Quaternary Science Reviews, Vol. 11, pp. 173–179, 1992.
Printed in Great Britain. All rights reserved.

0277-3791/92 $15.00

DOSE–RESPONSE AND THERMAL BEHAVIOUR OF THE ESR SIGNAL AT g = 2.0006 IN CARBONATES

Michael Barabas, Manfred Mudelsee, Ralf Walther and Augusto Mangini
Heidelberger Akademie der Wissenschaften, c/o Institut für Umweltphysik der Universität Heidelberg, Im Neuenheimer Feld 366, D-6900 Heidelberg, F.R.G.

Growth curves of the ESR dating signal at $g = 2.0006$ on irradiation have been carefully examined. They revealed that a description by a single exponential saturation function is only a good approximation in the dose range smaller than 1 kGy. In this dose range the saturation dose, D_0, for carbonates was found to be between 400 and 800 Gy. The systematic deviations from this function and statistical uncertainties limit the reliable AD range to about 250 Gy. Expanded functions and models that explain the observed deviations are given.

The usual way of determining the thermal life time of ESR signals (isothermal annealing and Arrhenius plot) is critically discussed and additional specific complications (trap decay, different components of the signal) of the signal at $g = 2.0006$ are shown. A different method of detecting long term fading was used, in which the natural signal growth is compared with artificial growth curves on γ-irradiation. Evaluation of measurements from the sediment core RC17-177 revealed a thermal stability lower than previously assumed for foraminifera. The data fit best with the assumption that the dating signal contains a component (about 50%) that has a very low thermal stability (with a lifetime of about 50 ka at 2°C). Annealing experiments indicate that this may be the case in other carbonates as well. This would drastically limit the dating applicability of the signal at $g = 2.0006$.

INTRODUCTION

The paramagnetic centre with the g-factor at $g = 2.0006$ is accepted to be the most reliable ESR signal for dating of fossil carbonates (see for example Grün, 1989). There are materials of various origin in which this signal appears and on which dating has been attempted so far: foraminifera from deep-sea sediments (Sato, 1981, 1982; Barabas *et al.*, 1988), corals from various reefs (Radtke and Grün, 1988), molluscs from marine sediments (Katzenberger and Grün, 1985; Hütt *et al.*, 1985; Radtke *et al.*, 1985; Molodkov and Hütt, 1985; Molodkov, 1986, 1988, 1989), travertines (Grün, 1985) and speleothems (Yokoyama *et al.*, 1983).

The signal at $g = 2.0006$ has well defined ESR properties — which are not dependent on the specific origin — and has been unambiguously identified in various carbonates (Barabas *et al.*, 1992).

However, the general approach in ESR dating was to examine the properties of a specific material. Different results have been obtained for molluscs, foraminifera or corals (e.g. Grün, 1989).

Our aim is to approach a more generalized method of ESR dating carbonates using the signal at $g = 2.0006$, and we want to study dating-relevant properties in different carbonates of various origin.

Furthermore, in this paper we want to focus on the AD determination. Two main subjects are to be discussed: the problem of correct description of the signal-growth curve and the long-term stability.

In ESR-dating the AD is determined via extrapolation with the additive-dose method. A correct analytical description of the growth curves on irradiation is essential to exclude systematic errors. Meanwhile most of the researchers accept the description of the irradiation curve of the signal at $g = 2.0006$ in carbonates by a saturation type function (e.g. Grün, 1989). However, it will be shown by exact measurements from various carbonates that a precise description of the growth curves of this signal needs a more complex model than assumed. Consequences for AD determination will be discussed.

The more severe question is the problem of long-term fading of the signal at $g = 2.0006$ in carbonates. Several attempts to determine the life time of this ESR signal in calcium carbonates by isothermal annealing and Arrhenius plot are reported (Yokoyama *et al.*, 1983; Smith *et al.*, 1985; Wieser *et al.*, 1985; Grün, 1985; Molodkov, 1988; Barabas, 1989).

We want to compare here outcomes from isothermal annealing experiments with results from new approaches that are based on the difference between the natural signal growth that takes place in geological times and the signal growth on γ-irradiation (Barabas *et al.*, 1988; Mejdahl, 1988; Hütt and Jaek, 1989). It has been shown elsewhere (Sato, 1982; Siegele and Mangini, 1985; Barabas *et al.*, 1988) that cores of deep-sea sediments with known ages (from $\delta^{18}O$) are ideally suited for this purpose as they represent a time record of the natural signal growth.

DOSE–RESPONSE CURVE OF THE ESR SIGNAL AT g = 2.0006

All measurements of the signal at $g = 2.0006$ have been carried out with an X-band spectrometer at high microwave power (> 20 mW) and with a modulation amplitude of 0.1 mT (see Barabas *et al.*, 1992).

