ESR Dating and Dosimetry (IONICS, Tokyo, 1985)

ESR-DATING WITHOUT DETERMINATION OF ANNUAL DOSE: A FIRST APPLICATION ON DATING MOLLUSC SHELLS

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ABSTRACT

Debuyst et al. (1984) showed, that in principle, it should be possible to date samples without determination of annual dose, when two ESR-centers of different thermal stabilities are present. The annual dose can be correlated with the thermal stability of an ESR-center and the equivalent dose (ED), which can be derived from this center. In this paper, the method as described by Debuyst et al. (1984) is applied to a well dated Italian mollusc shell (5e-terrace) using ESR-centers with g-values of 2.0018 and 2.0014.

Aragonitic mollusc shells display normally five ESR-signals in the region of g=2.00 (Fig.1). Two of these signals (g=2.0018 and g=2.0007) are sensitive to gamma-irradiation. Radtke et al. (1985) showed, that the ESR-signal with g=2.0018 is superimposed upon a broader peak with g about 2.0014, with a satellite peak at g=2.0007.

Annealing experiments gave the following results (Fig. 2):

- the retrapping process of electrons from the center with g=2.0018 is of second order kinetics,
- the ESR-signal g=2.0007 decreases with first order kinetics,
- the total peak with g about 2.0014, as indicated in Fig. 2, decreases at nearly the same rate as the signal with g=2.0007.

The signal with g=2.0018 decreases in the beginning of the annealing very rapidly until this sharp peak cannot be identified as a single peak anymore. The rest of the signal in this region decreases at the same rate as g=2.0007.

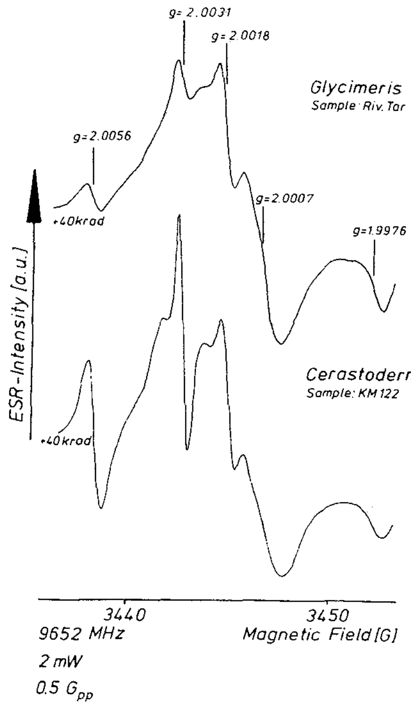

FIG. 1: ESR-Spectra of Aragonitic Mollusc Shells

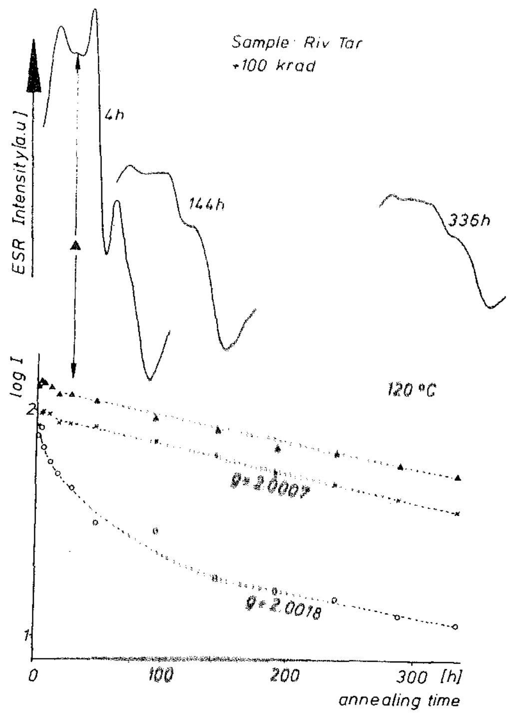

FIG. 2: Decay of the ESR-Signals along with Annealin-time. Trinangle Marks the Total Signal; x=Lower Signal; o=upper signal of the Splitted Line

