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Influence of the Mg-content on ESR-Signals in Synthetic Calcium Carbonate

M. BARABAS, A. BACH, M. MUDELSEE and A. MANGINI

Heidelberger Akademie der Wissenschaften, Im Neuenheimer Feld 366, 6900 Heidelberg, F.R.G.

Carbonate crystals doped with various concentrations of Mg^{2+}-ions have been grown by a gel-diffusion method. An increase of the Mg/Ca-ratio to more than about 1 caused a phase change in the crystal lattice from calcite to aragonite. The properties of the ESR-signals of the synthetic carbonates were studied and compared with natural marine carbonates. The following results were derived:

(a) In the presence of Mg^{2+}-ions the synthetic carbonates display the same ESR-signals as natural calcites of marine origin with similar properties (thermal stability, radiation sensitivity).

(b) The saturation value of the signal at $g = 2.0006$ in synthetic calcites was found to be strongly related with the Mg-content in the crystals.

(c) The signal at $g = 2.0036$ (axial symmetry) which is present in calcite was not influenced by the Mg-concentration. Its saturation value decreases when the crystal phase changed from calcite to aragonite and in complement the signal at $g = 2.0031$ appeared.

(d) The signals at $g = 2.0057$ and $g = 2.0031$ are most probably not of organic origin.

1. Introduction

Carbonate material that was formed in the ocean water (foraminifera, corals, moluscs) exhibits two narrow ESR-signals at $g = 2.0057$ (h1) and $g = 2.0006$ (h3) and a sharp line at $g = 2.0036$ (foraminifera) or at $g = 2.0031$ (corals, molluscs*) (Yokoyama *et al.*, 1983; Radtke and Grün, 1988; Skinner, 1983). Carbonates of continental origin (travertines, speleotherms) often show the signal at $g = 2.0006$ too (Grün, 1989; Grün *et al.*, 1988; Smith *et al.*, 1985).

Little is known about the origin of these different signals. Generally, the radiation sensitive centers observed in carbonates are assumed to be anion-centers, i.e. centers derived from the host lattice anion [CO_3^{2-}] or [HCO_3^-] and from impurity anions like [PO_3^{3-}], [AsO_2^{2-}] or [SO_3^{3-}] (Marfunin, 1979; Cass *et al.*, 1974; Serway and Marshall, 1967; Marshall and Serway, 1969). On the other hand impurity cations like Y^{3+} or Li^+ were reported to play an important role for stabilization of the different centers (Baquet *et al.*, 1975; Marshall *et al.*, 1968). Other centers which are commonly cited in alkali-halides like interstitials and ion vacancies (Royce, 1967) were not observed in carbonate spectra up to the present.

The relevant signals in the ESR-spectra of natural carbonates are:

—$g = 2.0057$ (h1): This line earlier was attributed to a humic acid–clay complex (Grün and De Canniere, 1984). However, in 1985 De Canniere *et al.* claimed that this is improbable because they observed a similar signal ($g = 2.0051$) in synthetic calcite without organic matter.

—$g = 2.0036$: This signal was already observed to be the $g_\perp$ of a center with $g_\parallel = 2.0021$ (De Canniere *et al.*, 1985; Rossi *et al.*, 1985) and attributed to the CO_3^{3-}-center because of its close relation to g-values of that center observed by Servay and Marshall, (1967).

—$g = 2.0031$: This signal—observed in corals and molluscs—was attributed to alanine (in molluscs; Ikeya, 1981).

—$g = 2.0006$ (h3): The most important signal for ESR-dating of carbonates could not be related to any known center. It was speculated to be a CO_3-type center (Grün, 1989) although none of the known centers (CO_2^{2-}, CO_3^{3-}, CO_3^-) fits this g-value (Marshall and McMillan, 1968; Servay and Marshall, 1967).

To get a better understanding of this problem the systematic approach is to study synthetic carbonate crystals grown under best controlled conditions. Besides spectra of chemical $CaCO_3$ (Wieser *et al.*, 1985) up to now only De Canniere *et al.* (1985, 1988) reported different spectra of synthetic carbonates. The main problem of synthetic growth is the purity of the ingredients used, because concentrations of impurities lower than 1 ppm should be detectable

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*In molluscs we find a strong superposition of the signal at $g = 2.0006$ by a broad line around $g = 2.0012$ and a sharp signal at $g = 2.0018$ (Radtke *et al.*, 1985; Katzenberger *et al.*, 1988).

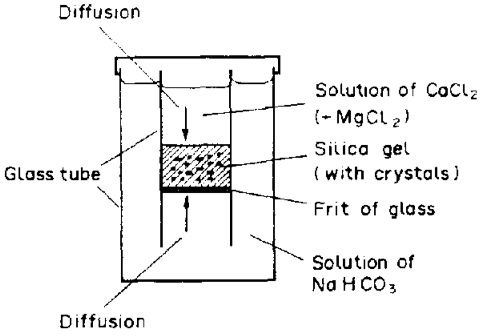

Fig. 1. The crystals are growing in the silica-gel by diffusion of the CO$_3^{2-}$-cation and the Ca^{2+}-anion within 2–4 weeks.

with ESR measurements (Plato and Schneider, 1971). In their experiment De Canniere *et al.* (1985) used concentrations of about 1% of humic acids for doping of the crystals in order to see detectable effects.

