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The Problem of Long-term Fading of Absorbed Palaeodose on ESR-dating of Quaternary Mollusc Shells

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Due to relatively low thermal stability of radiation-induced centres in biogenic carbonate of subfossil molluscs (mean life $\tau = 3.7 \times 10^5$ y at 10°C, $g = 2.0012$) correct dating of the latter by means of ESR-spectroscopy without considering natural relaxation of absorbed palaeodose may prove rather problematic. The long-term fading of palaeodose complicates correlation between absorbed natural radiation energy, and the value of the laboratory effect observed restricts the upper dating limit and may result in considerably younger ages on dating of the most ancient Quaternary samples. The present paper deals with the connection between the absorbed palaeodose value and the age of the sample, its dosimetric properties, as well as with the effect of different factors on the upper dating limit. Energetic parameters of CO_3^{3-} centres ($g = 2.0012$) have been determined for the shell's carbonate: trap depth $E = 1.52 \pm 0.01$ eV, frequency factor $s = 8 \times 10^{13}\,s^{-1}$, mean life $\tau = 1.14 \times 10^6$ y at 5°C. Mathematical models of the palaeodose accumulation in nature are discussed. The author suggests palaeodosimetric equations for calculating the age of shells and some other materials. The equations may be applied both to ESR- and TL-dating.

Introduction

The stability of absorbed palaeodose, proportional to the age of the sample, has proved a problem of topical interest on dating of Quaternary deposits with palaeodosimetric methods. Dosimetric characteristics and storage conditions in burial environment of many potential palaeodosimetric dating objects are found to be such that the probability of a partial loss of age information during a geologic time span cannot be excluded. Evidence can be derived from the results obtained through the dating of quartz (Moiseev and Rakov, 1977; Shlukov and Shachovets, 1987; Vlasov and Kulikov, 1987), meteorites (Durrani, 1982), deep-sea sediments (Mangini *et al.*, 1983; Barabas *et al.*, 1988), calcite (Nambi, 1983), archaeologic limestones (Vaz, 1983), loesses (Debenham, 1985; Balescu *et al.*, 1986) and feldspars (Mejdahl, 1986, 1988).

If the thermal stability of the electrons, that have been trapped in a crystal lattice of the mineral-palaeodetector, is not high enough, the relaxation of absorbed palaeodose during their storage in the burial environment is quite probable due to the thermal emptying of the traps. This complicates the correlation between the absorbed energy of natural radiation and the value of the laboratory effect observed, restricts the upper dating limit, and may lead to a considerable underestimation of the ages on dating of older Late Cenozoic objects.

The aim of the present study was to elucidate the regularities of the natural accumulation and decay of radiation-induced ESR-centres in the biogenic carbonate of subfossil mollusc shells, to explain and quantitatively describe the process of the storage of natural radiation palaeodose in them. The results obtained may also prove useful for dating some minerals by both ESR and TL methods.

Before discussing kinetic dependences of palaeodose accumulation in the shells, let us deal with the possibilities of its estimation on the basis of ESR results and the main regularities elucidated by means of laboratory experiments.

Palaeodose Estimation

The palaeodose of background radiation equivalent to the natural concentration of paramagnetic centres in a shell substance can be determined by so-called additive-dose method (Aitken, 1974) or from the formula

$$P_{\text{lab}} = \mu^{-1}(\ln I_{\infty\,\text{lab}} - \ln \Delta I), \qquad (1)$$

where μ is the sensitivity to irradiation of the sample, $I_{\infty\,\text{lab}}$ is the analytical signal intensity for laboratory saturation dose, $\Delta I = I_{\infty\,\text{lab}} - I$, I is the natural intensity.

However, due to the specific mechanism of the relaxation of natural radiation dose, there seems to exist no direct connection between the values of the laboratory effect in the mineral-palaeodetector and background radiation energy accumulated within a long geological interval in nature. Therefore, the palaeodose P, reconstructed in the laboratory and corresponding to the value of stored palaeodose P_s, is always smaller than the dose P_A, absorbed in nature, by the dose of relaxation P_r

$$P_{lab} = P_s = P_A - P_r. \qquad (2)$$

Due to the relaxation, the concentration of the radiation-induced paramagnetic centres in the shells strives for a dynamic equilibrium level, which, as a rule, is considerably lower than the laboratory saturation level.

