

## GENERAL PROPERTIES OF THE PARAMAGNETIC CENTRE AT $g = 2.0006$ IN CARBONATES

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The ESR-signal at  $g = 2.0006$  ('dating'-signal) in carbonates has characteristic properties that do not depend on the origin nor on the crystal modification of the carbonate. It is shown how the dating signal is identified even in complex spectra by taking advantage of these properties. Independent methods of identification have been applied: Q-band measurements and computer-simulations. These methods reveal the presence of this signal in aragonitic molluscs. Signals that often superimpose the dating signal have been analyzed. A probable model for the paramagnetic centre that is responsible for the signal is a rapid rotating  $\text{CO}_2^-$  signal. This model is discussed and compared with the experimental findings. Systematic observations of the occurrence of the signal in different natural carbonates and comparisons with synthetic calcites show that the Mg/Ca ratio is the main factor that determines the density of the traps related to this signal.

### INTRODUCTION

The paramagnetic centre with the  $g$ -factor at  $g = 2.0006$  is present in a large number of fossil carbonates. It is accepted to be the most reliable signal for dating of carbonates (see for example Grün, 1989). Although this signal has been studied in a variety of carbonate materials, a more generalized treatment of the signal is lacking.

The purpose of the present study is:

- (a) to describe and to summarize the specific features and properties of this ESR signal as far as they are independent from the specific origin of the carbonate;
- (b) to demonstrate the principle of identification of a paramagnetic centre in a complex ESR spectrum applying the example of the dating signal;
- (c) to discuss a reasonable model of the nature of this signal;
- (d) to give a systematic overview of the occurrence of the signal in various carbonates and to correlate these observations with synthetic carbonate measurements.

A similar procedure as discussed here in a more general way may be applicable also to other ESR-signals observed in different materials. The relevant properties to dating — signal growth curves and long-term fading — of this signal are discussed in detail in Barabas *et al.* (1992).

### FEATURES OF THE SIGNAL AT $g = 2.0006$

Labelling of paramagnetic centres with  $g$ -factors must be handled with care because differences of 0.0003 between different measurements are common. Consequently they are not sufficient to characterize a certain paramagnetic centre. In addition the following characteristic properties have to be taken into consideration.

First, these are the *width* of the signal and its *response on microwave power*. These parameters can be regarded as invariable for a certain paramagnetic centre, because they are a function of the spin-lattice relaxation time exclusively (Plato and Schneider, 1971) in the case of high diamagnetic dilution of the paramagnetic centres and constant temperature — conditions that normally are fulfilled for the centres in question. The *temperature behaviour* can be as well an important feature to characterize a paramagnetic centre (*ibid.*). It is determined by the dependence of the relaxation processes on the temperature. The *line shape* (Lorentzian/Gaussian) gives information about a possible unresolved hyper-fine-structure.

Another important property of a paramagnetic centre is the *orientation dependence* of the centre, i.e. whether it is isotropic or not. Specific information can be derived from study of single crystals. However, in principle one can obtain sufficient information from the spectra of powdered samples (Atkins and Symons, 1967).

The properties of the ESR-signal at  $g = 2.0006$  have been studied extensively by several authors (Yokoyama *et al.*, 1983, 1985; Rossi *et al.*, 1985; Smith *et al.*, 1985; Barabas, 1989). A suitable material having a large and nearly undisturbed signal at  $g = 2.0006$  (Fig. 1) is aragonitic coral (Radtke and Grün, 1988).

*g-Factor*: Range from 2.0003 (Rossi and Poupeau, 1989) to 2.0009 (Molodkov, 1988). Our best measurements (NMR-gaussmeter and digital frequency-counter) indicate a  $g$ -value of  $g = 2.0006 \pm 0.0001$ .

*Line-shape*: Lorentzian shape (Rossi, *pers. commun.*).

*Orientation*: Isotropic (Rossi and Poupeau, 1988; Katzenberger, 1989).

*Signal width (peak-to-peak)*: About 1.5 G ( $\pm 0.1$ ) at room-temperature.

