GEOLOGOS 5 (2000)

PL ISSN 1426-8981 • ISBN 83-86682-45-0

CREM in application to EPR dating technique

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Abstract: The paper illustrates the application of CREM (a method for enhancement of spectral resolution) to the EPR spectra of a sample of tooth enamel of a cave bear (J. Nietoperzowa = Bat Cave), mammoth bone (Halicz on the Dniester river) and calcite from cave dripstones (J. Czarna = Black Cave). The application of CREM enabled an accurate determination of positions of EPR spectra lines corresponding to paramagnetic centres. It was proved that the use of CREM enabled a determination of the influence of such physical processes as heating or irradiation, e.g. UV-irradiation, on the dynamics of the paramagnetic centres in a sample studied.

Key words: Electron Paramagnetic Resonance (EPR), Computer Resolution Enhancement Method (CREM), EPR Method of Dating.

Introduction

The phenomenon of Electron Paramagnetic Resonance (EPR) was discovered in 1944 by E. K. Zawojski. The scope of possible applications of EPR is very large. In ionic crystals it enables determination of the structure of energy levels of paramagnetic centres, subtle elements of the crystal lattice and parameters characterising the electron dynamics. EPR makes it also possible to study crystal lattice defects, which is fundamental for its application in dating. EPR can be also used to study the structure of solvation shells in liquid solutions of salts and the properties of conduction electrons in metals and semiconductors (Altszuler & Kozyriew 1965).

In 1997 at the Institute of Physics A. Mickiewicz University, Poznań, the program of EPR investigation of geological materials was launched. The materials included fossil bones and teeth of cave bear, mammoth bones, cave dripstones, sandstone from Egyptian pyramids and fossil artefacts. Preliminary studies were conducted on single crystals of natural and synthetic calcite, in order to determine the g tensor.

The method of EPR dating was applied for calcite, aragonite, hydroxyapatite, quartz. Attempts were also made to apply this method for determination of the age of zirconium, halite, gypsum, feldspars, fossil ceramics, peat and meteorites (Smart & Frances 1991).

EPR study of tooth enamel of cave bear and natural calcite is the initial step towards EPR dating. For the first time the method of EPR dating has been described by Zeller *et al.* in 1967 and used by Ikeya in 1975. One of the most important advantages the method offers is the range of the measurable age from 10^3 to 10^7 years (Smart & Frances 1991), and a possibility of dating the materials which cannot be dated by other methods, e.g. tooth enamel samples of mass lower than 2 g.

The principle of the method is practically the same as that of thermoluminescence dating (TL). The sample acts as a natural dosimeter recording the cumulative radiation dose received at the sample site since deposition. EPR simply provides a means of measuring the cumulative effects of radiation on the sample and of calibrating the sensitivity of the sample to radiation. Ionising radiation, X-rays and cosmic rays cause excitation of electrons in solids, the majority of which recombine with holes (positive charge sites) relatively rapidly. However, some of the excited electrons become trapped at charge deficit sites associated with defects and impurities in the crystal lattice. For instance in calcite, Y^{3+} sometimes replaces Ca^{2+} and stabilises CO_3^{3-} formed by trapping of an electron on a CO_3^{2-} site. These density of trapped electrons from paramagnetic centres or radicals can be measured directly and non-destructively by EPR. The intensity of natural EPR signal of a sample is thus dependent on four factors: the average radiation flux or dose rate at the sample site, the sample age and the sensitivity of the sample in terms of charge of EPR signal intensity per unit radiation.

The EPR sensitivity is obtained by exposing the sample studied to additional gamma radiation dose in laboratory using the additive dose method. In practice the natural intensity and sensitivity are combined to determine the geological dose, which is a direct estimate of the cumulative radiation dose to which the sample has been exposed. If the average dose rate for the sample is known, then the age can be calculated as the ratio of the geological dose to the average dose rate (Smart & Frances 1991).