In principle, the instability of the center corresponding to g=2.0018 raises the possibility of establishing calibration curves as carried out by Langouet et al. (1976; 1979). For the TL-age determination of archaeological ceramics Langouet et al. (1976; 1979) investigated the TL-intensity ratio of an instable TL-peak (325 °C) and a stable (375 °C) (at a heating rate of 20 °C/sec) in quartz as a function of time. This ratio is increasing steadily because electrons are retrapped by a thermally unstable trap much faster than by a stable center. It was now possible to construct calibration curves using the intensity ratios of well dated samples. Essential assumptions for the use of these curves are the temporal constancy of annual dose and temperature as well as the same alpha-efficiency of both centers.

An unstable trap accumulates electrons according the following formula (Langouet et al., 1976; 1979):

$$N = N_o + k\ D_o \tau (1 - e^{-t/\tau}) \qquad (1)$$

N = number of trapped electrons
N_o = number of trapped electrons at t=0
D_o = annual dose
k = radiolytic sensitivity
τ = meanlife
t = time (age)

If N is proportional to the measured ESR-intensity I, the formula can be rewritten:

$$I = I_o + E\ D_o \tau\ (1 - e^{-t/\tau}) \qquad (2)$$

E = ESR-sensitivity

Assuming $I_o = 0$ (i.e. no ESR-signal at the time of the formation, the essential assumption for ESR-dating) and

$$(ED)_t \propto E\ (I)_t \qquad (3)$$

(2) can be simplified when measuring the equivalent dose to:

$$ED = D_o \tau\ (1 - e^{-t/\tau}) \qquad (4)$$

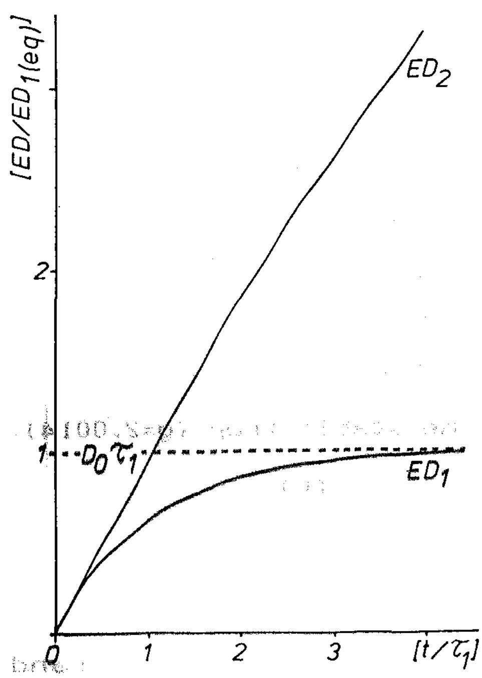

FIG. 3: Temporal Development of two EDs ($\tau_2 = 10\ \tau_1$)

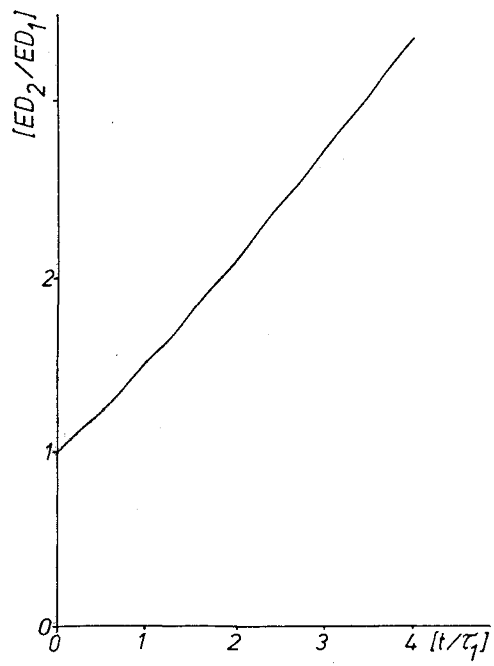

Fig. 4: Temporal Development of the Ratio ED_2/ED_1 According Fig. 3.