*Microwave power*: At room temperature it cannot be

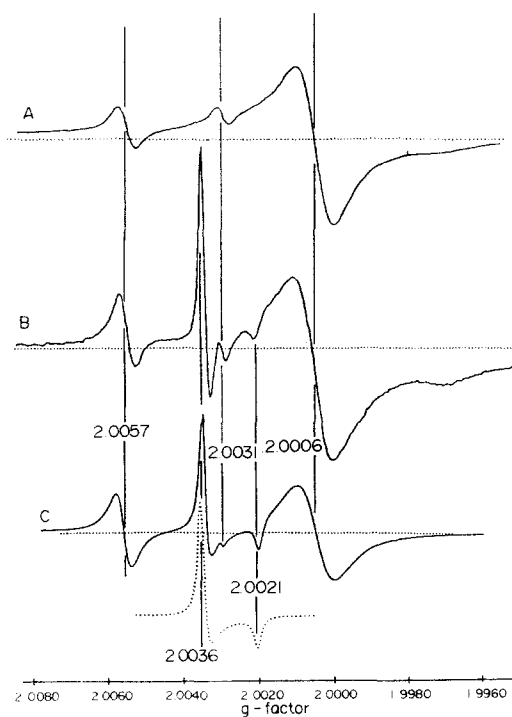


FIG. 1. An ESR spectrum (A) of a coral (irradiated with about 1 kGy) in general displays a large signal at  $g = 2.0006$  which is nearly not disturbed by other signals (at  $g = 2.0057$  and  $g = 2.0031$ ). Foraminifera spectra (B) differ only slightly as they show in the central region a signal with axial symmetry ( $g_{pp} = 2.0036$ ,  $g_{par} = 2.0021$ ; simulation dotted) instead of  $g = 2.0031$ . The  $g$ -values and other properties indicate that both may originate from the same paramagnetic centre. (C) Computer-simulation of (B).

saturated by conventional microwave powers (200 mW) (Lyons *et al.*, 1988).

**Temperature-dependency:** By lowering the cavity temperature two effects have been observed: first, the signal width decreases with temperature down to 1 G (at 220 K) which causes a strong increase of the signal amplitude. Then, at temperatures lower than about 200 K, the signal suddenly disappears and is not measurable any more even at very low microwave power (Yokoyama *et al.*, 1985; Katzenberger *et al.*, 1989; Rossi and Poupeau, 1989).

All measurements suggest that these features are independent of the specific origin of the carbonate material and as well of the crystal modification (calcite/ aragonite).

## METHODS OF IDENTIFICATION

Various researchers disagree on defining which is the most suitable dating signal in molluscs. It has been reported that the dating signal at  $g = 2.0006$  is not present in the complex spectrum of molluscs but, instead, different signals at  $g = 2.0012$  or  $g = 2.0014$  can be utilized for dating (Molodkov and Hütt, 1985; Molodkov, 1986, 1988; Radtke *et al.*, 1985). Using the example of the complex ESR spectrum of aragonitic mollusc shells, we will outline independent ways to

identify a certain paramagnetic centre. Our results lead to the conclusion that the paramagnetic centre at  $g = 2.0006$  is generally present in aragonitic shells, however, it is superimposed by other signals.

### Properties

In Fig. 2 a spectrum of an aragonitic shell is plotted at low and at high microwave power, respectively. At low microwave power the dating signal is not easy to recognize, whereas at high microwave power its amplitude increases (i.e. it does not saturate) while the other signals are saturated and become relatively small. This clearly shows that there is a signal at the same  $g$ -factor with the same width as compared to foraminifera and with a matching response on microwave power.

Another property that can be used for identification, is the disappearing of this signal at low temperatures ( $< 200$  K) that can be observed in molluscs (Katzenberger *et al.*, 1989) as well as in other carbonates (own measurements).

### Q-Band Measurements

Q-band means the use of a microwave frequency that is higher by a factor of 3 compared to X-band (i.e. around 30 GHz). As the magnetic field has to be enhanced by the same factor, the distance between close by signals (i.e. with nearby  $g$ -factors) increases likewise by a factor of three, whereas the signal width remains unchanged (because it is a measure of the absolute uncertainty of the energy levels).