Electron paramagnetic resonance theory

Interaction of an external magnetic field with magnetic moments of unpaired electrons in a sample under study leads to a splitting of the electron energy levels. An EPR signal is observed when the quantum of the electromagnetic wave energy incident on the sample is equal to the energy difference between the neighbouring energy levels:

$$E_2 - E_1 = h\nu = g\mu_B B, \qquad (1)$$

where: h is the Planck constant (6.626176(36) * 10^{-34}Js), ν – is the electromagnetic field frequency, E_1 and E_2 – energy of the first and the second level, respectively, g – spectroscopic splitting constant, μ_B – Bohr magneton (9.27407555(31) * 10^{-24} JT^{-1}), B – the intensity of the resonance field.

The g value is calculated from the known frequency of the electromagnetic wave and the intensity of the resonance field. It describes the contribution of the orbital and spin movement into the atom magnetic moment and is characteristic of paramagnetic centres of a certain kind. EPR is used in investigation of paramagnetic centres in organic materials (radicals or ionradicals, organometallic complexes), inorganic materials (transition metal ions, rare earth ions, conduction electrons in metals) and substances with crystal lattice defects (Kęcki 1972).

The instrument used for EPR signal observation is an EPR spectrometer (Fig. 1). It is composed of a microwave block, a detector, a magnetic field drive, a resonator, a power supply unit and a recorder. Microwaves generated in the microwave block fall into the resonator with a sample studied, which is placed between the electromagnet poles. The waves reflected from the sample are directed to the detector, amplified and recorded as an EPR spectrum, which is a derivative of the absorption spectrum. In EPR spectrometers clistrons working in different frequency bands are used as microwave generators, e.g. X band (9.4 GHz) Q band (35.0 GHz).

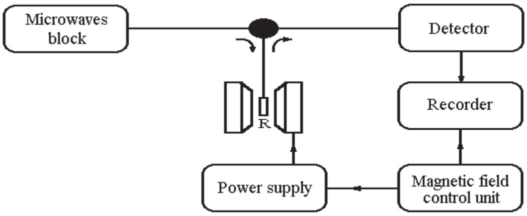

Fig. 1. A block diagram of an EPR spectrometr.

Experimental

Matherials

Natural calcite used in the study was collected from dripstones in the Jaskinia Czarna (Black Cave) in the western Tatra mountains. The tooth enamel of cave bear was found in the Jaskinia Nietoperzowa (Bat Cave) in the Kraków–Częstochowa Upland. The mammoth bones come from a site near Halicz on the river Dniester. The material was powdered in a mortar. The tooth enamel was sieved through a sieve of mesh diameter $\Phi = 0.063$ mm in order to separate it from dentine. The mass of each of the enamel samples was m = 0.035±0.001 g, while the mass of a sample of mammoth bones was m = 0.1311±0.0001 g.

EPR measurements

Measurements were performed using spectrometers made by Radiopan, working in the X (9.6 GHz) and Q (36 GHz) bands. Measurements of natural calcite were carried out for temperatures 300–900 K, using compressed nitrogen for temperature control. Samples of the tooth enamel were irradiated at the Nuclear Technology Department of the Academy of Agriculture, Poznań, using ^{60}Co source; the irradiation doses were: 25, 50, 100, 150, 200 and 300 Gy. The accuracy of mass measurements was $\Delta m = 0.001$ g. The mammoth bones were powdered and exposed to sunlight for about 20 weeks (summer), and to UV radiation from a low-pressure mercury lamp (EMITA VP – 60) of 410 W in power, for 15 hours directly in the resonance cavity. EPR measurements of the powdered bones exposed to sunlight were made at one week intervals, monitoring the sample mass.

