MODELAGE – A PROGRAM FOR EXTRACTION OF DIAGENETIC AND DETRITAL AGES AND OF $^{40}K_{detrital}/^{40}K_{diagenetic}$ RATIO FROM K-Ar DATES OF CLAY FRACTIONS

Marek Szczerba[1] and Jan Środoń[1]
[1] Institute of Geological Sciences Polish Academy of Sciences, Senacka 1, 31-002 Kraków, Poland,

Last revised: March 24, 2009
For additional information and in case of any problems with the program write or e-mail to:
Marek Szczerba
Institute of Geological Sciences Polish Academy of Sciences
Senacka 1 31-002 Krakow Poland
ndszczer@cyf-kr.edu.pl

CONTENTS

INTRODUCTION

It has been known since Hower *et al.* (1963) that illite in shales should be considered as a mixture of minerals of diagenetic and detrital origin. 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 detrital component can offer a substantial support for constraining the sedimentary material provenience. Because of such interest there has been several attempts of extracting these ages from measured mixed ages.

Physical separation of usually coarser detrital material from the diagenetic one 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 component in three (or more) different grain size fractions and on the linear extrapolation of the K-Ar dates measured for these fractions, plotted against the weight percent of detrital illite ($\%I_{d(I\text{-}S)}$) in the total population of illite layers (detrital + diagenetic):

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

where $\%I_{in(I\text{-}S)}$ is the percent of illite layers in illite-smectite, measured by XRD and wt.% corresponds to the mass of discrete illite or illite-smectite. It is assumed that illite is purely detrital, and illite-smectite – diagenetic. Środoń (2000) demonstrated that, as a result of variable amounts of potassium 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 $\%I_{d(I\text{-}S)}$ for the variable K contents ($\%K_{detrital}$ and $\%K_{diagenetic}$) of illite layers:

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

The corrected value ($\%I_{d(K)}$) can be understood as the percent 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 2*M*1 polytype considered as representing detrital illite (van der Pluijm *et al.*, 2001). However, in the quoted work the problem of variable K content of illite has not been taken into account. It was assumed without direct explanation that 1*M*d and 2*M*1 polytypes have the same potassium 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 higher (approaching 1 for very thick crystals), and the potassium 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 form linearity (Środoń, 1999).

It is very difficult to constrain analytically the potassium content of different polytypes. As the separation of detrital from diagenetic material is extremely difficult, it is possible only to constrain the amount of potassium in mixtures of different polytypes. 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.

Any value other than zero can be substituted for $\%K_{ideal}$ in Equation 2, because these values cancel out. Therefore, the Equation (2) can be rewritten to the following form:

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

$wt.\%_{illite(detrital)}$ has been substituted by $wt.\%_{detrital}$ to underline that both 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. Effectivelly, $\%I_{d(K)}$ 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 plotting not the mixed ages of different fractions but the $^{40}Ar^*/K$ ratios measured for these fractions against $\%I_{d(K)}$, and calculating the end-member ages from the extrapolated $^{40}Ar^*/K$ ratios. This effect is demonstrated in Figure 1, which compares age vs. $\%I_{d(K)}$ plot with $^{40}Ar^*/K$ vs. $\%I_{d(K)}$ plot. Both were obtained by mixing 1500 Ma illite of 9.2% K_2O with 200Ma illite of 10.4% K_2O (the procedure described by Środoń, 1999), and by calculating $\%I_{d(K)}$ using the Equation 3. This approach is equivalent to the one proposed by van der Pluijm *et al.* (2001) because $^{40}Ar^*/K$ is linearly related to $\exp(\lambda t) - 1$:

