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EXTRACTION OF DIAGENETIC AND DETRITAL AGES AND OF THE $^{40}K_{detrital}/^{40}K_{diagenetic}$ RATIO FROM K-Ar DATES OF CLAY FRACTIONS

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Abstract—Illite age analysis (IAA) is a classical method for extracting diagenetic and detrital ages from mixed ages measured by K-Ar. This approach is based on measuring the masses of diagenetic and detrital illitic components in a few different grain-size fractions of one rock sample and measuring the mixed ages of these fractions. The 1*Md* illitic polytype is usually considered to be diagenetic, while $2M_1$ is considered detrital. A plot of the function: $\exp(\lambda t)-1$ (where t is time and λ is the decay constant) *vs.* weight percent of the detrital fraction is constructed. On the basis of linear extrapolation to end-member fractions, the diagenetic and the detrital age is obtained. This approach does not take into account various K contents in different polytypes ($\%K_{detrital}$ and $\%K_{diagenetic}$). In order to do that, the detrital mass fraction ($wt.\%_{detrital}$) should be recalculated into the percentage of detrital K ($\%I_{d(K)}$):

$$\%I_{\mathrm{d(K)}} = \frac{\mathrm{wt.\%_{detrital}} \times \mathrm{\%K_{detrital}}}{\mathrm{wt.\%_{detrital}} \times \mathrm{\%K_{detrital}} + \mathrm{wt.\%_{diagenetic}} \times \mathrm{\%K_{diagenetic}}} \times 100$$

Analytical constraint of the K content of different polytypes is very difficult, so a new approach to this problem has been developed. In the present study, the plot of $^{40}Ar^*/^{40}K$ *vs.* $\%I_{d(K)}$ for a precisely determined ratio of $^{40}K_{detrital}/^{40}K_{diagenetic}$ was observed to be linear. On the basis of this observation, a computer program, *MODELAGE*, was written in the *Java* programming language using as input a few measured detrital illite mass fractions along with the mixed K-Ar ages of the relevant grain fractions. It then calculates the end-member ages and the $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio using genetic algorithms.

The errors in diagenetic and detrital illite mass-fraction determination mean that the $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio and the end-member ages can be evaluated only with some uncertainty. The best results are obtained if the measured mass fractions represent a relatively broad range. Constraining one of the unknowns (particularly the $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio) improves the results significantly.

Evaluation of data obtained from the literature using the proposed approach leads to the conclusion that the $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio is often >1.00, and some of 1*Md* illite polytype materials may be of detrital origin. If this is not the case, if a broad range of mass fractions is covered, and if the differences between end-member ages are relatively small, IAA analysis still gives appropriate results, even if the true $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio is different from 1.00.

Key Words—Diagenetic Age, Genetic Algorithms, Illite Age Analysis, K-Ar, Mixed Ages.

INTRODUCTION

Since the work by Hower *et al.* (1963), scientists have known that illite in shales should be considered as a mixture of minerals of both diagenetic and detrital origins. The ages of both components of this mixture can provide valuable information on various aspects of basin history. Diagenetic age gives information on the thermal evolution of a sedimentary basin, which is very important in hydrocarbon exploration (Pevear, 1999). The age of a detrital component can be very useful in constraining the provenance of sedimentary material. Because of the considerable interest, several attempts have been made to extract these ages from measured mixed ages.

Physical separation of usually coarser detrital material from diagenetic material has proven to be extremely difficult if not impossible. Even in the finest fractions (<0.02 μm), substantial amounts of the detrital component were found (Clauer *et al.*, 1997). Other approaches have also been tried: the calculation of end-member ages assuming that diagenetic and detrital components are mineralogically distinctive (*e.g.* Mossman *et al.*, 1992), and the use of $^{40}Ar/^{39}Ar$ thermal separation of diagenetic from detrital illite (*e.g.* Dong *et al.*, 2000; Fergusson and Phillips, 2001). The most popular approach, belonging to the first group, was proposed by Pevear (1992) and named 'illite age analysis' (IAA). This procedure is based on the XRD quantification of the ratio of diagenetic to detrital illitic components in three (or more) different grain-size fractions and on the linear extrapolation of the K-Ar dates measured for these fractions, plotted *vs.* the wt.% of detrital illite ($\%I_{d(I-S)}$) in the total population of illite layers (detrital + diagenetic):

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$$\%I_{d(I-S)} = \frac{wt.\%_{illite(detrital)}}{wt.\%_{illite(detrital)} + wt.\%_{I-S} \times \%I_{in(I-S)}} \times 100 \quad (1)$$

where $\%I_{in(I-S)}$ is the percent of illite layers in illite-smectite, measured by XRD and wt.% corresponds to the mass of discrete illite or illite-smectite. Assumptions are that illite is purely detrital and that illite-smectite is diagenetic. Środoń (2000) demonstrated that, as a result of variable amounts of K in illite, the plot of the K-Ar dates *vs*. mass fractions of illite is not linear. Ylagan *et al.* (2000) proposed a solution to this problem by correcting the $\%I_{d(I-S)}$ for the variable K contents ($\%K_{detrital}$ and $\%K_{diagenetic}$) of illite layers (equation 2).

The corrected value ($\%I_{d(K)}$) is understood to be the percentage of detrital layers in the population of layers with the same K content ($\%K_{ideal}$). Ylagan *et al.* (2000) demonstrated that the age *vs*. $\%I_{d(K)}$ plots are quasi-linear, and the deviation from linearity is related exclusively to the logarithmic nature of the age equation. This problem has been avoided by constructing a plot of $\exp(\lambda t)-1$ *vs*. mass fraction of $2M_1$ polytype considered to represent detrital illite (van der Pluijm *et al.*, 2001). However, in the cited work, the problem of the variable K content in illite was not taken into account. The authors assumed, without direct explanation, that the $1Md$ and $2M_1$ polytypes have the same K content, which may not be the case. Potassium ions are located only in the illite interlayers, therefore, for coarser crystals (these of detrital origin), the ratio of the number of interlayers to layers is greater (approaching 1 for very thick crystals), and the K content should be larger. Also, the two polytypes may differ significantly by the degree of Na^+ and NH_4^+ for K^+ substitution. If these differences are significant they may lead to a substantial deviation from linearity (Środoń, 1999).

