# APPLICATION OF ESR TO THE DATING OF SUBFOSSIL SHELLS FROM MARINE DEPOSITS

A. MOLODKOV
Institute of Geology,
Academy of Sciences of the E.S.S.R.
7, Estonia Boulevard,
Tallinn, Estonian S.S.R., U.S.S.R.

## INTRODUCTION

The attempts to use ESR spectroscopy for dating fossil shells by a number of workers (Ikeya and Ohmura, 1981,1984; Hutt et al., 1983, 1985; Molodkov and Hutt, 1985; Katzenberger and Grun, 1985; Radtke et al., 1985; Skinner, 1985) have established the scope of this method. With further development, ESR is expected to become a valuable tool for the dating of biogenic carbonates, especially within the time span 0.3-1 Ma BP which is a period where other methods are limited. In this paper we present the results of our preliminary ESR investigation of shells of different species and age which were collected from the coastal formation of ancient Baltic water bodies and the Polar Basin.

The possibility of cross checking the results of the ESR dating of shells and the TL dating of the same deposits exists for these samples and this is valuable since we may obtain information concerning the conditions associated with the formation of deposits of different genesis.

## PROCEDURE

For ESR dating it is necessary, as is the case for TL, to determine the accumulated dose during burial (palaeodose, P) and the annual dose-rate, D. We have found, as in other laboratories, that the main difficulty in ESR dating lies in the estimation of P. This arises from the uncertainty which is associated with the choice of ESR spectral lines suitable for dating, and the significant variation of P evaluations resulting from the use of derivative lines of microwave absorption. An additional problem is the determination of the annual dose-rate in shells; each dose-rate comprises alpha, beta and gamma components of natural radiation from the surrounding deposits and from internal sources. Moreover, the calculation of annual dose-rate and palaeodose differs for the dating of Holocene and Pleistocene shells.

### The Age Equation

The ESR age was calculated using the formula

$$A = \frac{P}{D_C + D_{ex,\gamma} + D_{ex,\beta} + kD^{U}_{in,\alpha} + D^{U}_{in,\beta} + D^{Th}_{in}(t)} \qquad (1)$$

where, $D_C$ = cosmic ray contribution, calculated according to Yokoyama et al., (1982), $D_{ex\gamma,\beta}$ = external annual dose-rate, corrected for water content,

determined by means of gamma-spectrometric analysis of sediments and using Bell's data (Bell, 1979), $D_{in\ \alpha,\beta}$ = internal annual dose-rate, and k = efficiency of alpha radiation.

**External dose-rate**

Since gamma-quanta in shells with wall thicknesses of a few mm are substantially the same as that for the infinite burial volume, the calculation of gamma dose-rate is not a problem.
The external beta dose-rate was determined using the formula of Yokoyama et al., (1982):

$$G_{E\beta} = (1-e^{-\mu\beta L}) / \mu_\beta L \qquad (2)$$

where, $G_{E\beta}$ is the attenuation-correction factor for the reduction of beta radiation, L is the thickness of the sample and $\mu_\beta$ is the attenuation coefficient of the ß-rays.
The external beta dose-rate can also be determined from tables of average beta dose ( expressed as a percentage of the infinite matrix dose) for aragonite and calcite (Grun, 1986). The external alpha dose-rate was not considered since the shell surface is removed by etching in dilute HCl.

**Internal dose-rate**

For Holocene shells, the main source of internal dose, $D^U_{in\ \alpha,\beta}$ , is uranium, which is incorporated during crystallization of the shell. Its components were evaluated using the following formulae (Hutt et al., 1985, Molodkov and Hutt, 1985):

$$D^u_{in,\alpha} = C^U_\alpha . Q . k \qquad (3)$$

$$D^u_{in,\beta} = D^u_\beta . Q . (1- G_{E\beta}) \qquad (4)$$

where, $D^u_{\alpha,\beta}$ represents the annual dose-rates for $\alpha$ and ß components from U-238 to Th-230, Q is the U-238 concentration in the shell, and k is the efficiency of alpha radiation, for which we adopted a value of $0.15 \pm 0.05$.