Figure 3 shows a comparison of Q-band spectra of an aragonitic coral and a mollusc. Both spectra display in principle identical signals although with different amplitudes. The signal at  $g = 2.0006$  is unambiguously separated from the other signals in both spectra.

Unfortunately, the reproducibility for Q-band meas-

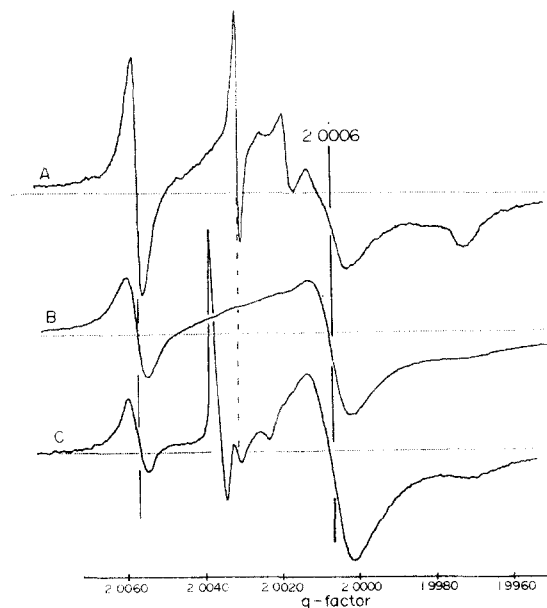


FIG. 2. ESR spectrum of molluscs. At low microwave power (2 mW, A) the signal at  $g = 2.0006$  is superimposed by others. However, at high microwave power (200 mW, B) the signal clearly appears as shown by a comparison with a foraminiferal spectrum at 2 mW (C).

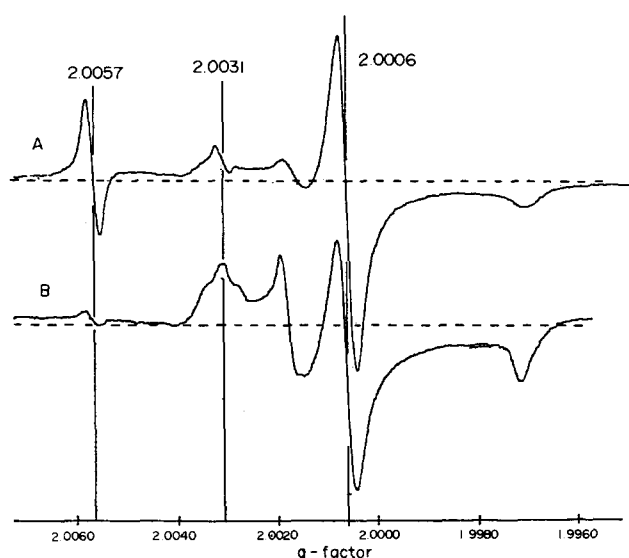


FIG. 3. In the Q-band-spectra (about 32 GHz, 9.4 kG) the signal at  $g = 2.0006$  can easily be distinguished from the others. The difference between coral (A) and mollusc (B) spectra is mainly due to the relative amplitudes of the signals.

urements is only in the range of about 50% (Hüttermann, *pers. commun.*). Thus the Q-band method cannot be applied to ESR dating.

#### Computer Simulation of ESR Spectra

Computer simulation is based on the knowledge of the principal shape of the signals in powder spectra (Kneubühl, 1960; Ibers and Swalen, 1962; Callens *et al.*, 1986). In a first approximation they consist of two kinds of signals (Lorentzian/Gaussian) each of which can exhibit three different orientation dependencies (cubic, axial or orthorhombic symmetry) (see for example Atkins and Symons, 1967). Using the principal line shapes we can adjust the  $g$ -factors and the signal widths to closely approach the measured ESR spectrum and thus to verify the constitution of the spectrum of its components.

Results are shown for simple ESR spectra of foraminifera (see Fig. 1). Figure 4 shows in detail the addition of different signals to a complex spectrum which resembles the measured spectrum of a mollusc.

From these observations it can be concluded that the paramagnetic centres responsible for the signal at  $g = 2.0006$  are present in aragonitic molluscs. The superimposed signals that also appear in several other carbonates, will be briefly described in the following section.