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

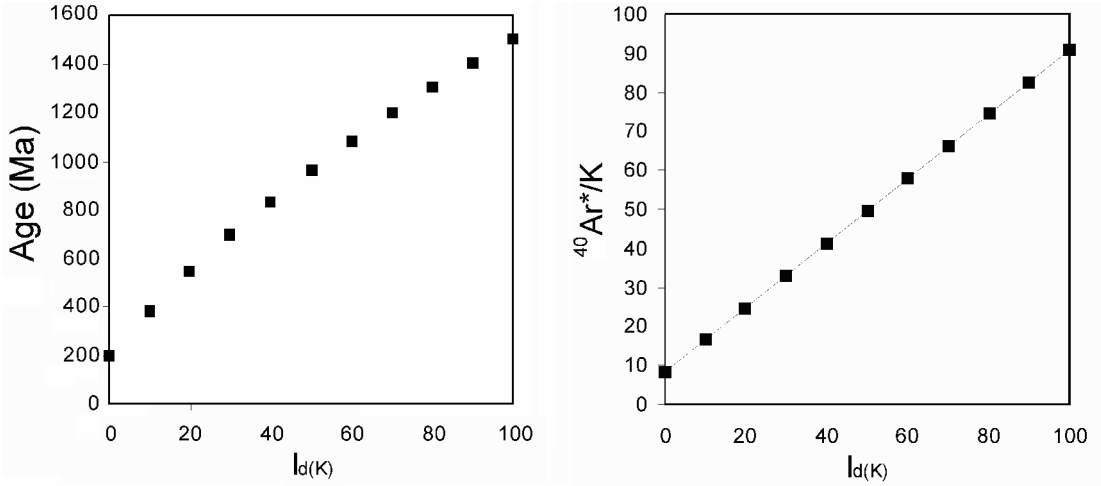


Figure 1. Comparison of age vs. $\%I_{d(K)}$ plot with $^{40}Ar^*/K$ vs. $\%I_{d(K)}$ plot. Visible nonlinearity of the former one.

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 component. Firstly, the "measured $^{40}Ar^*/K$ ratios" were calculated, by assuming the ages and the K_2O contents (and therefore 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 against $\%I_{d(K)}$. Values of $^{40}Ar^*$ and ^{40}K for different $\%I_{d(K)}$, calculated using Equation 3, were obtained as weighted means:

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

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

It was found that "measured $^{40}Ar^*/K$" vs. $\%I_{d(K)}$ plot remains linear if the "guessed" $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio is identical to the "measured" one (Figure 2a). Otherwise it becomes concave if the ratio is too high (Figure 2b), or convex if it is too low (Figure 2c). The departure from linearity is quite strong if the "guessed" $^{40}K_{detrital}/^{40}K_{diagenetic}$ differs by a few tens 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: diamonds).

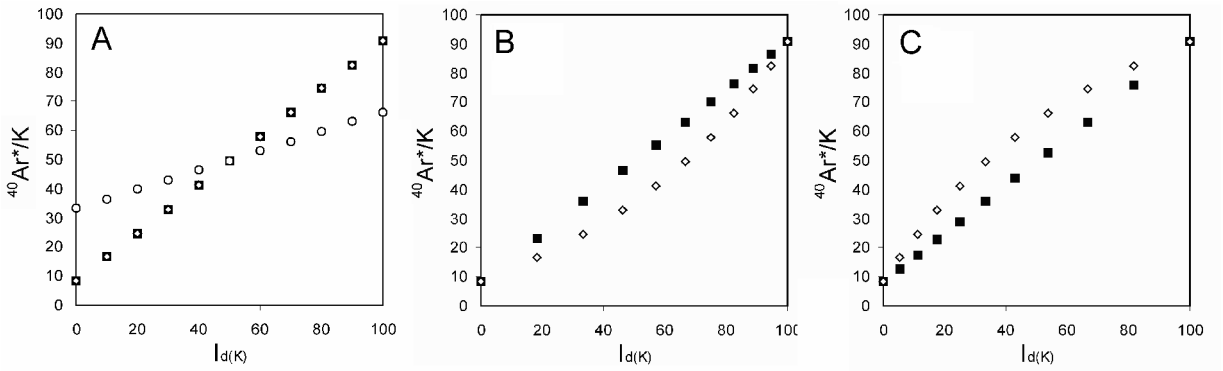


Figure 2. $^{40}Ar^*/K$ vs. $\%I_{d(K)}$ plots for different estimated ("guessed") $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratios compared to the "measured" ones (rectangles): a) "guessed" $^{40}K_{detrital}/^{40}K_{diagenetic}$ equals "measured", "guessed" $^{40}Ar^*/K$ ratio is different (circles) or equal (diamonds) to "measured". b) "guessed" $^{40}K_{detrital}/^{40}K_{diagenetic}$ (diamonds) is 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).

