma$ ) for 5 independent measurements made during the study. These reproducibility tests and the obtained values were considered to be satisfying, and no

Table 1. K-Ar data before and after alkylamine hydrochloride treatments.

Samples	K <sub>2</sub> O (%)	K <sub>2</sub> O depletion (%)	Ar* (%)	<sup>40</sup> Ar* (10 <sup>-6</sup> cm <sup>3</sup> /g)	<sup>40</sup> Ar* removal (%)	Age (±2s) (Ma)	Age decrease (%)
<b>&lt;0.1 μm</b>							
Untreated	7.07		94.9	124.07		475.9 ± 10.5	
C18 (72 h)	6.26	-11.5	95.7	103.96	-16.2	453.3 ± 10.0	-4.7
C12 (72 h)	6.71	-5.1	97.5	112.14	-9.6	455.9 ± 9.8	-4.2
<b>0.1-0.4 μm</b>							
Untreated	6.69		95.7	136.32		542.1 ± 11.9	
C18 (4 h)	5.73	-14.3	97.2	108.68	-20.3	509.4 ± 11.2	-6.0
C18 (72 h)	5.35	-20.0	95.8	103.35	-24.2	517.6 ± 11.6	-4.5
C12 (72 h)	6.39	-4.5	84.6	121.48	-10.9	510.4 ± 12.6	-5.8

Ar\* and <sup>40</sup>Ar\* stand for radiogenic Ar and radiogenic <sup>40</sup>Ar, respectively.

corrections were applied to the raw data. The concentrations of K were measured by emission flame photometry with a reproducibility of ±1.5% (2σ). The K-Ar dates were calculated with the usual decay constants (Steiger and Jäger 1977), the overall accuracy being about ±2% (2σ).

## RESULTS

The following observations may be made from the K-Ar data for the untreated samples and for the solids recovered after the different treatments (Table 1):

1) The K-Ar dates of the finer untreated fraction were found to be lower than those of the coarser untreated fraction, a trend which agrees with that of the Rb-Sr dates of the same fractions given by Gorokhov et al. (1994, Table 4). These dates are within the range of Rb-Sr and K-Ar dates obtained earlier for the Lontova clays (Gorokhov et al. 1994 and references cited therein). The higher K-Ar dates for the coarser fraction (0.1-0.4 μm) than for the finer (<0.1 μm) may be attributed to the former having lower K<sub>2</sub>O and higher radiogenic <sup>40</sup>Ar contents.

2) K<sub>2</sub>O content of the clays decreased by 4.5 to 20% after the alkylammonium treatments.

3) For a given fraction, the loss of K<sub>2</sub>O is higher for longer-chain alkylammonium cations and for longer reaction times, a trend that is consistent with observations previously reported on such exchange reactions.

4) The K-Ar dates obtained for the alkylammonium-treated fractions are lower by 20 to 30 Ma compared to that for the starting material, greater decreases occurring in the coarser fraction.

## INTERPRETATION

The lower K-Ar date of the untreated <0.1 μm fraction compared to that of the untreated 0.1-0.4 μm fraction suggests a higher concentration of authigenic illite in the finer fraction, a phenomenon which has been repeatedly observed for clay minerals in shales due to finer crystal size of authigenic illite or I-S. This interpretation for variations of isotope dates of the

same material has already been presented by Gorokhov et al. (1994). It is consistent with the transmission electron microscopy (TEM) observations of two illite morphologies and the presence of 2M<sub>1</sub> and 1Md mica polytypes in the Lontova samples. As the K-Ar dates of the finest fractions are lower than the sedimentary age of the shale, the clay mineral assemblage must contain a diagenetic (postsedimentary) fraction.

For interpretation of the K-Ar dates of the clays treated variously by different alkylammonium ions, we have assumed that no preferential removal of K or radiogenic <sup>40</sup>Ar occurred during the treatment. Although this assumption needs to be thoroughly verified, it seems justified at present by the high-resolution TEM (HRTEM) observations of the mechanism of layer opening by the alkylammonium-ion exchange. If this assumption is accepted, then the decrease of K-Ar dates after the alkylammonium treatments indicates that the detrital component is preferentially opened by exchange with the alkylammonium cations. If % radiogenic <sup>40</sup>Ar removed is plotted against % K<sub>2</sub>O removed, it becomes clear that the rate of this preferential opening is not constant (Figure 2). The detrital

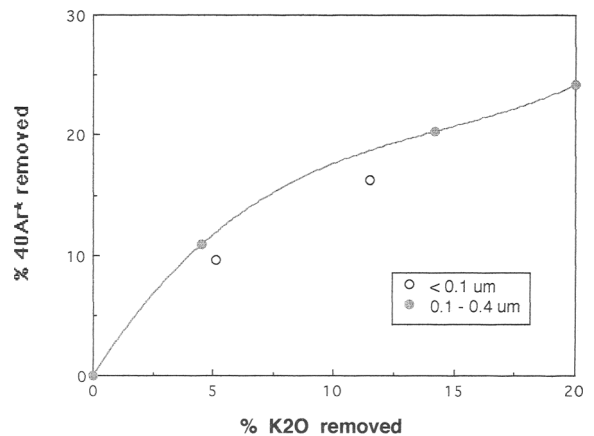


Figure 2. Relation between % K<sub>2</sub>O and % <sup>40</sup>Ar\* removed by different treatments, indicating a selective opening of older material at the early stages of the reaction.