Analytical constraint of the K content of different polytypes is difficult. As the separation of detrital from diagenetic material is extremely difficult, only constraining the amount of K in mixtures of different polytypes is possible. Linear extrapolation to end-member values is valid only if other K minerals are absent and K-free minerals are absent or have been quantified (Środoń *et al.*, 2002). In other cases the end-member values can be constrained only approximately.

The problem of non-linearity and the effect of variable K content stimulated the present research, aimed at finding a general solution, which would allow extension of IAA analysis to all possible fields of interest.

THEORETICAL APPROACH

Any value other than zero can be substituted for $\%K_{ideal}$ in equation 2, because these values cancel out. Therefore, equation 2 can be rewritten as equation 3.

Wt.% $_{illite(detrital)}$ has been substituted by $wt.\%_{detrital}$ emphasizing that wt.% and %K do not have to refer to illite but to any K-bearing phases (*e.g.* two illite-smectites or diagenetic illite and detrital K-feldspar, *etc.*). In other words the $\%I_{d(K)}$ correction makes the $\%I_{d(I-S)}$ correction irrelevant. Effectively, $\%I_{d(K)}$ corresponds to the wt.% of detrital K in the mass of total K in a mixture containing two K-bearing phases.

An elegant solution, which solves the logarithmic non-linearity problem, is to plot the $^{40}Ar^*/K$ ratios measured for these fractions against $\%I_{d(K)}$, rather than the mixed ages of different fractions, then to calculate the end-member ages from the extrapolated $^{40}Ar^*/K$ ratios. This effect is demonstrated in Figure 1, in which the plot of age *vs*. $\%I_{d(K)}$ is compared with the plot of $^{40}Ar^*/K$ *vs*. $\%I_{d(K)}$. Both were obtained by mixing 1500 Ma illite of 9.2% K_2O with 200 Ma illite of 10.4% K_2O (the procedure described by Środoń, 1999), and by calculating $\%I_{d(K)}$ using equation 3. This approach is equivalent to that proposed by van der Pluijm *et al.* (2001) because $^{40}Ar^*/K$ is linearly related to $\exp(\lambda t)-1$:

$$\frac{^{40}Ar^*}{^{40}K} = \frac{\lambda_{Ar}}{\lambda_{total}} \times (e^{\lambda t} - 1) \quad (4)$$

An *Excel*™ spreadsheet was applied to investigate the procedure of modeling the measured $^{40}Ar^*/K$ ratios of different fractions of a sample by 'guessing' the ages and the K_2O contents of the detrital and the diagenetic components. First, the 'measured $^{40}Ar^*/K$ ratios' were calculated, by assuming the ages and the K_2O contents (and therefore the amounts of ^{40}K) of the two components. Then, different 'guessed $^{40}Ar^*/K$ ratios' and corresponding $\%I_{d(K)}$ values were calculated by trying different ages and K_2O contents, and both 'measured' and 'guessed' $^{40}Ar^*/K$ ratios were plotted *vs*. $\%I_{d(K)}$. Values of $^{40}Ar^*$ and ^{40}K for different $\%I_{d(K)}$, calculated using equation 3, were obtained as weighted means:

$$^{40}Ar^* = (^{40}Ar^*_{detrital}\ wt.\%_{detrital} + {}^{40}Ar^*_{diagenetic}\ (100-wt.\%_{detrital}))/100 \quad (5)$$

$$^{40}K = (^{40}K_{detrital}\ wt.\%_{detrital} + {}^{40}K_{diagenetic}\ (100-wt.\%_{detrital}))/100 \quad (6)$$

$$\%I_{d(K)} = \frac{wt.\%_{illite(detrital)} \times \frac{\%K_{detrital}}{\%K_{ideal}}}{wt.\%_{illite(detrital)} \times \frac{\%K_{detrital}}{\%K_{ideal}} + wt.\%_{illite(diagenetic)} \times \frac{\%K_{diagenetic}}{\%K_{ideal}}} \times 100 \quad (2)$$

$$\%I_{d(K)} = \frac{wt.\%_{detrital} \times \%K_{detrital}}{wt.\%_{detrital} \times \%K_{detrital} + wt.\%_{diagenetic} \times \%K_{diagenetic}} \times 100 \quad (3)$$

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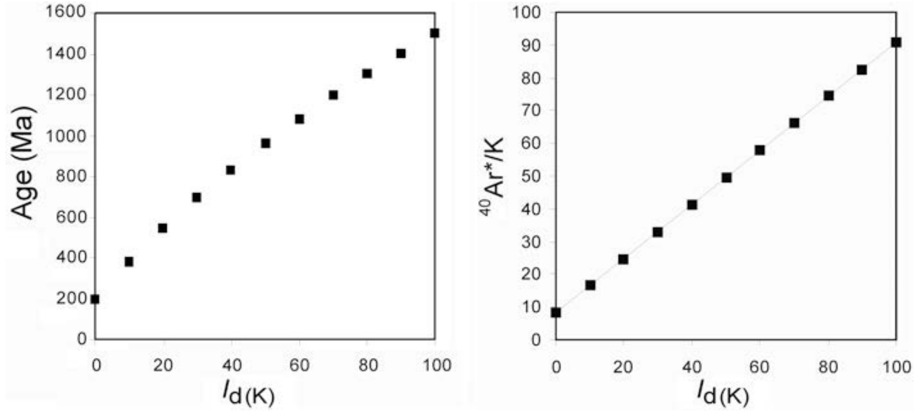

Figure 1. Comparison of (a) age *vs.* %$I_{d\ (K)}$ plot; (b) $^{40}Ar^*/K$ *vs.* %$I_{d\ (K)}$ plot. Non-linearity is evident in a.

The 'measured $^{40}Ar^*/K$' *vs.* %$I_{d(K)}$ plot remained linear if the 'guessed' $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio was identical to the 'measured' one (Figure 2a). Otherwise it became concave if the ratio was too high (Figure 2b), or convex if it was too low (Figure 2c). The departure from linearity is quite severe if the 'guessed' $^{40}K_{detrital}/^{40}K_{diagenetic}$ differs by a few tens of percent from the 'measured' one. Once linearity has been established (correct $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio, Figure 2a: circles), the correct fit requires 'guessing' the end-member ages (Figure 2a: squares).