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, it should be possible to determine how accurate are the guessed ages of the end-members and the guessed $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio. By employing an algorithm that optimizes the departure of "guessed" from "measured" $^{40}Ar^*/K$ values, it should be possible to find 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, and in consequence to the measured mixed ages.

In order to implement the concept described above, a program MODELAGE, that uses genetic algorithms (GA) as a minimalization procedure (*e.g.* Koza, 1992), was written in "Java" with the help of JGAP library (http://jgap.sourceforge.net).

GA 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 takes 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 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, 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 chromosomes at some values or ranges was added. The phenotype function F is defined as follows:

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

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

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, whilst the differences are not essential. Therefore for the purposes of the program, offsets are taken vertically.

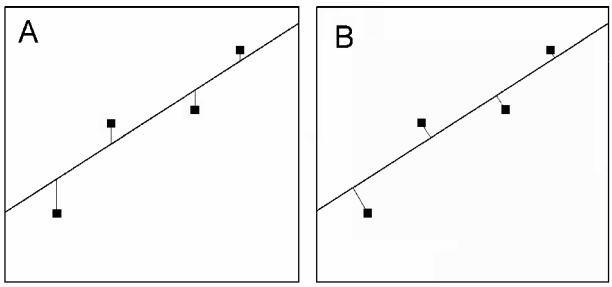


Figure 3. Visualization of a) vertical offsets and of b) perpendicular offsets.

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, denominator of function F to 1, and the function F itself reaches the maximum close to 1000. After a selected number of the evolutionary cycles (usually a few thousands to obtain good precision) the best solution is displayed.

In real situations there are some uncertainties in 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 mineralogical analysis used to calculate the illite mass fractions, thus the former was neglected in further considerations. The uncertainty of the illite wt.% determination was estimated by van der Pluijm *et al.* (2001) as about ±2.5% and by Grathoff (1999) as 2.5-5% (according to the experience of the present authors this uncertainty can be even larger).

In order to check how the proposed technique performs in non-ideal circumstances, random errors can be added to the mass fraction values. A very valuable 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 can be available (*e.g.* the detrital age from dating coarse-grained micas or the $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio from detail chemical analyses and illite crystal thickness data). On the other hand, the age of diagenesis, *e.g.* obtained from illite-smectite in bentonites can possibly lead, by employing this approach, to determination of the $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio of the sample. In such case it would be possible to evaluate, if the assumption of the same amounts of potassium in 2*M*1 and 1*M*d illite, used in the past by several authors, can be justified or not.

Also the effect of systematic errors can be evaluated. Such errors may arise, for example, from the assumption that 1*M*d polytype is of purely diagenetic origin, whilst 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 %2*M*1 mass fraction underestimates systematically the detrital component. In the proposed approach the systematic error means that an assumed percent (%1*M*d $_{detrital}$) of the mass of 1*M*d polytype (wt.%$_{1M\text{d}}$) is also of detrital origin:

$$\text{wt.\%}_{1M\text{d detrital}} = \%1M\text{d}_{\text{detrital}} \times \text{wt.\%}_{1M\text{d}}$$

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

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

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

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

Both approaches assume for simplicity that the 1*M*d illite of detrital origin contains the same amount of potassium as the diagenetic 1*M*d illite.