General Behaviour

A general observation is that the signal amplitude, S, tends to approach a certain maximum value, S_{max}, on irradiation (Fig. 1). One reasonable explanation (Barabas *et al.*, 1988) is that a crystal contains only a limited number of traps that can be filled (with electrons or holes). The saturation value is proportional to the total number of traps. The probability of capturing an electron by a certain trap can be described by a sensitivity constant, $1/D_0$.

This approach leads to an analytical description of the signal, S, as a function of the dose, D:

$$S(D) = S_{max}*(1-\exp[-D/D_0]) \qquad (1)$$

The inverse of the sensitivity constant, $1/D_0$, is the characteristic parameter of the growth curves, the so-called saturation dose, D_0. It is equal to the dose needed to reach $(1-1/e)*S_{max}$, i.e. it determines how strong the curvature of the growth curve is or how fast a saturation will be reached (Fig. 1). In a first approximation this gives a fairly good description of the growth curves of the signal at $g = 2.0006$, at least for a certain dose range (0–1000 Gy).

Many measurements on various carbonates (corals, foraminifera, molluscs, synthetic calcites) indicate that the saturation dose, D_0, is only slightly dependent on the material (Katzenberger, 1989; Barabas, 1989; Walther *et al.*, 1992). Values run from 400 to 800 Gy in the dose range less than 1 kGy, only few smaller saturation doses have been observed in molluscs (Katzenberger, 1989; although in these cases the ESR signal was not precisely defined).

Deviations from the Single Saturation Function

Assuming that this simple model is correct there should be no growth of the signal for a dose larger than about 3000 Gy (saturation). However, this is not the case. Some examples will illustrate the deviations.

(a) *Molluscs*: A fit according to Eq. 1 in a low dose range describes the measured values quite well. However, for higher doses the measured values deviate distinctly from this fit (Fig. 2a).

(b) *Foraminifera*: using the fit function (Eq. 1) the parameter D_0 depends on the dose range used for fitting: it increases from about 600 Gy (fit range: 0–800 Gy) to 1200 Gy (0–8000 Gy) (Mudelsee *et al.*, 1992). Similar observations have been obtained from corals and molluscs.

(c) *Corals and foraminifera*: A plot of the logarithm of the slope of the signal curve versus the absorbed dose, D, should give a straight line with the slope $1/D_0$ (see Katzenberger, 1989). Fig. 2b shows that this is not the case for the signal at $g = 2.0006$. The slope of S is derived for each radiation step by fitting a second order polynomial to each 5 sequential points.

These experimental results can be empirically described assuming that the saturation dose, D_0, is not a constant for the whole dose range but a function of the absorbed dose. Two *empirical* approaches have been

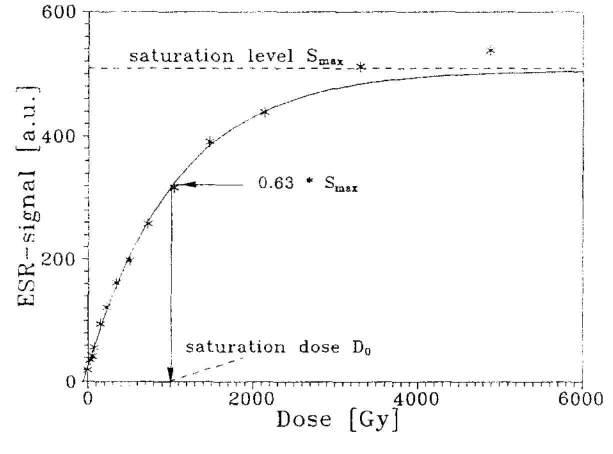

FIG. 1. Signal growth curve of the ESR signal $g = 2.0006$ in foraminifera (* = measured values; — = best fit). The principal parameters of the fit function are shown.

