Ancient TL

Dispersive decay kinetics and dose responses of isotropic radicals in natural carbonates

R. Debuyst, S. Idrissi and F. Dejehet

Université catholique de Louvain
Laboratoire de chimie inorganique et nucléaire,
2, chemin du Cyclotron, B-1348 Louvain-la-Neuve, Belgium

Abstract : *The isotropic signals at g = 2.0006 and g = 2.0057 in marine carbonates are due to freely rotating CO_2^- and SO_2^- radicals respectively. We have investigated the kinetics of these signals by selecting a fossil coral exhibiting a simple ESR spectrum. Various kinetic approaches were considered, including diffusion-controlled mechanisms and dispersive kinetics with time-dependent rate constant. The best decay description was found to be the second-order equal concentrations dispersive equation. Some dose response curves of modern coral and mollusc shell obtained by Çetin et al (1993) could be fitted with a single dispersive model with a time-dependent radical-creation efficiency. These dispersive models allow satisfactory fittings over the entire ranges of doses or time, with a minimum number of parameters.*

Introduction

Kinetics

The isotropic ESR signals at g = 2.0006 and g = 2.0057, due to rapidly rotating CO_2^- and SO_2^- radicals, are potential dating signals (Ikeya, 1993; Brumby and Yoshida, 1994; Martinez-Walter, 1994). They are thought to be located in the occluded water surroundings of the constituent crystallites of the material (Callens *et al.*, 1994; Idrissi *et al.*, 1996).Their thermal stability at room temperature is normally estimated by extrapolating Arrhenius plots from higher temperature isothermal annealing data. These isothermal annealing curves have been described in the literature by different mechanisms : first-order, two or three first-order reactions occurring simultaneously and independently of each other with different rates, 1.5 - or second-order or even third-order reactions (Debuyst *et al.*, 1995 and references therein). The purpose of the present work is to look at this problem by adding other kinetic descriptions and to try to fit the annealing curves with a minimum of parameters. Therefore, good quality experimental data are necessary. This is not a trivial problem for the following reasons. First, the concentration of the radicals should be measured by the double integral of the ESR signal, but the results are doubtful because of the overlapping of Lorentzian lines and contribution of anisotropic signals. Spectrum deconvolution is a tedious and not always unambiguous procedure. The ESR intensity is usually estimated by the peak to peak height of the signal but the line width should then be checked to be a constant during the thermal annealing or irradiation. Secondly, when a natural sample is irradiated with a γ source, anisotropic signals with variable thermal stabilities are also produced, which again perturb the isotropic signals ("shoulders and dips" appear) and alter line shape, line width and height. The annealing time needed to get rid of these perturbations varies from sample to sample. Thirdly, after laboratory irradiation, the ESR intensity often decreases only after an initial increase of the signal, revealing the presence of a precursor feeding the isotropic signals (see also Lyons, 1996). In the case of the SO_2^- radical, this "initial" increase is sometimes the only feature observed even after a long time period (Martinez-Walter, 1994; Brumby and Yoshida, 1995). Finally, the decay kinetics should be performed over a long annealing time period, which is not frequently encountered in the literature. We tried to avoid some of these difficulties by selecting a fossil coral sample from the Barbados (Kendal Hill) (given to us by U. Radtke, with an approximate age of 2.10^5 years) exhibiting an apparently simple ESR spectrum consisting principally of the two isotropic lines of CO_2^- and

SO$_2^-$ with a small contribution of a signal at g = 2.0032 due to SO$_3^-$ (Barabas, 1992) whose decay has not been studied. The derivative ESR spectrum with a small dip at g = 1.9972 around 3490 Gauss and the corresponding integrated spectrum reveal the presence of anisotropic CO$_2^-$ species and show the long wings of the isotropic Lorentzian line shapes (Fig. 1). The signals were sufficiently high so that no laboratory irradiation was needed and no initial increase observed. Furthermore, the line width of the two species were found to be constant during the annealing time : 1.65 ± 0.05 Gauss for CO$_2^-$ and 0.72 ± 0.01 Gauss for SO$_2^-$ so that we used the peak-to-peak height for estimating the radical concentration. In doing so, the values of the CO$_2^-$ signal at the end of the thermal annealing are slightly overestimated because of the presence of a small anisotropic CO$_2^-$ residue.
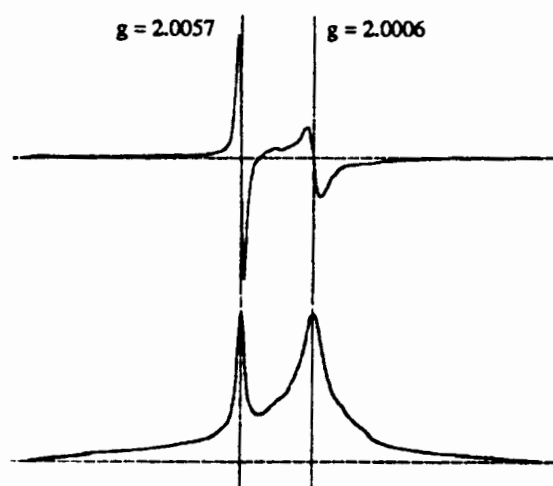
Experimental