RUNNING THE MODELAGE

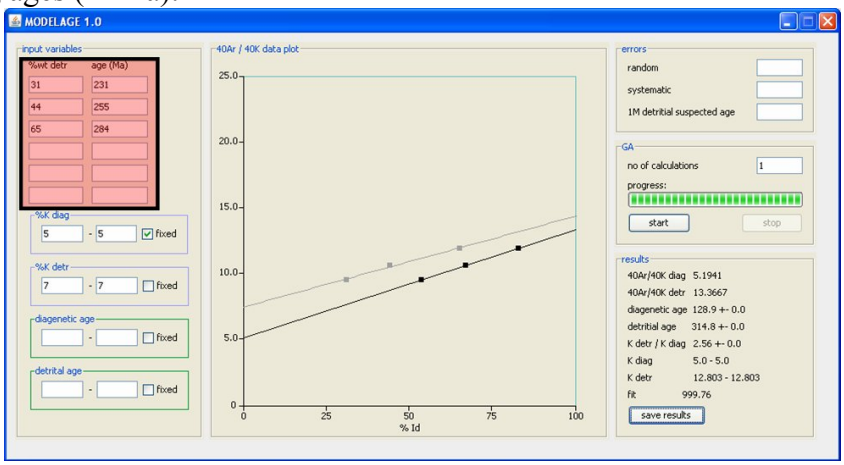
The program consists of three files: Run_MODELAGE.bat, MODELAGE.jar and jgap.jar. The main program file is the MODELAGE.jar. The jgap.jar is Genetic Programming component provided as a Java framework, which is distributed under GNU Lesser Public License. The latest version of this software can be download from: http://jgap.sourceforge.net.

In order to be able to run the program you need to have Java Runtime Environment (JRE) installed on your computer, which can be freely download for example from the following page: http://java.sun.com/javase/downloads/index.jsp.

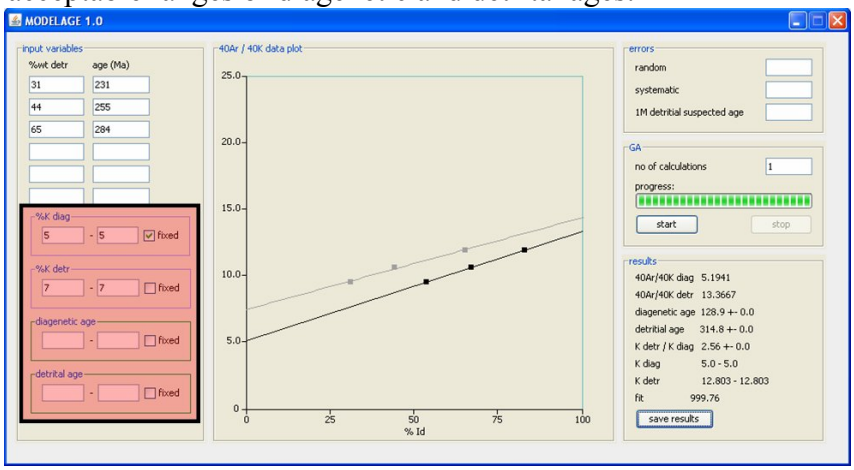
Then you just to have put o put all these three files into one folder and double click on the Run_MODELAGE.bat to run the program.

STARTING THE CALCULATIONS

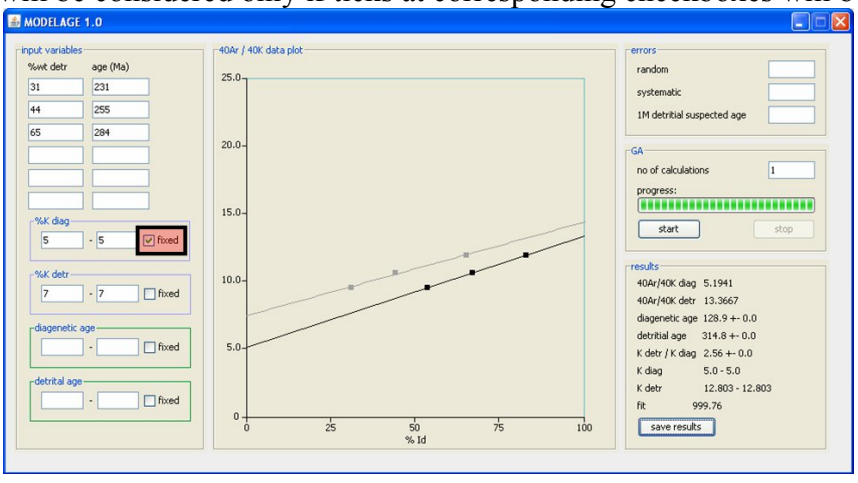
You can provide up to 6 values of mass of detrital fraction (%wt. detr.) with corresponding ages (in Ma):