Fig. 3 shows the temporal development of two EDs derived from two ESR-signals g_1 and g_2, where the meanlife $\tau_2 = 10\tau_1$. Fig. 4 displays the temporal growth of the ratio ED_2/ED_1. In the following text X_{14} and X_{18} are parameters corresponding to the centers with g=2.0014 and 2.0018, respectively. A first attempt to establish calibration curves on a set of circumarctic molluscs (see Katzenberger & Grün, 1985) failed. The reason therefore might be that it was not possible to get identical species from well dated terraces. Additionally, the annealing experiments on Glycimeris showed that the meanlife varied to some extent between different individuals. On the other hand it was obvious, that the ED_{14}/ED_{18}-ratios of circumartic molluscs were about 1.5-2 whereas Italian molluscs of the same age (stage 5), but of course higher storage temperatures, displayed values of 5-10. It might be possible to use this ratio to calculate long term average temperatures. This would be useful, e.g., for aminoacid-dating, which is very dependent on temperature.

Debuyst et al. (1984) expanded the model of Langouet et al. (1976; 1979) to the general case, that an age can be determined directly when measuring the lifetimes and the EDs of the traps. This procedure can be deduced from Fig. 3 & 4:

$$(ED)_t = f(\tau)_t \qquad (5)$$

The mathematical treatment of this problem was given in detail by Debuyst et al. (1979). In order to date a mollusc shell via the unstable trap with g=2.0018 the following assumptions are made:

- the center correlated with the ESR-signal g=2.0014 is stable over the entire dating-range and retrapping can be neglected,

- the alpha-efficiency of both signals is equal. DeCanniere et al. (1985) showed, that this assumption can be made within the given uncertainties,

- the steady state density of spins at the center with g=2.0018 is well below the saturation level for that center.

Normally, the age is calculated via the stable trap (g=2.0014):

$$Age = ED_{14}/D_o \qquad (6)$$

and according equation (4):

$$ED_{18} = D_o \tau_{18} \ (1 - \exp\ (-t/\tau_{18}) \qquad (7)$$

For $t \geq 5\tau$, ED_{18} is less than 1% from a steady-state value and we obtain:

$$D_o \cong ED_{18}/\tau_{18} \qquad (8)$$

The age results from:

$$Age\ (a) = ED_{14}\ \tau_{18}/ED_{18} \qquad (9)$$

This formulation was used for the sample Riv. Tar., which was selected from an Italian 5e-terrace (see Radtke, 1983).

As shown in Fig.2, the signal with g=2.0018 affears to decrease according to 2nd order kinetics, because of the interference of the signal with g=2.0014. In order to obtain the lifetime of the center with g=2.0018 a linearly extrapolated part of the curve for the g=2.0014 signal was substracted from the total curve (see Fig. 5). The differences (lower dotted line) gives the decay of the unstable center. The lifetime of an electron captured by a trap can be calculated according the Arrhenius equation:

$$1/\tau = v_o \exp(- E_a/k\ T) \qquad (10)$$

v_o = preexponential factor
E_a = activation energy
k = Boltzmann constant
T = temperature (K)

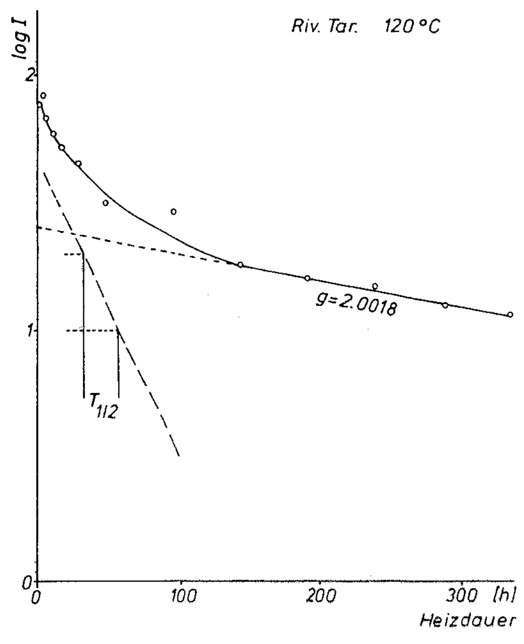

FIG. 5: Thermal Decay of the ESR-Signal with g=2.0018 of an Aragonitic Mollusc Shell