In summary, three values (end-member ages and $^{40}K_{detrital}/^{40}K_{diagenetic}$) have to be predicted in order to obtain the correct fit. Therefore, by evaluating how far the predicted results depart from the experimental ones and from the linearity on the $^{40}Ar^*/K$ *vs.* %$I_{d(K)}$ plot, determination of the accuracy of the guessed ages of the end-members and the guessed $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio should be possible. By employing an algorithm that optimizes the departure of 'guessed' from 'measured' $^{40}Ar^*/K$ values, finding the end-member ages and $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio that gives the best fit to the experimentally measured $^{40}Ar^*/K$ ratios should be possible, as well as a consequence to the measured mixed ages.

METHODS

In order to implement the concept described above, the program *MODELAGE*, which uses genetic algorithms (GA) as a minimalization procedure (*e.g.* Koza, 1992), was written in *Java* with the help of the JGAP library (the program is freely available at www.ing.pan.pl. Using GA for such a simple problem (just three genes) is not crucial because the problem is rather uncomplicated and few local minima are expected. Alternative optimization procedures, which are usually faster, are also available, *e.g.* simulated annealing or gradient procedures. However, they are less effective at finding the global minimum of the analyzed function. This problem was solved during studies of GA implementation in *Java* by one of the authors (MS) and was the approach adopted for routine use as it gives results of an acceptable quality.

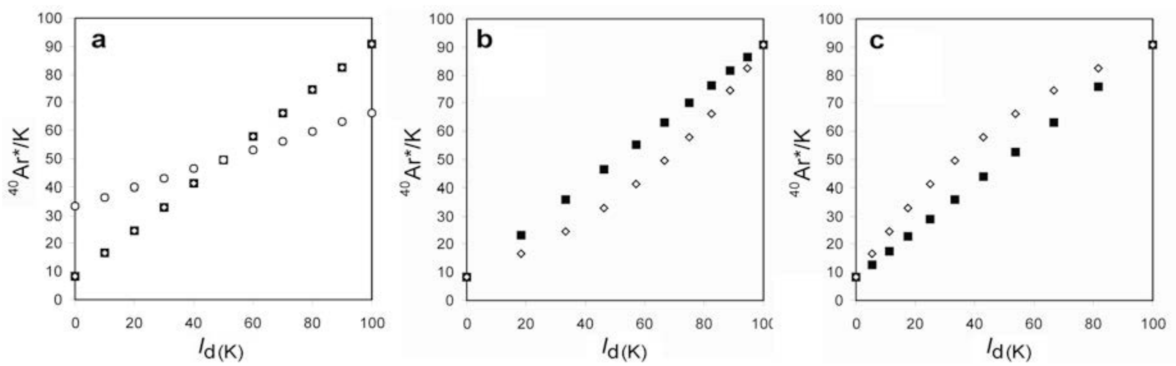

Figure 2. $^{40}Ar^*/K$ *vs.* %$I_{d\ (K)}$ plots for different estimated ('guessed') $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratios compared to the 'measured' ones (rectangles): (a) 'guessed' $^{40}K_{detrital}/^{40}K_{diagenetic}$ equals 'measured', 'guessed' $^{40}Ar^*/K$ ratio is different (circles) or equal (diamonds) to 'measured'. (b) 'guessed' $^{40}K_{detrital}/^{40}K_{diagenetic}$ (diamonds) values are too high, and (c) too low. Notice that values of $I_{d(K)}$ for points in (b) and (c) are shifted in comparison to (a).

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Genetic algorithms are based on concepts inherited from evolutionary biology, such as genes, chromosomes, genotype, phenotype, *etc.* The parameters undergoing optimization are denoted as genes in the populations of chromosomes that reproduce, crossover, and undergo mutations. In order to check how good the results (genes, corresponding to optimized parameters) are, a phenotype function is defined. This function uses as input variables the values of genes (genotype) for each chromosome and describes the possibility of crossover in the next step of evolution (optimization). Therefore, this function describes the population of the chromosome's offspring in the next cycle of evolution.

The program reads as input variables wt.%$_{detrital}$ values for a few (n) different clay fractions along with their $^{40}Ar^*/K$ values. These are denoted as 'measured' values. In GA, the guessed $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio and diagenetic and detrital $^{40}Ar^*/K$ values of the end-member components are taken as genes. Therefore, chromosomes consist only of these three genes. Also, the possibility of constraining these genes at some values or ranges was added. The phenotype function F is defined as follows:

$$F = 1000/(1 + S) \quad (7)$$

where:

$$S = \sum_{i=1}^{n}(t_i - y_i)^2$$

t_i is the 'measured' $^{40}Ar^*/K$ value for the analyzed mixture with % $I_{d(K)}$ constrained by selecting a value of the $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio, and y_i the 'guessed' $^{40}Ar^*/K$ value of this mixture. This is a converse of the function used by the least-squares method, which is a classic mathematical approach for finding the best-fitting curve to a set of points by minimizing the sum of the squares of the offsets of the points from the curve. These offsets can be calculated in two ways: vertically (Figure 3a) or perpendicularly (Figure 3b). The latter approach is algorithmically more demanding, while the differences are not essential. Therefore, for the purposes of the program, offsets are taken vertically.

For the best solutions, with the 'guessed' values of $^{40}Ar^*/K$ (y_i) close to the 'measured' ones (t_i), S tends to zero, the denominator of function F to 1, and the function F itself reaches the maximum close to 1000. After a selected number of evolutionary cycles (usually a few thousand to obtain good precision) the best solution is displayed.

RESULTS AND DISCUSSION

Theoretical calculations

In order to investigate if the proposed approach is valid, calculations using a few ideal values of $^{40}Ar^*/K$ and mass fractions of detrital material have been performed. For testing purposes, three values of $^{40}Ar^*/K$ were chosen, corresponding to the grain-size fractions with 30, 50, and 70% of the detrital component. The $^{40}Ar^*/K$ ratios for these fractions were calculated using the spreadsheet described in the theoretical approach section. The results of GA calculations (Table 1) demonstrate that, under ideal circumstances, this approach reconstructs, almost ideally, the detrital and the diagenetic ages, as well as the $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio.