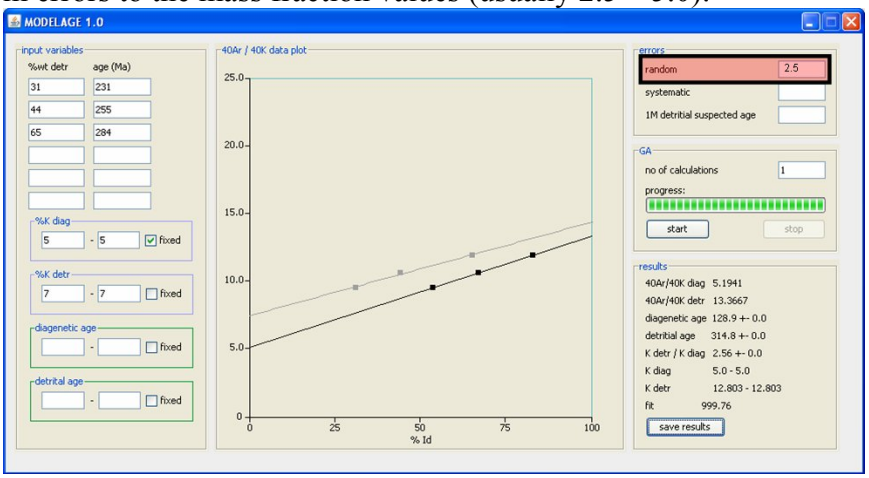
Then you can constrain suspectable ranges of potassium amounts in diagenetic and detrital fractions. Note that for this calculations only $\%K_{detrital}/\%K_{diagenetic}$ ratio is important. You can also constrain acceptable ranges of diagenetic and detrital ages:



These values will be considered only if ticks at corresponding checkboxes will be checked:

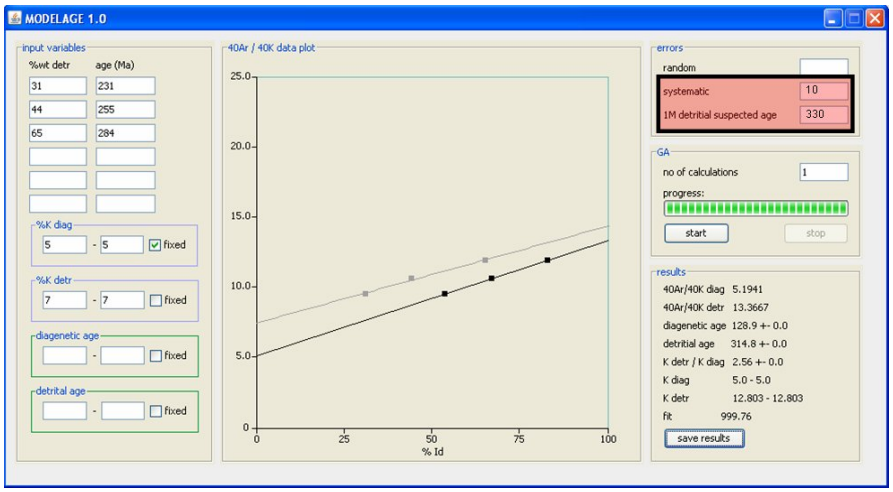


If you want to check how the proposed technique performs in non-ideal circumstances, you can put random errors to the mass fraction values (usually 2.5 – 5.0):

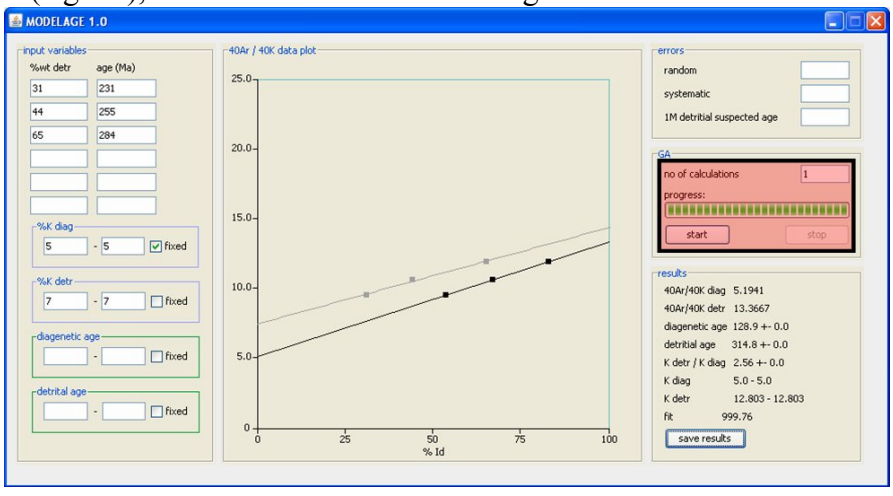


Do not give too broad range (e.g. 50) because the results will be meaningless.

