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## František RYŠAVÝ ${ }^{1}$ <br> THE POTASSIUM-CALCIUM METHOD ON BASIS OF GAMMASPECTROMETRY WELL-LOGGING DATA LIKE THE METHOD OF DETERMINATION OF THE ROCK AGE <br> KALIUM-ARGONOVÁ METODA VYCHÁZEJÍCÍ Z GAMASPEKTROMETRICKÝCH KAROTÁŽNÍCH DAT JAKO METODA STANOVENÍ STÁŘÍ HORNIN


#### Abstract

This paper presents way how to determine the rock age from the continuous curve of the real bygone time expressed like function of depth. Inputs of well-logging data are two continuous curves registered for two elements: ${ }_{19}^{40} \mathrm{~K}$ and ${ }_{20}^{40} \mathrm{Ca}$. Both you get with the help of gamma-spectrometry for the natural gamma-ray and for the spectrometric neutron-gamma method. Both curves are computed to create the only curve of ratio reporting about quantities of the mentioned elements.

The ratio curve is transformed into time domain to be formed the only curve remarked as the curve of the apparent time. Relations for transformation can be various; here are two, after author and after Hamilton.

This curve of the apparent time has two components; global and local ones. The global is presented with the curve of trend for rocks being not carbonates. The above trend has various shapes: exponential, linear, polynomial up to sixth degree or all other. We expect that this curve presents the one of the real bygone time which is used for determination of the rock age.


#### Abstract

Abstrakt Přípěvek představuje cestu ke stanovení stáří hornin z kontinuální křivky reálného minulého času vyjádřené jako funkce hloubky. Vstupní karotážní data jsou dvě kontinuální křivky zaznamenané pro dva prvky: ${ }_{19}^{40} \mathrm{~K} \mathrm{a}_{20}^{40} \mathrm{Ca}$. Obě lze získat z gamaspektrometrie přirozeného gama záření a spektrometrie neutron-gama metody. Přepočtem z obou křivek je získán poměr poskytující informaci o množstvích zmíněných prvků.

Poměrová křivka je přepočtena do časové oblasti k získání jediné křivky označované jako zdánlivý čas. K transformaci jsou dispozici dva vztahy, autorův a Hamiltona.


[^0]Křivka zdánlivého času má dvě složky: globální a lokální. Globální představuje trendovou křivku pro bezkarbonátové horniny. Tento trend má různé tvary: exponenciální, lineární, polynomický šestého řádu a další. Očekává se, že tato křivka představuje reálný uplynulý čas, který je možno použít pro stanovení stáří hornin.

## Introduction

Determination of the absolute time of archeological artefacts and rocks knows several well-verified methods of geochronology. The all use decay of radioactive chemical elements; an isotope of element decays on the other one which remains stable. The potassium-calcium method is characterized by that ${ }_{19}^{40} \mathrm{~K}$ decays on ${ }_{20}^{40} \mathrm{Ca}$. The above process is active for millions of years yet; quantity of calcium on planet Earth is its final product.

The problem is that calcium is such element being easy dissolved in water and just this is why that calcium well migrates. This element is present in remains of animals, is secreted by sea-weeds and through these organic processes creates the gigantic massifs of carbonates there. Beside of that there are formed, too, travertine from water being rich of calcium like result of chemical processes.

Both mentioned processes very often combine one other and they end by various sorts of limestones and dolomites.

For the closed system when the created calcium remains it is easy to count the rock age, however, for the open system it is big problem, because part of calcium migrates out and in and there remains only tiny part of ${ }_{20}^{40} \mathrm{Ca}$ at that original domain. We cannot know how to separate that local component presented result of chemical and organic processes and the global component which reflects that original process of radioactive decay of ${ }_{19}^{40} \mathrm{~K}$ on ${ }_{20}^{40} \mathrm{Ca}$.

The aim of this paper is an attempt to offer interpretation of the open system for the rock age; it is about how to get from well-logging data the continuous curve with the borehole depth which is presented like the curve of the bygone time for rocks and how to separate that mentioned curve on global and local components.

## Principles of method after author

It is known that isotope ${ }_{19}^{40} \mathrm{~K}$ decays on two stable isotopes: ${ }_{20}^{40} \mathrm{Ca}$ and ${ }_{18}^{40} \mathrm{Ar}$. This double transmutation is passing simultaneously. It is known, too, that $89 \%$ of ${ }_{19}^{40} \mathrm{~K}$ is decayed like $\beta$-decay. The following equation is equation of this decay:

$$
{ }_{19}^{40} K \rightarrow{ }_{-1}^{0} e+{ }_{20}^{40} C a
$$

The remaining $11 \%$ of ${ }_{19}^{40} \mathrm{~K}$ is transmuted by K -capture of electron. Here is equation of this process:

$$
{ }_{19}^{40} \mathrm{~K}+{ }_{-1}^{0} e \rightarrow{ }_{18}^{40} \mathrm{~A} r
$$

Dual transmutation has different the decay constants - it holds that $\lambda_{\beta}=$ $4.962 \times 10^{-10}\left[\mathrm{yrs}^{-1}\right]$ and $\lambda_{K}=0.581 \times 10^{-10}\left[\mathrm{yrs}^{-1}\right]$; after Dubanský A., Zamarský V. (1982).