Provided that under the effect of ionizing radiation the trap-filling process follows a first-order reaction, and no new traps are being formed, the rate of trap-filling may be expressed by the following differential equation (Ivanov, 1970):

$$\mathrm{d}n/\mathrm{d}t = \mu q \dot{D}(n_\infty - n) - \eta n, \qquad (3)$$

where n is the number of filled traps at time t, equivalent to absorbed palaeodose, μ is the probability per unit dose of filling one of the above traps, in Gy^{-1}, q is the attenuation-correction factor, $\dot{D}$ is the dose rate, in $\mathrm{Gy\,s}^{-1}$, n_∞ is the initial concentration of the traps, corresponding to the value of the saturation level due to laboratory irradiation, η is the decay constant, in s^{-1}, corresponding to the probability of the release of electron per time unit from the trap of depth E, in eV at temperature T, in kelvin

$$\eta = \frac{1}{\tau} = s\exp(-E/kT), \qquad (4)$$

where s is the frequency factor, in s^{-1}, k is Boltzmann's constant, τ is the mean life of trapped electrons, in s, for storage at a temperature T, in kelvin.

According to equation (3) the accumulation rate of radiation-induced paramagnetic centres $\mathrm{d}n/\mathrm{d}t$ in the shell substance is determined by two competing processes: first, the increase in the number of centers under the effect of natural radiation field, and, second, their destruction.

In nature, under the conditions of weak radiation fields, dynamic equilibrium is established between the number of newly formed and destroyed centres, i.e. the following conditions are fulfilled

$$\mu q \dot{D}(n_\infty - n) = \eta n, \qquad (5)$$

$$\mathrm{d}n/\mathrm{d}t = 0. \qquad (6)$$

From the above, with $n \to n_{\infty\,nat}$, where $n_{\infty\,nat}$ represents dynamic-equilibrium, or steady-state conditions, the value of n reached under natural radiation, we obtain the criteria for kinetics equilibrium, determined by the fulfillment of equation (7):

$$n_{\infty\,nat} = \frac{n_\infty}{1 + 1/\tau\mu q \dot{D}}. \qquad (7)$$

Thus, from equation (7), it follows that the level of natural equilibrium is governed by the sensitivity and geometry of the mineral-detector, dose rate of environmental radiation, mean life of the trapped charges, initial concentration of the empty traps and also, according to equation (4), by the average storage temperature.

Analysing equations (3) and (7), it becomes evident that as a result of an extraordinarily wide variation of radiation, thermal, radiospectroscopical (but also thermoluminescent) properties of natural minerals, the steady-state level cannot be identical, even for objects within one variety. Thus, for example, for abut 10 quartz samples, the value μ appears to range from 1×10^{-4} up to $6.5 \times 10^{-4}\,\mathrm{Gy}^{-1}$ (Vlasov *et al.*, 1979). However, as is known, the environmental dose rate and storage temperature may show even greater variations. In this connection, the attempts to correct the age of materials, proceeding from an unknown steady-state level in nature for a concrete object (Hütt and Jaek, 1989) should be considered as insufficiently grounded. An exception (rather rare in Quaternary palaeodosimetry) is when, with sufficiently deep traps, natural equilibrium of charge concentration $n_{\infty\,nat}$ may practically coincide with the maximum concentration of $n_{\infty\,lab}$ at laboratory saturation dose. For example, according to equation (7), on dating of quartz by the TL method with the mean effective dose rate $\dot{D}_\Sigma = 2\,\mathrm{mGy\,y}^{-1}$ and sensitivity coefficient $\mu = 5 \times 10^{-4}\,\mathrm{Gy}^{-1}$, the condition $n_{\infty\,nat} \geqslant 0.95\,n_{\infty\,lab}$ is fulfilled with $\tau \geqslant 2 \times 10^7$ y. As for quartz $\tau = 10^8$ y ($T_m = 325$°C, $T = 10$°C, Wintle, 1977), and the levelling off of the natural dose–response takes place up to 70,000–200,000 y, then on TL dating of Quaternary deposits with the quartz inclusion method the long-term fading of palaeodose may evidently be neglected.