For Pleistocene shells, the time dependent component of internal dose, $D^{Th}_{in}$ (t), reflects the in-growth of Th-230 with daughters in the shell during its buried state. Correction of the age for Pleistocene shells was achieved using the set of curves shown in figure 1, which have been obtained on the basis of calculation of the increasing internal annual dose-rate due to in-growth of Th-230 and its radioactive daughters with various concentrations of parent uranium in the shell.

**Palaeodose**

The palaeodose P was determined, using an additional dose method, by extrapolation of the dose response curve to the dose axis.

Pleistocene samples

For Pleistocene samples the area under the absorption curve, obtained by double integration of the first derivative spectra, was used as a measure of the concentration of radiation defects (method S). As a variant of this method,

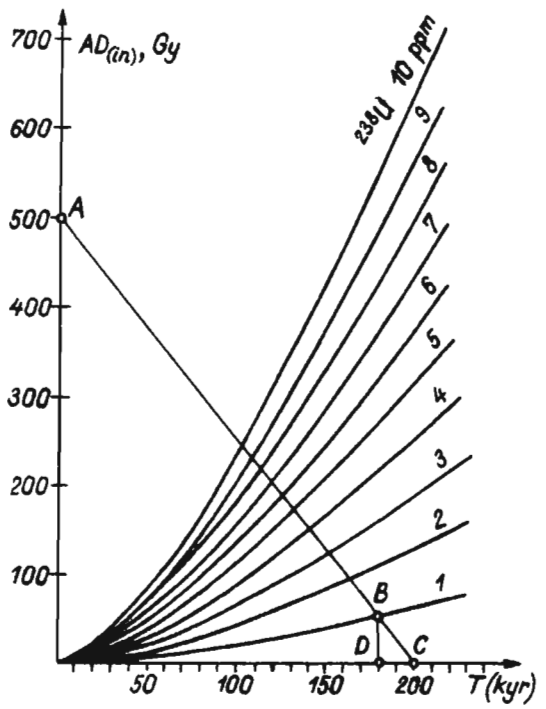


*Figure 1. Time dependence of internal palaeodose, $P_{in}$, for a shell of 0.5 mm wall thickness, vs different U-238 concentrations. Correction for the time-dependent component, $D^{Th}_{in}(t)$, is achieved using the following procedure for a shell containing 1 ppm U-238: Points A and C represent P and $P/(D_c + D_{ex} + D^{u}_{in})$ respectively, and the linear curve drawn between these two points and curve 1 intersect at point B, the T-coordinate of which provides the true age (point D).*

the magnitude of the absorption curve was also used in the region of the magnetic field which produced a good plateau (method A) and the first derivative signal, but with strong (up to 1 mT) overmodulation (method OM, Molodkov and Hutt, 1985). The reproducibility of measurements was better than 3%.
The behaviour of dose-response curves for derivative lines under conditions of artificial or natural irradiation is difficult to predict because of the strong interference of various components of complex ESR spectra. In contrast to this, the dose-response curves obtained by methods S, A and OM, are well represented by the exponential equation of first order kinetics:

$$I = I_{\infty}[1 - e^{-\mu(\gamma + P)}] \qquad (5)$$

where, I is the signal intensity for a gamma dose, $\gamma$, $I_{\infty}$ is the saturation intensity, $\mu$ is the sensitivity coefficient, and P can be determined by plotting $-\ln(1 - I/I_{\infty})$ vs $\gamma$ dose, (Apers et al., 1981).
The values of P obtained using the three methods determine the same quantity, and increased precision was obtained by calculating the mean value, P. For calcite shells, the ESR spectra of which contain intense $Mn^{2+}$ lines, P was determined by subtraction of the background signal of the forbidden $Mn^{2+}$ transition line (the amplitude of which does not change under the artificial irradiation) from the ESR signal of interest.