Quantity of ${ }_{19}^{40} \mathrm{~K}$ which is registered is directed by equation:

$$
\begin{equation*}
m^{(K)}=m_{0}^{(K)} \times\left[0.89 \times \exp \left(-\lambda_{\beta} \times t\right)+0.11 \times \exp \left(-\lambda_{K} \times t\right)\right] \tag{1}
\end{equation*}
$$

where $\mathrm{m}_{0}^{(\mathrm{K})}=$ the original quantity of ${ }_{19}^{40} \mathrm{~K}[\mathrm{~g} / \mathrm{g}]$, $\mathrm{m}^{(\mathrm{K})}=$ the recent quantity of ${ }_{19}^{40} \mathrm{~K}[\mathrm{~g} / \mathrm{g}]$, and $\mathrm{t}=$ the bygone time [yrs]; it is the apparent time.

Quantity of ${ }_{20}^{40} \mathrm{Ca}$ is presented by equation as follows:

$$
\begin{equation*}
m^{(C a)}=0,89 \times m_{0}^{(K)} \times\left[1-\exp \left(-\lambda_{\beta} \times t\right)\right] \tag{2}
\end{equation*}
$$

What is important is that this isotope is final product of decay; the next decay is not executed.

Now, you have to define the time function like it is made in the following formula:

$$
\begin{equation*}
f(t)=\frac{m^{(C a)}}{m^{(K)}}=0.89 \times\left[\frac{1-\exp \left(-\lambda_{\beta} \times t\right)}{0.89 \times \exp \left(-\lambda_{\beta} \times t\right)+0.11 \times \exp \left(-\lambda_{K} \times t\right)}\right] \tag{3}
\end{equation*}
$$

This relation is depicted in fig. 1 being remarked as the real relation. However, it is very difficult, rather impossible, to express directly attribute of time from formula (3).


Fig. 1 Depiction of real and polynomial time relations

Nevertheless, the real relationship could be replaced by the following one:
$f^{*}(t)=0.001 \times t^{2}+4.4162 \times t$.
Such equation can be adjusted into form:
$f^{*}(t)=0.001 \times(t+2208.1)^{2}-0.001 \times(2208.1)^{2}$.

It needs to say that the decay constants $\lambda_{\beta}$ and $\lambda_{\mathrm{K}}$ must be adjusted too for formula (3); if $\lambda_{\beta}=4.962 \times 10^{-4}$ and $\lambda_{K}=0.581 \times 10^{-4}$, then factor of time has relation to one million of years - it holds that $\mathrm{t} \equiv\left[10^{-6} \mathrm{yrs}\right]$. However, formula (4) can be expressed like this:

$$
\begin{equation*}
f^{*}(t)=0.001 \times t^{2}+0,89 \times \lambda_{\beta} \times 10^{4} \times t \ldots \text { for } t \geq 0 \tag{6}
\end{equation*}
$$

You can make sure that equation (6) and (4) are identical. It is possible to write down for formula (5) that it holds:

$$
\begin{align*}
& f^{*}(t)=0.001 \times(t+A)^{2}-\frac{A^{2}}{1000}  \tag{7}\\
& A=2208.1\left[10^{-6} \mathrm{yrs}\right] \tag{8}
\end{align*}
$$

Formula (7) presents relation being parabolic where coordinates of vertex of parabola are these: $(-\mathrm{A})$ and $\left(-\mathrm{A}^{2} / 1000\right)$. Now, we replace formula (3) by formula (7):

$$
\begin{equation*}
f^{*}(t)=\frac{m^{(C a)}}{m^{(K)}}=0.001 \times(t+A)^{2}-0,001 \times A^{2} \tag{9}
\end{equation*}
$$

This is formula being very convenient for expression of the time factor.

$$
\begin{equation*}
t=A \times\left[\sqrt{\left.1+k \times 10^{-4} \times\left(\frac{m^{(C a)}}{m^{(K)}} \times 10^{4}\right)-1\right]},\right. \tag{10}
\end{equation*}
$$

$$
\begin{align*}
& A=2208.1, \text { and } \\
& k=2.0509851 \times 10^{-4} . \tag{11}
\end{align*}
$$

The unit of time is related to one million of years; $t \equiv\left[10^{-6} \mathrm{yrs}\right]$. The input values of ratio calcium/potassium are in the following form: $\left[\mathbf{m}^{(\mathrm{Ca})} / \mathbf{m}^{(\mathrm{K})}\right] \times 10^{4}$. Formula (10) can be adjusted, too, in the form as follows:
$t=A \times \sqrt{1+k \times 10^{-4} \times\left(\frac{m^{(C a)}}{m^{(K)}} \times 10^{4}\right)} \times \exp \left\{-\operatorname{Argsinh}\left[\sqrt{1+k \times 10^{-4} \times\left(\frac{m^{(C a)}}{m^{(K)}} \times 10^{4}\right)}\right]^{-1}\right\}$.

Both amounts of $\mathrm{m}^{(\mathrm{K})}$ and $\mathrm{m}^{(\mathrm{Ca})}$ you are able to register with the help of spectral observations of energy for gamma-photons. You can use for that the method of neutron-gamma and the method of natural gamma-radiation. The trouble is that besides
of ${ }_{20}^{40} \mathrm{Ca}$ created by radioactive decay there exists big amount of calcium being dependent on chemical and organic processes.