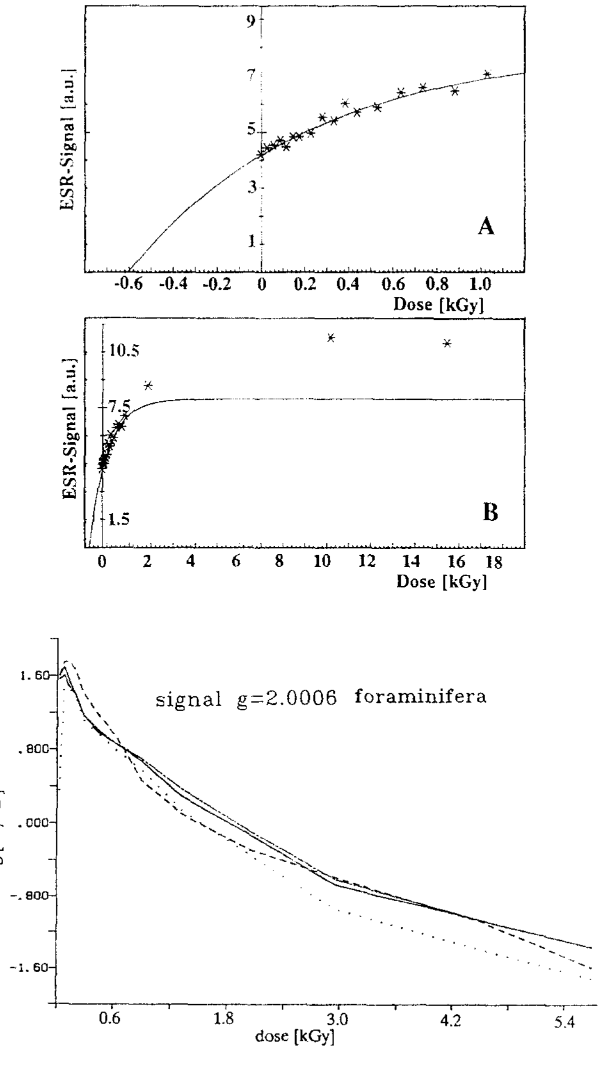

FIG. 2. (a) The function that describes the low-dose data; (A) deviates strongly from the measured values for higher doses (B) (fossil shell). (b) Logarithm of the slope dS/dD of the signal growth curve (numerically evaluated) vs. the dose received. This would result in a linear relationship for a single exponential saturation function (data from sediment core RC17-177, different depth).

shown to give a better description over a larger dose range (Fig. 3a).

(a) A sum of at least two saturation functions with different D_0. The second function (large D_0) can be approximated by a linear function.

(b) If we assume D_0 to be a function of the dose, D; itself $D_0(D) = D_0'^*D^{(1-\gamma)}$ with γ in the range of 0.8 (according to Grün, 1989).

The resulting functions describe the growth curves in a range up to around 1500 Gy sufficiently well (Fig. 3b). However, both introduce at least one additional parameter, that has to be determined and that increases the statistical uncertainty (see below). Similar results have been obtained by Grün (1990) and Walther *et al.* (1992) for corals. Different models may explain these functions and the observed behaviour at least qualitatively (e.g. Mitchell *et al.*, 1961). For the observed behaviour either the creation of new traps due to irradiation or different sensitivities of existing traps (see also Grün, 1990; Walther *et al.*, 1992) may be responsible.

AD DETERMINATION

The only source of knowledge about the functional relationship between signal amplitude and absorbed dose is the measured response on artificial irradiation. The assumption of the additive-dose method for AD determination is that we can extrapolate the growth curve on artificial irradiation, i.e. it is assumed that there is no difference between the response on natural low dose rates and artificial high dose rates.

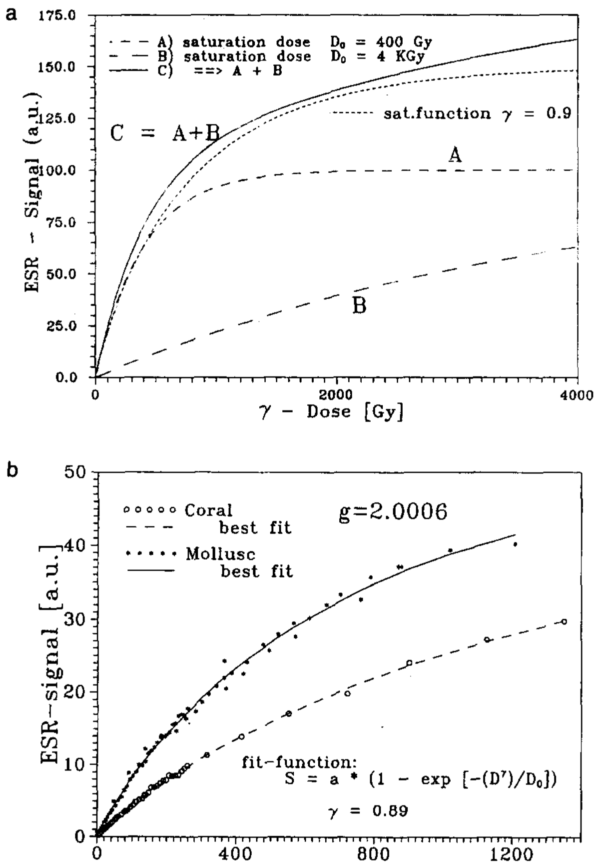

FIG. 3. (a) Principle composition of the growth curve of saturation functions with different saturation doses, D_0, and comparison with the second model (γ-function). (b) Best fit of data to this function: $\gamma = 0.89$.

Systematic Deviations

As shown above the description of the signal growth curves using a single exponential saturation function is only an approximation for small dose ranges. As a consequence the use of a single saturation function as a fit function for AD determination introduces a systematic error. This is shown in Fig. 4. As a data base we used the measured values of recent mollusc samples (40 irradiation steps) and thus tried to verify the ADs.

The systematic overestimating increases with the dose range (i.e. the radiation steps) that is used for the fit. From our observations on corals and molluscs a total dose range (AD + γ-dose) of less than about 500 Gy leads to a good approximation of the true AD if a single exponential saturation function is used. This limits the reliable AD range to about 250 Gy for this signal.

