

Further comments on decay kinetics of isotropic radicals in carbonates

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Abstract : This work is a continuation of previous investigations on decay kinetics of isotropic radicals in carbonates (Ancient TL, 1997, 15, 30-35). It rules out a model implying only chemical reactions between CO_2^- and CO_3^- radicals, questions the use of a sum of first-order kinetics and supports the dispersive second-order equal concentration kinetics with a time-dependent rate constant.

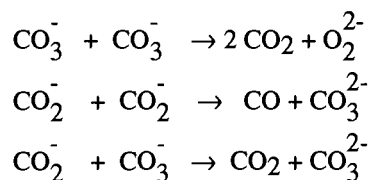
Introduction

Recently, we studied the decay kinetics of isotropic radicals (CO_2^- , CO_3^- , SO_2^-), located in a disordered environment of protons of the occluded water (Callens *et al.*, 1994; Idrissi *et al.*, 1996), in synthetic monohydrocalcite and natural carbonates (Debuyst *et al.*, 1995, 1997). We considered various kinetic approaches including diffusion-controlled mechanisms and dispersive kinetics with a time-dependent reaction rate of the form $k(t) = Bt^{\alpha-1}$ (B and $0 < \alpha \leq 1$ are constants). The best decay description was found to be the second-order equal concentrations dispersive equation (Plonka, 1991), as, with only two parameters, it could satisfactorily fit all the kinetic data (provided that the annealing temperature is lower than that of the water departure). The radicals are supposed to diffuse and recombine together (2CO_2^- or 2CO_3^-), as was previously proposed (Hisatsume *et al.*, 1970) or react with an equal number of complementary centers (electron center + hole center, $\text{CO}_2^- + \text{CO}_3^-$) (Ikeya, 1993), but with an in-time-decreasing reaction rate. Dispersive models have been successfully applied to reaction kinetics of radiation produced species in condensed media (i.a. ice, polymers, drugs) (Plonka, 1990; Kantoglu *et al.*, 1995; Miyazaki *et al.*, 1994). A distribution of reaction rates or activation energies may indeed be expected in disordered, non-homogeneous systems.

The parameter α is a measure of the dispersion of reactivity due to spatial, temporal or energetic disorder of the system. So, the model has also a well-founded physical basis and seems to be suitable to an occluded water environment.

In the present note, we further investigated kinetics for the following reasons. First, some colleagues (chemists) criticized us for not having explicitly considered the chemical reactions between CO_2^-

and CO_3^- which are the only radicals observed in the ESR spectra of irradiated synthetic monohydrocalcite. The following reactions may be proposed (Hisatsume *et al.*, 1970) :



The corresponding differential equations for both **coupled** radicals can be solved **numerically**. In case of satisfactory fitting, this model based on chemical reactions and constant reaction rates may be an alternative to the dispersive model.

Second, we reconsider also the possibility that each kinetic curve is a sum of exponential functions. This is the model generally used in dating : several first-

order reactions occurring simultaneously and independently of each other with different rates. Çetin *et al.*, 1993, e.g., proposed for their data a sum of three exponentials. Using their data, we demonstrated that dispersive kinetics explained just as easily the entire decay curves with fewer parameters (Debuyst *et al.*, 1995). The number of localization sites (three) seemed to us also quite arbitrary in the multi-exponential model. Different environments with different activation energies for the radical can, however, be considered e.g. in the bulk or at the surface of the constituents of the material (here, the occluded water). A similar situation is encountered e.g. in tooth enamel, where two types of anisotropic CO_2^- radicals with very similar g-values are produced and are difficult to distinguish in EPR powder spectra (Callens, 1997). The multi-exponential model is thus again reconsidered here by means of the "spectral analysis" used by one of us (M.B.) in another research field (Cunningham and Jones, 1993).