Description of the experimental methods

Computer Resolution Enhancement Method (CREM)

The Computer Resolution Enhancement Method (CREM) converting the experimental spectrum into a spectrum with enhanced resolution. It based on Fourier transform. The shape of the spectrum is described by a function of the following form.

$$F(x) = \int_{-\infty}^{\infty} K(x - x')\psi(x')dx', \tag{2}$$

where the function $\Psi(x')$ determines the positions and intensities of particular lines in the spectrum, and $K(x–x')$ is so-called core i.e. the function describing the shape of individual lines. In order to determine the positions and intensities of the lines we have to find the function $\Psi(x)$. The Fourier transform of $F(x)$ may be written as:

$$\tilde{F}(y) = (2\pi)^{-\frac{1}{2}} \int_{-\infty}^{\infty} F(x)\exp(-iyx)dx. \tag{3}$$

Similarly, denoting by $\tilde{K}(y)$ the Fourier transform of $K(x - x')$, we find the unknown function from equation Eq. (4):

$$\psi(x) = (2\pi)^{-\frac{1}{2}} \int_{-\infty}^{\infty} \frac{\tilde{F}(y)}{\tilde{k}(y)} \cdot \exp(-ixy)dy. \tag{4}$$

Therefore, aiming at determination of the function $\Psi(x)$ we have to calculate successively the Fourier transform of the core i.e. of the function describing the shape of the individual lines, and finally the retransform of the quotient of these two transforms (Krzyminiewski *et al.* 1998).

CREM enables exact determination of position of a line characteristic of a given paramagnetic centre. If an EPR comes from a single paramagnetic centre, both the EPR spectrum and its absorption curve may appear as single sharp lines (Fig. 2a). In the case of presence of a greater number of paramagnetic centres the spectrum is composed of many lines or is asymmetric (Fig. 2b).

The application of CREM allows a separation of the components of the EPR spectrum, which ensures a possibility of accurate calculation of the g-factor (Eq. 1), characterising a given centre. The enhancement CREM ensures enables determination of the number of paramagnetic centres, their splitting and amplitude (Fig. 3).

For instance from the EPR spectrum of a cave bear tooth enamel (Fig. 4a), recorded on a spectrometer working in the X band, three values of the g-factor were obtained: $g_1 = 2.0022$, $g_2 = 2.0002$, $g_3 = 1.9972$ (±0.0007). After CREM analysis four values of the g-factor were found: $g_1 = 2.0022$, $g_2 = 2.0003$, $g_3 = 2.0001$,

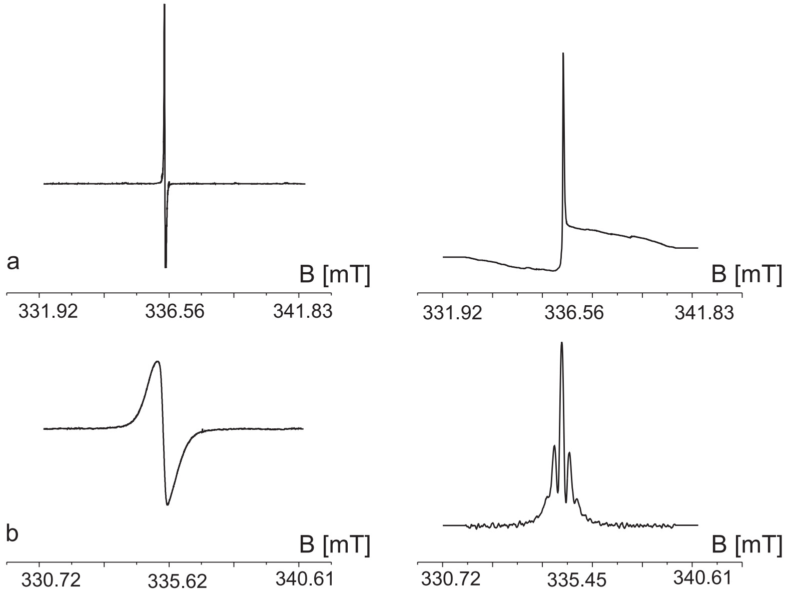

Fig. 2. A single sharp line EPR spectrum of TCNQ standard (**a**) and asymmetric EPR spectrum of a carbon standard (**b**). On the left the absorption curves derivatives and on the right the absorption curves.