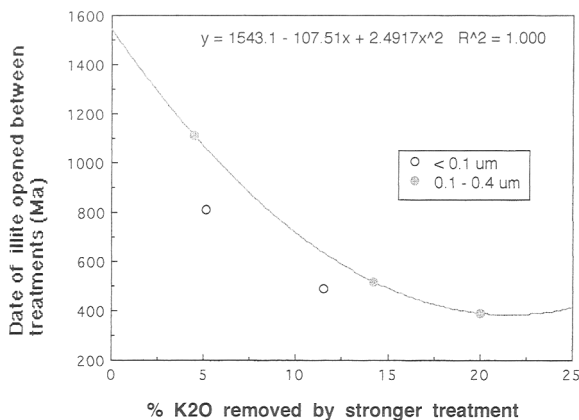


Figure 3. Relation between the reaction progress, measured by %  $K_2O$  removed at the end of a given step, and the age of illite opened during this step, that is, between the consecutive treatments (data from Table 2). The detrital age of about 1550 Ma and the diagenetic age of 380 Ma are inferred by extrapolation from this plot.

component is opened at a higher rate at the beginning of the reaction, as evidenced by the decreasing slope of the curve.

The K-Ar dates of the illite fractions opened at the subsequent steps of the treatment can be calculated by consecutive subtractions of  $K_2O$  and radiogenic  $^{40}Ar$  values from the data presented in Table 1. The results have to be interpreted cautiously, because the analytical uncertainties cumulate in the calculations (Table 2). In Figure 3, these K-Ar dates are plotted against %  $K_2O$  removed by the alkylammonium treatments. The plot for the 0.1–0.4  $\mu m$  fraction is a smooth curve which drops from 1550 Ma extrapolated for zero removed  $K_2O$  to almost no change at ca. 380 Ma, corresponding to the removal of about 20%  $K_2O$ . This date is 162 Ma younger than that of the untreated fraction. The 2 data points obtained for the <0.1  $\mu m$  fraction plot below, probably on a parallel line. Figure 3 is consistent with the interpretation of selective opening of detrital illite layers at the early stages of the exchange reaction. It still can be a mixing curve in the steep part, but it seems to be approaching a true diagenetic age in its flat part. This interpretation implies that the detrital material of Lontova shale is at least as old as Late Proterozoic and that the diagenetic illite is not older than Devonian, that is, 150 Ma younger than the stratigraphic age (Tommotian: 530–534 Ma, see Mens et al. 1990). Our interpretation of the Lontova illite dates differs from that of Gorokhov et al. (1994) in that we are extrapolating a detrital age of >1550 Ma instead of >700 Ma and a diagenetic age of  $\leq$ 380 Ma instead of <470 Ma, which allows us to explain the isotope data without making an assumption of the presence of a synsedimentary illite component as Gorokhov et al. (1994) did. Recently, Kirsimae et al. (1997) reported additional Rb-Sr dates of very fine

Table 2. Ages of illite opened by alkylammonium cations between the consecutive treatments, calculated from the differences in %  $K_2O$  and radiogenic  $^{40}Ar^*$  values reported in Table 1.

Samples	$\Delta K_2O$	$\Delta ^{40}Ar^*$	Age (Ma)
<b>&lt;0.1 <math>\mu m</math></b>			
Untreated— $C_{12}$	0.36	11.93	813
$C_{12}$ — $C_{18}$	0.45	8.18	490
<b>0.1–0.4 <math>\mu m</math></b>			
Untreated— $C_{12}$	0.30	14.84	1110
$C_{12}$ — $C_{18}$ (4 h)	0.66	12.80	519
$C_{18}$ (4 h)— $C_{18}$ (72 h)	0.38	5.33	390

fractions (<0.06  $\mu m$ ) of the Lontova shales yielding a range of ages with the minimum values that are similar to our estimated diagenetic age (150 Ma after sedimentation).