As will be seen in the Results, the dispersive model seems to us still the most satisfactory one. Kinetic curves exhibiting an initial increase are here also analysed within the framework of this model. An initial increase is indeed quite common to both laboratory- irradiated synthetic and natural carbonates. Moreover, α values for the radicals in monohydrocalcite in a wide range of temperature (303-443 K) are also presented.

Experimental data

The following experimental data were used in this work :

a) the data for CO_2^- and CO_3^- of Debuyst *et al.*, 1995, where γ -irradiated (2700 Gy) synthetic monohydrocalcite was thermally annealed at 371, 391, 417 and 443 K ; new experimental data at 303, 333 and 403 K (for the last temperature at 3000 and 9000 Gy) were added ;

b) the data of Çetin *et al.*, 1993, concerning CO_2^- in a fossil mollusc annealed at 493, 513 and 522 K.

Theory

For both following methods, the parameters of the models were fitted to the data using the Levenberg-Marquardt algorithm (Press *et al.*, 1990).

Differential equations for connected kinetics

The decay of both CO_2^- and CO_3^- can be described by the following equations (1) :

$$\frac{d[\text{CO}_2^-]}{dt} = -p_1[\text{CO}_2^-]^2 - p_2[\text{CO}_2^-][\text{CO}_3^-] - p_4[\text{CO}_2^-]$$

$$\frac{d[\text{CO}_3^-]}{dt} = -p_2[\text{CO}_2^-][\text{CO}_3^-] - p_3[\text{CO}_3^-]^2$$

where p_1 , p_2 , p_3 and p_4 are the parameters to be fitted to the data. The first three parameters correspond to the chemical reactions presented in the Introduction, whereas the fourth is a supplementary one describing a possible first-order reaction mechanism for CO_2^- . Equations (1) (with and without parameter p_4) were numerically solved by ordinary differential equations method implemented as ODE 23 in Matlab software. The fitting procedure can be applied to the data of each radical separately.

Exponential functions

Because the number of exponential functions is initially not known and only some functions are retained from as much as 50 functions used to fit the data, this method is called spectral analysis (Cunningham and Jones, 1993). The data of the radical were assumed to be a combination of n exponential functions (2) :

$$f(t) = c_1 \exp(-b_1 t) + c_2 \exp(-b_2 t) + \dots + c_n \exp(-b_n t)$$

where the coefficients c_i ($i = 1, n$) are non-negative constants. t is the sampling time of the curve and is a column vector of size m . The number of terms n is initially arbitrarily chosen to be large enough to explore the range of physical true constants ($n = 50$). The exponents b_i sequentially take the n values from an arbitrarily small value ($b = 10^{-5}$) to $b = 1$. Equation 2 can be written in a matrix form:

$$[E] \cdot [C] = [F_2] \quad (3)$$

where the $m \times n$ matrix $[E]$ is formed by the exponential functions, $[C]$ is the n elements vector of coefficients and $[F_2]$ is the m data points to be fitted. The coefficients c_i can be obtained by solving equation (3) using the non-negative least square (nnls) algorithm (Lawson and Hanson, 1974). The few c values satisfying both equation 3 and the non-negativity constraint, together with their corresponding b values, form the requested exponential functions (in general, only 2 to 6 terms are obtained from the initial 50). This technique

generally gives some parameters split in two values and this effect is due to the finite sampling of the b values. These two values can be averaged to form one exponential function and these parameters are further fitted to more precisely adjust the data.

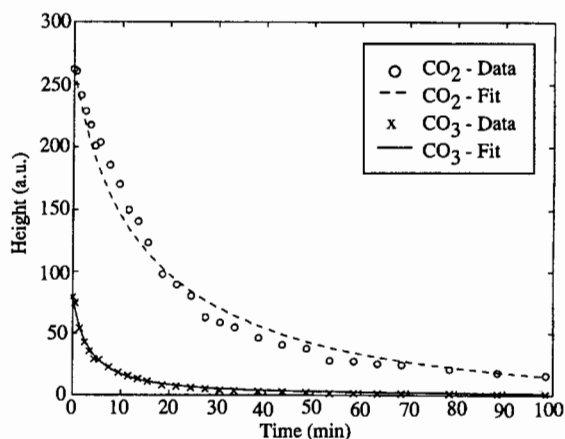


Figure 1.

