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ELECTRON PARAMAGNETIC RESONANCE IN DATING OF FOSSIL ORGANIC REMAINS

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Abstract. The EPR method of dating is based on measurements of the concentration of paramagnetic centres generated by ionising radiation. The age (t) of a given sample is defined as the ratio of the geological dose (AD) to the annual dose (D). The geological dose is determined on the basis of the extrapolation of the EPR signal intensity dependence on the laboratory irradiation dose. The annual dose is the sum of an external (D_{ext}) and internal (D_{int}) doses. The external dose is measured at the site of the sample as intensity of γ radiation. The internal dose is determined by spectroscopic methods on the basis of the concentrations of uranium, thorium and potassium in the sample.

This paper reports a determination of the geological dose of cave bear tooth enamel found in the Nietoperzowa Cave (Cracow Plain), performed at the Institute of Physics, Adam Mickiewicz University in Poznań.

1. 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, ν – magnetic field frequency, E_1 and E_2 – energy of the first and the second level, respectively, g – spectroscopic splitting constant, μ_B – Bohr magneton, B – the intensity of the resonance field.

The value of g 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 which have 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, detector, magnetic field drive, resonator, power supply unit and recorder. Microwaves generated in the microwave block fall into the resonator with a sample studied 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) and Q band (35.0 GHz).

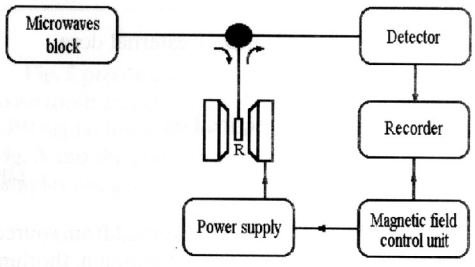

***Fig. 1.** A block diagram of an EPR spectrometer.*

2. EPR IN DATING

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 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. 2**). Part of them is then trapped in the electron traps. 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 centre. If the depth of the traps is E_a, the mean time τ the electrons stay in the traps at a temperature T is:

$$\tau = Ae^{\frac{E_a}{kT}} \tag{2}$$

where: A is a constant and k – Boltzmann constant.

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:

$$t = \frac{AD}{D} \tag{3}$$

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:

$$D = D_{ext} + D_{\text{int}} \tag{4a}$$

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

The internal dose is described by:

$$D_{\text{int}} = D_U + D_{Th} + D_K \tag{4b}$$

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

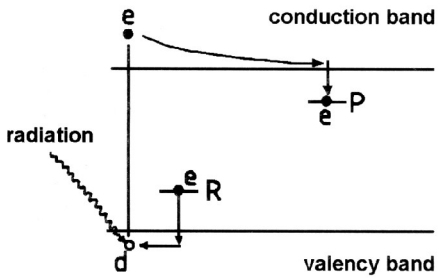

Fig. 2. *A simplified scheme of the energy levels – illustration of the mechanism of filling the electron traps; p – the trap level, R – recombination centre, e – electron, d – hole (after Hercman, 1991).*

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. 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, 1988; Ikeya, 1978). Dating by EPR has been considered a much promising method first of all because each kind of electron trap is ascribed to a specific EPR signal. Therefore, the EPR spectrum gives information on the amount and kind of electron traps characterising the material of the sample. It also informs about the presence of different admixtures unrelated to the electron traps. Another important advantage of this method is repeatability of measurements, because EPR is not an invasive method and does not destroy the electron structure in the trapped band, as it happens when the thermoluminescence method is used. Therefore it is possible to study grains of different size and monolith fragments, which is of importance in archaeology. Determination of a geological dose is relatively quick and takes usually a few days. The drawbacks of the EPR based method of dating stem from the fact that either the assumptions of the method are not satisfied or the annual external dose has changed. One of the assumptions of the method is the stability of annual internal dose, however, often it is not satisfied as the dose emitted by uranium isotopes changes in time. The external dose is assumed to be constant, which implies unchanged geometry and structure of environment. However, in certain circumstances, e.g. in a cave, the amount of deposits, their distribution, the amount of flowing water or the moisture content may change. In certain cases, e.g. when dating a dripstone by different methods, and getting overestimated age determined by EPR or thermoluminescence relative to that obtained by the $^{230}Th/^{234}U$ method, we can assess the time at which the dripstone was covered with more active deposits. Another factor disturbing determination of the age is partial fulfilment of electron traps already at the

moment of crystallisation; this results in overestimation of the age of a given sample. In disadvantageous conditions, such as high temperature or exposure to ultraviolet radiation, electrons can pass from the trap band to the ground band, which results in underestimation of the sample age. The dependence of intensity of EPR signal on the laboratory dose may not be linear due to the saturation effect-taking place when large doses, greater than 10^4-10^5 Gy (Hercman, 1991) have been absorbed. This effect restricts determination of the maximum age. Assuming that typical annual doses are $5*10^{-3}$-$1*10^{-2}$ Gy, the maximum age determined by the EPR method is $1*10^7$ years. This value depends on the kind of the substance studied, absorbed dose and conditions in which the sample remained. A limited sensitivity of an EPR spectrometer and the minimum detectable concentration of paramagnetic centres in a sample delimit the bottom bound of dating by the EPR method as $1*10^3$ years (Smart, 1991).