Interpretations presented in the last 2 paragraphs are based on  $K_2O$  and radiogenic  $^{40}Ar$  contents measured with respect to a variable mass of the clay (Table 1): after the alkylammonium treatments, the mass of the clay increases, because heavy organic cations substitute for K and the exchange cations. In fact, this mass increase has no effect on the K-Ar dates calculations of different fractions, but Figure 2 and the calculations presented in Table 2 and Figure 3 are affected. The error resulting from this simplification was evaluated as follows: the clay was assumed to be pure I-S, completely dehydrated when analyzed untreated. From the  $K_2O$  content, a structural formula was assumed using the data of Środoń et al. (1986). Then, using an Excel spreadsheet, all exchange cations and an appropriate part of K was substituted with an alkylammonium cation in order to obtain the measured  $K_2O$ . Then a corrected  $K_2O$  content was calculated with respect to the structural formula of the untreated clay, thus putting it on the same basis as  $K_2O$  of the untreated sample. The ratio of measured  $K_2O$ /corrected  $K_2O$  was used to correct the radiogenic  $^{40}Ar$  measurements, and from the corrected values a new Table 1 was prepared. This operation was repeated for 2 slightly different I-S compositions (differing by the content of exchange cations). It was found that the correction would produce curves of the same shape as presented in Figure 3, extrapolating to even higher detrital ages, but consistently flattening at about 380 Ma. Thus, the last value can be considered reliable, but the detrital age evaluated by this technique is very imprecise and should be considered as a minimum value. The true effect should be smaller than calculated, because the untreated sample is most probably hydrated to some extent. Future experiments along these lines should be more rigorous in this respect.

The presented technique allowed for discrimination of detrital vs. diagenetic illite in one particular sample. Whether mixed-illite assemblages in other samples

Table 3. Modeling the experimental data (ages and radiogenic  $^{40}\text{Ar}^*$ ) and calculation of the percentage of detrital illite (% detr.) resulting from the mixing of detrital 1550 Ma illite of 8 or 9%  $\text{K}_2\text{O}$  with diagenetic 380 Ma illite–smectite of 7%  $\text{K}_2\text{O}$ . The  $^{40}\text{Ar}^*$  corr. are modeled values, corrected for the effect of dilution (see text).

Samples	Experimental data			Model 1 (8/7% $\text{K}_2\text{O}$ )			Model 2 (9/7% $\text{K}_2\text{O}$ )		
	Age (Ma)	$^{40}\text{Ar}^*$	% detr.	Age (Ma)	$^{40}\text{Ar}^*$	% detr.	Age (Ma)	$^{40}\text{Ar}^*$	$^{40}\text{Ar}^*$ corr.
Untreated <0.1 $\mu\text{m}$	475.9	124.07	5.3	476	124	4.7	476	125	
Untreated 0.1–0.4 $\mu\text{m}$	542.1	136.32	9.1	542	145	8.2	542	146	
$\text{C}_{18}$ (72 h) <0.1 $\mu\text{m}$	453.3	103.96	4.0	453	117	3.6	454	118	104
$\text{C}_{18}$ (72 h) 0.1–0.4 $\mu\text{m}$	517.6	103.35	7.7	518	140	6.9	518	138	103

may be dated by a process of alkylammonium ion exchange remains to be verified. The study by Sears et al. (1995) seems to indicate an effect that is opposite to what we have observed, that is, preferential opening of the detrital component by the same  $\text{C}_{18}$  alkylammonium cation.

Table 3 presents the modeling of the experimental data performed according to the procedure for “mixed ages” developed by Środoń (1998). A detrital end-member age of 1550 Ma and a diagenetic end-member age of 380 Ma were assumed. The  $\text{K}_2\text{O}$  content of the diagenetic component (20% S in I–S) was set at 7% according to the data of Środoń et al. (1986), while 8 or 9%  $\text{K}_2\text{O}$  contents were assumed for the detrital illite. Values of the “mixed ages”, proportions of the components and contents of radiogenic  $^{40}\text{Ar}$  of the mixtures were calculated for the untreated and the treated fractions. In case of the untreated samples, both models produced excellent results for the <0.1 mm fraction, predicting 4.7 to 5.3% of detrital illite in the clay assemblage. For the coarser fraction, 8.2 to 9.1% detrital clay was calculated, but the content of radiogenic  $^{40}\text{Ar}$  was overestimated. This is expected, because the model assumes the occurrence of 100% illitic material, whereas the coarse fraction also contains significant amounts of dilutant minerals (mostly chlorite). Normalizing the calculated radiogenic  $^{40}\text{Ar}$  to the measured one, we could evaluate the content of chlorite in the coarse sample at 7%.