Systematic error corresponds to the assumption that part of 1*M*d polytype is of detrital origin. You can assume also the expected age of this 1*M*d detrital fraction, but it is not necessary. If not, the age of this fraction is assumed to be equal to diagenetic end member age.

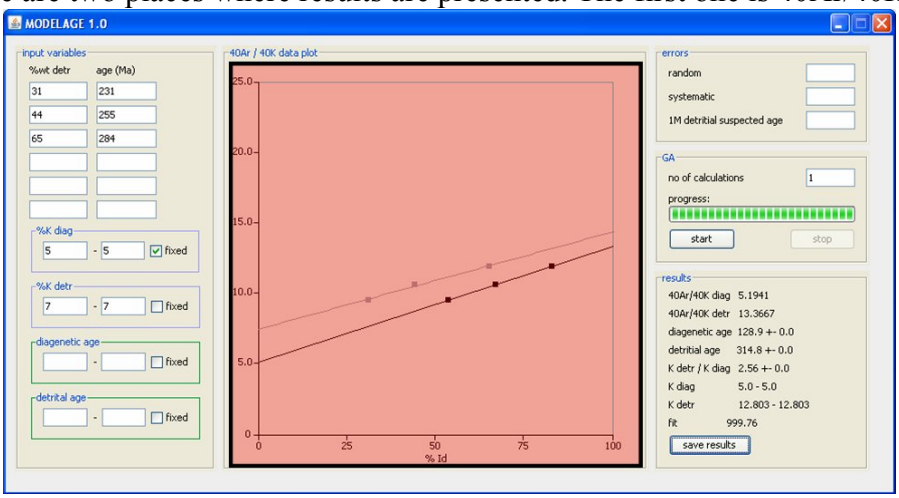


Then set the number of calculations – to obtain reasonable standard deviations use larger number (e.g. 10), and click “start” button to begin the calculations.



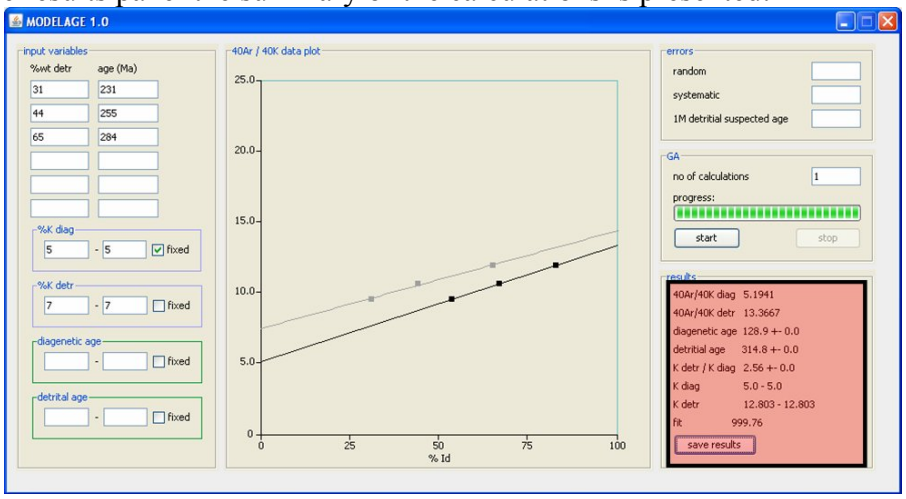
RESULTS

There are two places where results are presented. The first one is 40Ar/40K data plot:



The grey line and grey squares represents classical linear extrapolation (corresponding to IAA approach). The black line and squares corresponds to MODELAGE approach.