ESR spectra have been recorded at room temperature with a Bruker ER 200tt X-band spectrometer, connected to a Stelar computer system, at a power of 20 mW and a modulation amplitude of 0.5 Gauss. The spectrum of an independent Mn^{++} sample was taken as a reference before and after each annealing experiment. The temperature at which the sample has to be annealed should be neither too high (the radicals are surrounded by water molecules whose departure must be avoided) nor too low (for evident duration considerations). A temperature of 160°C has been chosen. The annealings were performed by putting the sample into an oven and regularly removing it for ESR measurement. The CO$_2^-$ radicals disappeared completely after approximately 10 days annealing (Fig. 2), whereas the SO$_2^-$ radicals were still present after 40 days (Fig. 3).
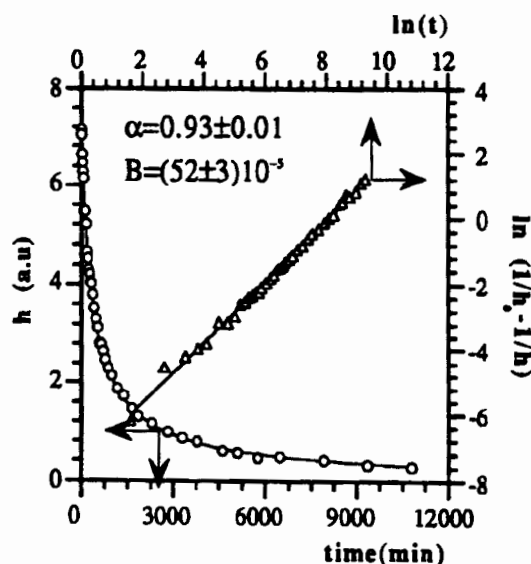

Figure 1.
First-derivative and absorbtion ESR spectra of the fossil coral showing the SO$_2^-$ signal at g= 2.0057 on the left and the CO$_2^-$ signal at g = 2.0006 on the right.

Figure 2.
Decay of CO$_2^-$ at 160°C in fossil coral, fitting equation (1) in normal (height versus time) and linearized (logarithmic) forms. The arrows indicate the relevant axes.

Dose response

It is well known that a single saturation curve is not able to fit dose response curves at high doses (> 10^3 Gy). Several models have been suggested in order to improve the fittings : linear or exponential creation of additional traps by irradiation , decrease of the radical-creation efficiency, combination of two or three single exponential saturation functions (Çetin *et al.*, 1993 and references therein). Because our kinetic results are in favour of a time-dependent rate constant, we tried to reproduce the dose response data of Çetin *et al.* (1993) with analogous time-dependence of the radical-creation efficiency.

Results and discussions

Kinetics

For a rapid checking of the relevance of the various kinetic models, linearized forms were used for both CO_2^- and SO_2^- decays. Plots of $\ln(I_o/I)$, where I is the ESR intensity (height) and I_o the initial intensity, I_o/I, $(I_o/I)^2$, $(I_o/I)^{0.5}$ versus t (time) allow to eliminate the classical first-, second-, third- and 1.5- order reactions. A second-order reaction with a non-decaying fraction has been investigated by plotting $t/(I_o-I)$ versus t (Dole, 1988). A mixture of first- and second-order reactions has been tested by plotting $\ln((I/I_o + I_o\lambda\tau)/(1 + I_o\lambda\tau))$ versus t (τ and λ are the first-order decay time and the second-order rate constant respectively) (Ikeya, 1992). Diffusion-controlled reactions need plots of $\ln(I_o/I)$ versus $t^{0.5}$ (first-order) and $(1/I -1/I_o)t^{0.5}$ versus $t^{0.5}$ (second-order) (Kantoglu et al., 1995). Plots of I versus $\ln(t)$ have also been proposed by Brumby and Yoshida (1995). Finally, non-classical, inhomogeneous or dispersive kinetics with a time-dependent rate constant ($k(t) = Bt^{\alpha-1}$, B and α are constants, $0 < \alpha \leq 1$) (Plonka, 1991a) have been investigated with $\ln(\ln(I_o/I))$ versus $\ln(t)$ (first-order) and $\ln(I_o/I)$ versus $\ln(t)$ (second-order equal concentrations). The decay of both radicals was found to be best described with the latter model (Fig. 2 and 3) involving the following equation :