#### Characteristics of Interfering Signals

(a) 'A-signal complex':  $g_x \approx 2.0030$ ,  $g_z \approx 2.0015$ ,  $g_y \approx 1.9973$

Our own analysis (Barabas, 1989) and the work of Rossi and Poupeau (1989), Decanniere *et al.* (1988), Debuyst *et al.* (1991) and Katzenberger *et al.* (1989) revealed that carbonates contain at least two orthorhombic signals with the principal  $g$ -factors close to those attributed to the  $\text{CO}_2^-$  radical by Marshall *et*

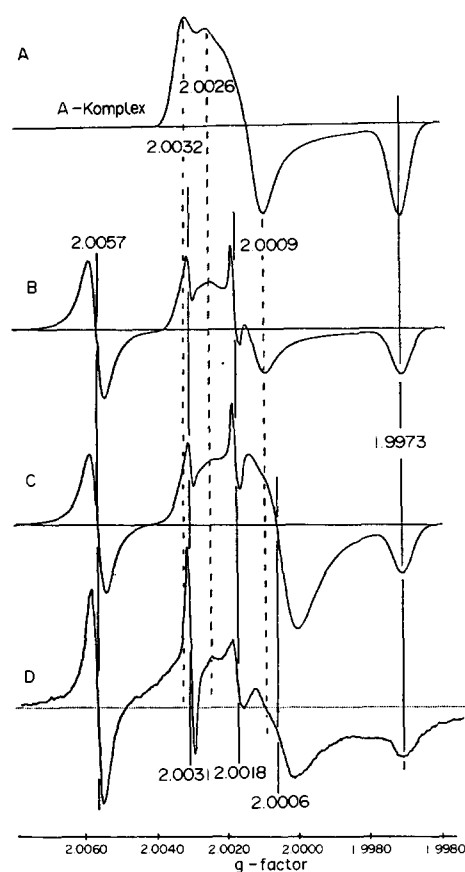


FIG. 4. The computer simulation of the mollusc spectrum shows the different components contributing to the complex signal observed in aragonitic shells (D). It shows that the signal at  $g = 2.0006$  may be strongly influenced by others, especially by the A-signal: (A) A-complex; (B) including signals at  $g = 2.0057$ ,  $g = 2.0031$  and  $g = 2.0018$ ; (C) addition of the dating signal  $g = 2.0006$ ; (D) measured spectrum of a mollusc.

*al.* (1964). The signal width is in the range of 1.5–3 G, but increases at high microwave power due to saturation effects. The signals have different thermal stabilities observed in aragonitic molluscs as well as in synthetic carbonates (Debuyst *et al.*, 1991). The central  $g$ -factor (2.0018–2.0012) may interfere with the dating signal at  $g = 2.0006$  at its low field side (Fig. 5a).

This complexity of signals has been observed in various carbonates, however it is generally most pronounced in aragonitic shells. It was also found to be large in marine aragonite (ooids) and in synthetic aragonites (Barabas, 1989).

(b) 'Grinding signal':  $g = 2.0001$

This signal was observed in various carbonates (e.g. in coral crust) and could be identified as an axial species ( $g_{pp} = 2.0003$ ,  $g_{par} = 1.9996$ ; Fig. 5b). Saturation power is low ( $< 1$  mW) (Lyons *et al.*, 1988). It can be removed by etching. Interference can be observed at the high field side of dating signal.

(c) 'Short-living signal':  $g = 2.0023$

Unstable signal (Fig. 5c) with probably orthorhombic symmetry ( $g$ -factors: 2.0027, 2.0020, 2.0009; observed in foraminifera). It only appears immediately after