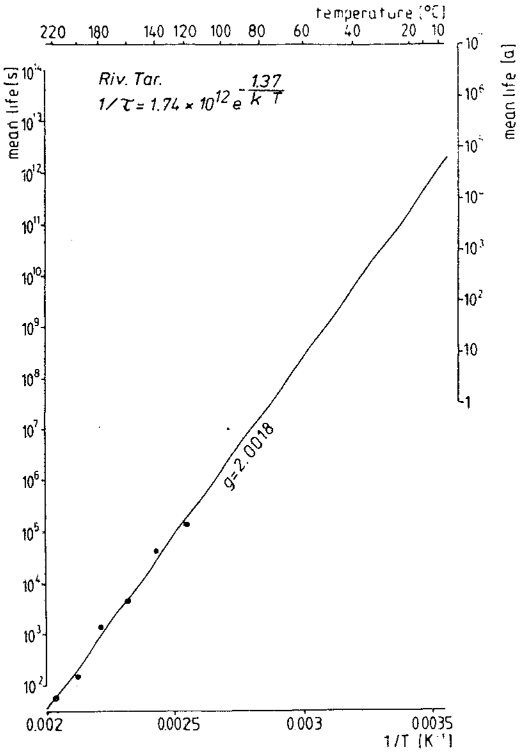

FIG. 6: Arrhenius Plot of the ESR-Signal with g=2.0018 of an Aragonitic Mollusc Shell

Fig. 6 shows the plot of 1/T against the annealing time and it is possible to determine the lifetimes of the center at different temperatures. The meanlife of the center corresponding to the ESR-signal g=2.0018 of the sample Riv. Tar. is according the recent average annual temperature (16.2 °C) 12 100 a.

The age calculation gives:

$$\text{Age} = (ED_{14}/ED_{18})\,\tau_{18} = (24.4\ \text{krad}/3.5\ \text{krad})\ 12.1\ \text{ka} = 84\ 400\ \text{a}$$

This value is certainly too low as compared to the expected age (approximately 125 000 a). This can be put down to the fact, that the signal height of g=2.0018 does not display thermal equilibrium, because during the last 5 meanlifes (ca. 60 ka) the average temperature was certainly lower than today due to the last glaciation. In order to apply a thermal correction a temperature model has to be established. One was developed by Grün (1985; see Fig. 7 & Tab. 1) based on various paleoclimatic indicators such as the $\delta^{18}O$ record of the deep sea core V28-238 (Shackleton & Opdyke, 1973), speleothem growth rates (Hennig et al., 1983), average July-temperature (Zagwijn & Paepe, 1982) and specific Mediterranean details (Brunnacker et al., 1982; Brunnacker, pers. comm.): the last 82 000 a were subdivided in 12 segments with constant temperatures (see Tab. 1, column 1-3).

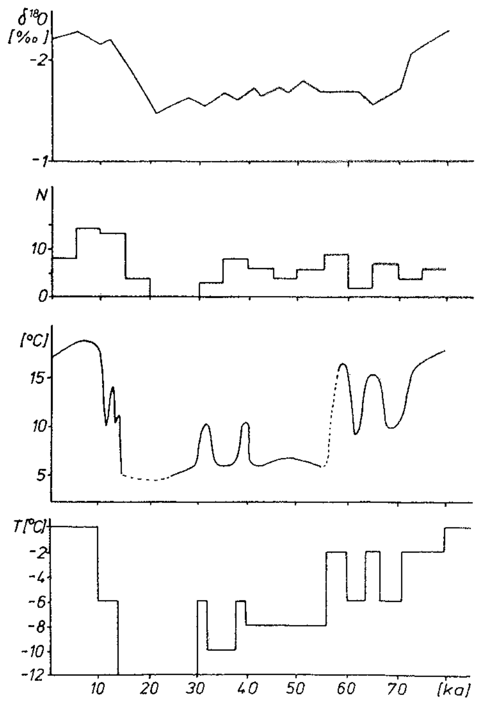

FIG. 7: Various Indications of the Paleoclimate: Top: $\delta^{18}O$-Deep-Sea Record V28-238 (Shackleton & Opdyke, 1973); Below: Speleothem-Growth (Hennig et al., 1983) Below: Average July-Temperature (Zagwijn & Paepe, 1968); Below: Modeltemperature for Thermal Correction