Formula (10) is presented in fig. 1 like the polynomial relation of second degree. It is relation being much closer to the real relation according to formula (3). The ratio $\mathrm{f}^{*}(\mathrm{t}) / \mathrm{f}(\mathrm{t})$ in tab. 1 allows us to estimate systematic error formed by replacement of formula (3) by formula (9).

$$
\begin{equation*}
\frac{\Delta f(t)}{f(t)}=\frac{f^{*}(t)}{f(t)}-1<+0.010 \tag{13}
\end{equation*}
$$

This inequality presents lower value than $1 \%$.

| $\mathrm{t}\left[10^{6} \mathrm{yrs}\right]$ | f (t) | f*(t) | f*(t)/f (t) | $\begin{gathered} \mathrm{t} \\ {\left[10^{6} \mathrm{yrs}\right]} \end{gathered}$ | f (t) | f*(t) | $\begin{gathered} \mathbf{f}^{*}(\mathbf{t}) / \mathbf{f} \\ (\mathbf{t}) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 0 | 0 | 0 |  | 60 | 268.169 | 268.572 | 1.002 |
| 1 | 4.417 | 4.417 | 1.000 | 70 | 313.490 | 314.034 | 1.002 |
| 2 | 8.836 | 8.836 | 1.000 | 80 | 358.992 | 359.696 | 1.002 |
| 3 | 13.256 | 13.258 | 1.000 | 90 | 404.674 | 405.558 | 1.002 |
| 4 | 17.679 | 17.681 | 1.000 | 100 | 450.539 | 451.620 | 1.002 |
| 5 | 22.103 | 22.106 | 1.000 | 200 | 919.289 | 923.240 | 1.004 |
| 6 | 26.529 | 26.533 | 1.000 | 300 | 1406.808 | 1414.860 | 1.006 |
| 7 | 30.957 | 30.962 | 1.000 | 400 | 1913.656 | 1926.480 | 1.007 |
| 8 | 35.386 | 35.394 | 1.000 | 500 | 2440.394 | 2458.100 | 1.007 |
| 9 | 39.817 | 39.827 | 1.000 | 600 | 2987.581 | 3009.720 | 1.007 |
| 10 | 44.250 | 44.262 | 1.000 | 700 | 3555.775 | 3581.340 | 1.007 |
| 20 | 88.677 | 88.724 | 1.001 | 800 | 4145.529 | 4172.960 | 1.007 |
| 30 | 133.282 | 133.386 | 1.001 | 900 | 4757.391 | 4784.580 | 1.006 |
| 40 | 178.066 | 178.248 | 1.001 | 1000 | 5391.898 | 5416.200 | 1.005 |
| 50 | 223.028 | 223.310 | 1.001 |  |  |  |  |

Tab. 1 Comparison of the real and polynomial functions

Thus, equation (9) or (7) can be well-used for replacement and the derived formula (10) presents that basic one for calculation of the apparent time which makes transformation into time domain.

You can also analyze the above formula (10). If it holds that $\mathrm{m}^{(\mathrm{Ca})} \gg \mathrm{m}^{(\mathrm{K})}$ you will attain simpler formula:

$$
\begin{equation*}
t=A \times \sqrt{1+k \times 10^{-4} \times\left(\frac{m^{(C a)}}{m^{(K)}} \times 10^{4}\right)}, \ldots \text { for } m^{(C a)} \gg m^{(K)} \tag{14}
\end{equation*}
$$

This relation is characteristic for carbonates, at all. It expresses an extraordinary import of calcium. Derivation of formula (14) is easier from formula (12), because for condition that $\mathrm{m}^{(\mathrm{Ca})} \gg \mathrm{m}^{(\mathrm{K})}$ it holds that the exponential term is equal to one.

If there is condition that $\mathrm{m}^{(\mathrm{Ca})} \ll \mathrm{m}^{(\mathrm{K})}$ it means that the term $0.001 \times \mathrm{t}^{2} \rightarrow 0$. Then you will get this formula:

$$
\begin{equation*}
t=\left[0.89 \times \lambda_{\beta} \times 10^{4}\right]^{-1} \times\left(\frac{m^{(C a)}}{m^{(K)}} \times 10^{4}\right), \text { for... } m^{(C a)} \ll m^{(K)} \tag{15}
\end{equation*}
$$

This is linear relation valid for weakly calcareous formations.
Thanks to relation (6) it is possible to express coefficients A and k like function of constant $\lambda_{\beta}$ :

$$
\begin{align*}
& A=445 \times \lambda_{\beta} \times 10^{4}, \text { and }  \tag{16}\\
& k=\frac{1000}{A^{2}}=0.005049867 \times \lambda_{\beta}^{-2} \times 10^{-8} . \tag{17}
\end{align*}
$$

Formula (10) presents basic equation for transformation of the ratio curve in time domain. By that you get the curve of the apparent time with depth. Formula (17) can be expressed in other way, as well.

$$
\begin{align*}
& k=(\eta)^{-1}, \text { and }  \tag{18}\\
& \eta=\frac{A^{2}}{1000} \tag{19}
\end{align*}
$$

where $\eta=$ constant related to one milliard of years.
Dimension of $\eta$ follows from this adjustment:

$$
\frac{\left[10^{-12} \times \mathrm{yrs}^{2}\right]}{\left[10^{3} \times 10^{-6} \times \mathrm{yrs}\right]}=\left[10^{-9} \times \mathrm{yrs}\right]
$$

It holds that $\eta=4.8757 \times 10^{-9}$ yrs. This can be adjusted like $\eta \times 10^{9}=4.8757$ milliards of years or better like $\eta \times 10^{9}=4875.7 \times 10^{6} \mathrm{yrs}$.

This constant is expressed in milliards of years. For $\eta=4.8757\left[10^{-9} \mathrm{yrs}\right]$ it is possible to suppose that it is somewhere very close to the age of the Earth. This is supported by fact that for $\mathrm{t}=0$, i.e, the moment when a fictive stopwatch was pushed,
you receive according to formula (7) difference $(\eta-\eta)=0$ which means that $f^{*}(t)=0$, too; only then it holds that ratio $\mathbf{m}^{(\mathrm{K})}=\mathrm{m}_{0}^{(\mathrm{K})}$ and $\mathbf{m}^{(\mathrm{Ca})}=0$.