Unfortunately, a vast majority of potential ESR- (and TL-) dating objects (e.g. mollusc shells, feldspars, calcite formations, etc.) are characterized

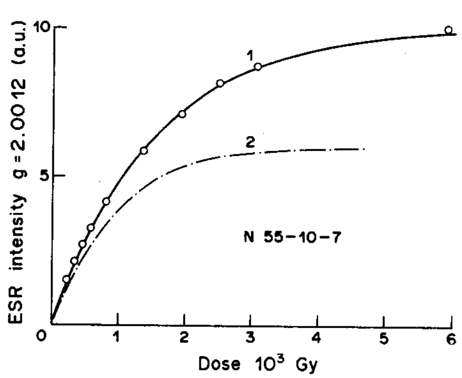

Fig. 1. Theoretical plot of the $g = 2.0012$ ESR signal of shell vs γ-dose D_γ, calculated from equation (9) for $I_{\infty lab} = 10$ a.u., $\mu = 8.377 \times 10^{-4}\,\mathrm{Gy}^{-1}$ and from equation (12) for $I_{\infty lab} = 10$ a.u., $\eta = 10^{-6}\,\mathrm{y}^{-1}$, $\mu = 8.377 \times 10^{-4}\,\mathrm{Gy}^{-1}$, $\dot{D}_\Sigma = 1.8\,\mathrm{mGy\,y}^{-1}$; the circles are experimental values of the $g = 2.0012$ signal intensity I vs D_γ.

by lower thermal stability of the trapped electrons and their life-times are often comparable with the age of the sample. Therefore, due to the presence of the relaxation term $-\eta n$ in equation (3), the flattening of the natural dose–response will take place, according to equation (7), at a considerably lower quasi-equilibrium level $n_{\infty \mathrm{nat}}$ (Fig. 1). The laboratory dose–response will differ appreciably from the natural one. And therefore, under conditions unfavourable for the age-information storage (e.g. relatively high average burial temperature, short mean life of the trapped charges, old sample etc.), the evaluation of the palaeodose with the additive-dose method may lead to inadmissable errors in the dating of geological objects, if the natural relaxation of absorbed dose is neglected.

Dose–Effect Function

The process of the accumulation of radiation-induced paramagenetic centres in the shells may be described by equation (3). On added irradiation, the relaxation term may be omitted. Then the dose–effect function is described by the following equation:

$$\mathrm{d}n/\mathrm{d}t = \mu q \dot{D}(n_{\infty \mathrm{lab}} - n). \qquad (8)$$

The solution of equation (8) is given by the well-known exponential equation of first-order kinetics:

$$I = I_{\infty \mathrm{lab}}[1 - \exp(-\mu D_{\gamma})]. \qquad (9)$$

For plotting of I vs radiation dose, D_{γ}, shell samples (N 55-07-7) were irradiated by a calibrated ^{60}Co γ-ray source delivering 1 Gy min^{-1}. To eliminate unsuitable paramagnetic centres, the irradiated samples were kept at 100°C for 100 min.

Concentration measurements were carried out according to the methods described in detail elsewhere (see e.g. Molodkov, 1988b).

The shape of the dose–response curves obtained experimentally for the studied shells, by using the amplitude of an analytical signal at $g = 2.0012$ as an absorbed dose equivalent, was in good agreement with that calculated from equation (9) (Fig. 1). Thus, in view of the simulation of the palaeodose accumulation in nature, quite an important fact was elucidated: the kinetics of absorbed radiation energy accumulation in shell substances correspond to the first-order reaction, described by equation (9).

Decay of Carbonate Centres

In the first approach the determination of the kinetics of natural decay of paramagnetic centres and substantiation of a model of long-term fading is to be based on the results of laboratory thermal investigations, with the succeeding extrapolation of the thermal experimental data in the region of low temperatures at which their relaxation takes place in natural conditions.

As a model sample in thermal experiments, an ancient shell of *Astarte borealis* (about 550,000 y B.P.) gave a stored palaeodose of natural radiation of 1072 Gy. It should be stressed here that the thermal experiment was carried out on a naturally irradiated shell, as there is every reason to suggest that radiation paramagnetic centres, induced by artificial irradiation, may have other fading properties, e.g. considerably lower annealing temperature (Moiseev, 1985).

The experiment with *Astarte borealis* was performed by thermostating of different portions of the sample at six temperature values between 180 and 100°C. On the measurements of the paramagnetic centre concentration, use was made of the analytical signal amplitude at $g = 2.0012$.