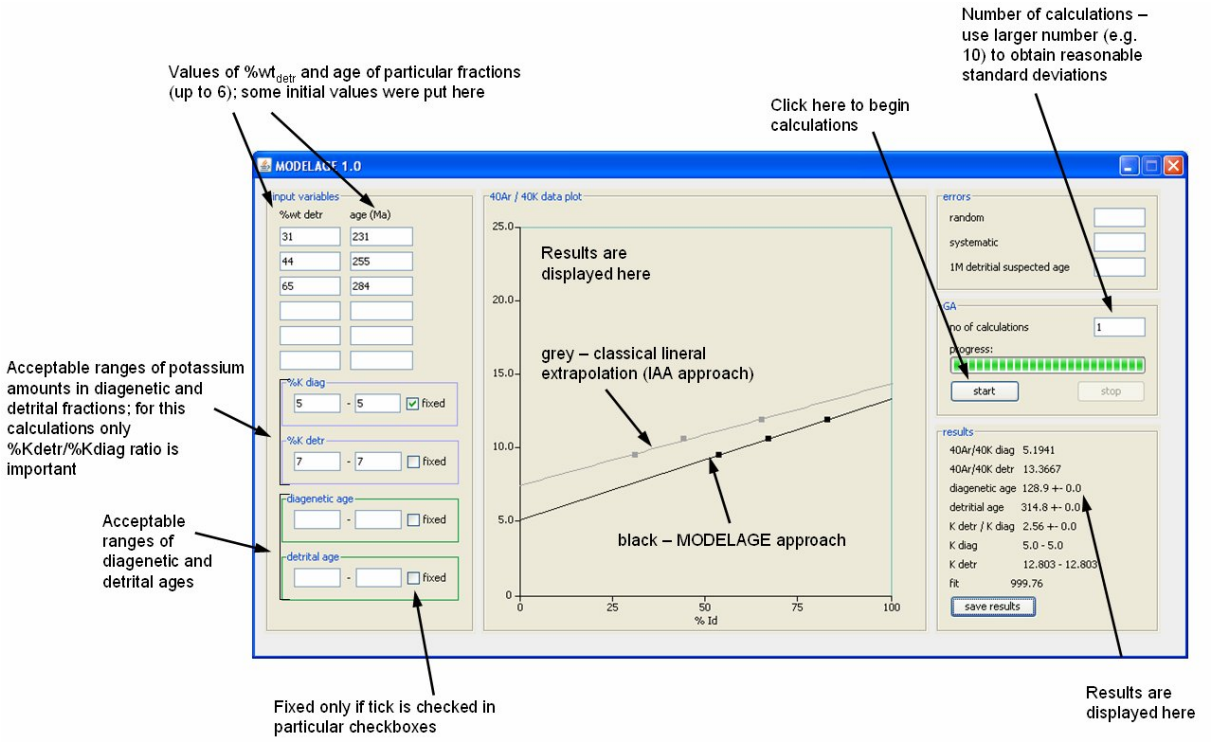
In the results panel the summary of the calculations is presented:



40Ar/40K diag – represents 40Ar/40K ratio for end member diagenetic fraction (expressed in nl/g of ^{40}Ar per % of K),
40Ar/40K detr – 40Ar/40K ratio for end member detrital fraction,
diagenetic age – is diagenetic end member age with standard deviation (different from 0 if more than 1 calculations were performed),
detrital age – represents detrital end member age,
K detr/ K diag – represents $K_{detrital}/K_{diagenetic}$ ratio (with standard deviation),
K diag – ranges of potassium amount in diagenetic end member fraction – it is calculated if tick is checked in %Kdiag and/or %Kdetr checkbox,
K detr – ranges of potassium amount in detrital end member fraction,
fit – represents how good the results are – the best results are with fit value close to 1000 (but it is not always possible to be close to this value). Using this value you can check if this approach works properly or discard poor results.

FINAL REMARKS

The summary of description from the two previous paragraphs is presented here:



In case of any questions, any problems, or especially if you find any errors in the program please contact me:

Marek Szczerba
Institute of Geological Sciences Polish Academy of Sciences
Senacka 1 31-002 Kraków, Poland
ndszczer@cyf-kr.edu.pl