Many authors were concerned with a correlation between the results obtained by the EPR method and other dating techniques. For example Blackwell *et al.* (1991) compared the results of dating the fossil teeth found at the site La Chaise-de-Vouthon (France). Their age determined by EPR was from 37 to 94 ka, with an error of 2-6 ka, while the method $^{230}Th/^{234}U$ gave from 101±12 ka to 147±7 ka. The deviation of the results was of about 20%, and it could be explained by accumulation of uranium from the surrounding deposit in the teeth, which means that the assumptions of the EPR method were not fulfilled. Another example is the study by Bahein *et al.* (1991) in Italy on fossil teeth from the site of Isernia la Pineta. EPR gave their age as 144-242 ka, depending on the assumed model of uranium accumulation in the sample, whereas the method $^{230}Th/^{234}U$ gave 154±14 ka to 455±157 ka and the K-Ar method gave 736±40 ka. Avery good correlation between the results of EPR and ^{14}C dating was reported by Ikeya *et al.* (1983) for corals. The EPR method gave from 1.92±0.02 ka to 2.30±0.02 ka, while the age obtained on the basis of the ^{14}C method was 2.170±0.085 ka. The result obtained by the ^{14}C method is within that determined by the EPR method. Therefore, the result is significantly affected by the kind of material and physical and chemical processes the sample undergoes in time.

3. DETERMINATION OF THE GEOLOGICAL DOSE

The procedure is as follows. The pretreated sample is irradiated by different controlled doses of γ-radiation. After each irradiation EPR spectra of the sample are taken. From the spectra a dependence of the EPR signal intensity on the amount of γ-radiation dose is made. The dependence is extrapolated for the laboratory dose (**Fig. 3**), and the geological dose is read out.

The EPR dating has been applied for calcite (cave dripstones, skeletons of small organisms), aragonite (corals and molluscs), hydroxyapatite (fossil bones and teeth), and quartz (volcanic and sedimentary rocks, skeletons of small marine organisms). Attempts were also made to apply this method for determination of the age of zirconium, halite, gypsum, feldspars, fossil ceramics, peat and meteorites (Smart *et al.*, 1991).

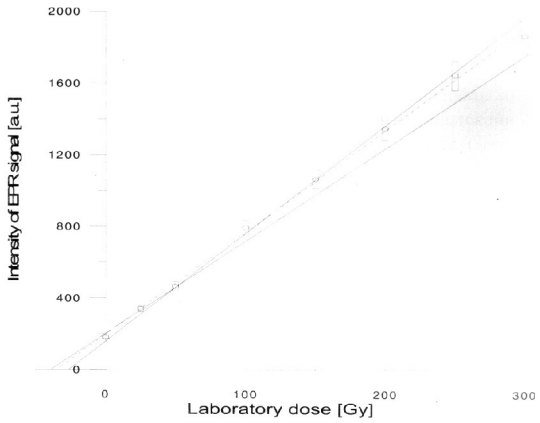

Fig. 3. *EPR signal intensity versus the laboratory irradiation dose for tooth enamel of a cave bear found in the Nietoperzowa Cave (Cracow Plain).*

4. THE APPLICATION OF THE EPR METHOD FOR DETERMINATION OF GEOLOGICAL DOSE OF ORGANIC FOSSIL REMAINS

In 1998, at the Institute of Physics, A. Mickiewicz University, Poznań, a study was undertaken to determine the geological dose of a sample of tooth enamel (**Fig. 4**) and bones of a cave bear. The samples were found in the Nietoperzowa Cave (Cracow Upland) at a geological site. The method applied was EPR. Analysis was made of hydroxyapatite of the chemical formula $Ca_{10}(PO_4)_6(OH)_2$ (Swang, 1964). From the measurements performed in the X and Q band, the spectroscopic splitting constants were calculated (**Table 1**).

Table 1. *Spectroscopic splitting coefficients calculated for fossil tooth enamel of cave bear, $\Delta g = 0.0006$.*

g_1	g_2	g_3	g_4
2.0022	2.0003	2.0001	1.9972

Fig. 5 presents exemplary EPR spectra of γ-radiated fossil tooth enamel of cave bear. The dependence of the EPR signal intensity on the laboratory dose is shown in **Fig. 3** and the geological doses calculated for different samples are given in **Table 2**.