Figure 2 shows a set of thermal decay plots of radiation-induced centres vs isothermal annealing time; the lowering of the isothermal annealing temperature was accompanied by a straightening of decay curves $P(t)/P_0$ vs ln τ, i.e. by a transition from more complex decay mechanisms to first-order kinetics. It provides a basis for the supposition that the first-order reaction is maintained, when extrapolating the results of laboratory investigations to the normal temperatures of the burial environment; and also that in nature the process of temporal abatement of paramagnetic centres concentration follows the law of isothermal decay on low-temperature annealing

$$n/n_0 = \exp(-\eta t), \qquad (10)$$

where the ratio n/n_0 is the relative number of radiation-induced charges remaining in the traps after time t.

According to the present results, both the process of accumulation of radiation-induced paramagnetic charges and their low temperature annealing follows

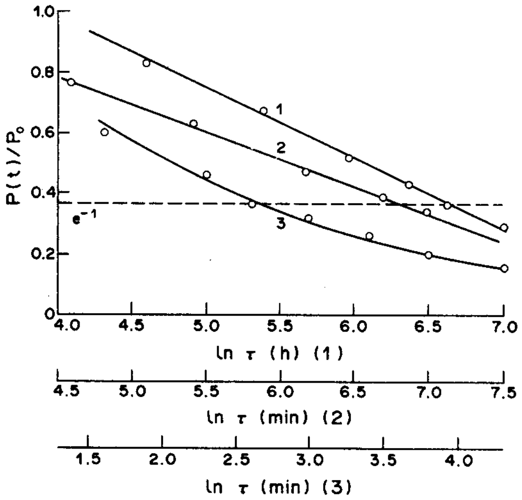

Fig. 2. The kinetics of low-temperature relaxation of the palaeodose $P_0 = 1072$ Gy stored in the carbonate skeleton of the mollusc *Astarte borealis* (N 10-12-4) and the thermal annealing temperatures 100°C (1), 140°C (2) and 180°C (3).

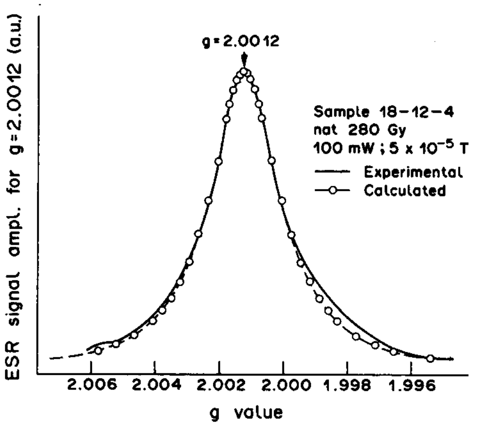

Fig. 3. A calculated Lorentz line (circles) and the experimental ESR absorption curve at $g = 2.0012$, separated in the ESR spectrum of the shell (N 18-12-4).

the first-order reaction which proves to be common for the mollusc shells. It indicates that the ESR-signal with $g = 2.0012$, used for concentration measurements and reconstruction of palaeodose on ESR-dating of subfossil mollusc shells (Molodkov, 1988b), belongs to one type of centre in biogenic $CaCO_3$ which is likely to be related to the paramagnetic ion CO_3^{3-}, stabilized by the ions Y^{3+} (Marshall *et al.*, 1968) or Mn^{3+} (Low and Zeira, 1972). This conclusion is corroborated also by the good fitting of the calculated Lorentz line with the experimental ESR absorption curve at $g = 2.0012$, separated in the ESR spectrum of the shell (N 18-12-4) (Fig. 3).

Energetic Parameters

Determination of the parameters of paramagnetic centres in the biogenic carbonates is a complicated task due to the problems related to the interferencial distortions of individual lines of ESR differential spectrum. This leads to incorrect results when interpreting the data of concentration measurements and estimating the dose stored in minerals, determining their age and so on. An additional problem is the relatively low thermal stability of the marine carbonates; after heating above 300°C irreversible phase transformations occur in the crystalline structures and deformation of their ESR spectra.