In real situations uncertainties remain in the determination of the values of $^{40}Ar^*/K$ and the mass fractions of the detrital material. The analytical method of $^{40}Ar^*/K$ determination is several times more accurate than the mineralogical analysis used to calculate the illite mass fractions, thus the former was ignored in further considerations. The uncertainty of the illite wt.% determination was estimated by van der Pluijm *et al.* (2001) as ~±2.5% and by Grathoff *et al.* (1998) as 2.5–5% (the present authors suggest that it can be even larger).

In order to check how the proposed technique performs in non-ideal circumstances, random errors from the range of ±2.5% were added to the mass-fraction values. Twenty subsequent calculations were performed in each case, and then mean values and standard deviations of single measurement for these results were calculated (Table 2). The results show that the values obtained are substantially uncertain if the range of mass fractions is narrow. Therefore, in order to improve the reliability of the calculations, the mass-

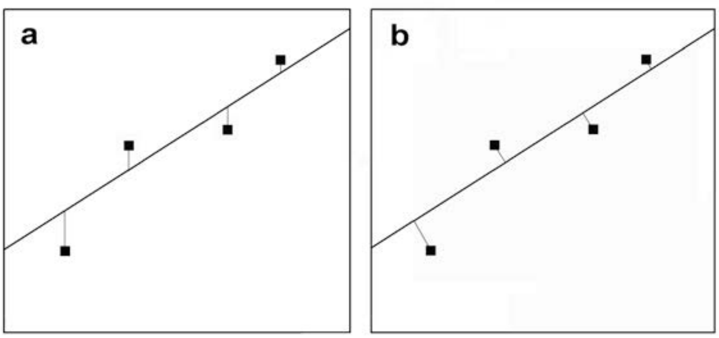

Figure 3. Visualization of: (a) vertical offsets; and (b) perpendicular offsets.

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Table 1. Results of GA calculations performed for different assumed end-member ages and $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratios. Three fractions with 30, 50, and 70 wt.% of the detrital material were used. Free optimization of all values was allowed.

Assumed values		Calculated values		
Ages (Ma)	$^{40}K_{detrital}/^{40}K_{diagenetic}$	Diagenetic age (Ma)	Detrital age (Ma)	$^{40}K_{detrital}/^{40}K_{diagenetic}$
10–50	1.0	10.0±0.3	50.0±0.3	1.00±0.03
	2.0	9.9±0.5	50.0±0.1	2.01±0.06
50–300	1.0	49.4±1.8	299.7±1.8	1.01±0.03
	2.0	49.0±3.3	299.7±0.9	2.02±0.07
200–1500	1.0	196.8±10.2	1499.2±5.5	1.01±0.02
	2.0	194.7±12.6	1499.6±2.3	2.01±0.04

fraction range should be as broad as possible. Using more than three data points in the analysis should also lead to some improvement. A very valuable piece of information is the value of one of the end-member ages and particularly of the $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio. In certain circumstances such independent data may be available (*e.g.* the detrital age from dating coarse-grained micas or the $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio from detailed chemical analyses and illite crystal-thickness data). On the other hand, the age of diagenesis, *e.g.* obtained from illite-smectite in bentonites, may lead to the determination of the $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio of the sample. In such a case, the justification for assuming whether or not the same amounts of K in $2M_1$ and $1Md$ illite, as used in the past by several authors, can be evaluated.

The potential errors related to the erroneous assumption of the $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio have been evaluated by fixing this ratio at values different from the true one and then performing the optimization calculations. The results (Table 3) show that such error can influence sustantially the end-member ages obtained. Therefore, in order to evaluate these ages properly, the $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio should be quantified. If this is not possible, the value can be optimized using the program constructed. Moreover, if one suspects that the range of $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio can be narrowed down, the program allows the ratio to be fixed at the expected range. However, as was previously shown, the precision of such calculations is satisfactory only if the mass fractions are from a broad range.

The effect of systematic errors should be evaluated also. Such errors may arise, for example, from the assumption that the $1Md$ polytype is of purely diagenetic origin, while part of this polytype can also be detrital, contributed by erosion of sedimentary rocks (*e.g.* Elliott *et al.*, 2006). In such circumstances, the measured $\%2M_1$ mass fraction underestimates systematically the detrital component. In the proposed approach, the systematic error means that an assumed percent ($\%1Md_{detrital}$) of the mass of $1Md$ polytype (wt.$\%_{1Md}$) is also of detrital origin:

$$\text{wt.}\%_{1Md\ \text{detrital}} = \%1Md_{\text{detrital}}\ \text{wt.}\%_{1Md}$$

If the age of the detrital $1M$ illite is unknown, then the age equal to the $2M_1$ illite has to be assumed. In order to perform calculations, the initial value of wt.$\%_{detrital}$ was recalculated according to the following equation:

$$\text{wt.}\%_{\text{detrital(final)}} = \text{wt.}\%_{\text{detrital}} + \text{wt.}\%_{1Md\ \text{detrital}}$$

Table 2. Results of GA calculations performed for different mass fractions of the detrital material, assuming random errors of these values from the range of ±2.5%. For some calculations, one of the age values or the $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio were fixed at an ideal initial value (bold).

Initial values			Calculated values		
Ages (Ma)	$^{40}K_{detrital}/^{40}K_{diagenetic}$	Detrital wt.%	Diagenetic age (Ma)	Detrital age (Ma)	$^{40}K_{detrital}/^{40}K_{diagenetic}$
50–350	2.00	30–50–70	54.0±39.5	354.1±15.0	1.96±0.62
		30–40–45–55–60–70	39.5±38.8	349.3±10.9	2.17±0.59
		20–50–80	45.8±24.5	350.9±6.6	2.06±0.4
		20–30–40–50–60–80	48.4±27.7	351.3±5.4	2.01±0.4
		30–50–70	**50.0**	351.5±7.3	1.99±0.2
		30–50–70	38.3±29.1	**350.0**	2.13±0.27
		30–50–70	51.6±11.3	351.0±4.3	**2.00**
		20–30–40–50–60–80	50.7±8.0	349.5±2.4	**2.00**

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Table 3. Results of GA calculations performed for 30, 50, and 70 wt.% mass fractions of the detrital material (no random errors of these values assumed). $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratios were fixed at assumed values.