In principle the use of a fit that describes the curves more precisely will lead to a better approximation. However, this increases the statistical uncertainty as well. If it could be verified that some parameters are constant this would reduce the number of variables that have to be determined. Further work has to be done on this point.

Statistical Errors

The use of ESR data (i.e. signal amplitudes versus γ-doses) for fitting and AD determination leads to a standard error of the AD itself — even if we know the correct function — because all measured data have a certain *statistical* uncertainty.

For a single exponential saturation function, this

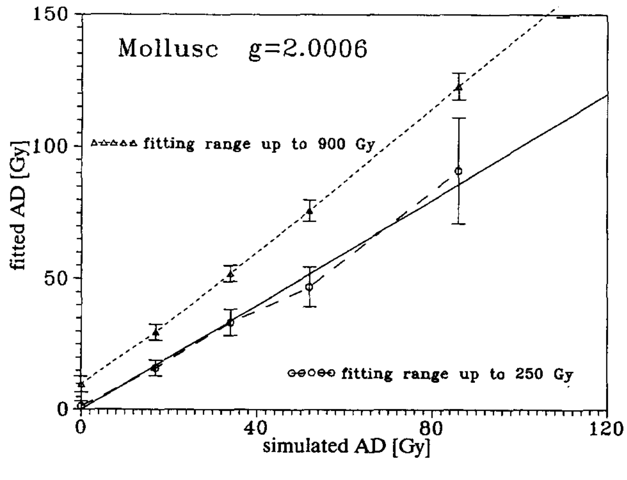

FIG. 4. AD determination with Eq. 1 (= fitted AD) using different fit ranges. Simulated AD = dose of the minimum value used for fitting. Data are from measurements on recent molluscs (as shown in Fig. 3). If the range is too large systematic deviations (dotted line) from the 1:1 correlation (solid line) occur.

error depends on various parameters: standard deviation of a single measurement, number of data points, maximum dose range used for fitting, the curvature (saturation dose) of the growth curve and the AD value itself.

In order to check the influence of the different parameters on the AD uncertainty we made Monte Carlo simulations, i.e. we generated data with a random scatter and fitted Eq. 1 to them. These simulations show (Fig. 5) that in order to achieve a reasonable accuracy of the AD (i.e. less than ± 10% standard error), the following procedures have to be applied:

- at least 12–15 data points are required each of which has to be measured with a maximum precision (normalization!);
- the dose range used for fitting (i.e. maximum radiation step) has to be at least in the same range as the saturation dose, D_0 (i.e. > 400–800 Gy for carbonates);
- the AD has to be smaller than one third of the saturation dose, D_0.

This means that we can measure ADs up to 150–300 Gy using the signal at $g = 2.0006$ in carbonates with a satisfying precision. In principle the AD range can be expanded by using a larger number of data points. However, for practical use a number of 15 measurements is already a maximum. These limitations are a consequence of the statistical uncertainty.

Conclusion/Practical Solution

Because of statistical and even more because of systematic deviations the AD that can be evaluated from the signal at $g = 2.0006$ in carbonates is limited to about 250 Gy. It could be obtained by using a single exponential saturation fit with at least 12 irradiation steps and a *maximum additional* γ*-dose* of about 250 Gy. The AD range can be expanded to a certain extent by increasing the number of measurements or by establishing generalized parameters for the growth curves.

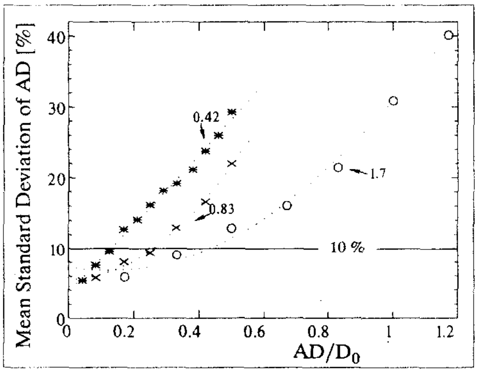

FIG. 5. Monte Carlo simulations to test the algorithm for AD determination: the relative standard error of the fitted AD is shown as a function of the AD (expressed in units of the saturation dose, D_0). We have calculated 17 equidistant data points for each fit, each of which has a standard error of 3%. Three curves are shown for three different ranges of additional γ-irradiation (parameter = maximum γ-dose/saturation dose, D_0).

THERMAL BEHAVIOUR AND LONG-TERM FADING

Arrhenius Plot Life Times

The thermal life time of a signal limits the age that can be obtained from this signal. To get a reliable age the life time should be at least 5 times this age (Barabas, 1989). Otherwise, a correction factor has to be applied (Barabas *et al.*, 1988, Mejdahl, 1988).

The conventional way of determining life times of ESR signals is to accomplish isothermal annealing experiments at several elevated temperatures and then to extrapolate the life time to ambient temperatures (Arrhenius plot).