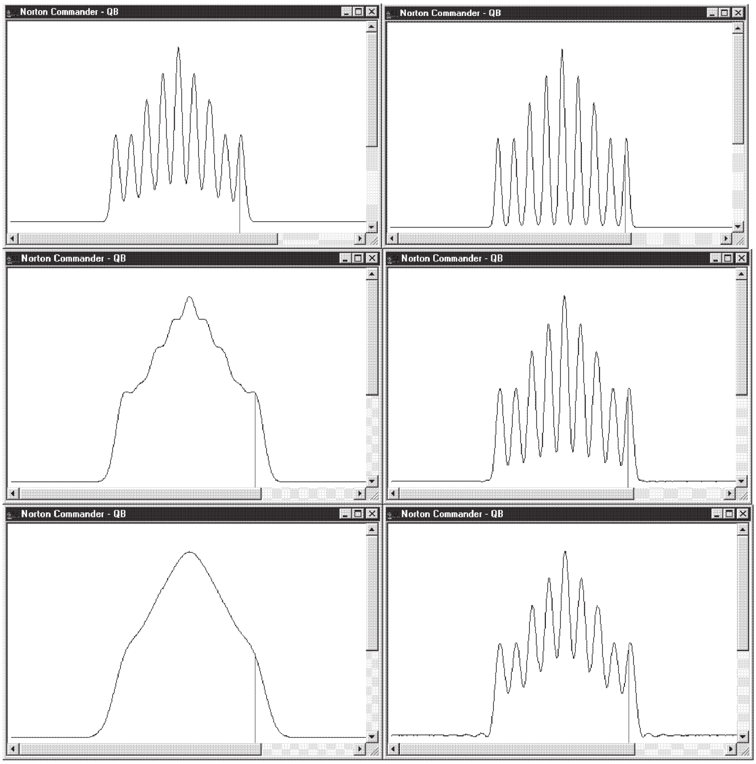

Fig. 3. The absorption curves of exemplary EPR spectra before (left) and after (right) CREM analysis of gradually deteriorating resolution of the well-resolved spectrum presented at the top.

g_4 = 1.9972 (±0.0007). The presence of four paramagnetic centres was confirmed by measurements on a Q-band spectrometer. In the case of dripstone calcite it was possible to determine five values of the *g*-factor (and six for mammoth bones) while CREM analysis gave the eight (and the eight for mammoth bones) *g*-factor values (Fig. 4b, c).

By the application of CREM it is also possible to follow the dynamics of the paramagnetic centres during different physical processes such as annealing, γ or UV-irradiation (Fig. 5).

From a comparison of EPR spectra of particular geological materials shown in Fig. 4 and Fig. 5, it is apparent that the above mentioned physical processes influence the structure of the paramagnetic centres in the substances studied. The application of CREM evidences in the spectrum of tooth enamel after γ-irradiation the intensity of the line corresponding to the paramagnetic centre g_2 increased much more than that of the lines assigned to the other three paramagnetic centres. Without CREM it would only be possible to calculate the increase of the EPR signal intensity after γ-irradiation to that in the spectrum before the irradiation. The situation is similar for the spectra of dripstone calcite and mammoth bone.