Initial values: Ages (Ma)	Initial values: $^{40}K_{detrital}/^{40}K_{diagenetic}$	Fixed values: $^{40}K_{detrital}/^{40}K_{diagenetic}$	Calculated values: Diagenetic age (Ma)	Calculated values: Detrital age (Ma)
200–1500	1.0	1.4	24.8±1.0	1438.8±0.3
		1.2	113.6±0.9	1464.9±0.4
		1.0	199.7±0.9	1500.0±0.5
		0.8	284.4±0.6	1550.3±0.3
10–50	1.0	1.4	6.4±0.1	47.4±0.1
		1.2	8.2±0.1	48.5±0.1
		1.0	10.0±0.1	50.0±0.1
		0.8	11.8±0.1	52.2±0.1

If constraining the age value of the 1*Md* detrital fraction is possible, another approach is proposed. The $(^{40}Ar^*/K)_{1M}$ value obtained for the diagenetic fraction should be considered as the linear combination of $(^{40}Ar^*/K)_{1Md\ diagenetic}$ and $(^{40}Ar^*/K)_{1Md\ detrital}$:

$$(^{40}Ar^*/K)_{1M} = (\%1Md_{\ detrital}\ (^{40}Ar^*/K)_{1Md\ detrital} + (100-\%1Md_{\ detrital})\ (^{40}Ar^*/K)_{1Md\ diagenetic})/100$$

Both approaches assume, for simplicity, that the 1*Md* illite of detrital origin contains the same amount of K as the diagenetic 1*Md* illite.

The results of the evaluation of a case assuming systematic errors (Table 4) indicate that the diagenetic end-member age is underestimated, while the detrital one, as well as the $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio, are left unchanged (first row in Table 4 and filled squares in Figure 4). Knowing the ratio $^{40}K_{detrital}/^{40}K_{diagenetic}$ or the detrital age fails to improve the results much if a systematic error is involved.

Comparison with experimental data

The results obtained from theoretical calculations lead to the conclusion that the values modeled by the program are reliable if mineralogical analyses were performed with perfect precision and are exact. Unfortunately, analytical results do not always offer such a confidence level. Therefore, the outcomes from the program are reliable only if one of the end-member ages and $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio are known, or if a broad range of mass fractions is covered. Some published results of IAA analysis were evaluated taking these conclusions into account.

Artificial mixtures. Środoń *et al.* (2002) prepared a set of artificial mixtures of pure Miocene illite ('diagenetic clay' in this mixture) and Triassic illite-smectite ('detrital' clay). For mixed and homogenized samples, K_2O and radiogenic Ar measurements were performed, and ages of particular mixtures were calculated (Table 5).

The data corresponding to 25, 50, and 75% of the older fraction were available, and the following approaches were considered (Table 5):

(1) assumption of $^{40}K_{detrital}/^{40}K_{diagenetic}$ = 1.00 and optimization of detrital and diagenetic ages (diamonds in Figure 5);

(2) full optimization of all variables without any constraints;

(3) constraining the diagenetic age at 21.1 Ma (measured value) and optimization of detrital age and $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio;

(4) constraining the detrital age at 213.1 Ma (measured value), and optimization of diagenetic age and $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio;

(5) constraining the $^{40}K_{detrital}/^{40}K_{diagenetic}$ at 0.215, calculated from $\%K_2O$ of the end-member phases and optimization of diagenetic and detrital ages (filled squares in Figure 5).

As expected, constraining the $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio at 1.00, *i.e.* far from the true value, led to unacceptably erroneous results (approach 1 in Table 5

Table 4. Results of GA calculations performed for different mass fractions of the detrital material, assuming 10% systematic errors of these values. For some calculations, one of the age values or the $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio were fixed at ideal, initial values (bold).

Initial values: Ages (Ma)	Initial values: $^{40}K_{detrital}/^{40}K_{diagenetic}$	Initial values: Detrital wt.%	Calculated values: Diagenetic age (Ma)	Calculated values: Detrital age (Ma)	Calculated values: $^{40}K_{detrital}/^{40}K_{diagenetic}$
50–350	1.0	30–50–70	12.9±1.3	349.7±1.2	1.01±0.02
		30–50–70	**50.0**	389.3±0.7	0.57±0.01
		30–50–70	13.3±0.2	**350.0**	1.00±0.11
		30–50–70	13.6±0.4	349.7±0.6	**1.00**

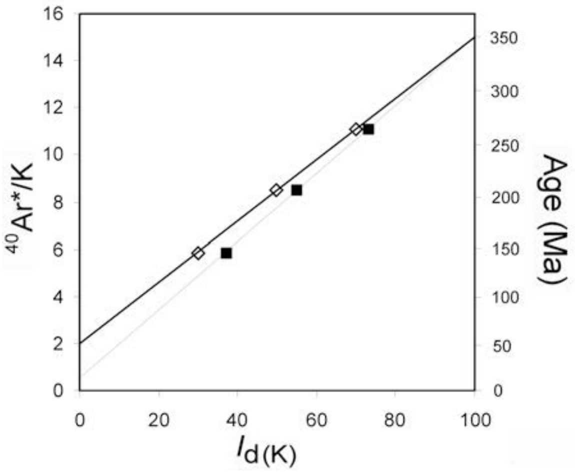

Figure 4. $^{40}Ar^*/K$ *vs.* $\%I_{d\ (K)}$ plot for different mass fractions of the detrital material, with (filled squares) and without (diamonds) the assumption of 10% systematic error in these values (data from Table 4). The vertical axis is also calibrated for age.