It ought to be remembered that the input calcium/potassium is directed by inequality:

$$
\begin{equation*}
0 \leq\left(\frac{m^{(C a)}}{m^{(K)}} \times 10^{4}\right)<\infty \tag{20}
\end{equation*}
$$

## Implement of correction like consequence of replacement the real time function

Systematic error was said to be lower than $1 \%$. That means you can neglect it within calculation. However, for very accurate calculations you should implement correction making you completely remove the systematic error. Fig. 2 shows how to do that.


Fig. 2 Principle of correction between real and polynomial relation

As $f^{*}(t)>f(t)$ it holds that ratio $f^{*}(t) / f(t)>1$. Because we use for interpretation the polynomial function remarked as $\mathrm{f}^{*}(\mathrm{t})$ the interpreted time remarked as $\mathrm{t}^{*}$ will be lower than the real time after the real function being remarked like $\mathrm{f}(\mathrm{t})$. It holds that $\mathrm{t}^{*}<$ $t$. The starting value for interpretation is ratio $\left[\mathbf{m}^{(\mathrm{Ca})} / \mathbf{m}^{(\mathrm{K})}\right]$.

As we want to reach the time remarked as $t$, we need to have higher starting value $\left[\mathbf{m}^{(\mathrm{Ca})} / \mathbf{m}^{(\mathrm{K})}\right]$. Therefore this ratio is adjusted after formula:

$$
\begin{equation*}
\left[\frac{m^{(C a)}}{m^{(K)}} \times 10^{4}\right]^{*}=\frac{f^{*}\left(t^{*}\right)}{f\left(t^{*}\right)} \times\left[\frac{m^{(C a)}}{m^{(K)}} \times 10^{4}\right] \tag{21}
\end{equation*}
$$

where $\left[\mathbf{m}^{(\mathrm{Ca})} / \mathbf{m}^{(\mathrm{K})}\right]=$ the ratio calcium/potassium registered, $\left[\mathbf{m}^{(\mathrm{Ca})} / \mathbf{m}^{(\mathrm{K})}\right]^{*}=$ the ratio calcium/potassium corrected, $\mathrm{f}\left(\mathrm{t}^{*}\right) \quad=$ the real time function for uncorrected time $\mathrm{t}^{*}$ and
$\mathrm{f}^{*}\left(\mathrm{t}^{*}\right) \quad=$ the polynomial time function uncorrected time $\mathrm{t}^{*}$.

You suppose you have $t^{*}=1000 \times 10^{6}$ years. The ratio $\mathrm{f}^{*}\left(\mathrm{t}^{*}\right) / \mathrm{f}\left(\mathrm{t}^{*}\right)=1.005$. The registered ratio $\left[\mathrm{m}^{(\mathrm{Ca})} / \mathbf{m}^{(\mathrm{K})}\right] \times 10^{4}=\mathrm{f}\left(\mathrm{t}^{*}\right) \times 10^{4}=5391.898$. Then the corrected ratio is following: $\left[\mathbf{m}^{(\mathrm{Ca})} / \mathbf{m}^{(\mathrm{K})}\right]^{*} \times 10^{4}=5418.857$.

If you use the formula for polynomial relation remarked as (10) or (12) you will attain this result: $\mathrm{t}=1000.414 \times 10^{6}$ years. This is that accurate value without any systematic error.

## Spectrometry of the natural gamma-radiation

I think, in this domain there are no problems. It is one of standard well-logging methods. You make registration of three continuous curves with the borehole depth for these elements: ${ }_{19}^{40} \mathrm{~K},{ }_{92}^{238} \mathrm{U}$ and ${ }_{90}^{232} \mathrm{Th}$. Those elements have their characteristic energies; for ${ }_{19}^{40} \mathrm{~K}$ it is $\mathrm{E}=1.46 \mathrm{MeV}$. Calibration of curves is made in $[\mathrm{g} / \mathrm{g}]$. Interpretation of gamma-spectrometry is well-verified; with the curve of ${ }_{19}^{40} \mathrm{~K}$ there should to be no problems. We register two levels of energy; the first is for $\mathrm{E}>1.3 \mathrm{MeV}$ when you register potassium, thorium and uranium together, the second is for $\mathrm{E}>1.6$ MeV when there are registered only thorium and uranium together.

What is remarkable is the quantity of ${ }_{19}^{40} \mathrm{~K}$ in carbonates. It is extraordinary low, lowest of all sediments, whereas, the amount of calcium is very high there, almost dominating.

## Spectrometry of the prompt gamma-radiation of the neutron-gamma method

For registration of ${ }_{20}^{40} \mathrm{Ca}$ you need to have a power source of neutrons around 666 GBq . It is recommended to use higher length of tool, because the distance between source and detector ought to be higher. I suppose that the distance being $400-600 \mathrm{~mm}$ is enough. It is because of influence of gamma-photons belonging to inelastic dispersion of fast neutrons to come to detector with certain delay. You register spectrum of prompt gamma-radiation and the influence of spectrum evoked by inelastic dispersion presents
interference being not desirable. For energy $\mathrm{E}>3 \mathrm{MeV}$ there are two significant elements ${ }_{8}^{16} \mathrm{O}$ with $\mathrm{E}_{\gamma}=6.1 \mathrm{MeV}$ and ${ }_{6}^{12} \mathrm{C}$ with $\mathrm{E}_{\gamma}=4.42 \mathrm{MeV}$; both are not convenient, because both are the product of inelastic dispersion of fast neutrons.