We present here ESR-powder-spectra of Mg^{2+}-doped carbonate crystals. The reasons for the choice of Mg in our first systematic approach are that:

(a) Mg^{2+}-ions easily substitute for Ca in the lattice of calcite, for the size of this ion is smaller (0.66 Å) than that of Ca^{2+} (1 Å) (Goldsmith and Graf, 1958).

(b) The amount of magnesium in ocean water—where most carbonates are generated—is five times that of calcium and the concentration of other cations (except Na) is far smaller.

(c) The ratio of calcium and magnesium has a strong influence on the lattice structure of calcium carbonate: it determines whether calcite or aragonite crystals are grown (Folk and Land, 1972).

(d) Comparison of mollusc and coral spectra show that the signal at $g = 2.0006$ is largest in corals having the larger content of Mg^{2+}.

(e) Our own preliminary experiments showed that the doping of crystals with Mg^{2+} suppresses the manganese lines and increases the signal at $g = 2.0006$.

The range of Mg in natural carbonates is from about 100 ppm (molluscs) to > 10,000 ppm (pricks of sea-urchin) (our own measurements).

The questions we address with our work are the following:

—Is it possible to grow carbonate crystals exhibiting the same ESR-signals as natural carbonates?
—Can we detect any influence of impurity ions on the ESR signals?
—Is there a difference between signals in calcite and in aragonite?
—Why do most carbonates exhibit the signal at $g = 2.0006$ but others do not?
—Can we get additional information on the nature of the different centers?
—Is it possible to draw conclusions for ESR-dating with carbonates?

2. Experimental

2.1. *Synthesis of the carbonate crystals*

The crystals were grown using a gel-diffusion-method (described in detail by Henisch, 1970) in a glass tube from solutions of 0.2 M CaCl$_2$ and 0.2 M (NaH)CO$_3$ separated by a gel made of 0.2 M Na meta-silicate (Fig. 1) at room temperature (pH = 8). The crystals grew at the diffusion front in the gel within 2–4 weeks up to a size of 0.2 mm (maximum about 2 mm). The yield was between 100 and 200 mg carbonate in each tube. The crystals were then washed from the gel with distilled water and dried at 60°C.

We preferred this gel-diffusion-method for crystal formation because it is slower than the precipitation method (described by De Keyser and Degueldre, 1950; Wray and Daniels, 1957) and thus comes a little closer to crystal formation in nature. Additionally it is possible to dope the crystals continuously while growing by adding solutions of impurity ions. One disadvantage of this method is that a small amount of the sodium silicate gel (< 1%) may be incorporated in the crystals. Preliminary studies with precipitated crystals yielded ESR-spectra like those from chemical CaCO$_3$ (see Wieser *et al.*, 1985).

2.2. *Doped crystals*

Preliminary experiments were carried out with pure solutions of CaCl$_2$ and NaHCO$_3$ to which dissolved impurity ions in concentrations of about 1% (Al^{3+}, Sr^{2+}, Mg^{2+}, K$^+$; NO$_3^-$, SO$_4^{2-}$) were added. Some of the spectra are shown in Fig. 2. The main problem in this series were the large ESR-signals of manganese overlapping the other signals except for CaCO$_3$ crystals that were doped with Mg^{2+} where the signal at $g = 2.0006$ is also more pronounced.

In a second series of experiments we consequently used p.a. or suprapur substances with trace element concentrations < 5 to 20 ppm (Mn: 5 ppm). The Mn-lines in the ESR-spectra of these crystals were smaller by about a factor of 10. We doped the solution of CaCl$_2$ with solutions at 12 different concentrations of MgCl$_2$, starting from a Mg/Ca ratio of 4×10^{-4} (100 ppm) to a Mg/Ca ratio of 4.

2.3. *AAS and x-ray diffraction*

The Mg^{2+}-content of the crystals was measured subsequently by atomic absorption spectroscopy (AAS) at a precision of 5%, because of the small sample weights used (10 mg).

The crystal structure was checked with x-ray diffraction in order to determine the content of calcite and/or aragonite in the crystals at least qualitatively.