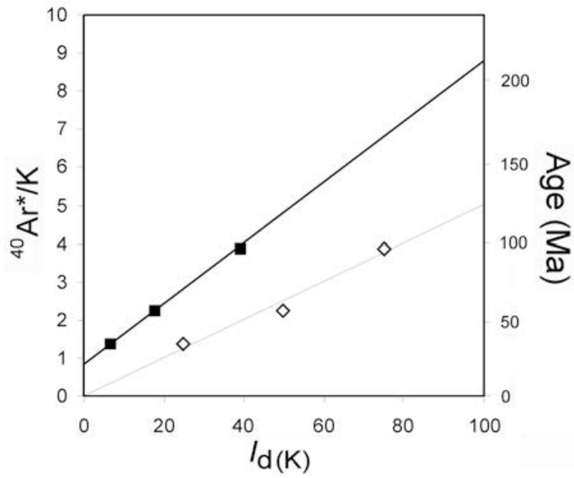

Figure 5. Results of GA calculations for the artificial mixtures described by Środoń *et al.* (2002). Diamonds – assumption of $^{40}K_{detrital}/^{40}K_{diagenetic}$ = 1.00 and optimization of detrital and diagenetic ages (corresponding to the IAA approach); filled squares – optimization of diagenetic and detrital ages, constraining the $^{40}K_{detrital}/^{40}K_{diagenetic}$ at 0.215 (data from Table 5). True values: diagenetic age, 21.1 Ma; detrital age, 213.1 Ma, $^{40}K_{detrital}/^{40}K_{diagenetic}$ = 0.215.

and diamonds in Figure 5). The modeling without any constraints gave quite good results (approach 2 in Table 5 and filled squares in Figure 5). The discrepancies arise from the fact that the measured ages for mixtures were obtained with some error (as shown in figure 7 of Środoń *et al.*, 2002). Constraining one of the variables at the correct value led to markedly improved results. Another finding was that the $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio is extremely sensitive to errors. This value was obtained from the linearity of the diagram, an attribute that is very responsive to errors in wt.% detrital.

This analysis confirms, using experimental data, that the conclusions drawn above from studying the theoretical cases (if the wt.% detrital is known accurately, and even in unconstrained modeling) predicts the end-member ages quite accurately.

Illinois Basin. Grathoff *et al.* (1998) measured K-Ar ages of the Silurian Waukesha illite from Illinois Basin (southeastern Wisconsin). This illite consists of a mixture of two polytypes $2M_1$ and $1Md$, which were quantified, assigned as detrital and diagenetic, respectively, and analyzed by IAA under the assumption that $^{40}K_{detrital}/^{40}K_{diagenetic}$ = 1.00. These results of Grathoff *et al.* (1998) were evaluated by modeling, using the following approaches (Table 6):

(1) assumption that $^{40}K_{detrital}/^{40}K_{diagenetic}$ = 1.00 with modeling of the results with no random error of the wt.% determinations (diamonds in Figure 6),

(2) assumption that $^{40}K_{detrital}/^{40}K_{diagenetic}$ =1.00 with modeling of the results with 3.0% random error;

(3) full optimization with no constraints and no random error (filled squares in Figure 6);

(4) full optimization with no constraints and with 3.0% random error.

The modeling illustrated that if a broad range of mass fractions was used and differences between end-member ages were relatively small, the random error of 3% had little effect on the results. An additional advantage was that even a major error in evaluating $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio (1.00 assumed *vs.* 1.9 modeled) affected the end-member ages by <5%. This is an important finding,

Table 5. K-Ar dates and the results of calculations for artificial mixtures measured by Środoń *et al.* (2002). The numbers correspond to different approaches described in the text. Bold – values that were constrained.

Data				Models			
Wt.% old clay	K_2O (%)	^{40}Ar (10^{-6}cm/g)	Age (Ma)	Approach	Diagenetic age (Ma)	Detrital age (Ma)	$^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio
100	1.94	14.14	213.1	1	0.0	124.8	**1.00**
75	3.79	12.16	96.9	2	19.2±0.3	179.8±1.5	0.30±0.01
50	5.45	10.18	57.1	3	**21.1**	182.5±0.2	0.28±0.01
25	7.30	8.16	34.4	4	22.1±0.1	**213.1**	0.21±0.01
0	9.04	6.19	21.1	5	21.9±0.1	208.2±0.1	**0.215**

Table 6. Results of optimizations for a sample of the Waukesha illite measured by Grathoff *et al.* (1998). Approaches 1–4 are specified in the text. Bold – fixed values.

Data			Models			
Size fractions (μm)	% $2M_1$	K-Ar ages (Ma)	Approach	Diagenetic age (Ma)	Detrital age (Ma)	$^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio
<0.2	11	325.1	1	315.3±0.2	450.0±0.2	**1.00**
0.2–0.5	31	363.4	2	314.5±2.2	451.0±2.6	**1.00**
<0.5–1	49	386.5	3	299.7±1.0	434.8±0.7	1.84±0.05
1–2	66	404.7	4	296.8±8.0	434.5±2.2	1.91±0.27
2–4	79	419.4	Grathoff *et al.* (1998)	316	451	**1.00**

because it shows that for such a case, the classic IAA analysis can still give appropriate results even when assuming the $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio of 1.00.

Fore-Sudetic monocline. Bechtel *et al.* (1999) quantified $2M_1/(1M+1Md)$ polytype ratios in numerous samples of the Permian Kupfershiefer Shale from the Fore-Sudetic monocline (SW Poland) and used these values to extrapolate the end-member K-Ar ages from the IAA plot (Table 7). The extrapolated diagenetic ages fall in the range 190–216 Ma. In the same area, 159–188 Ma ages of filamentous illites separated from the Weissliegendes sandstones underlying the Kupferschiefer Shale were measured (Michalik, 2001). These ages were measured only for the <0.2 μm fraction, which could have been contaminated with an older detrital component (*e.g.* Clauer *et al.*, 1997). In such a case the youngest date should be considered as potentially the least contaminated and thus closest to pure diagenetic age. Therefore in the GA modeling for the present study, the 159 Ma age was used.