It is also possible to construct special tools having two neutron sources; $\mathrm{Am} / \mathrm{Be}$ with average energy $\mathrm{E}=4.99 \mathrm{MeV}$ and $\mathrm{Po} / \mathrm{Be}$ with energy $\mathrm{E}=3.07 \mathrm{MeV}$. The source presented like $\mathrm{Am} / \mathrm{Be}$ is affected by inelastic dispersion, whereas, $\mathrm{Po} / \mathrm{Be}$ is not. Both spectrums are compared and there are counted corrections, namely for specification quantity of gamma photons produced by thermal neutrons belonging to the source with higher average energy. Nevertheless, using of longer distance between source and detector seems me simpler.

The spectrum of the prompt gamma-radiation is well-registered like the line spectrum for domain of energy $\mathrm{E}>3 \mathrm{MeV}$. For $\mathrm{E}<3 \mathrm{MeV}$ there is possible to register only the continuous spectrum of energy; there exists interference of primary spectrum and the spectrum of dispersed radiation.
${ }_{20}^{40} \mathrm{Ca}$ have the following lines of energy: $\mathrm{E}_{\gamma}=6.41 \mathrm{MeV}$ for 22 gamma-photons, $\mathrm{E}_{\gamma}=4.42 \mathrm{MeV}$ for 12 gamma-photons and $\mathrm{E}_{\gamma}=1.94 \mathrm{MeV}$ for 39 gamma-photons. The above photons are those emitted as a consequence of the capture of one hundred thermal neutrons by nuclei of atoms. These data carry information about intensity of gammaradiation.

It is clear that for registrations of ${ }_{20}^{40} \mathrm{Ca}$ there are the lines of energy for 6.41 MeV and 4.42 MeV . Unfortunately, here is just present ${ }_{6}^{12} \mathrm{C}$ having energy 4.42 MeV , too. You see that both mentioned elements have common line of energy. That is also why we try to limit effect of inelastic dispersion by selection of the distance between source and detector.

Nevertheless, in spite of all troubles with registration ${ }_{20}^{40} \mathrm{Ca}$ we are able to record continuous curve with the borehole depth. Registration of potassium and calcium can be made simultaneously within the only run in the borehole. Both curves are calibrated in [ $\mathrm{g} / \mathrm{g}]$.

What is important too is the spectrum of energy is almost independent on density and wetness of rocks; the spectrum does not depend on the borehole effect. As the detectors there are expected sensitive $\mathrm{Ge}(\mathrm{Li})$-detectors.

## The error of the apparent time

The error is deduced with the help of first derivatives after $\mathbf{m}^{(\mathrm{Ca})}$ and $\mathbf{m}^{(\mathrm{K})}$. It holds that:

$$
\begin{equation*}
\frac{d t}{d m^{(C a)}}=+A \times \frac{k}{2} \times\left[\frac{m^{(C a)}}{m^{(K)}}\right] \times\left[1+k \times \frac{m^{(C a)}}{m^{(K)}}\right]^{-\frac{1}{2}} \times \frac{1}{m^{(C a)}}, \text { and } \tag{22}
\end{equation*}
$$

$$
\begin{equation*}
\frac{d t}{d m^{(K)}}=-A \times \frac{k}{2} \times\left[\frac{m^{(C a)}}{m^{(K)}}\right] \times\left[1+k \times \frac{m^{(C a)}}{m^{(K)}}\right]^{-\frac{1}{2}} \times \frac{1}{m^{(K)}} \tag{23}
\end{equation*}
$$

The error is defined as follows:

$$
\begin{equation*}
\Delta t= \pm A \times \frac{k}{2} \times 10^{4} \times\left(\frac{m^{(C d}}{m^{(K)}} \times 1 \theta^{\phi}\right) \times\left[1+k \times 10^{4} \times\left(\frac{m^{(C)}}{m^{(K)}} \times 1 \theta\right)\right]^{-\frac{1}{2}} \times \sqrt{\left[\frac{\Delta m^{(C)}}{m^{(C)}}\right]^{2}+\left[\frac{\Delta m^{(K)}}{m^{(K)}}\right]^{2}} . \tag{24}
\end{equation*}
$$

If you use values that $\mathrm{A}=2208.1$ and $\mathrm{k}=2.0509851 \times 10^{-4}$ and substitute them into formula (24) you will get numeric form of this relation:

$$
\begin{align*}
\Delta t & = \pm 2264.39 \times 10^{-4} \times\left(\frac{m^{(C a)}}{m^{(K)}} \times 10^{4}\right) \times\left[1+2.0509851 \times 10^{-8} \times\left(\frac{m^{(C a)}}{m^{(K)}} \times 10^{4}\right)\right]^{-\frac{1}{2}} \times \\
& \times \sqrt{\left[\frac{\Delta m^{(C a)}}{m^{(C a)}}\right]^{2}+\left[\frac{\Delta m^{(K)}}{m^{(K)}}\right]^{2}} . \tag{25}
\end{align*}
$$

where $\Delta \mathbf{m}^{(\mathrm{K})}=$ the error of determination of potassium-quantity $[\mathrm{g} / \mathrm{g}]$,
$\Delta \mathbf{m}^{(\mathrm{Ca})}=$ the error of determination of calcium-quantity $[\mathrm{g} / \mathrm{g}]$, and
$\Delta \mathrm{t}=$ the error of the apparent time [10-6yrs].
For condition that $\mathbf{m}^{(\mathrm{Ca})} \gg \mathbf{m}^{(\mathrm{K})}$ it is clear you can use this identity:

$$
1+k \times 10^{-4} \times\left(\frac{m^{(C a)}}{m^{(K)}} \times 10^{4}\right)=k \times 10^{-4} \times\left(\frac{m^{(C a)}}{m^{(K)}} \times 10^{4}\right)
$$

The formula for error will get simpler:

$$
\begin{equation*}
\Delta t= \pm \frac{A}{2} \times \sqrt{1+k \times 10^{-4} \times\left(\frac{m^{(C a)}}{m^{(K)}} \times 10^{4}\right)} \times \sqrt{\left[\frac{\Delta m^{(C a)}}{m^{(C a)}}\right]^{2}+\left[\frac{\Delta m^{(K)}}{m^{(K)}}\right]^{2}} . \tag{26}
\end{equation*}
$$

This case is very frequent, because in rocks there exist rather more calcium than potassium. The next case is less frequent; for $\mathbf{m}{ }^{(\mathrm{Ca})} \ll \mathbf{m}^{(\mathrm{K})}$ the error tends to zero. It results clearly from equation (24).