To overcome these problems in the present work, the parameters of paramagnetic centres were determined by the isothermal annealing method at relatively low temperatures (between 100 and 180°C), with the time of thermostating up to 1000 h with a precision of ±1°C. As an equivalent of dose, the amplitude of the analytical ESR-signal at $g = 2.0012$ (Molodkov, 1988b) was used. The results are presented in Fig. 4. The energetical trap depth E and frequency factor s were determined from the plot of $\ln \tau$ vs T^{-1} and equation (4), transformed into the linear one:

$$\ln \tau = \frac{E}{kT} - \ln s. \tag{11}$$

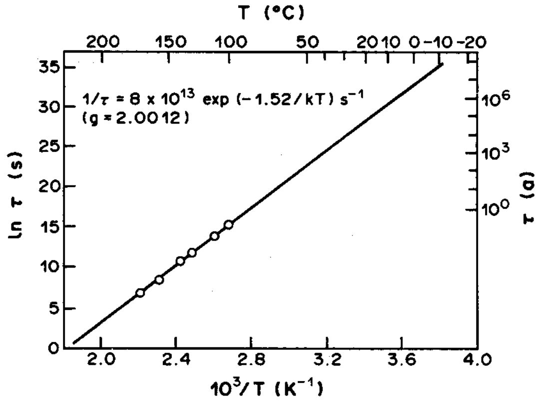

Fig. 4. Arrhenius plot $\ln \tau$ vs T^{-1} corresponding to low-temperature reaction decay of radiation-induced paramagnetic centres in the mollusc shell substance. On the basis of the experimental data, energetic parameters of CO_3^{3-} centres ($g = 2.0012$) were calculated: $E = 1.52 \pm 0.01$ eV, $s = 8 \times 10^{13}\ s^{-1}$, $\tau = 1.14 \times 10^6$ Gy at $T = 5°C$.

The following energetic parameters of paramagnetic CO_3^{3-} centres in the biogenic carbonate of the mollusc shells were obtained: $E = 1.52 \pm 0.01$ eV, $s = 8 \times 10^{13}\ s^{-1}$. According to the results obtained and from equation (4), it follows that the mean life values of the CO_3^{3-} molecule–ion in the shell carbonate at −5°C and +5°C are 12×10^6 and 1.14×10^6 y, respectively.

Simulation of Absorbed Palaeodose Natural Accumulation and Long-term Fading

The change of concentration of radiation-induced CO_3^{3-} radicals in the shells, n, with time, t, is described by equation (7). Its solution is given by equation (12) with the assumption that the effective environmental dose rate $q\dot{D} = \dot{D}_\Sigma$ is constant and the number of CO_3^{3-} radicals $n = 0$ at $t = 0$:

$$I = \frac{I_{\infty \mathrm{lab}}\,\mu \dot{D}_\Sigma}{\mu \dot{D}_\Sigma + \eta}\,[1 - \exp(-(\mu \dot{D}_\Sigma + \eta)t)] \tag{12}$$

where $I_{\infty \mathrm{lab}}$ is the intensity of the signal at laboratory saturation dose, proportional to the total number of electron traps $n_{\infty \mathrm{lab}}$, I is the natural intensity, proportional to n, $\dot{D}_\Sigma$ is the dose rate (in Gy y^{-1}), μ is the sensitivity coefficient (in Gy^{-1}), equal to relative number of radiation centres, Δn, induced by a unit of dose ΔD.