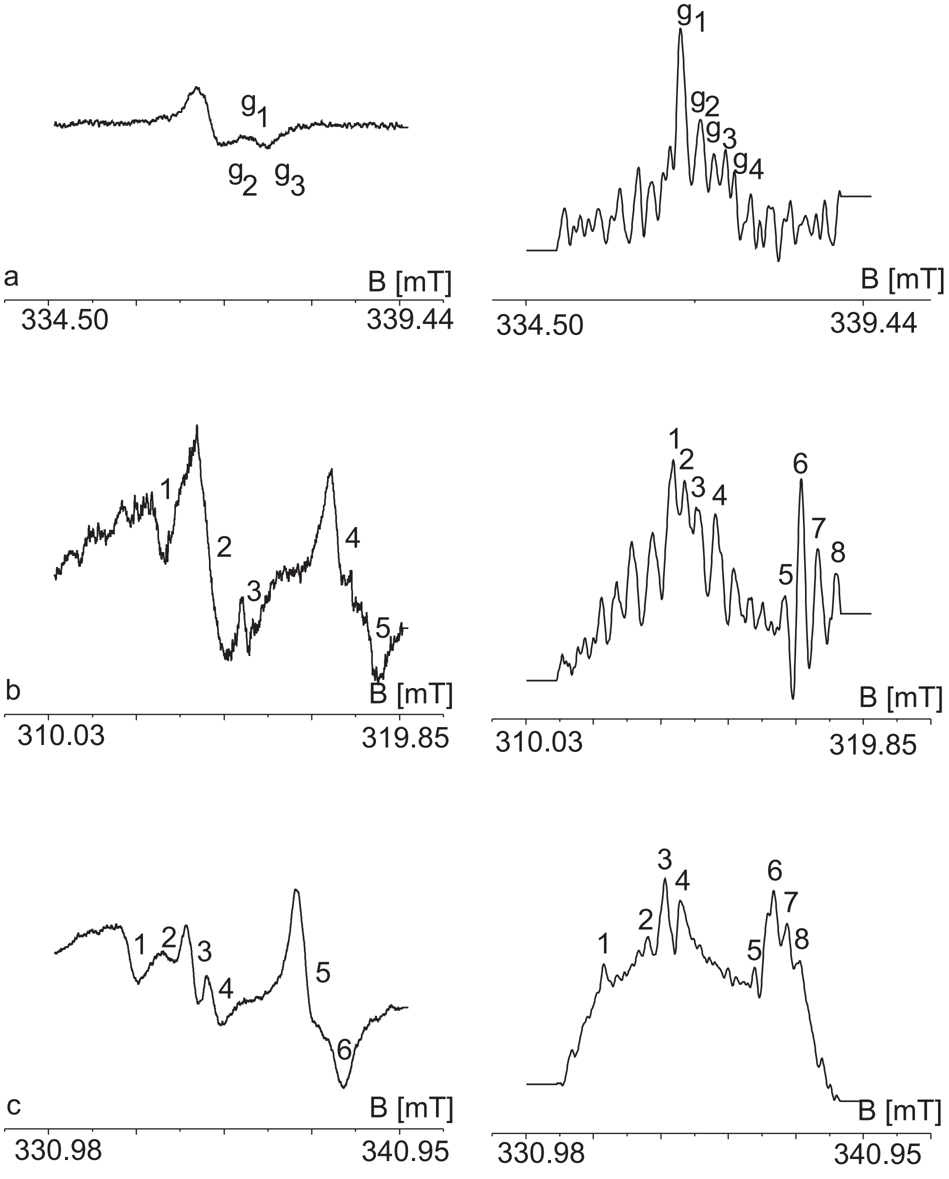

Fig. 4. EPR spectra of a cave bear tooth enamel (**a**), dripstone calcite (**b**) and mammoth bone (**c**), before (left) and after (right) CREM analysis.

EPR dating method

During crystallisation in natural conditions some defects appear in the crystal lattice, which act as electron traps. To these defects are attributed additional energy levels in the forbidden band. In a newly formed crystal the traps are