If you return to formula (14) you can deduce formula for the relative error of the apparent time:

$$
\begin{equation*}
\frac{\Delta t}{t}= \pm 0,5 \times \sqrt{\left[\frac{\Delta m^{(C a)}}{m^{(C a)}}\right]^{2}+\left[\frac{\Delta m^{(K)}}{m^{(K)}}\right]^{2}} \ldots \text { for } m^{(C a) \gg} m^{(K)} \tag{27}
\end{equation*}
$$

Due to this formula it is also possible to determine the highest error of the apparent time. Such error arise when it is valid that $\Delta \mathbf{m}^{(\mathrm{Ca})} \rightarrow \mathbf{m}^{(\mathrm{Ca})}$ and, simultaneously, $\Delta \mathbf{m}^{(\mathrm{K})} \rightarrow \mathbf{m}{ }^{(\mathrm{K})}$.

$$
\begin{equation*}
\frac{\Delta t}{t}= \pm \frac{\sqrt{2}}{2} \ldots \text { for } m^{(C a) \gg} m^{(K)} \tag{28}
\end{equation*}
$$

It is all evident that it holds that $(\Delta t / t)< \pm 70.7 \%$. This is highly significant result of analysis.

## Other record of the time relation

Hamilton (1965) used other way of statement for the time relation. He wrote that:

$$
\begin{equation*}
f(t)=\frac{m^{(C a)}}{m^{(K)}}=\frac{\lambda_{\beta}}{\left(\lambda_{K}+\lambda_{\beta}\right)} \times \exp \left\{\left(\lambda_{K}+\lambda_{\beta}\right) \times t-1\right\} . \tag{29}
\end{equation*}
$$

In such case the attribute of time is following:

$$
\begin{equation*}
t=\left(\lambda_{K}+\lambda_{\beta}\right)^{-1} \times \ln \left\{1+\left(\frac{\lambda_{K}+\lambda_{\beta}}{\lambda_{\beta}}\right) \times 10^{-4} \times\left(\frac{m^{(C a)}}{m^{(K)}} \times 10^{4}\right)\right\} . \tag{30}
\end{equation*}
$$

It needs to mention Hamilton both expressions used for argon, not for calcium. However, both are useable for calcium in the form having been presented for argon.

For $\lambda_{\beta}=4.962 \times 10^{-4}$ and $\lambda_{K}=0.581 \times 10^{-4}$ you attain formula (30) in the adjusted numeric form:

$$
\begin{equation*}
t=1804.077 \times \ln \left\{1+1.117089883 \times 10^{-4} \times\left(\frac{m^{(C a)}}{m^{(K)}} \times 10^{4}\right)\right\} \tag{31}
\end{equation*}
$$

I should like to note again that the input ratio is in the form remarked like relation (20). The apparent time is resulted in millions of years. Tab. 2 carries data needed for
depiction of relation (29) and for its comparison to relation (3). Both are in fig. 3 there. Hamilton's relation provides time data being lower than it is for Ryšavý's relation. Both relations are possible and I let it for future which of them will be the right. Data needed for fig. 3 are in tab. 2 there.

| $\mathbf{t}\left[\mathbf{1 0}^{\mathbf{6}} \mathbf{y r s}\right]$ | $\mathbf{f}_{\mathbf{1}}(\mathbf{t}) \times \mathbf{1 0}^{\mathbf{4}}$ | $\mathbf{f}_{\mathbf{2}}(\mathbf{t}) \times \mathbf{1 0}^{\mathbf{4}}$ | $\mathbf{t}\left[\mathbf{1 0}^{\mathbf{6}} \mathbf{y r s} \mathbf{}\right.$ | $\mathbf{f}_{\mathbf{1}}(\mathbf{t}) \times \mathbf{1 0}^{\mathbf{4}}$ | $\mathbf{f}_{\mathbf{2}}(\mathbf{t}) \times \mathbf{1 0}^{\mathbf{4}}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 0 | 0 | 0 | 60 | 268.169 | 302.726 |
| 1 | 4.417 | 4.963 | 70 | 313.490 | 354.167 |
| 2 | 8.836 | 9.930 | 80 | 358.992 | 405.893 |
| 3 | 13.256 | 14.898 | 90 | 404.674 | 457.907 |
| 4 | 17.679 | 19.870 | 100 | 450.539 | 510.210 |
| 5 | 22.103 | 24.844 | 200 | 919.289 | 1049.499 |
| 6 | 26.529 | 29.822 | 300 | 1406.808 | 1619.525 |
| 7 | 30.957 | 34.801 | 400 | 1913.656 | 2222.040 |
| 8 | 35.386 | 39.784 | 500 | 2440.394 | 2858.895 |
| 9 | 39.817 | 44.770 | 600 | 2987.581 | 3532.048 |
| 10 | 44.250 | 49.758 | 700 | 3555.775 | 4243.567 |
| 20 | 88.677 | 99.792 | 800 | 4145.529 | 4995.639 |
| 30 | 133.282 | 150.105 | 900 | 4757.391 | 5790.575 |
| 40 | 178.066 | 200.697 | 1000 | 5391.898 | 6630.819 |
|  | 223.028 | 251.570 |  |  |  |