Fitting CO_3^- data of monohydrocalcite annealed at $T=443$ K as described by eq 1 without parameter p_4 , followed by fitting CO_2^- data with p_4 (see text).

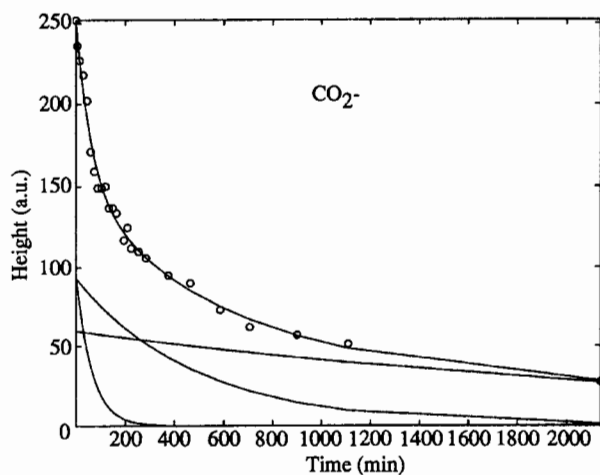


Figure 2.

Decomposition of CO_2^- radicals in monohydrocalcite in their exponential functions for data at 417 K. Here, the decomposition was constrained to 3 components. Their sum is shown to accurately fit the data.

Spectral analysis provides all the exponential functions giving the best approximation to the data. However, statistical fluctuations in the data can generate one or more components recognisable by their shape, which can be omitted and the remaining

parameters are fitted to the data, thus constraining the decomposition to physical components.

Results

A. Kinetics

The kinetic data of CO_2^- and CO_3^- in monohydrocalcite are connected in Equations (1). These equations, without parameter p_4 , were not able to fit both kinetic curves. The best results were obtained by fitting first, satisfactorily, the curve of CO_3^- , and afterwards, but badly, that of CO_2^- . Figure 1 shows the data at 443 K with a good fit for CO_3^- ($p_3/p_2 \cong 8$)

The calculated values for CO_2^- are however already too high after about ten minutes heating time (not shown on the figure). Keeping these values of p_1 , p_2

and p_3 , a better but insufficient fit for CO_2^- was obtained by adding the fourth parameter p_4 ($p_4 \gg p_1, p_2$) (shown on figure 1). Similar or worse results are obtained for the other data of Debuyst *et al.*, 1995 plus the new ones at 403 K. This model should thus be abandoned.

B. Sum of exponentials

The program of spectral analysis was used with the experimental data of both monohydrocalcite and fossil mollusc. Two options were chosen: no constraint at all for the number of components and elimination of too small components followed by a new fit with a fixed number of components. Even with no constraint, only three components were found for the data of the fossil mollusc, whereas, in the case of monohydrocalcite, up to six components appeared that could be reduced to three or two after elimination of small contributions (see Fig. 2 as an example). Figures 3 and 4 show the Arrhenius plots

obtained for CO_2^- in both compounds. The values indicated in these figures are those of the coefficients c expressed in %. At 403 K, the data for 3000 Gy yielded two components (noted \diamond in figure 4), whereas those for 9000 Gy had three components. The results for the fossil mollusc are better than those for monohydrocalcite: the corresponding c values at different temperatures are close to each other. Those of monohydrocalcite (CO_3^- included,

whose results are not shown) are definitely less conclusive.