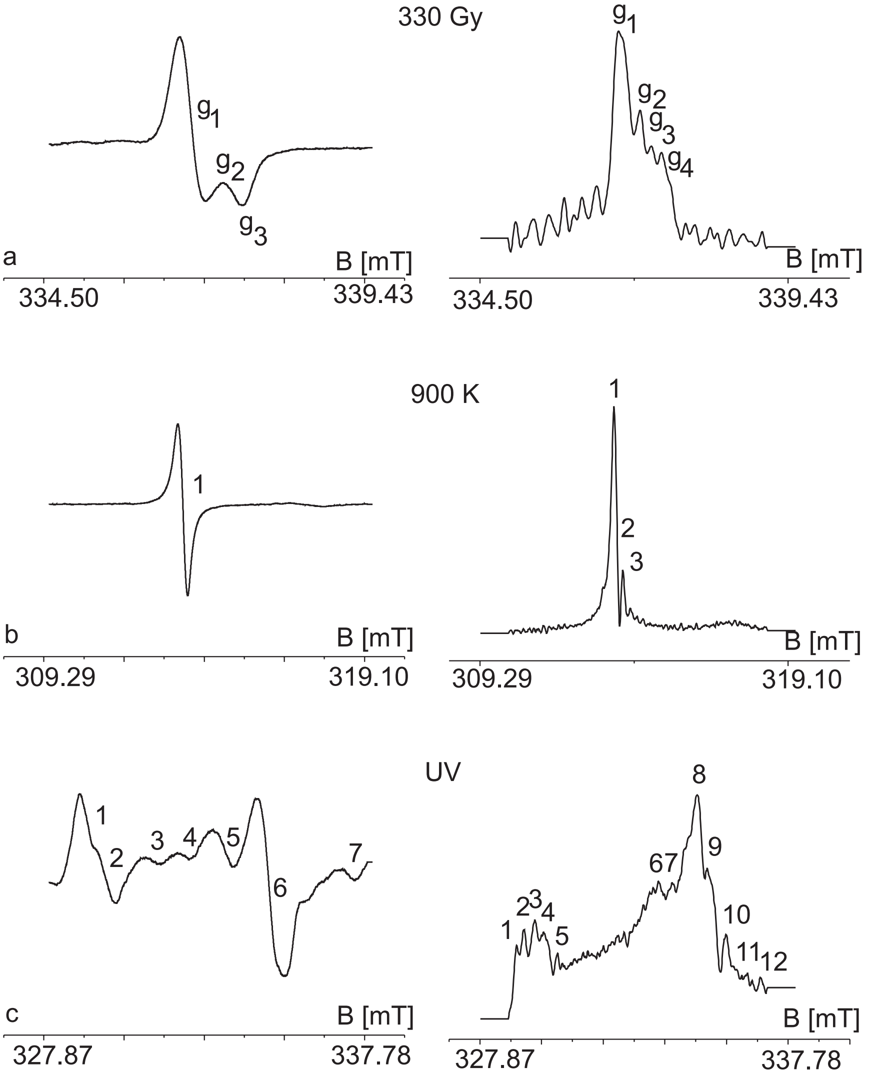

Fig. 5. EPR spectra of a cave bear tooth enamel after γ-irradiation with a dose of 300 Gy (**a**), dripstone calcite after annealing to 900 K (**b**) and mammoth bone after exposure to sunlight for about 18 weeks (**c**); before (left) and after (right) CREM analysis.

not populated. Nuclear radiation of trace radioactive admixtures present in the crystal and in the surrounding environment knocks out electrons from the valence band into the conduction band, Fig. 6 (Smart & Frances 1991). The number of traps depends on the radiation dose absorbed by the crystal. The time the electrons stay in the traps in natural conditions varies from fraction of a second to million years and depends on the energy difference between the bottom of the conduction band and the trap level, depth of traps and temperature of the environment. Long times of electron stay in a trap are related to the path of coming back to the valence band, which leads through the conduction band and recombination centres.

If the depth of the traps is E_a, the mean time the electrons stay in the traps τ at a temperature T is, Eq. (5):

$$\tau = Ae^{E_a/kT}, \tag{5}$$

where: A is a constant, k is the Boltzman constant (1.380662(44) * 10^{-23} JK^{-1}.

Dating by EPR is based on determination of the concentration of paramagnetic centres generated by the ionising radiation in given environmental conditions. The age of a given sample is defined as a ratio of the geological dose to the annual dose, Eq. (6):

$$t = \frac{AD}{D}, \tag{6}$$

where: t is the age of a sample, AD – geological dose, D – annual dose.