$$c^{-1} - c_o^{-1} = B\alpha^{-1} t^\alpha \qquad (1)$$

where c and c_o are the radical concentrations at t and $t_o = 0$. With a non-decaying fraction A, the equation becomes

$$(c-A)^{-1} - (c_o-A)^{-1} = B\alpha^{-1}t^\alpha \quad (2),$$

which can be rewritten as

$$(c_o-c)^{-1} = (c_o-A)^{-1} + \alpha/(Bt^\alpha(c_o-A)^2) \quad (3).$$

The parameter values indicated in the figures were obtained from the linearized forms. In dispersive kinetics, the activation energy increases with time and the parameter α is interpreted as a measure of the dispersion of the activation energy in these disordered systems.

In the case of SO_2^-, the fitting was optimized by taking account of a non-decaying fraction A, corresponding to the existence of a plateau. Such plateaus were observed by Martinez-Walter (1994), who used them for dating purposes. The dispersive second-order model has been already

found convenient for isotropic CO_3^- and CO_2^- radicals in laboratory irradiated synthetic monohydrate and biocarbonates where activation energies could be calculated (Debuyst et al., 1995). It implies only 2 parameters : B and α, eventually 3 if A is unknown.
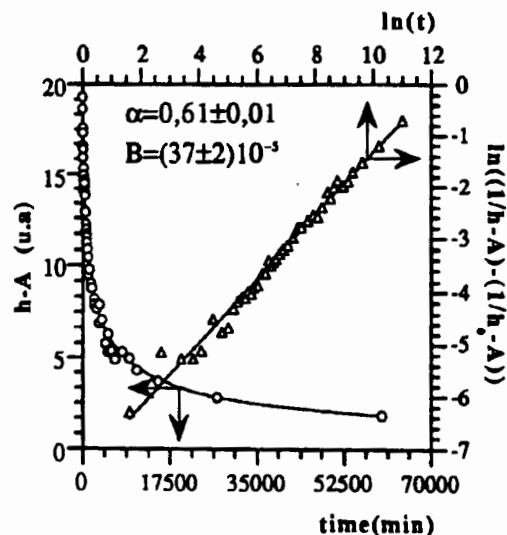

Figure 3.
Decay of SO_2^- at 160°C in fossil coral, fitting equation (2) in normal (h-A versus time) and linearized (logarithmic) forms. Here A = 5 a.u.

Dose response

Çetin et al. (1993) described their dose response curves for the isotropic CO_2^- in modern aragonitic coral and shell samples by a combination of three single exponential saturation functions. They also described their isothermal decay curves by the combination of three first order decay functions. We tried to fit their dose response data (table 1, p. 676 in Çetin et al., 1993) with models implying less parameters. The possibility of a linear creation of traps yields the following function :

$$I = (K_o - b/a) (1 - \exp(-aDt)) + bDt \qquad (4),$$

where K_o is the number of traps before the irradiation, D the dose rate, a (and b) the radical - (and trap-) creation efficiency (Levy, 1989). By analogy with the dispersive kinetic model, we consider a time-dependent radical-creation efficiency $a = a't^{\alpha-1}$ ($0 < \alpha \leq 1$). The following function is then derived by integration :
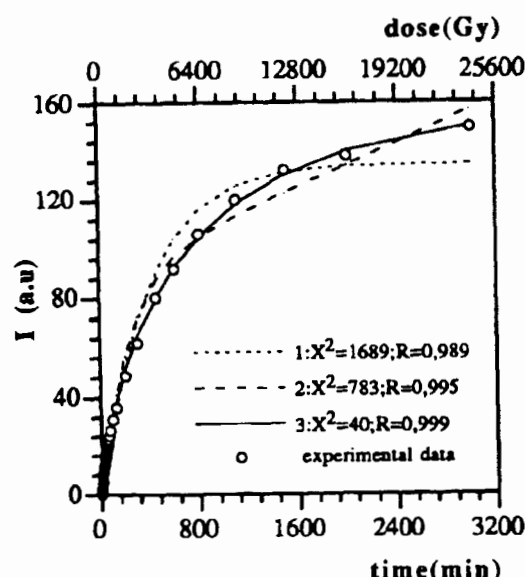
$$I = K(1-\exp(-a'Dt^\alpha/\alpha)) \qquad (5).$$

Figure 4.
Dose response of a modern shell (data of Cetin et al., 1993). Model 1 : single exponential saturation function ; model 2 : equation (4) ; model 3 : equation (5).