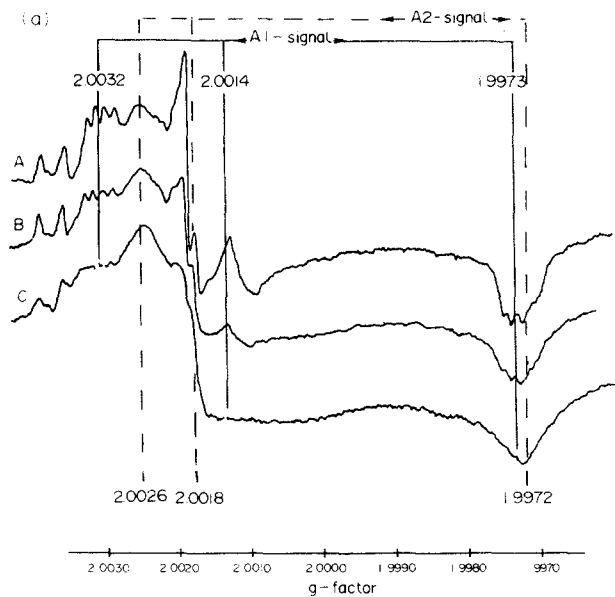


FIG. 5a. Composition of the 'A-signal complex' as derived from annealing experiments: (A) annealed and re-irradiated; (B) plus annealing 2hr/160°C; (C) 5hr/160°C. The 'A1-signal' is less stable and disappears due to heating.

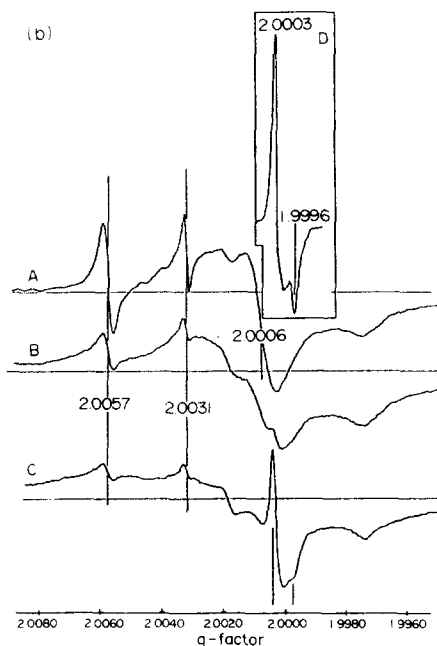


FIG. 5b: The evolution of a coral spectrum (A) due to (natural) grinding (B) and formation of coral crust (C). The so-called 'grinding signal' appears at the high-field side of the signal at  $g = 2.0006$ . Its axial symmetry can clearly be recognized (D) at low microwave power (0.2 mW) and small modulation amplitude (0.01 mT).

irradiation and can be removed by heating at 90°C for 5 days or storage for 2 weeks at room temperature. The microwave saturation occurs at about 2 mW.

(d)  $g = 2.0018$

This signal is exclusively observed in shells (Figs 2 and 4). Microwave saturation is at about 5 mW and the signal width about 0.8 G. The lifetime is comparatively low.

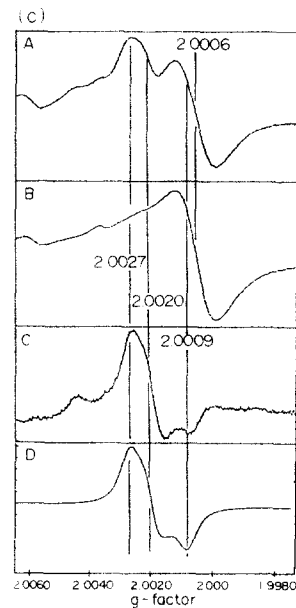


FIG. 5c. Directly after irradiation (A) in foraminifera, a signal superimposes the dating signal at  $g = 2.0006$  which has probably orthorhombic symmetry ( $g$ -factors: 2.0029, 2.0021, 2.0010). It disappears rapidly (B) after gentle heating (90°C). (C) The difference between A and B is due to the unstable signal; (D) computer-simulation of C.

#### Recommendations for the Measurement of the Signal at $g = 2.0006$

Taking into account the properties of the interfering signals and of the dating signal, we can deduce some optimum conditions for measuring the signal at  $g = 2.0006$ .

In order to enhance the dating signal it is recommended to use high microwave power because it is the only signal in this region that does not saturate and, hence, at high microwave power this signal typically dominates the ESR spectrum (Fig. 2). Furthermore the signal-to-noise ratio will be enhanced which increases the accuracy of the measurement.