Table 2. *Geological doses of irradiation determined for fossil tooth enamel of cave bear.*

Excavation	Layer	Geological dose [Gy]	Confidence interval [Gy]
III	10	9.0	7.8 - 15.6
III	15	35.3	20.7 - 43.7
IVc	10	35.3	25.3 - 39.1
V	9	18.9	18.0 - 33.3

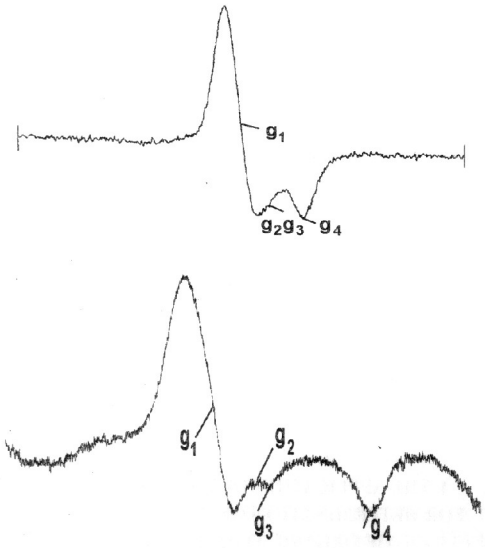

Fig. 4. *The EPR spectra of the cave bear tooth enamel: taken in the X band (the top one): range 10 and resonance field 336.700 mT, and taken in the Q band (the bottom one): range 10 and the field values for particular g-factors (see Table 1) are B_1=1272.600, B_2=1273.680, B_3=1273.880 and B_4=1273.820 mT.*

The samples of fossil tooth enamel of cave bear were found at the geological site in the Nietoperzowa Cave. The plan of the site is shown in **Fig. 6** (Madeyska-Niklewska, 1969).

5. CONCLUSIONS

The results confirmed the usefulness of the EPR method in determination of geological doses of fossil remains. The next stage of the studies, already under way, concerns determination of an eternal dose, attempts at determination of an internal dose, and testing of different models of accumulation of uranium in bones. Another problem of interest is the influence of ionising radiation on the structure of EPR spectra of calcite originating from cave dripstones (Wojcieszów). The studies towards this aim have been already started and are to be the preparatory stage for working out a method of dating of different materials by the EPR technique.

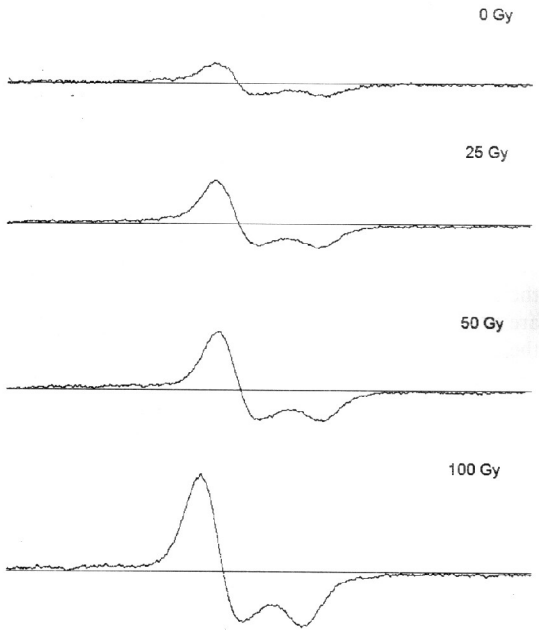

Fig. 5. *The EPR spectra of tooth enamel irradiated with the doses: 0, 25, 50 and 100 Gy; field: 334.50-339.43 mT, frequency: 9.4336 GHz.*

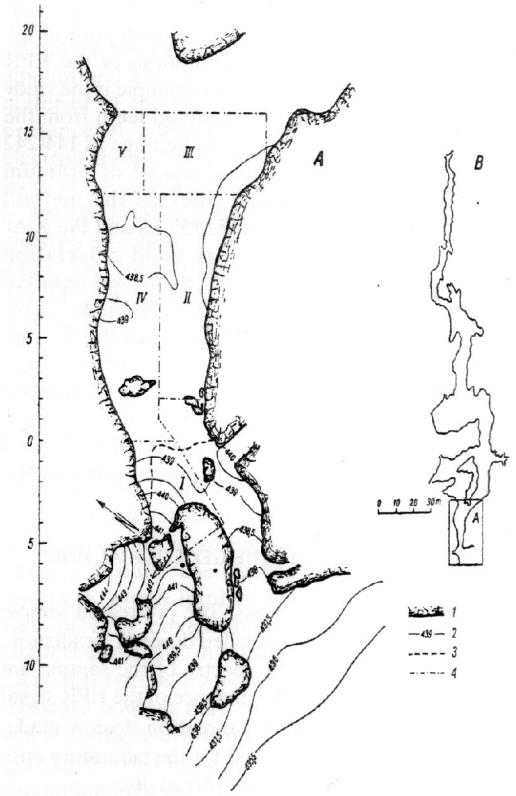

Fig. 6. *A plan of Nietoperzowa Cave. A – the part near the opening after W. Chmielewski. B – the central part after Z. Cietak: 1 – rock walls, 2 – isohypses in meters above the sea level, 3 – overlap of cave, 4 – the profile contours.*

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