Tab. 2 Comparison of relations after Ryšavý and Hamilton


Fig. 3 Depiction of time relations after Ryšavý and Hamilton

Nevertheless, let's try to implement condition that for $\mathbf{m}^{(\mathrm{Ca})} \ll \mathbf{m}^{(\mathrm{K})}$, it holds that:

$$
\ln \left\{1+\left(\frac{\lambda_{K}+\lambda_{\beta}}{\lambda_{\beta}}\right) \times 10^{-4} \times\left(\frac{m^{(C a)}}{m^{(K)}} \times 10^{4}\right)\right\}=\left(\frac{\lambda_{K}+\lambda_{\beta}}{\lambda_{\beta}}\right) \times 10^{-4} \times\left(\frac{m^{(C a)}}{m^{(K)}} \times 10^{4}\right)
$$

In such case you receive linear relation in the following form:

$$
\begin{equation*}
t=\frac{1}{\lambda_{\beta} \times 10^{4}} \times\left(\frac{m^{(C a)}}{m^{(K)}} \times 10^{4}\right) \ldots \text { for } m^{(C a)} \ll m^{(K)} \tag{32}
\end{equation*}
$$

This formula is valid only for tiny calcareous rocks.

## Derivation of error after Hamilton's formula

First derivatives after $\mathbf{m}^{(\mathrm{Ca})}$ and $\mathbf{m}^{(\mathrm{K})}$ are these:

$$
\begin{align*}
& \frac{d t}{d m^{(C a)}}=+\frac{1}{\lambda_{\beta}} \times\left[\frac{m^{(C a)}}{m^{(K)}}\right] \times\left[1+\left(\frac{\lambda_{K}+\lambda_{\beta}}{\lambda_{\beta}}\right) \times \frac{m^{(C a)}}{m^{(K)}}\right]^{-1} \times \frac{1}{m^{(C a)}}, \text { and }  \tag{33}\\
& \frac{d t}{d m^{(K)}}=-\frac{1}{\lambda_{\beta}} \times\left[\frac{m^{(C a)}}{m^{(K)}}\right] \times\left[1+\left(\frac{\lambda_{K}+\lambda_{\beta}}{\lambda_{\beta}}\right) \times \frac{m^{(C a)}}{m^{(K)}}\right]^{-1} \times \frac{1}{m^{(K)}} \tag{34}
\end{align*}
$$

Thanks to both above equations it results that:
$\Delta t= \pm \frac{1}{\lambda_{\beta} \times 10^{4}} \times\left(\frac{m^{(C a)}}{m^{(K)}} \times 10^{4}\right) \times\left[1+\left(\frac{\lambda_{K}+\lambda_{\beta}}{\lambda_{\beta}}\right) \times 10^{-4} \times\left(\frac{m^{(C a)}}{m^{(K)}} \times 10^{4}\right)\right]^{-1} \times \sqrt{\left[\frac{\Delta m^{\left(C_{a}\right)}}{m^{(C a)}}\right]^{2}+\left[\frac{\Delta m^{(K)}}{m^{(K)}}\right]^{2}}$.

If you return to formula (32) you will be able to write formula for the relative error of the apparent time.
$\frac{\Delta t}{t}= \pm\left[1+\left(\frac{\lambda_{K}+\lambda_{\beta}}{\lambda_{\beta}}\right) \times 10^{-4} \times\left(\frac{m^{(C a)}}{m^{(K)}} \times 10^{4}\right)\right]^{-1} \times \sqrt{\left[\frac{\Delta m^{(C a)}}{m^{(C a)}}\right]^{2}+\left[\frac{\Delta m^{(K)}}{m^{(K)}}\right]^{2} .}$

This formula can be analyzed for partial cases. If sedimentary rocks are weakly calcareous there holds condition that $\mathbf{m}^{(\mathrm{Ca})} \ll \mathbf{m}^{(\mathrm{K})}$.

$$
\begin{equation*}
\frac{\Delta t}{t}= \pm \sqrt{\left[\frac{\Delta m^{(C a)}}{m^{(C a)}}\right]^{2}+\left[\frac{\Delta m^{(K)}}{m^{(K)}}\right]^{2} \rightarrow \sqrt{2} \ldots \text { for } m^{(C a)} \ll m^{(K)} . . . ~ . ~} \tag{37}
\end{equation*}
$$

The sediments like carbonates are have condition that $\mathbf{m}{ }^{(\mathrm{Ca})} \gg \mathbf{m}^{(\mathrm{K})}$. For them there holds this sub-condition:

$$
\left[1+\left(\frac{\lambda_{K}+\lambda_{\beta}}{\lambda_{\beta}}\right) \times \frac{m^{(C a)}}{m^{(K)}}\right]^{-1}=\left(\frac{\lambda_{\beta}}{\lambda_{K}+\lambda_{\beta}}\right) \times\left[\frac{m^{(C a)}}{m^{(K)}}\right]^{-1} \rightarrow 0
$$

You will get formula like this:

$$
\begin{equation*}
\frac{\Delta t}{t}=0 \ldots \text { for } m^{(C a)} \gg m^{(K)} \tag{38}
\end{equation*}
$$

Let's try to compare the relative errors after author and after Hamilton.

$$
\begin{aligned}
& 0 \leq \frac{\Delta t}{t}<\frac{\sqrt{2}}{2}, \text { and } \\
& \sqrt{2} \geq \frac{\Delta t}{t}>0
\end{aligned}
$$

The left boundary of intervals is presented by values 0 and $\sqrt{2}$; it is for condition that $\mathbf{m}^{(\mathrm{Ca})} \ll \mathbf{m}^{(\mathrm{K})}$. The right boundary is given by values $\sqrt{ } 2 / 2$ and 0 - it presents condition $\mathbf{m}^{(\mathrm{Ca})} \gg \mathbf{m}^{(\mathrm{K})}$. This fact results in consequence that the relative errors are reciprocally inverse.