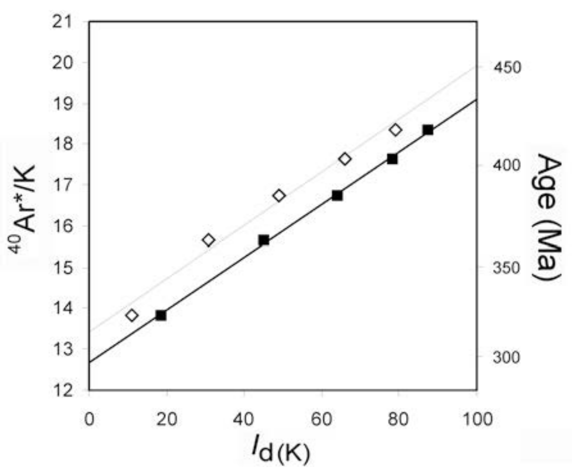

Figure 6. Results of GA calculations for the Illinois Basin (Grathoff *et al.*, 1998). Diamonds – assumption of $^{40}K_{detrital}/^{40}K_{diagenetic}$ = 1.00 and optimization of detrital and diagenetic ages (corresponding to the IAA approach); filled squares – full optimization of all variables without constraints (data from Table 6).

During the Late Rotliegendes, Poland was eroded to the peneplain, and only the Sudetes, the Fore-Sudetic block, the Wolsztyn highlands, the Mazury elevation, and the Pomeranian elevation supplied clastics to the basin (Pokorski, 1988). In SW Poland, stratigraphic gaps from the Lower Carboniferous to the Rotliegendes occur, especially in the Wolsztyn highlands (Górecka-Nowak, 2008). Therefore, some $1M+1Md$ illite in Permian sediments of the Fore-Sudetic monocline feasibly came from the redeposition of the Upper Carboniferous clastics, which had undergone diagenesis soon after their deposition, *i.e.* at ~300 Ma. This is only a simplified model, because older, diagenetically altered rocks may also have been eroded and redeposited in the basin (*e.g.* sediments from the Sudetes, which had not been heated above 250ºC during the Variscan orogenesis).

The age of the detrital $2M_1$ fraction is difficult to evaluate, because different micas may have been eroded from the neighboring Hercynian mountain ranges, *e.g.* from Variscan granites, 290–310 Ma (*e.g.* Turniak *et al.*, 2007); from Variscan metamorphic rocks, 330–340 Ma (*e.g.* Schneider *et al.*, 2006); and from early Variscan metamorphic rocks, 350–380 Ma (*e.g.* Mazur *et al.*, 2006). Therefore assuming a precise value for the age of the detrital $2M_1$ fraction is not possible.

In order to evaluate the data obtained by Bechtel *et al.* (1999), the following approaches were considered:

(1) assumption of $^{40}K_{detrital}/^{40}K_{diagenetic}$ = 1.00 and modeling results with no random error (close to Bechtel approach, diamonds in Figure 7);

(2) assumption of $^{40}K_{detrital}/^{40}K_{diagenetic}$ = 1.00 and modeling results with 3% random error (evaluation of error in Bechtel approach only due to random error);

(3) assumption of $^{40}K_{detrital}/^{40}K_{diagenetic}$ = 1.00 and modeling results with 3% random error, plus allowing for systematic error in wt.$\%_{detrital}$ ($1M+1Md$ detrital component present, but not accounted for) to find out how large an error should be assumed in order to obtain an ~159 Ma age of diagenesis. For the $1M+1Md$ detrital component the age of 300 Ma was assumed;

(4) constraining the diagenetic age at 159 Ma and allowing the $^{40}K_{detrital}/^{40}K_{diagenetic}$ optimization with no random error (circles in Figure 7);

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Table 7. Results of optimizations for samples from the Fore-Sudetic monocline measured by Bechtel *et al.* (1999). Approaches 1–5 are specified in the text. Bold – fixed values.

	Data			Models				
Sample no.	Size fractions (μm)	% $2M_1$	K–Ar ages (Ma)	Approach	Diagenetic age (Ma)	Detrital age (Ma)	$\%1Md_{detrital}$	$^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio
				1	195.2±0.1	329.8±0.2	–	**1.00**
				2	194.4±4.4	330.0±3.6	–	**1.00**
	<1	30	237	3	158.0±5.8	339.8±5.4	**25.0**	1.00
Be 3	1–2	44	255	4	**159.0**	311.9±0.2	–	2.22±0.01
	2–5	65	284	5	201.6±2.0	338.8±3.3	–	0.78±0.06
				Bechtel *et al.* (1999)	196	331	–	**1.00**
				1	201.9±0.1	341.6±0.2	–	**1.00**
				2	202.1±3.2	339.1±4.0	–	**1.00**
	<1	18	227	3	160.1±5.0	356.5±7.7	**29.6**	**1.00**
Be 5	1–2	32	249	4	**159.0**	305.5±0.2	–	3.56±0.01
	2–5	56	281	5	194.0±1.2	326.3±1.9	–	1.46±0.07
				Bechtel *et al.* (1999)	202	344	–	**1.00**
				1	216.3±0.1	324.7±0.2	–	**1.00**
				2	215.5±5.3	325.2±6.9	–	**1.00**
	<1	28	249	3	158.0±6.8	340.3±8.8	**39.8**	**1.00**
Be 11	1–2	40	258	4	**159.0**	300.1±0.1	–	3.99±0.01
	2–5	58	281	5	235.2±0.4	915.5±145.8	–	0.05±0.01
				Bechtel *et al.* (1999)	216	327	–	**1.00**
				1	189.5±0.1	311.1±0.2	–	**1.00**
				2	190.7±3.6	310.4±3.2	–	**1.00**
	<1	25	223	3	160.1±4.8	312.4±5.1	**20.9**	1.00
Be 17	1–2	37	232	4	**159.0**	292.4±0.2	–	2.34 ± 0.01
	2–5	62	267	5	210.5±0.5	850.4±127.9	–	0.05±0.02
				Bechtel *et al.* (1999)	190	312	–	**1.00**