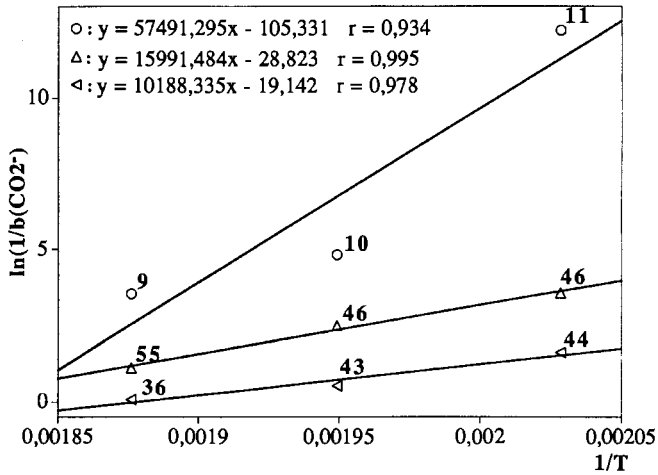


Figure 3.
Arrhenius plots for the three exponential functions (symbols : circle, triangle up and triangle left) of CO_2^- in fossil mollusc annealed at $T = 493, 513$ and 533 K. The numbers beside the symbols represent the coefficients of the exponentials.

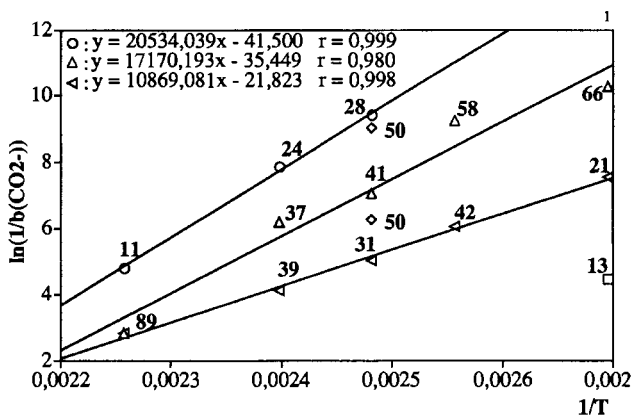


Figure 4.
Arrhenius plots for the three or two exponential functions of CO_2^- in synthetic monohydrocalcite annealed at $T = 371, 388, 403, 417$ and 443 K.

C. Dispersive model

Satisfactory fits with the dispersive model for radicals in synthetic monohydrocalcite, fossil mollusc and coral have already been presented in Debuyst *et al.* (1995, 1997). This model remains our

favourite one. The previous works, however, did not consider the presence of an initial increase in the isothermal data. To our knowledge, this increase does not exist in non-laboratory-irradiated fossil samples ; in the case of synthetic monohydrocalcite, it lasts some minutes for CO_3^- and some tens of minutes for CO_2^- , and has been removed in the previous analyses.

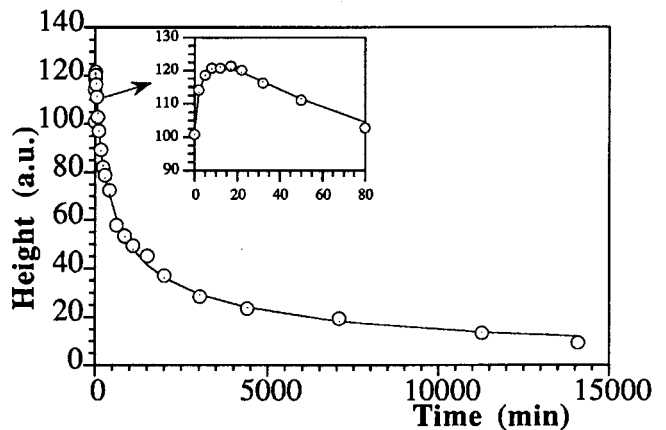


Figure 5.
Curve fitting with the dispersive model for CO_2^- in 9000 Gy-monohydrocalcite annealed at 403 K.