According to annealing experiments the life times of the signal at $g = 2.0006$ *at higher temperatures* (200°C) differ by a factor of up to 50 (between molluscs and speleothems), also within the same material (speleothems: two orders of magnitude; Rossi and Poupeau, 1989).

Corresponding *life times at 0°C* deduced from Arrhenius plots range between 3 Ma (molluscs (overmodulated signal); Molodkow, 1989), 10 Ma (foraminifera; Barabas, 1989) and 4–80 Ma (speleothems; Yokoyama *et al.*, 1985).

These results indicate that the life time is not an invariable attribute of the paramagnetic centre but is dependent strongly on the specific material. Furthermore, the determination of life times with the Arrhenius method delivers large errors for principle reasons:

(a) The Arrhenius plot extrapolation results in uncertainties at least with a factor of 3 or more (Barabas, 1989; Grün, 1989).

(b) It is not proven that the Arrhenius equation holds exactly over the whole range of temperatures with a constant frequency factor (McKeever, 1985).

(c) Other processes like diffusion of point defects or recrystallization of carbonates that can take place during annealing may have an influence on the results (ibid.). For aragonitic carbonates there is a strong tendency to transform into calcite unless it is not in a marine environment. These processes may become much more important at low temperatures than can be deduced from the high temperature behaviour.

In the special case of the signal at $g = 2.0006$ in carbonates additional problems exist making the determination of the life time questionable.

- Smith *et al.* (1985) detected an unstable component during annealing experiments. Rossi and Poupeau (1989) found that the order of the decay of the signal is between first and second (1.5). Our experiments with marine carbonates (foraminifera and corals) indicate that the general form of the isothermal decay curves displays a higher decay order or consists of at least two components that differ by about a factor of 20 (Fig. 6). Hence, the life time may depend on the relative contribution of the different components.
- Barabas *et al.* (1988) and Katzenberger *et al.* (1989) found that heating of the sample leads to partial or

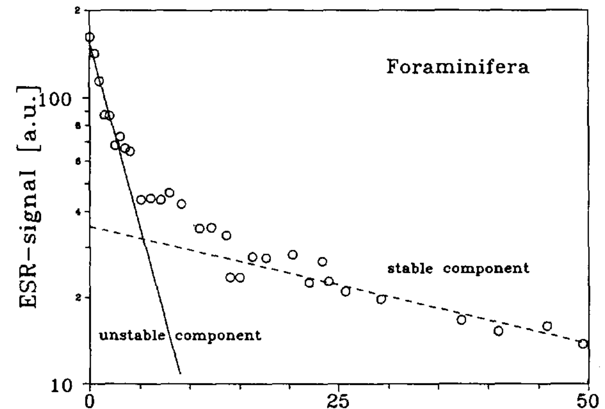

FIG. 6. Semi-log plot of the signal amplitude in foraminifera vs. heating time at 160°C. It can be interpreted as consisting of two components each displaying first order kinetics.

total destruction of the sites where the paramagnetic centres can be built (trap decay), i.e. after sufficient heating of the sample the signal cannot be recreated by irradiation. This effect (observed in foraminifera (Barabas *et al.* 1988), shells and corals (Katzenberger *et al.*, 1989, Walther *et al.*, 1992)) contributes to the observed decrease of the signal amplitude and may thus lead to wrong conclusions about the life time of the signal.

In the results mentioned above, no special care has been taken of probably existing short-life components nor of the observed trap decay of this signal. So those values are just indicating the general range of life time.

Determination of the Life Time from Sediment Cores

Another approach of the determination of the signal life time or the detection of long-term fading is the comparison of the growth of a signal on artificial irradiation with its natural growth (i.e. during burial time by environmental radiation). It is assumed that the difference is due to the fading of the signal. Details are given in equivalent models by Barabas *et al.* (1988), Mejdahl (1988), and Hütt and Jaek (1989).

Sediment cores with known ages and known dose rates enable us to calculate the accumulated dose a sample (foraminifera) has received. Comparing the natural (normalized) signal amplitude of a specific sample with the signal amplitude that is caused by the same quantum of γ-radiation allows the calculation of the life time for this sample numerically taking into account its age. By this method Barabas *et al.* (1988) showed that the signal at $g = 2.0006$ in foraminifera is far less stable than expected from isothermal annealing experiments. Assuming a constant dose rate a life time of about 450 ka (at 2°C) was derived which results in ADs too small for samples older than about 50 ka.

We have analyzed the growth behaviour of the signal at $g = 2.0006$ with a higher precision in the deep-sea sediment core RC17-177 and derived more precise conclusions about the long-term stability of the signal at $g = 2.0006$.

EXPERIMENTAL

Calcitic foraminifera samples from sediment core RC17-177 were measured from 40 depths and a span of about 800 ka ($\delta^{18}O$ stratigraphy). The $\delta^{18}O$-ages of each sample were known up to a maximum age of about 750 ka (Shackleton, *pers. commun.*).