For each sample the value μ may be calculated according to the equations

$$\mu = \frac{\Delta n}{\Delta D(I_{\infty \mathrm{lab}} - I)} \tag{13}$$

or

$$\mu = P_s^{-1} \ln \frac{I_{\infty \mathrm{lab}}}{\Delta I} \tag{14}$$

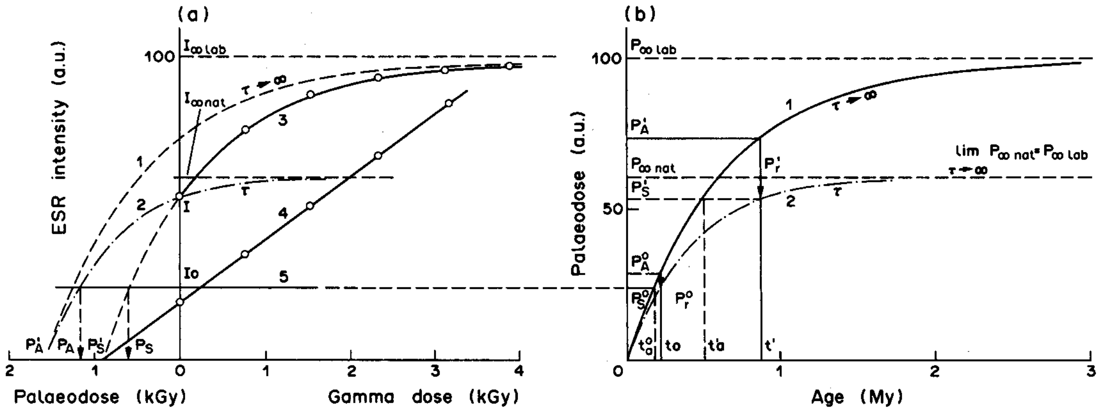

Fig. 5. (a) Calculated characteristic dependences of paramagnetic centres accumulation in a mineral-palaeodosimeter on natural (1, 2) and artificial (3) irradiation. The value of stored palaeodose P'_s (or P_s if the progenetic concentration (5) of the centres $n_0\,(I_0) \neq 0$) was determined by plotting $-\ln(1 - I/I_{\infty\,\mathrm{lab}})$ vs increasing radiation dose D_γ. (b) The appearance of the function of palaeodose accumulation dependent on the mean life of the electrons in traps with: 1, $\tau \to \infty$, 2, $\tau = 10^6$ y and $\dot{D}_\Sigma = 1.8$ mGy y^{-1}. The true age of the sample $t = t' - t_0$ can be calculated from equations (16) and (20) in consideration of the natural fading P_r of the absorbed palaeodose P'_A and dose P^0_A equivalent to the progenetic concentration of the trapped electrons n_0.

where $\Delta I = I_{\infty\,\mathrm{lab}} - I$, P_s is the natural radiation dose accumulated during a geological time interval, determinable by plotting $-\ln(1 - I/I_{\infty\,\mathrm{lab}})$ vs an increasing radiation dose D_γ (Apers *et al.*, 1981).

Using the known parameters $I_{\infty\,\mathrm{lab}}$, μ, $\dot{D}_\Sigma$, I, P_s and η from equation (12), we obtain the formula for calculating the age of the sample, t, equivalent to change of paramagnetic centre concentration from $I_0 = 0$ to I value with regard for natural relaxation of the absorbed palaeodose (Molodkov, 1988a):

$$t = -\ln\left(1 - \frac{I(\mu\dot{D}_\Sigma + \eta)}{I_{\infty\,\mathrm{lab}}\,\mu\dot{D}_\Sigma}\right)(\mu\dot{D}_\Sigma + \eta)^{-1}. \qquad (15)$$

If the post-sedimentational accumulation of radiation-induced centres has started from an initial progenetic level $n_0 \neq 0$ ($I_0 \neq 0$) (Fig. 5), the actual age of the sample may be determined from equation (15) by subtracting the temporal component t_0, equivalent to the initial amount of electron centres n_0 and signal intensity I_0:

$$t = \ln\left(1 - \frac{I_0 A}{I_{\infty\,\mathrm{lab}} B}\right) - \ln\left(1 - \frac{IA}{I_{\infty\,\mathrm{lab}} B}\right) A^{-1}, \qquad (16)$$

where

$$A = \mu\dot{D}_\Sigma + \eta, \; B = \mu\dot{D}_\Sigma.$$

The use of equations (1), (2) and (16) enables one to determine the value of the long-term fading of absorbed palaeodose of natural radiation (the relaxation dose P_r):

$$P_r = \left(\mu t\dot{D}_\Sigma + \ln\frac{I_{\infty\,\mathrm{lab}}}{\Delta I_0} - \ln\frac{I_{\infty\,\mathrm{lab}}}{\Delta I}\right)\mu^{-1}, \qquad (17)$$

where

$$\Delta I_0 = I_{\infty\,\mathrm{lab}} - I_0, \; \Delta I = I_{\infty\,\mathrm{lab}} - I.$$

If $n \ll n_\infty$, i.e. if the number of charge defects in the sample is quite large, equation (3) can be rewritten as

$$\mathrm{d}n/\mathrm{d}t = \mu q\dot{D}n_\infty - \eta n. \qquad (18)$$

The solution of equation (18) gives

$$P'_s = \dot{D}_\Sigma(1 - \exp(-t\eta))/\eta, \qquad (19)$$

where $P'_s = n/\mu n_\infty$ is the accumulated palaeodose that is measured in the laboratory. It is equivalent to the number of filled traps, n, out of the maximum number of traps, n_∞, that is possible to be filled under given conditions. With equilibrium (when the time $t \to \infty$ and absorbed dose $P'_A \to \infty$), n_∞ represents the steady-state value of n and stored palaeodose P'_s remains invariable and equal to the μ^{-1} value (Fig. 6).