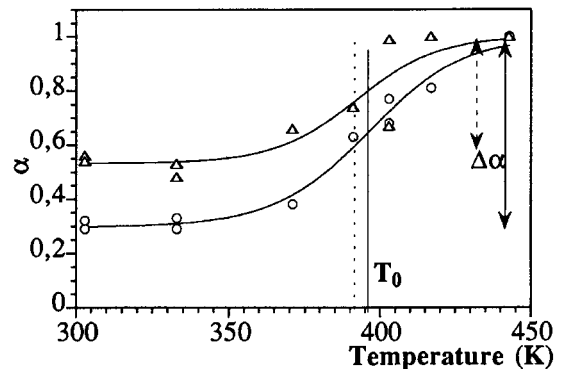


Figure 6.
 α -values for CO_2^- (o) and CO_3^- (Δ) radicals in irradiated monohydrocalcite as a function of the annealing temperature

This initial increase can be explained by the presence of a precursor feeding the radical in the first step of the thermal annealing. As this phenomenon is common to both radicals, we believe that this increase is due to anisotropic radicals which, following their diffusion or the diffusion of nearby

partners, rotate more and more easily and become isotropic. In fossil samples, this diffusion is achieved nowadays and no increase is observed. Figure 5 shows a complete curve

for CO_2^- at 403 K using the following equations solved numerically with Matlab software :

$$\begin{aligned} dr/dt &= -Bt^{\alpha-1} r^2 + Ct^{\alpha-1} p \\ dp/dt &= -Ct^{\alpha-1} p \end{aligned} \quad (4)$$

where r and p represent the concentrations of the radical and the precursor, α is supposed to have the same value for both species. A first-order reaction for the precursor yielded a slightly better fit than a second-order one.

Two experiments at low temperatures (303 and 333 K, during around 45 weeks) were also performed in order to have a broader field of α values. At these low temperatures, the initial increase is weak or hardly visible and the intensity of the ESR signal only decreases after some time (several hours at 333 K and a hundred hours at 303 K). The values of α at 303, 333 and 403 K obtained using equations (4) are presented in figure 6 together with the values at the other temperatures obtained previously. The experimental data show a sigmoid behaviour : below nearly 353 K, α remains constant for both species, but with a lower value for the more stable CO_2^-

radical (0.3 compared to 0.5 for CO_3^- and reaches the value of 1 (i.e. the classical second-order) at around 413 K for CO_3^- and 443 K for CO_2^- . A function of the form $\alpha = 1 - (\Delta\alpha(1 + \exp m(T - T_0)))^{-1}$, where $\Delta\alpha$ is the total difference in the α -values, T is the temperature, T_0 the temperature at which a mean value of α is obtained and m is a parameter related to the slope of the curve, was used to fit the data. The experiments were duplicated at 303 and 333 K with the same dose (3000 Gy), whereas at 403 K the dose was 3000 for one of the samples and 9000 Gy for the other. The experimental uncertainties are larger for the less stable CO_3^- . A sigmoid behaviour also appears, in the dispersive model, for the distribution function of the activation energy at a given temperature (Plonka, 1991).

Conclusions

The present work rules out a model implying only chemical reactions between CO_2^- and CO_3^- radicals.

The distribution of rates for a given decay reaction proposed in dispersive kinetics seems, in disordered systems, more logical than a superposition of a limited number of exponential decays. The reason for having a precise number of first-order reactions is not clear, the Arrhenius plots (specially in figure 4) are not convincing and the number of parameters used in the fits is quite high. Nevertheless, the experimental uncertainties are larger for unstable compounds (monohydrocalcite compared to natural carbonates) and less stable radicals (CO_3^-

compared to CO_2^-). In this respect, the Arrhenius plots for the more stable fossil mollusc (figure 3) could be considered as not too bad. It is hoped that this work will incite colleagues to utilize both multi-exponential and dispersive models. As for dose response curves, multiple samples and repeated measurements should improve the quality of the data and make the choice of an appropriate model easier.

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Reviewer

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