Signal amplitudes were recorded (Bruker ESP-300 Spectrometer) as a function of the artificial γ-dose (^{60}Co; calibration with alanin-dosimeter) with 15 irradiation steps for each sample (up to 8 kGy).

The concentrations of ^{238}U, ^{232}Th, and ^{40}K have been measured. The excess ^{230}Thorium, Th_{xs}, was measured in the samples younger than 200 ka (initial $Th_{xs} = 5.55$ dpm/g); the k_α factor was measured to be 0.1; the water content was estimated to range between 50 and 60%. For the calculation of the time dependent dose rate (dose-conversion tables given by Nambi and Aitken, 1986) an infinite matrix radiation field was assumed. Details are given elsewhere (Mudelsee *et al.*, 1992).

RESULTS

According to Barabas *et al.* (1988) the natural growth of a signal is given as:

$$dS(t)/dt = P(t)/D_0 * [K - S(t)] - S(t)/\tau \qquad (2)$$

The first term presents the growth of the signal size, S, proportional to the amount of unfilled traps, $(K-S)$, and the dose rate, P, the second the (first order) thermal decay with the life time, τ. From Eq. 2 the natural increase of the signal can be calculated numerically, taking into account the *time-dependent dose rate* resulting from excess ^{230}Thorium. The parameters D_0 (= saturation dose) and K (= number of traps = saturation level S_{max}) can be derived from the signal increase on γ-irradiation (Eq. 1).

From the differences between natural (measured) signal and calculated signal (Fig. 7), the life time for

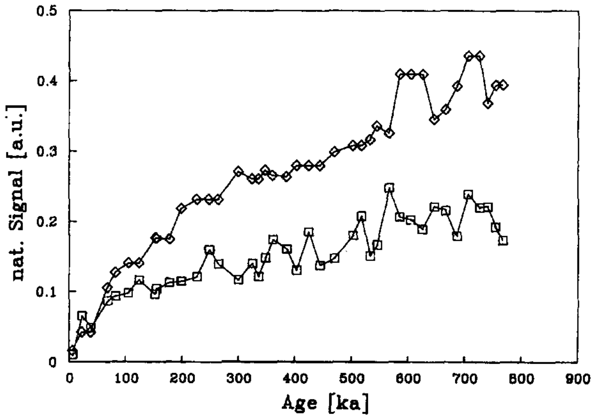

FIG. 7. Comparison of the (normalized) natural measured signal at $g = 2.0006$ (□) and the signal amplitude as calculated from the total dose the sample has received (from U, Th, K content) and the saturation dose as determined from the signal growth curves on artificial irradiation (◇). The difference is due to fading of the signal and increases with age.

each depth was calculated (Fig. 8). It exhibits the same range that was deduced earlier (ibid.) but displays a distinct increase of the signal life time with the age of the samples. Obviously the use of this model (one component, first order kinetics) has not been correct.

In order to explain the strange behaviour we calculated the signal growth for various assumptions (Fig. 9a,b). Finally this resulted in a model that assumes two (equal weighted) components one of which has a short life time of about 50 ka, while the other was assumed to be stable on the time scale in question (Fig. 9b). In this case a good agreement was found between measured and calculated values.

It has to be noted that the behaviour could not be well described by assuming a higher than first order kinetics.

CONCLUSION

(a) *Signal-Growth Curves*

From our (and other) experiments, followed that the signal growth curves can be described by a single saturation function only in a small dose range of not more than 1 kGy. In this low dose range, the parameter D_0 is varying by a factor of about 2 (400–800 Gy). However, this range seems to be valid for all carbonates.

An AD determination should be possible in the range < 250 Gy with a sufficient precision (better than 10%). Exceeding this range means to increase the statistical uncertainty and to introduce systematic errors.

The main question remaining in this complex is whether or not a trap creation takes places during γ-irradiation. It should be easy to carry out the adequate experiments. In future research it should also be investigated whether some parameters (saturation dose?, γ?) can be treated as constant generally, which would increase the fit accuracy even when using more complex fit functions. In this case the AD range could be enlarged.

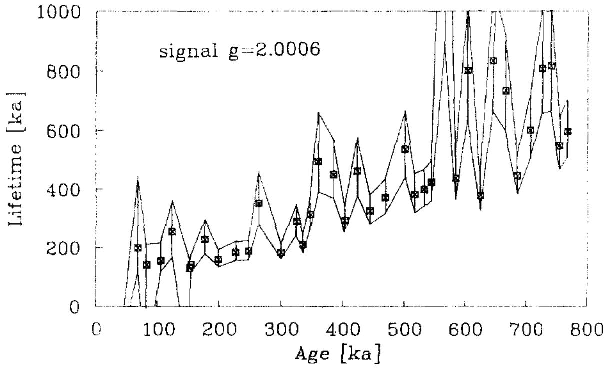

FIG. 8. Life times calculated numerically from the differences in Fig. 7. Error bars indicate life time results for ± 10% different natural signal amplitude. The life time seems to increase with the age of the sample.