Holocene Samples

The young (Holocene) shell samples yield a signal of up to 2.5 mT width that is probably associated with an organic protein radical. Because there is uncertainty in the content of this organic radical in shells of different species, age and conditions of burial, we prefer to estimate the palaeodose for Holocene shells by the amplitude of the derivative ESR line. As has been shown previously (Hutt et al., 1985, Molodkov and Hutt,1985), only the line at g = 2.0020 has been found to be suitable for this purpose since the use of other lines resulted in significant higher uncertainty (up to 3 times more) in the evaluation of P.

## EXPERIMENTAL

All measurements were made at room temperature using an ESR X-band spectrometer with a microwave power of 2 mW and a modulation amplitude of 4 μT at 100 kHz. The samples of shells were carefully washed in water: the remnant sand and clay minerals were removed in an ultrasonic bath. The shells were etched in 0.3N HCl for 3 min in order to remove the α-irradiated surface, and then crushed in an agate mortar. The 75-200 μm fraction was separated and portions of samples of 50-300 mg were irradiated in a Co-60 radiotherapy unit. After irradiation, the samples were either stored for 2-3 weeks or heated at 100°C for 10 min to remove the unstable defects. Sample preparation and experimental measurements were performed in diffuse daylight.

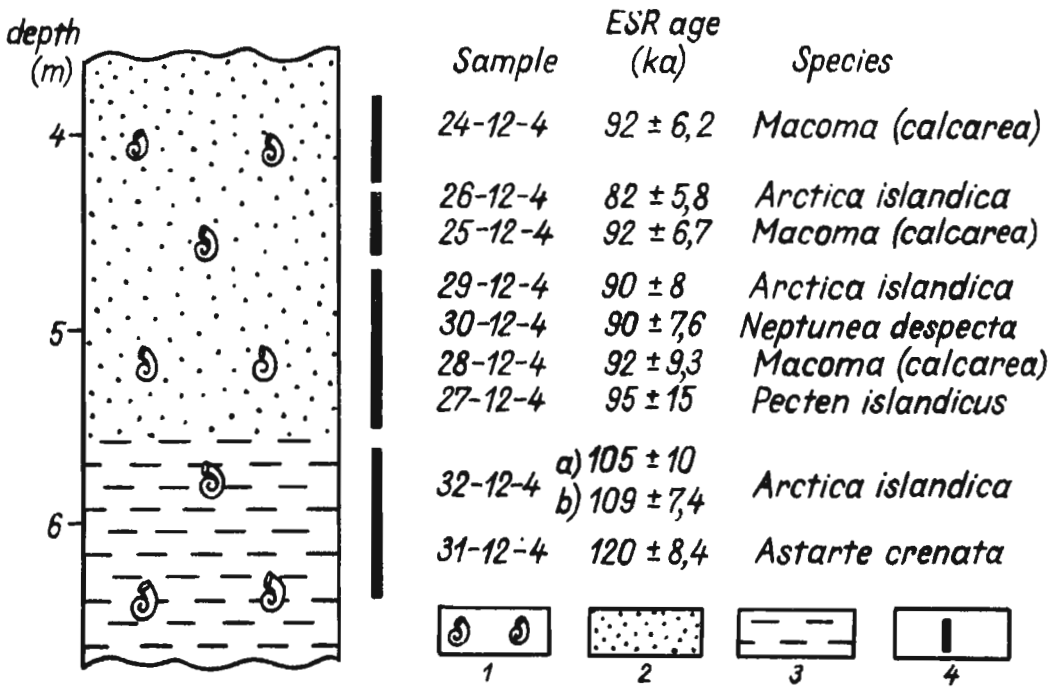


*Figure 2. A part of the section from the Arkhangelsk district with the results of the ESR dating of an Eemian formation . 1- shells 2- sand 3-fine sand 4- sampling horizons*

## RESULTS AND DISCUSSION

The results obtained for Holocene and Pleistocene shells are summarised in table 1 and figure 2 . The following conclusions were drawn from them:

1) The ESR ages, from the youngest to 300 ka, are in good agreement with the estimated dates, obtained using a number of analytical methods, including palynologic, micro-and macro-faunistic, diatomic, mineralogical, granulometric, radiocarbon and palaeomagnetic techniques.