Repeating the same calculation for the treated samples produced an overestimated amount of radiogenic  $^{40}\text{Ar}$  in both fractions. This is expected because both fractions contain dilutant minerals, that is, the illitic clay expanded by alkylammonium cations, which is as much as 11.5% of the total illite amount in the fine fraction and 20% in the coarse fraction (based on %  $\text{K}_2\text{O}$  depletion, Table 1). If the calculated  $^{40}\text{Ar}$  values are corrected for the contents of the dilutants, including 7% chlorite in the coarse fraction, a good agreement is obtained with the experimental values. Thus, about 5% of detrital component in the <0.1  $\mu\text{m}$  fraction and 8–9% in the 0.1–0.4  $\mu\text{m}$  fraction can explain the measured ages, the detrital component being the  $2M_1$  illite. Up to 5% of any clay being hardly detectable by XRD, the <0.1  $\mu\text{m}$  fraction appears as mono-

mineralic in the random XRD mount (Figure 1B), even though the TEM observations indicate its heterogeneity (Gorokhov et al. 1994). The dominant *IMd* diagenetic component appears in the oriented preparations as a mixture of illite and R1 clay, a phenomenon that has been documented in detail by HRTEM (Elsass et al. 1997).

#### GEOLOGICAL IMPLICATIONS

An illitic clay from a shale with 20% expandability corresponds normally to burial temperatures of about 135–140 °C. This estimate is based on the reasoning presented by Środoń (1995), using the data of Šucha et al. (1993) from the East Slovak Basin as a reference. The thermal history of this basin is well known (Clauer et al. 1997) and the maximum paleotemperatures were 5–10 °C higher than the present-day temperatures reported by Šucha et al. (1993, Figure 3). Such maximum paleotemperature estimation based on %S seems to apply also to Precambrian rocks. For instance, Price and McDowell (1993) have shown that, without experiencing sufficiently high temperatures sometime during their geological history, clays as old as Precambrian stay highly expandable.

According to the geological record, the Lontova shales have never been buried to depths corresponding to such a degree of illitization (>4 km at the average geothermal gradient). The maximum burial of these rocks is estimated as 800–1000 m (Kalle Kirsimae, personal information). Based on the current knowledge of the illitization mechanism, 2 processes could produce the observed degree of diagenetic illitization in Lontova clays: 1) a Devonian thermal event or the penetration of hot fluids in the study area, that is, processes which would significantly raise the rock temperatures at shallow depths, and 2) a Devonian incursion of highly alkaline fluids (pH  $\geq$ 10). It has been shown by field evidence (Hay et al. 1991) and by laboratory studies (Eberl et al. 1986, 1993) that alkaline fluids are capable of promoting illitization at low temperatures.

Both processes are feasible from the regional geology standpoint, and both have been considered already (Pichugin et al. 1977) as possible explanations for major tectonically controlled metasomatic dolomitization

in a zone situated some 20–30 km SE of our study area. The dolomitization is dated by field evidence for the end of Silurian or Early Devonian, which corresponds precisely to our estimate of the diagenetic age (380 Ma). The processes invoked by Pichugin et al. (1977) are 1) penetration of postmagmatic waters, like in the carbonatites of Kola Peninsula, which were genetically related to the Caledonian alkaline intrusions known in central Sweden and along the southern coast of the Gulf of Bothnia (alkaline waters), and 2) discharge of subsurface waters in the course of the Silurian–Devonian continental breakdown (hot waters). Perhaps further isotope studies will solve this alternative, but clearly the region was an area of long-lived fluid discharge along tectonic discontinuities, as evidenced by Hercynian Pb–Zn mineralization superimposed on older dolomitization (Pichugin et al. 1977).

### CONCLUSION

Alkylammonium treatment of shale samples, which removes K from the illite interlayers, can be selective with respect to detrital vs. diagenetic component. In the studied sample, the detrital  $2M_1$  illite was preferentially opened at the beginning of the experiments, inducing a decrease in the K–Ar dates of the treated material. The dates of illite opened during subsequent steps of the experiment, calculated by subtraction of the corresponding  $K_2O$  and radiogenic  $^{40}Ar$  values measured for the solids and plotted against the reaction progress (%  $K_2O$  removed), extrapolate to values for a minimum detrital age of 1550 Ma and a diagenetic age of 380 Ma.

The extrapolated detrital age is feasible for this site, and the diagenetic age corresponds well to the Devonian massive dolomitization event in the area. Diagenetic illitization due to fluid migration explains a higher degree of illitization than expected from an area that never went through a deep burial phase after the deposition of shales.

Modeling the untreated and treated samples as mixtures of 380-Ma and 1550-Ma illite produces an excellent fit of measured dates and radiogenic  $^{40}Ar$  contents, if the dilution effects are taken into account. The content of the detrital material calculated by the model corresponds well with the XRD estimations. The analytical technique presented in this paper is far from a mature stage, but it offers a new perspective for extracting diagenetic ages from shales.

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