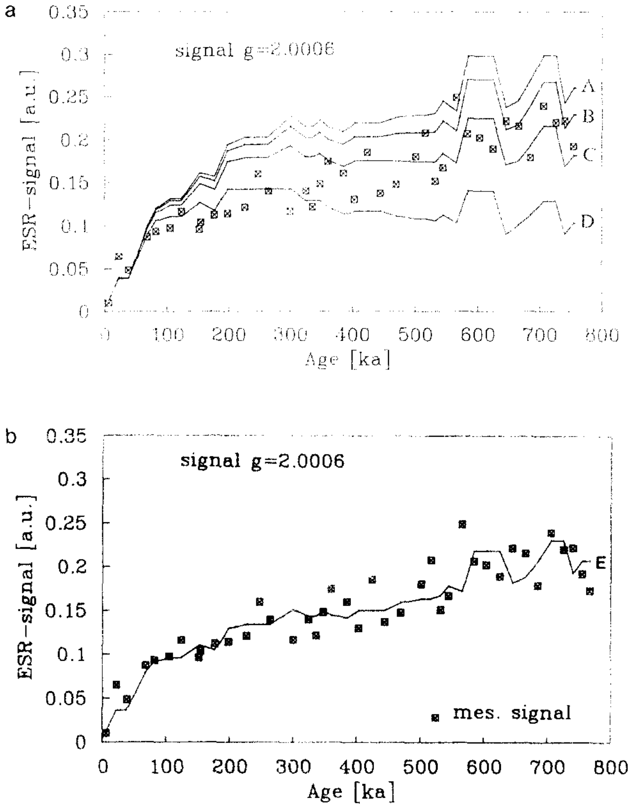

FIG. 9. Model calculation of the signal amplitudes (—): (a) assuming different life times and one component: A — 1 Ma, B — 750 ka, C — 500 ka, D — 250 ka; (b) E — assuming two components (1:1) one of which has a short life time of about 50 ka.

(b) *Stability/Fading*

In general the decay behaviour of the signal cannot be described with first order kinetics. As there is a connection between trap depth and probability of capturing an electron by this trap (i.e. between life time and saturation dose; Levy, *pers. commun.*) this finding fits with the observed growth curves on γ-irradiation, i.e. it is most probable that components with different properties contribute to the dating signal.

Furthermore the situation is complicated by the decay of traps (= sensitivity change due to heating), which may or may not have an influence on the long-term stability at ambient temperatures. Therefore the application of the Arrhenius plot seems inadvisable.

A derivation of the life time from the ratio between the natural signal growth and the growth on γ-irradiation as shown for sediment cores seems to be more trustworthy. Our findings from sediment cores as well indicate the existence of different components. The short life time of the unstable component of this signal derived from the sediment cores also demonstrate that conclusions from Arrhenius plots may be dramatically wrong.

If this unstable component would be a general property of the ESR signal at $g = 2.0006$ — that is what the decay behaviour of this signal in various carbonates indicates — it would mean that dating is not possible using this signal, even more as it seems to be less stable in aragonitic material.

The question remains: How do we get such old ages as 200 ka in corals without any indication for a systematic underestimation (Radtke and Grün, 1988)? This has to be checked carefully by precise comparisons of ESR ages and Th/U ages.

Another approach to derive life times uses very old samples that have reached the equilibrium between filling of the traps by radiation and thermal release of electrons (Barabas *et al.*, 1988; Hütt and Jaek, 1989). This, however, should only be applied to calcites because in very old aragonitic samples generally recrystallizations have occurred. We plan to expand our examination with sediment cores up to ages of 2 Ma. This will reveal how the signal growth continues in time and whether the assumed models are correct.

ACKNOWLEDGEMENTS

We gratefully acknowledge N. Shackleton (Cambridge) for providing us with the samples from RC17-177 and J. Scholten (Kiel) for recent foram samples. Thank you to Professor Neugebauer (MPI Heidelberg) and A. Wieser (GSF München) who placed their ESR machines at our disposal. This study was financially supported by the Deutsche Forschungsgemeinschaft (Ma 821/5).

REFERENCES

Barabas, M. (1989). ESR-Datierung von Karbonaten: Grundlagen, Systematik, Anwendungen. Ph.D. Thesis, Heidelberg, 161 pp.

Barabas, M., Bach, A. and Mangini, A. (1988). An analytical model for ESR-signals in calcite. *Nuclear Tracks and Radiation Measurements*, **14**, 231–235.

Barabas, M., Bach, A., Mudelsee, M. and Mangini, A. (1992). General properties of the paramagnetic centre at g = 2.0006 in carbonates. *Quaternary Science Reviews*, **11**, 165–171.

Grün, R. (1985). *Beiträge zur ESR-Datierung*. Geologisches Institat Universtät Köln, Sonderveröffentlichung No. 59, 157 pp.

Grün, R. (1989). *Die ESR-Altersbestimmungsmethode*. Springer, Berlin, 132 pp.