Geological dose, defined as the dose of radiation absorbed by the sample from the moment of its formation to the moment of measurement, is determined by measuring the concentration of paramagnetic centres in a sample, which is directly proportional to the intensity of the EPR signal. The annual dose is a sum of the external and internal dose, Eq. (7):

$$D = D_{ext} + D_{int}, \tag{7}$$

where: D is the annual dose, D_{ext} is external dose and D_{int} is internal dose.

The internal dose is described by:

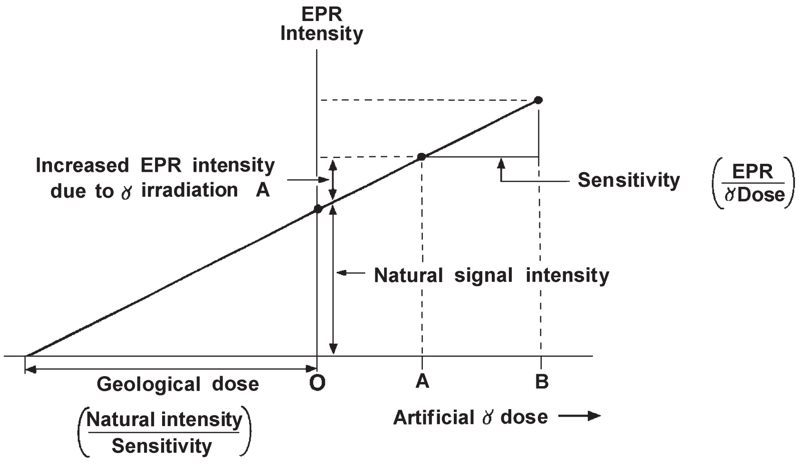

Fig. 6. The additive dose method for determination of sensitivity of a sample to radiation, and estimation of geological dose (*AD*) from the sensitivity and natural EPR signal intensity.

$$D_{int} = D_U + D_{Th} + D_K, \tag{8}$$

where: D_U, D_{Th}, D_K are the doses absorbed from sources of radiation being isotopes of uranium, thorium, and potassium – 40 isotope, respectively.

The external dose is proportional to the intensity of ionising radiation in the environment of the sample, and is measured at the site of the sample collection on the basis of measurements of γ-radiation intensity, Fig. 6 (Smart & Frances 1991).

The internal dose is determined by spectrometric methods on the basis of activities of radioactive isotopes occurring in the sample, measured by the scintillation method or neutron activation analysis (Hercman 1991; Ikeya 1978).

Determination of the geological dose. The procedure is as follows. The pretreated sample is irradiated by different controlled doses of γ-irradiation. After each irradiation EPR spectra of the sample are taken. On the basis of the spectra a dependence of the EPR signal intensity on the amount of γ-irradiation dose is obtained. The dependence is extrapolated for the laboratory dose and the geological dose is read out.

Conclusions

The application of CREM helps establish the number and type of paramagnetic centres present in a given sample and permits detection of dynamics of the paramagnetic centres both already present and generated during such physical processes as irradiation and annealing of geological materials. The possibility of laboratory reproduction of the physical processes taking place in the natural environment allows determination of factors which could obscure the result of EPR dating in a much shorter time than in the geological conditions. It was established that characteristic paramagnetic centres are generated during annealing of dripstone calcite and UV irradiation of mammoth bone. Their stability has not been well recognised yet, but they do not recombine immediately after cessation of the influence of the above mentioned external factors. The use of CREM for processing of EPR spectra of geological materials subjected to different physical processes in combination with determination of stability characterising the centres, enables an accurate analysis of geological history of a given sample. Since the main aim of the paper was to develop and verify the methodology of dating based on EPR measurements, and in particular analysis of behaviour of different kind paramagnetic centres generated in a given material, the results of the dating will be presented in a separate paper, after determination of the internal doses.

Acknowledgement: Financial support of the Polish State Committee for Scientific Research (KBN) within grant no. P04D 05615 is gratefully acknowledged.

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