The use of a very large modulation amplitude (i.e. 10 G = 'overmodulation' which was proposed by Molodkov (1986, 1988)) for aragonitic shells increases the measured amplitude of the broad A-signal block. Using these measurement conditions it is not clear which of the signals (that may have different properties, at least different thermal stabilities) contribute to the measured amplitude. This is also valid for the use of the so-called 'dating signal' at  $g = 2.0014$  (Radtke *et al.*, 1985), because it is a composition of at least two signals as well (Katzenberger *et al.*, 1989).

The use of the lower part of a signal (distance from low peak to the baseline) (Ikeda *et al.*, 1992) is not of advantage because there may be an offset from a broad signal component in the spectrum.

In the spectra of some molluscs the signal at  $g = 2.0006$  is too small that even at high microwave power it cannot be resolved from the other signals (Katzenberger, 1989; Hütt, *pers. commun.*) and therefore an interference with other signals has to be expected (Lyons *et al.*, 1988). Lowering the cavity temperature

to about  $-60^{\circ}\text{C}$  will enhance the amplitude of the signal at  $g = 2.0006$  by a factor of 3 (Rossi and Poupeau, 1989). Another approach would be to perform a computer analysis of the spectrum and thus to determine the amplitude of the signal at  $g = 2.0006$ . However, this procedure is very time consuming and may introduce additional uncertainties.

### PHYSICAL NATURE OF THE PARAMAGNETIC CENTRE

The physical nature of this certain paramagnetic centre is still not definitely known, although the very recent work of Debuyst *et al.* (1991) cleared up this point almost completely. From the present knowledge we discuss a model which is reasonable and which can explain the observed properties. This model has also been proposed by Debuyst (*ibid.*).

Our hypothesis is that the paramagnetic centre associated with the dating signal at  $g = 2.0006$  is a rapid rotating  $\text{CO}_2^-$  radical, probably at an interstitial position. This interpretation was also given by Callens *et al.* (1989) who observed carbonate signals in  $^{13}\text{C}$ -labelled synthetic apatite. It may have been created by trapping an electron at an (interstitial)  $\text{CO}_2$ -molecule or by separating an O-radical from a  $\text{CO}_3^{2-}$ -ion.

#### Discussion

*g-factor:* It agrees within the limits of error with the mean value of the orthorhombic  $\text{CO}_2^-$  centre, identified by Marshall *et al.* (1964) (*g*-factors:  $g_x = 2.0032$ ,  $g_z = 2.0016$ ,  $g_y = 1.9973$ ). The proposed motion about all three possible axes would lead to one isotropic narrow line at the mean *g*-factor (motional narrowing), if the frequency of motion is large compared to the microwave frequency (Atkins and Symons, 1967).

*Hyper-fine-structure:* This was observed by Debuyst *et al.* (1991) in synthetic carbonates that have been grown from  $^{13}\text{C}$ -labelled substances. They found the expected hyper-fine-structure with a splitting-constant that is very close to that of the  $\text{CO}_2^-$  radical and thus concluded that it is an isotropic species of this radical. This observation agrees with the model proposed above.

*Temperature dependency:* Below a certain temperature ( $< 200\text{ K}$ ) the signal cannot be observed even at very low microwave powers (0.02 mW). This behaviour can be explained by freezing of the rotational levels. This effect has already been described by McMillan and Marshall (1968) below 200 K for a rotation about one axis (perpendicular to the  $\text{CO}_3$  planes), which leads to an axial species.

*Saturation behaviour:* The transfer of energy from the spin-system to the motional energy levels would lead to an additional relaxation mechanism and thus could explain that the signal cannot be saturated even at high microwave powers.

*Trap fading:* If the traps are  $\text{CO}_2$  (precursors) it is

not unlikely that they are able to diffuse throughout the crystal lattice or that a higher order of the lattice disables the rotation of the  $\text{CO}_2^-$  radicals. Thus the number of traps will decrease on heating or even — during longer times — at ambient temperatures which may explain the observed trap decay.

A remaining question is the special position of this paramagnetic centre and the kind of ions stabilizing the radical. Also the dependency on the Mg/Ca ratio (see below) is not yet understood.