Grün, R. (1990). Dose response of the paramagnetic centre at g = 2.0007 in corals. *Ancient TL*, **8**(3), 20–22.

Grün, R. and McDonald, P.D.M. (1989). Non linear fitting of TL/ESR dose response curves. *Applied Radiation and Isotopes*, **40**, 1077–1080.

Hütt, G., Molodkov, A., Kessel, H. and Raukas, A. (1985). ESR dating of subfossil holocene shells in Estonia. *Nuclear Tracks and Radiation Measurements*, **10**, 891–898.

Hütt, G. and Jaek, J. (1989). Dating accuracy from laboratory reconstruction of palaeodose. *Applied Radiation and Isotopes*, **40**, 1057–1061.

Katzenberger, O. and Grün, R. (1985). ESR-dating of circumartic molluscs. *Nuclear Tracks and Radiation Measurements*, **10**, 885–890.

Katzenberger, O. (1989). Experimentelle Untersuchungen zur ESR-Datierung von Molluskenschalen. Ph.D. Thesis, Sonderveröffentlichungen Geologisches Institut Universität Köln, No. 72, 71 pp.

Katzenberger, O., Debuyst, R., DeCanniere, P., Dejehet, F., Apers, D. and Barabas, M. (1989). Temperature experiments on mollusc samples: an approach to ESR signal identification. *Applied Radiation and Isotopes*, **40**, 1113–1118.

Lyons, R.G., Bowmaker, G.A. and O'Connor, C.J. (1988). Dependence of accumulated dose in ESR dating on microwave power. *Nuclear Tracks and Radiation Measurements*, **14**, 243–251.

McKeever, S.W.S. (1985). *Thermoluminescence of Solids*. Cambridge University Press, Cambridge, 376 pp.

Mejdahl, V. (1988). Long-term stability of the TL signals in alkali feldspars. *Quaternary Science Reviews*, **7**, 357–360.

Mitchell, P.V., Wiegand, D.A. and Smoluchowski, R. (1961). Formation of F centres in KCl by X-rays. *Physics Reviews*, **121**, 484–498.

Molodkov, A. and Hütt, G. (1985). ESR dating of subfossil shells: some refinements. *In*: Ikeya, M. and Miki, T. (eds), *ESR-Dating and Dosimetry*, pp. 145–155.

Molodkov, A. (1986). Application of ESR to the dating of subfossil shells from marine deposits. *Ancient TL*, **4**, 49–54.

Molodkov, A. (1988). ESR dating of quaternary shells: recent advances. *Quaternary Science Reviews*, **7**, 477–484.

Molodkov, A. (1989). The problem of long-term fading of absorbed palaeodose on ESR-dating of quaternary mollusc shells. *Applied Radiation and Isotopes*, **40**, 1087–1093.

Mudelsee, M., Barabas, M. and Mangini, A. (1992). ESR dating of the quaternary deep-sea sediment core RC17-177. *Quaternary Science Reviews*, **11**, 181–189.

Nambi, K.S.V. and Aitken, M.J. (1986). Annual dose conversion factors for TL and ESR dating. *Archaeometry*, **28**, 202–205.

Radtke, U., Mangini, A. and Grün, R. (1985). ESR-Dating of marine fossil shells. *Nuclear Tracks and Radiation Measurements*, **10**, 879–884.

Radtke, U. and Grün, R. (1988). ESR dating of corals. *Quaternary Science Reviews*, **7**, 465–470.

Sato, T. (1981). ESR dating of calcareous microfossils in deep-sea sediment. *Rock Magnetism and Paleogeophysics*, **8**, 85–88.

Sato, T. (1982). ESR dating of planctonic foraminifera. *Nature*, **300**, 518–521.

Siegele, R. and Mangini, A. (1985). Progress in ESR-Studies on $CaCO_3$ of deep sea sediments. *Nuclear Tracks and Radiation Measurements*, **10**, 937–943.

Smith, B.W., Smart, P.L. and Symons, M.C.R. (1985). ESR signals in a variety of speleothem calcites and their suitability for dating. *Nuclear Tracks and Radiation Measurements*, **10**, 837–844.

Walther, R., Barabas, M. and Mangini, A. (1992). Basic ESR studies on recent corals. *Quaternary Science Reviews*, **11**, 191–196.

Wieser, A., Göksu, H.Y. and Regulla, D.F. (1985). Characteristics of γ-induced ESR spectra in various calcites. *Nuclear Tracks and Radiation Measurements*, **10**, 831–836.

Yokoyama, Y., Quaegebeur, J.P., Bibron, R. and Leger, C. (1983). ESR dating of Paleolithic calcite: Thermal annealing experiment and trapped electron life time. *PACT*, **2**, 371–379.

Yokoyama, Y., Bibron, R., Leger, C. and Quaegebeur, J.P. (1985). ESR dating of Paleolithic calcite: fundamental studies. *Nuclear Tracks and Radiation Measurements*, **10**, 929–936.