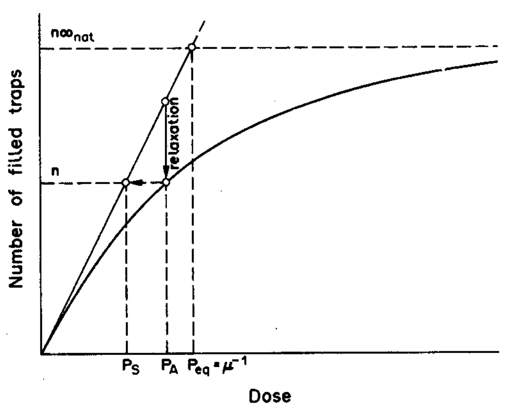

Fig. 6. The plot of number of filled traps, n, vs dose, P. If exponential thermal decay and linear growth potential are realized in nature, the stored palaeodose is expressed by $P'_s = n/\mu n_\infty$. With equilibrium, the stored palaeodose remains invariable and equal to μ^{-1} value.

Let us assume that $\eta \to 0$. In this case the effect-vs-natural dose function (19) is identical to the artificial dose–response (as on artificial irradiation the relaxation term $-\eta n$ may be neglected in equation (18)). The latter in its turn will be controlled for the real sample by the radiation sensitivity, the value of the absorbed dose and the feasible amount of radiation-induced paramagnetic centres in the sample.

The progress of radiation centres accumulation in the mineral-palaeodetector will also be described by equation (19), if exponential decay and exponential growth potential are realized in nature. Then the general solution of equation (19) for t is given by the following expression (Molodkov, 1988a):

$$t = \tau\left[\ln\left(1 - \frac{P_s^0}{\tau\dot{D}_\Sigma}\right) - \ln\left(1 - \frac{P_s'}{\tau\dot{D}_\Sigma}\right)\right], \quad (20)$$

where P_s^0 is the palaeodose equivalent to the residual progenetic concentration of paramagnetic centres, P_s' is the value of the stored palaeodose obtained by plotting $-\ln(1 - I/I_{\infty\,\mathrm{lab}})$ vs artificial dose D_γ.

The dose of relaxation for a given model can be derived from equations (1)–(3) and (20) (see also Fig. 5):

$$P_r = \dot{D}_\Sigma t + P_s^0 - P_s' = \tau\dot{D}_\Sigma\left[\ln\left(1 - \frac{\ln J}{\mu\tau\dot{D}_\Sigma}\right) - \ln\left(1 - \frac{\ln J_0}{\mu\tau\dot{D}_\Sigma}\right)\right] + \ln\frac{J_0}{J}\mu^{-1}, \quad (21)$$

where

$$J = I_{\infty\,\mathrm{lab}}/(I_{\infty\,\mathrm{lab}} - I),\ J_0 = I_{\infty\,\mathrm{lab}}/(I_{\infty\,\mathrm{lab}} - I_0).$$

It is easy to see that on dating of biogenic carbonates the value of $P_s^0 \to 0$ and equations (20) and (21) are essentially reduced.

Examples

As an illustration, the calculation of the ages was carried out for shells collected from synchronous beds which correlate with the Eemian horizon in North Europe, and with stage 5 of the deep-sea oxygen-isotope record (Shackleton and Opdyke, 1973). The shells from the Upper Khazarian deposits in the Caspian Sea Basin (N 55-07-7), Mikulian, on the White Sea coast (N 32-12-4) and Khazantsevo deposits on the Arctic islands (N 70-10-7) were subjected to dating.

Besides, a model dating of shells with "apparent" age $t^a = P_s/\dot{D}_\Sigma = 321{,}400$ y B.P. (N 50-00-0) has been performed to show possibilities of ESR dating of ancient samples with initial progenetic level I_0 and unfavourable environmental storage conditions (relatively high, ~5°C, average burial temperature).