### OCCURRENCE

One reason for establishing the signal at  $g = 2.0006$  as a dating signal was the widespread occurrence of this signal in various carbonates. Here we report some results of a systematic examination of the presence of this paramagnetic centre in marine carbonates in comparison with synthetic carbonates and the factors that influence this behaviour.

#### Natural Carbonates

One of the most remarkable observations in ESR dating of carbonates is that spectra are characteristic for the carbonate of marine origin (coral, foraminifera, molluscs), and that some signals appear in all marine carbonates, for example the signal at  $g = 2.0006$ . On the contrary, it is not possible to speak of the typical ESR spectrum of terrestrial carbonates (travertine, speleothems; Grün, 1989); in terrestrial carbonates the signal at  $g = 2.0006$  sometimes does not occur.

One reasonable assumption was therefore that the marine environment has a strong influence on the formation of specific paramagnetic centres in carbonates.  $\text{Mg}^{2+}$  is an ion with a high concentration in the sea water and the Mg/Ca ratio is about 5.  $\text{Mg}^{2+}$  also plays an important role for the formation of different modifications of carbonates (Katz, 1973).

We compared ESR spectra of relevant carbonate forming organisms. Focussing on the signal at  $g = 2.0006$ , we obtained the following results:

- All recent marine carbonates display the signal at  $g = 2.0006$  on irradiation, although in some aragonites (molluscs, ooids) it is relatively weak.
- In Mg-calcites (sea urchins, red algae, Fig. 6) the signal is significantly more (about a factor of 10) radiation sensitive than in calcites (foraminifera); the signal is smallest in aragonitic molluscs which normally have the lowest Mg content (Dodds, 1967).
- In very old molluscs or in carbonates that have been subject to diagenesis (coral crust) the signal does not occur any more.

In order to understand these results and to determine the biological influence we compared them with observations on synthetic  $\text{CaCO}_3$ .

#### Synthetic Carbonates

Synthetic crystals with different Mg/Ca ratios have been grown with a special method (Barabas *et al.*,

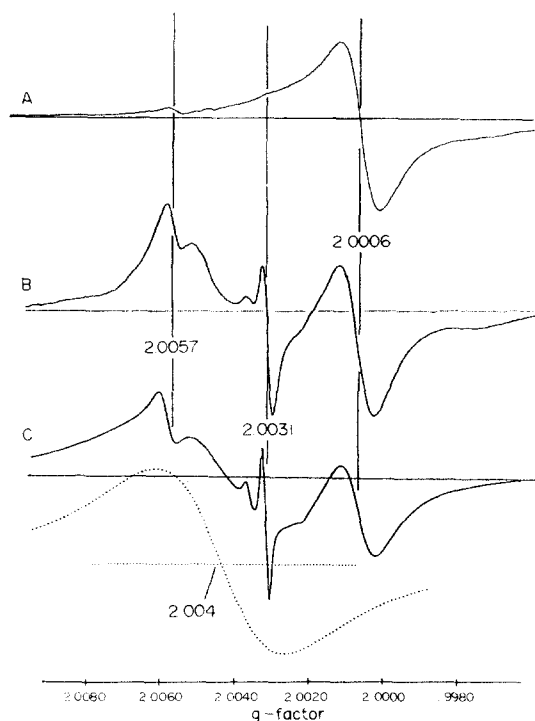


FIG. 6. Examples for natural Mg-calcite with a large signal at  $g = 2.0006$ : (A) red algae, (B) prickles of a sea-urchin; irradiation dose: 500 Gy; microwave power: 20 mW, (C) simulation of (B) (dotted: broad signal at  $g = 2.004$ ).

1989). In Fig. 7 the increase of the saturation level is shown as the function of the Mg content of the solution the synthetic crystals have been grown in. The saturation level is assumed to be a measure of the number of traps that can be filled by irradiation.

We found a strong, nearly linear increase of the dating signal with Mg/Ca ratio. Additional experiments showed that this dependence is indeed caused by the presence of  $Mg^{2+}$  ions and not by the specific process of crystal growing. However, the velocity of precipitation seems to have an influence on the number of traps that will be produced. Further work is needed on this point.