2) For the Pleistocene shells, the best agreement has been obtained when the palaeodose has been determined using methods S, A and OM. In the future, a better method for the determination of P might result from a decomposition of complex ESR spectra and detailed examination of the peculiarities of some of the components.

3) Although in some cases the use of lines g3, g4 and g5 of the first derivative signal gave values of P coinciding with expected values (e.g. for samples NN 10-12-4, 14-12-4), there is a serious doubt concerning the reliability of their wide application in dating Pleistocene shells.

4) The plateau-test for the circumarctic shells gave good results even for laboratory doses which were close to saturation levels. This suggests that the dominant components of the observed spectra are associated with radiation defects of similar lifetimes and saturation levels of dose. Thus, where these radiation defects have sufficient lifetimes , the procedures of palaeodose determination we have described appear to be suitable for dating shells throughout the Quaternary period.

5) The estimation of life-time is usually obtained from an Arrhenius plot. However, thermal annealing in the laboratory may seriously differ from the process of natural relaxation of defects that occurs at ambient temperatures during burial. The results obtained may not reflect the slow processes (e.g. diffusion of defects, its compensators and others) that occur during the burial period. Also, for aragonite shells, the low thermal stability of their structure may complicate the experiments at high temperature. Consequently, the exploration of the extent of the chronological range of the technique (and beginning of thermodynamic equilibrium between decayed and reformed radiation defects) by examining ancient samples from circumarctic regions within the age range 0.3-3 Ma is important because it gives the opportunity to estimate the real geological process of the destruction of defects during long periods.

6) The preliminary results show that the ESR dating method is a promising field of investigation. Although there are many unsolved problems, the first step to creating a new and promising tool for studying the history of the Earth has been taken.

**Acknowledgments**
The author wishes to thank Dr. G. Hutt for fruitful discussions, Dr. H. Kessel and Dr. V. Makeev for useful geological discussions and samples, and also H. Putnik for the donation of shell samples.

**Invited Paper**: This paper was first presented by the author at a conference "Methodology of TL Dating" held at Tallinn 20-24 April 1986. Two further papers given by Soviet scientists at the same meeting have been invited and we hope to be able to include them in future issues of Ancient TL.