The dating technique for shells used in this study has been described earlier in detail (see e.g. Molodkov, 1986, 1988b). According to the latter the amplitude of the analytical line (peak) at $g = 2.0012$ was used in the present work as an equivalent of paramagnetic centre concentration in shell substance.

Table 1. Ages of shells from Upper Pleistocene marine deposits (Nos 1–3) calculated from equations (16) and (20) and of model sample (No. 4) calculated from equation (16)

No.	Sample	$I_{\infty\,\mathrm{lab}}$ (a.u.)	I(a.u.)	I_0 (a.u.)	μ (10^{-4} Gy^{-1})	$\dot{D}_\Sigma$ (mGy y^{-1})	τ (y)	T (°C)	P_s' (Gy)	P_s (Gy)	Apparent ESR age, t^a	True ESR age, t Equation (16)	True ESR age, t Equation (20)
1	32-12-4	201	7.0	0	3.586	0.94	4.7×10^6	−1.0	98.84	0	105.1	106.4	106.3
2	55-07-7	231	34.6	0	8.377	1.80	1.0×10^6	5.5	194.00	0	107.8	114.2	114.0
3	70-10-7	164	8.8	0	5.150	1.11	70.0×10^6	−12.0	107.00	0	96.4	96.5	96.5
4	55-00-0	100	53.5	24.5	8.377	1.80	1.0×10^6	5.5	—	578.4	321.4	670.8	—

Notes: $I_{\infty\,\mathrm{lab}}$—ESR intensity at laboratory saturation dose; I—measured ESR intensity; I_0—progenetic ESR intensity; μ—sensitivity to radiation; $\dot{D}_\Sigma$—dose rate; τ—mean life; T—storage temperature; P_s'—stored palaeodose with $I_0 = 0$; P_s—stored palaeodose with $I_0 \neq 0$; t^a—apparent age ($t^a = P_s'/\dot{D}_\Sigma$, if $I_0 = 0$ and $t^a = P_s/\dot{D}_\Sigma$, if $I_0 \neq 0$).

On the basis of the comparison of the results obtained with the geological estimates on Eemian interglacial, as well as on the data of model dating (see Table 1), it may be supposed that the analytical models presented above seem to describe quite well the natural process of palaeodose accumulation in shells during the geologic time span. This enables one to hope that with obtaining more exact dosimetric characteristics of mineral-palaeodetectors, further studies on their radiospectroscopic (luminescent) properties and with the attainment of more reliable information about the conditions in which the accumulation of palaeodose took place, the results obtained by palaeodosimetric dating methods will contribute to ever-growing reliability in reflecting the succession of geological events in the Late Cenozoic.

Summary

The results of the present work may be summarized as follows:

(1) Kinetic studies showed that the processes of accumulation and thermal decay of paramagnetic centres follow the first-order reaction law in biogenic mollusc carbonates.

(2) The following energetic parameters of characteristic paramagnetic centres in biogenic carbonate of mollusc shells were determined: $E = 1.52 \pm 0.01$ eV, $s = 8 \times 10^{13}\,s^{-1}$, $\tau = 1.14 \times 10^{6}$ y at 5°C.

(3) The models presented describe the regularities of the natural accumulation and fading of absorbed palaeodose in shell substance and its display during geological time intervals in different burial conditions.

(4) It is stressed that the natural concentration of radiation-induced centres in mineral-palaeodetectors is a function of the thermal stability of the trapped charges, their creation efficiency in minerals, effective dose rate of environmental radiation, average temperature of the surrounding environment and burial time; all these factors are to be considered in the dating of ancient samples.

(5) The palaeodosimetric equations are suggested for the dating of subfossil mollusc shells in consideration of palaeodose fading and the factors affecting the process of the accumulation of paramagnetic centres in the biogenic $CaCO_3$.

(6) The proposed equations may also be used for dating of minerals from sedimentary deposits with different palaeodosimetric methods, such as ESR, TL and OSL, in consideration of the residual progenetic concentration of trapped charges.

(7) ESR applied to the dating of subfossil mollusc shells with its different aspects discussed both in the present and earlier papers, enables one to determine the age of shells in some cases up to about 10^6 years B.P. or even greater.

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