For the time before 82 000 a it is assumed that ED_{18} has reached equilibrium. In order to calculate a temperature correction the following calculations have to be carried out:

During a time interval of the time t_x with the average temperature T_x a given ED_0 from a center with τ_x decreases to:

$$ED_d = ED_0 \exp(-t_x/\tau_x) \quad (11)$$

If K is the ratio ED/ED(16.2 °C in thermal equilibrium) then:

$$K_d = K_0 \exp(-t_x/\tau_x) \quad \text{(Tab. 1, column 6)}$$

In the same interval electrons are trapped producing a dose ED_n. Normalized on ED(16.2 °C in equilibrium):

$$K_n = \tau_x/\tau_{16.2} (1 - \exp(-t/\tau_x) \quad \text{(Tab. 1, column 7)}$$

Hence, the temperature correction factor K_T at the end of the time interval is:

$$K_T = K_d + K_n \quad \text{(Tab. 1, column 8)}$$

TABLE 1

Calculation of the Temperature Correction Factor (See Text)

Inter see F	Duration (a)	T (°C)	τ_x (a)	$\tau_x/\tau_{16.2}$	K_d	K_n	K_T
1	10 000	16.2	12 200	1.0	1.53	0.44	1.97
2	4 000	10	38 000	3.1	2.88	0.64	3.52
3	16 000	4	129 000	10.7	2.41	1.21	3.62
4	2 000	10	38 000	3.1	2.57	0.15	2.72
5	6 000	6	85 400	7.1	2.22	0.48	2.70
6	2 000	10	38 000	3.1	2.23	0.15	2.38
7	17 000	8	56 500	4.7	1.13	1.21	2.34
8	4 000	14	17 460	1.4	1.23	0.29	1.52
9	4 000	10	38 000	3.1	1.23	0.32	1.55
10	4 000	14	17 460	1.4	1.08	0.29	1.37
11	4 000	10	38 000	3.1	1.04	0.32	1.36
12	9 000	14	17 460	1.4	0.60	0.56	1.16

$\tau_{16.2}$ = meanlife according the recent average annual temperature (16.2 °C)

The calculation of K_T was carried out for each temperature interval (assuming K_0 = 1). Tab. 1 shows that the measured ED_{18} is 1.97 times bigger than it would be if ED_{18} would displayed the steady-state dose corresponding to the modern annual temperature. This gives for the age:

$$\text{Age (a)} = (ED_{14}/ED_{18})\ \tau_{18}\ K_T = 166\ 300\ \text{a}$$

The purpose of this paper is only to demonstrate ,that mollusc shells show a potential to be dated without determination of annual dose. This method has, however, some disadvantages:

- the determination of the meanlife requires relative much material (5 - 10 g),

- the determination of the meanlife is very time-consuming,
- the temporal variation of the annual dose, e.g. caused by a disequilibrium in the U-238 decay chain) is not taken into account. This might be negligible, when the external gamma-dose is high relative to the internal dose,
- the uncertainty in the calculation based on the climatic model is about 10% (for the calculation only the last five intervals are essential),
- the uncertainty in the estimation of τ is about 18% per ^{o}C,
- the error in determining ED_{18} and ED_{14} is about 5% each.

All these error-sources give a total error of about 20-30%. This uncertainty itself could still allow satisfying results, but there is one essentially larger uncertainty:

The determination of τ in the manner described here can lead to values, which are about 3 times too large or too small (Debenham, 1983; Grün, unpublished data). As long as it is not possible to determine τ with smaller uncertainty, this method of age determination can give unfortunately only very unprecise ages. On the other hand, it may be possible to use this method in reverse, to determine the temperature history at a site where, e.g., precise ^{14}C-ages are available.

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