**TABLE 1**

| SAMPLE | ORIGIN | P(Gy) FOR DIFFERENT SIGNALS | | | | | | P | EXPECTED | ESR | GEOLOG. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | g3 2.0020 | g4 2.0009 | g5 1.9976 | OM | S | A | (Gy) | P (Gy) | AGE (ka) | AGE (ka) |
| 1-12-4 | Estonia | 15 | 22.5 | 12.5 | - | - | - | 15 | 14.9-15.8 | 6.6±0.4 | 6.5-7.0 |
| 2-12-4 | " " | 20 | 20 | 15 | - | - | - | 20 | 19.4-21.8 | 8.3±0.66 | 8.0-9.0 |
| 4-12-4 | " " | 16.5 | 22 | - | - | - | - | 16.5 | ≤17.3 | 8.1±0.5 | ≤8.5 |
| K-IV | " " | 15 | 26 | 27.5 | - | - | - | 15 | 14.8-15.4 | 6.83±0.57 | 6.5-7.0 |
| 10-12-4 | Novosibirsk is. | 1075 | 1075 | 790 | 1068 | 1078 | 1070 | 1070 | 600-1940 | 550±33 | 300-1000 |
| 11-12-4 | Severnaja Zemlya | 170 | 230 | 335 | 316 | 317 | 316 | 314 | 200-500 | 170±10 | 110-280 |
| 14-12-4 | " " | 80 | 80 | 80 | 80.1 | 81 | 80.5 | 80.5 | 68-86 | 65±8.7 | 55-70 |
| 15-12-4 | " " | 62 | 72 | 56 | 72 | 71 | 72 | 72 | 68-86 | 56±4.2 | 55-70 |
| 18-12-4 | " " | 194 | 420 | 176 | 270 | 280 | 280 | 280 | ~276 | 105±10.5 | ~100 |
| 24-12-4 | Arkhangelsk distr. | 85 | 132 | 110 | 114 | 113 | 114 | 114 | 102-130 | 92±6.2 | ~100 |
| 25-12-4 | " " | 53 | 83 | 113 | 119 | 110 | 113 | 114 | ~127 | 92±6.7 | ~100 |
| 26-12-4 | " " | 44 | 97 | 53 | 80 | 85 | 83 | 83 | ~102 | 82±5.8 | ~100 |
| 31-12-4 | " " | 66 | 72 | 128 | 121 | 117 | 121 | 120 | ~100 | 120±8.4 | ~100 |
| 32-12-4 | " " | 111 | 125 | 155 | 103 | 104 | 103 | 103 | ~95 | 109±7.4 | ~100 |

# APPLICATION OF ESR TO THE DATING OF SUBFOSSIL SHELLS FROM MARINE DEPOSITS

A Molodkov.

## REFERENCES

Apers, D., Debuyst, R., De Canniere P., Dejehet, F. and Lombard, E. (1981): A criticism of the dating by ESR of the stalagmitic floors of the Caune de l'Argo at Tautavel, in de Lumley, H. and Labeyrie,I. (eds), *Absolute dating and isotope analysis in prehistory - methods and limits.* 533-550. Proceedings.

Bell, W.T. (1979): Thermoluminescence dating; radiation dose-rate data, *Archaeometry*, **21**, 243-245.

Hutt, G., Molodkov, A., Punning, J-M. and Pung, L. (1983): The first experience in ESR dating of fossil shells in Tallinn, *PACT J.*, **9**, 433-438.

Hutt, G., Molodkov, A. and Kessel, H. (1985) : ESR dating of fossil shells in the Estonian territory, *Nucl. Tracks*, **10**, 891-898.

Grun, R. (1986): Beta dose attenuation in thin layers, *Ancient TL*, **4(1)**, 1-8.

Ikeya, M. and Ohmura, K. (1981): Dating of fossil shells with elektron spin resonance, *J. Geol.*, **89**, 247-250.

Ikeya, M. and Ohmura, K. (1984): ESR age of Pleistocene shells measured by radiation assessment, *Geochem. J.*, **18**, 11-17.

Katzenberger, O. and Grun, R. (1985): ESR dating of subfossil shells: some refinements, in Ikeya, M. and Miki, T. (eds), *ESR dating and dosimetry*, 145-155.

Radtke, U., Hennig, G. I., Linke, W. and Mungersdorf, I. (1981): Th-230, U-234 and ESR dating problems of fossil shells in Pleistocene marine terraces, *Quaternaria*, **23**, 37-50.

Skinner, A.F. (1985): Comparison of ESR and Th-230/U-234 ages in fossil aragonitic corals, in Ikeya, M. and Miki, T. (eds), *ESR dating and dosimetry*, 135-138.

Yokoyama, Y., Nguyen, H. V, Quagebeur, J.P. and Poupeau, G. (1982): Some problems encountered in the evaluation of the annual dose-rate in the electron spin resonance dating of fossil bones, *PACT J.*, **6**, 101-115.

## Errata

Correction to formula 3 on p50:

$$D^{U}_{in,\alpha} = D^{U}_{\alpha}. Q. k$$