## Separation of the time function on the local and global components

By transformation of the ratio curve remarked as $\mathbf{m}^{(\mathrm{Ca})} / \mathbf{m}^{(\mathrm{K})}$ into the time domain you receive the curve of the apparent time; it is the continuous curve with the borehole depth. It was said that we distinguish two basic categories of rocks for this method: the weakly calcareous sediments with $\mathbf{m}^{(\mathrm{Ca})} \ll \mathbf{m}^{(\mathrm{K})}$ and carbonates having $\mathbf{m}^{(\mathrm{Ca})} \gg \mathbf{m}^{(\mathrm{K})}$.

If you have continuous curve of the apparent time, you will have to admit, too, an existence of two components of this curve. They are global and local ones; their sum presents then the curve of the apparent time.

The global component of time reflects original amount of $\mathrm{a}_{20}^{40} \mathrm{Ca}$ created by radioactive decay. Unfortunately, the reality is that this element migrates out and in. In
one bed can be deficit of calcium, whereas, the other bed has redundancy of the same element. As far as ${ }_{19}^{40} \mathrm{~K}$ - it is known that this element migrates too, but, its migration is not so fast and easy.

Therefore it is possible to come out of premise that it is the curve of trend inverted through values of the apparent time for category of the weakly calcareous sediments which presents the curve of the true time. This is model admitting only calcification. According to that we can determine the rock age. The shape of this can be various; it can be linear, exponential, polynomial or all other. What is important is that it depends on the borehole depth. It is function of depth for registered interval.

The linear trend can be observed in case that the drilled rocks are in position in situ, i.e, the oldest rocks are deep down, whereas, the youngest are near to the surface of earth. This could be presented by relations remarked as (15) after author or (32) after Hamilton. Both are linear and almost identical.

$$
\begin{aligned}
& t=\frac{1}{\lambda_{\beta} \times 10^{4}} \times\left(\frac{m^{(C a)}}{m^{(K)}} \times 10^{4}\right) \ldots \text { for } m^{(C a)} \ll m^{(K)}, \text { and } \\
& t=\frac{1}{0.89 \times \lambda_{\beta} \times 10^{4}} \times\left(\frac{m^{(C a)}}{m^{(K)}} \times 10^{4}\right) \ldots \text { for } m^{(C a)} \ll m^{(K)} .
\end{aligned}
$$

As most of rocks are folded it is possible rather to expect that linear trend will be exception; nearly to reality there will be polynomial trend of various degrees.

The local component presents effect of subsequent processes acting after radioactive decay. This component can be negative and positive values. Local component you get like difference between values of the apparent time and the real time. This component can be also regarded as a systematic error of the global component.

If I return to both categories of rocks; the important are the weakly calcareous rocks. Just these determine the global component. Limestones and dolomites present big exception; they are colossal anomaly, they are the only gigantic local component. Carbonates falsify the curve of the apparent time. Consequence of that is where the carbonates are only it is impossible to insert the curve of the global component. And just this is the limiting condition using the potassium-calcium method. Therefore I think that the borehole should start and end in the weakly calcareous rocks. Only under these conditions we are able to have the curve of the real time over all drilled interval.

On other hand I have to say that better solution can be using of the gliding trend. Namely, if the time values fast oscillate. This is next model admitting both calcification and decalcification. We have also to admit that the original rocks can be extremely decalcificated too. In such case it could be false to select weakly calcareous rocks. Maybe, the curve of gliding trend could be better than the curve of polynomial trend; for very oscillating values of time I am sure.

## Conclusions

Owing to the analysis made before here are the following conclusions:

1) Thanks to the gamma-spectrometry we can register two continuous curves like function of depth. The first is for ${ }_{19}^{40} \mathrm{~K}$, the second for ${ }_{20}^{40} \mathrm{Ca}$. By computation we create the new curve being also dependent on the depth; it is the ratio curve of quantities $\mathbf{m}^{(\mathrm{Ca})} / \mathbf{m}^{(\mathrm{K})}$.
2) This ratio curve is transformed into time domain. There are used two different time relations. The first made after author of this paper and the second after Hamilton (1965). The expected result is in both cases the only continuous curve of the apparent time. The values, read after Hamilton, are lower than those after author. Nevertheless, both relations are right and possible.
3) The curve of the apparent time has global and local components. The global one is presented with the curve of trend for values of the apparent time belonging to the weakly calcareous rocks. This also continuous curve being dependent on the depth and having linear, exponential and polynomial shape can be referred to as the curve of the real time for determination of the rock age. This is model admitting only calcification.
4) Next model admits both calcification and decalcification. It uses gliding trend like the curve of the global component. This is perhaps closer to real geologic situation.

## References

[1] BORSUK , A.M. Kriterii nadezhnosti metodov radiologitcheckogo datirovanya. Nauka, Moscow 1979.
[2] DUBANSKÝ ,A. \& ZAMARSKÝ, V. Metody jaderné geochronologie, part 1. VŠB, Ostrava, 1982.
[3] HAMILTON, E. I. Applied Geochronology. Academic Press, London and New York, 1965.

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