$Zn^{2+}$  ions which have very similar properties to

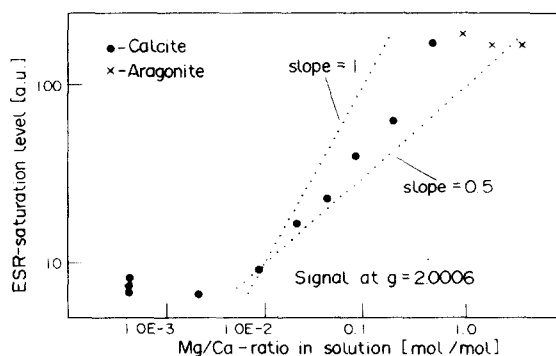


FIG. 7. Saturation level (equivalent for the number of traps) of the signal at  $g = 2.0006$  as a function of the Mg/Ca ratio of synthetic carbonates, grown with a gel-diffusion method (Barabas *et al.*, 1989) (double-log-scale!). The signal amplitude increases by a factor of about 25.

$Mg^{2+}$  (ion radius and electron configuration) induce a similar effect. Also terrestrial carbonates with a high Mg content can be found, that display no signal at  $g = 2.0006$  (A. Wieser, *pers. commun.*).

These results indicate that the paramagnetic centre is not directly associated with one of these cations.

#### Discussion

From the comparison of ESR measurements of the natural and synthetic carbonates it can be concluded that it is the marine environment that plays a major role for originating specific paramagnetic centres in carbonates. The influence of the biological organism seems to determine the Mg/Ca ratio and by it the crystal modification and the amount of traps. This explains the occurrence of the signal at  $g = 2.0006$  in marine carbonates, whereas terrestrial carbonates may not display this signal.

Due to the observed dependency of the trap density on the Mg/Ca ratio, Ikeda *et al.* (1990) proposed a model where the rotating  $CO_2^-$  radical is stabilized by  $Mg^{2+}$  ions. However, as no HFS-splitting has been observed from  $^{25}Mg$  (10% abundance) this model is rather unlikely. No further proof has been published so far.

Mg also plays an important role for the formation of the crystal lattice (Katz, 1973) and may enhance the formation of specific defects. Lattice distortions caused by incorporation of  $Mg^{2+}$  ions (Goldsmith and Graf, 1958) may lead to rotating (isotropic)  $CO_2^-$  by creating larger interatomic distances. An alternative explanation is that water molecules which may be related to this centre (Debuyst, *pers. commun.*) are introduced together with the  $Mg^{2+}$  ions (Wollast and Loijens, 1983) into the crystal lattice.

An indication that the effect of the Mg ions is on the lattice as a whole, and not on a specific centre, results from the dependency of the common ESR signals at  $g = 2.0057$  and  $g = 2.0031$  (in synthetic carbonates) on the Mg/Ca ratio being similar to that of the signal at  $g = 2.0006$  (Barabas *et al.*, 1989).

#### CONCLUSIONS

We have summarized different properties of the ESR signal at  $g = 2.0006$  in carbonates, which enable us to identify this signal unambiguously in carbonates without relying on the  $g$ -factor exclusively. These properties are not dependent on the specific origin nor on the modification of the carbonate.

We have shown how to find the dating signal by different methods, even if it is superimposed by other signals, e.g. in molluscs. For practical purposes the use of a high microwave power is most important. The authors hope that the detailed review of the properties of the dating signal and the description of the methods of analysis of ESR spectra will help to find an agreeable method of treating for example ESR dating of molluscs.

We have given and discussed a reasonable model for

the physical nature of the signal at  $g = 2.0006$ , although some open questions remain concerning the specific surrounding of the radical. It may be a task of theoretical research to understand the possibility of a rotating  $\text{CO}_2^-$  radical in the carbonate lattice.

It has been shown that the Mg concentration is an important parameter for the formation of this specific signal in nature as well as in synthetic carbonates. However, further work has to be done to understand its mode of operation.

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### POSTSCRIPT

Meanwhile it turned out as a well-known fact that the  $\text{CO}_3^{2-}$  ions in carbonate are rapidly rotating at room temperature.