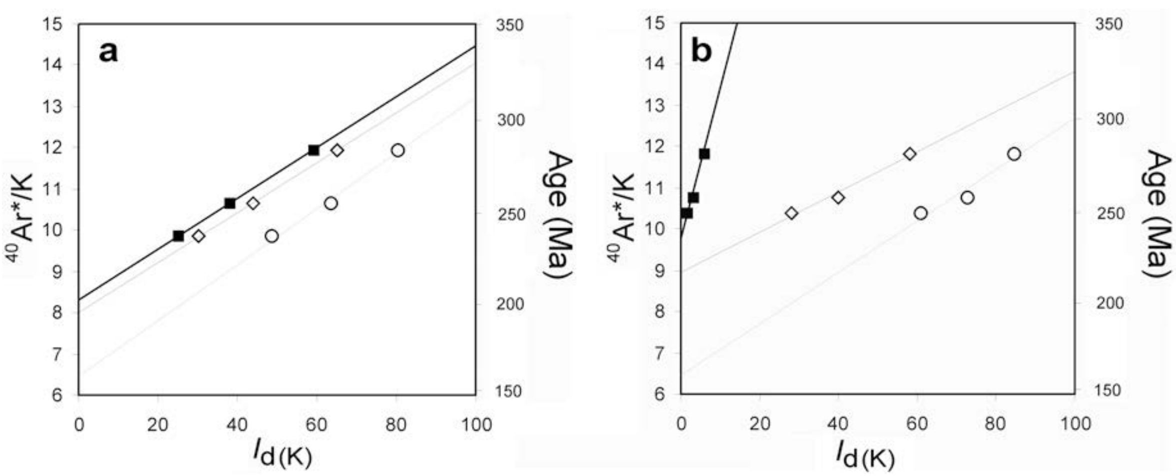

Figure 7. Results of GA calculations for the Fore-Sudetic monocline (Bechtel *et al.*, 1999): (a) sample Be 3; (b) sample Be 11; diamonds – assumption that $^{40}K_{detrital}/^{40}K_{diagenetic} = 1.00$ and optimization of detrital and diagenetic ages (corresponding to the IAA approach); filled squares – full optimization of all variables without constraints; circles – constraining the diagenetic age at 159 Ma, allowing the optimization of $^{40}K_{detrital}/^{40}K_{diagenetic}$, and modeling without random error (data from Table 7).

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(5) full optimization without any constraints and with no random error (filled squares in Figure 7).

For the purpose of these calculations sample no. Be 9 (Bechtel *et al.*, 1999) was excluded because the data points for this sample were in such close proximity that calculations and interpretation based on these data would be too erroneous.

As in the case of the data from Grathoff *et al.* (1998), the random error alone has little effect on the results. For the narrow compositional ranges of size fractions used in this study, the unconstrained optimization produces very erratic and thus unreliable results, with the end-member ages differing by >50% from the results of IAA analysis, and huge variations in modeled $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio (approach 5 and filled squares in Figure 7).

On the other hand, the assumption of a 159 Ma diagenetic age and the presence of a detrital 1*M*+1*Md* component offers a solution which cannot be discarded: a large proportion of the Permian-basin fill coming from erosion of the Carboniferous sedimentary rocks (1*M*+1*Md* illite) and the rest from the Variscan and Caledonian crystalline rocks ($2M_1$ illite). Also, the assumption of a 159 Ma diagenetic age results in a very consistent set of modeled data: the detrital age within the 292–313 Ma range and the $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio of 2.2–4.0. This result is judged as quite feasible, as the range of detrital ages is Variscan and the high $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio is very probable in these black shales, often containing >10% marine organic matter (Sawłowicz, 1989; Sun, 1998), and thus able to supply the diagenetic illite with a lot of NH_4^+ (Lindgreen *et al.*, 2000).

The exercise presented above illustrates how *MODELAGE* can be used to investigate alternative models based on a given set of assumptions. The measurement of inorganic ammonium in these shales would help to validate the proposed models. Also, homogeneity of the ages of the fibrous illites should be investigated to verify the 159 Ma diagenetic illite age. Before this is done, the results above should be considered with caution, only as an alternative hypothesis. If a 188 Ma age of diagenesis is accepted, often no need exists to assume that some of 1*M*+1*Md* illite was of diagenetic origin and the $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio can be close to or only a little greater than 1.0.

If the proposed model is correct, it implies that the mineralization event, which produced the Kupfershiefer metal-sulfide deposits, and was of Middle to Late Triassic age (Jowett *et al.*, 1987; Kosakowski *et al.*, 2007) or younger – from Triassic to Lower Cretaceous (Kucha, 1993; Kucha and Przybyłowicz, 1999), did not reset the detrital illite ages. According to the available age data alone, the diagenetic illite may have formed during an ore mineralization event and/or during younger or older diagenesis. The former hypothesis is supported by the observation of Bechtel *et al.* (1999, fig. 3), who documented the relative enrichment of 1*M* and 1*Md* with respect to $2M_1$ illites in the mineralized zones as compared to the barren zone.

CONCLUSIONS

(1) A new method of analysis of the K-Ar ages of illite-smectite mixtures has been developed (*MODELAGE* program). It deals with the non-linearity in illite age analysis and with different amounts of $^{40}K_{detrital}$ and $^{40}K_{diagenetic}$. Under ideal circumstances, this new approach would allow accurate determination of end-member ages as well as the $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio. In practice, the random errors in the detrital mass-fraction determination mean that these numbers can only be evaluated with a degree of uncertainty. The best results are obtained if the wt.$\%_{detrital}$ values used for the modeling are taken from a relatively broad range and/or the $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio is known. For a given set of data the method permits evaluation of the ranges of expected errors.

(2) The evaluation of literature data by the proposed approach leads to the conclusion that the $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio is often >1.00. Smaller crystal thicknesses of the diagenetic illite and the replacement of some of the K^+ by NH_4^+ or Na^+ in the diagenetic illite may produce such a result.

(3) If the $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio is suspected to be different from 1.00 (visible non-linearity of $^{40}Ar^*/K$ *vs.* wt.$\%_{detrital}$ plot), the proposed approach gives better results than IAA analysis. However, IAA analysis still gives quite accurate results even if the true $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio is different from 1.00, if a broad range of mass fractions is covered and the differences between end-member ages are relatively small.

(4) Overestimation of the diagenetic end-member age can occur if the 1*Md* polytype of the detrital origin is not accounted for. Such a situation is suspected, for example, in the Fore-Sudetic monocline.

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