Figure 5.
Dose response of a modern coral (data of Cetin et al., 1993). Same models as in figure 4.

This equation is equivalent to that of Grün and McDonald (1989) with their phenomenological exponent Γ. Indeed, as pointed out by Barabas *et al.* (1992) and Walther *et al.* (1992), the latter equation assumes $a = a'(Dt)^{\Gamma-1}$ which yields by integration $I = K(1-\exp(-a'(Dt)^{\Gamma}/\Gamma))$. Time-dependent radical-creation efficiencies were also considered by Çetin *et al.* (1993) and Martinez-Walter (1994). Figures 4 and 5 show the fitting with a normal exponential saturation function and the two aforementioned functions. The dispersive model yields the fitting with the best statistical characteristics (χ^2 and R with the KaleidaGraph program). Çetin *et al.* (1993) found also good results with an equivalent model but they prefered globally the combination of three exponential saturation functions. The data of Grün (1990) were best described with the model including a production of defects by irradiation. The model with the exponent Γ was rejected because Γ was found to decrease as more data were added in the fittings ($\Gamma =1$ for ~ 200 Gy compared to $\Gamma=0.85$ for ~ 700 Gy, the maximum dose used in this study). The dose interval in Çetin's data is much higher (0-2.10^4 Gy). As also stressed by Martinez-Walter (1994), the exponent α allows a quite satisfactory fitting of the curvature at higher doses (here, around 5-6000 Gy). In the case of modern mollusc shell (see Fig. 4) which offers the broadest dose interval and number of aliquots (59), the fitted parameters are $K = 160 \pm 1$ a.u., $a = 0.736 \pm 0.005$ and $a' = (136 \pm 3)10^{-5}$ $Gy^{-1}min^{1-\alpha}$
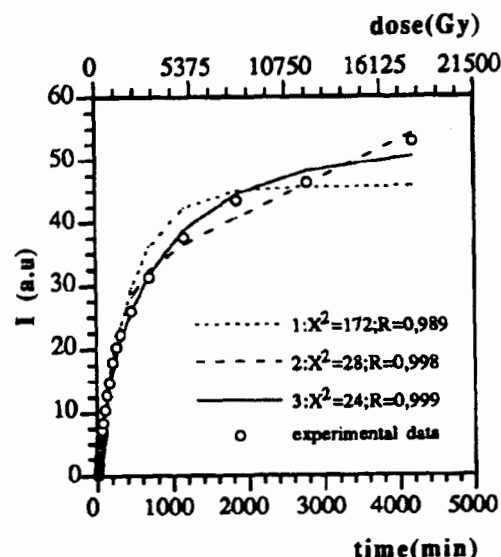
If data are removed one by one from the high to the low dose region, the same set of values is able to fit the experimental data, provided that this set is introduced as guessed values in KaleidaGraph. The value of a remains 0.74 ± 0.04 from 21000 to ~250 Gy. Below ~250 Gy, it tends to increase progressively and reaches 0.88 at ~ 100 Gy, but the role of α in this region is weak and the errors in K and a' are tremendous (100% around 350 Gy). So, in our opinion, dispersive dose response should be reconsidered all the more as dispersive kinetics yield satisfactory results.

Conclusions
Decay kinetic and dose response curves over long time periods could be fitted with models implying time-dependent rate constant and radical-creation efficiency : the probability for radical decay or creation is supposed to decrease with time. The transition from classical to dispersive models implies the replacement of time by $(time)^{\alpha}$. In dispersive kinetics, the increase in activation energy with time is due either to depletion from the system of more reactive species or to local matrix relaxation making all species progressively less reactive. (Plonka, 1991b). In dose response, the creation of radicals could decrease with irradiation time due to the creation of more and more competitive species. The dispersive models which are able to fit the data of the isotropic radicals (CO_2^-, CO_3^-, SO_2^-) in natural and synthetic carbonates should be considered in ESR dating.

Acknowledgements

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Reviewer
R. Grün

Comments : We can be grateful to Debuyst *et al.* to present a comprehensive model for the thermal decay and dose response of the paramagnetic centre at g=2.0007 in corals. Although the time

dependent radical creation model seems best suited to describe the overall dose response of this centre, there are some problems in the lower dose range ($< \sim 250$Gy) where the exponent α changes. However, for dating purposes, this dose range has to be exactly known as most samples (<250,000 years) will have dose values of < 250 Gy.