2.4. *Gamma-ray irradiation and ESR-measurements*

All crystals were irradiated with a ^{60}Co source (dose rate about 50 Gy/min) in 5 steps up to 5 kGy (which was expected to be the saturation level). After each irradiation step the samples were heated at

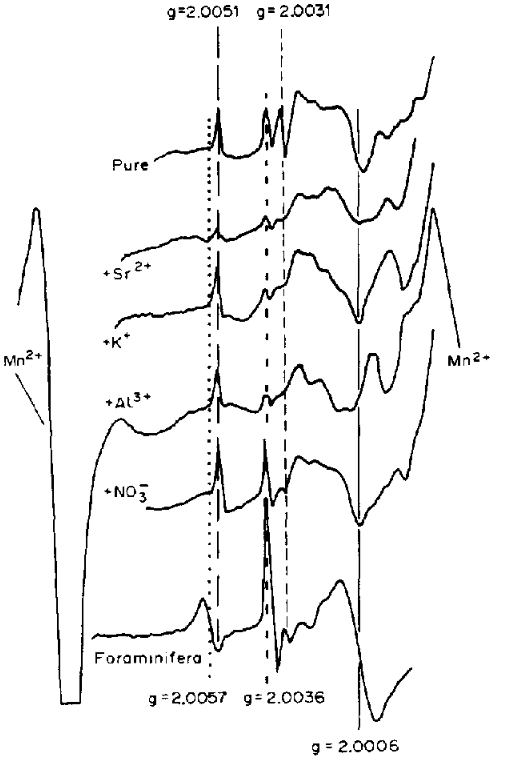

Fig. 2. The spectra shown are doped with various impurities in comparison with a spectrum of natural carbonate (foraminifera). They do not display the characteristic carbonate signals (except the signal at $g = 2.0036$) and are superimposed by large Mn^{2+}-hyperfine lines.

160°C for 1 h to remove unstable signals. The ESR-measurements were carried out at room temperature with a Bruker ESP-300 spectrometer (GSF, München) at 20 resp. 2 mW and 0.4 G modulation amplitude in the range from $g = 2.0100$ to $g = 1.9980$. As no significant change in the signal width was observed we took the peak-to-peak height of the first derivative spectra as being proportional to the number of traps.

2.5. Additional annealing experiments

After these procedures the crystals were heated once at 184°C for 1 h to test the stability of the observed signals and compare it with that of natural samples. In two samples the signals have been completely annealed (14 h at 200°C) and irradiated subsequently to test the regeneration behavior of the signals.

3. Results and Discussion

3.1. Transfer of Mg^{2+}-ions into the crystals

The results of the AAS measurements are shown in Fig. 3. We used a log–log plot because of the large range of concentrations and of signals. We find a nearly linear relationship for low Mg-concentrations with a transfer factor of about 0.37. Only the first sample (with no Mg added) shows some deviation from this relationship. This offset may originate from a small Mg contamination (in the range of 50 ppm) in the solutions of $CaCl_2$ and $(NaH)CO_3$ and in the gel respectively.

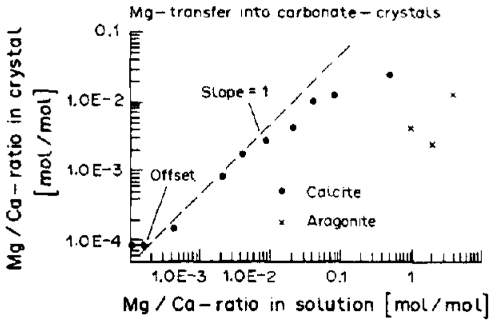

Fig. 3. Molecular ratio of Mg/Ca in the crystals as determined by AAS measurements vs the molecular ratio of Mg/Ca in the solution of $CaCl_2$. For the samples with the highest Mg-concentration aragonite was detected by x-ray diffraction.

For higher Mg-concentrations we find a sub-linear behavior up to a Mg/Ca ratio of 0.5 (transfer factor decreases to about 0.05; see Katz, 1973: 0.06 at 25°C, at similar concentrations). Increase of the Mg concentration in the solution beyond this value does not lead to an increment of the magnesium content in the crystal: it decreases dramatically (by a factor of about 10). This is related with a transfer factor of about 0.0025.

The observed behavior for crystals from Mg rich solutions indicates a *phase change* in the crystal lattice from calcite to aragonite which is expected for high magnesium content in the liquid (Folk, 1974). This was confirmed by x-ray diffraction of the crystals: in the samples plotted with an asterisk the content of aragonite in the crystals exceeds 30% (increasing with Mg-concentration), while the samples grown at lower Mg-concentration consist of almost pure calcite.

In the Mg-doped solutions trace element concentrations are about 5×10^4 lower than Mg.

3.2. Comparison of ESR-spectra with natural carbonates

The spectrum of crystals grown at low Mg-concentration (1000 ppm) and irradiated with 500 Gy is compared with calcitic foraminifera (500 Gy) in Fig. 4(a). Qualitatively, there is a very good correspondence of the three signals at $g = 2.0006$, $g = 2.0036$ (unsymmetrical, with a small line at $g = 2.0021$ belonging to it) and $g = 2.0057$. Additionally we find a small signal at $g = 2.0051$ in the synthetic crystals, probably the same that was observed by De Canniere *et al.* (1985) in synthetic calcite and which is present in chemical $CaCO_3$. This signal is only present in the crystal with lowest Mg-concentrations.

The concordance between natural and artificial samples is also very good when we compare the

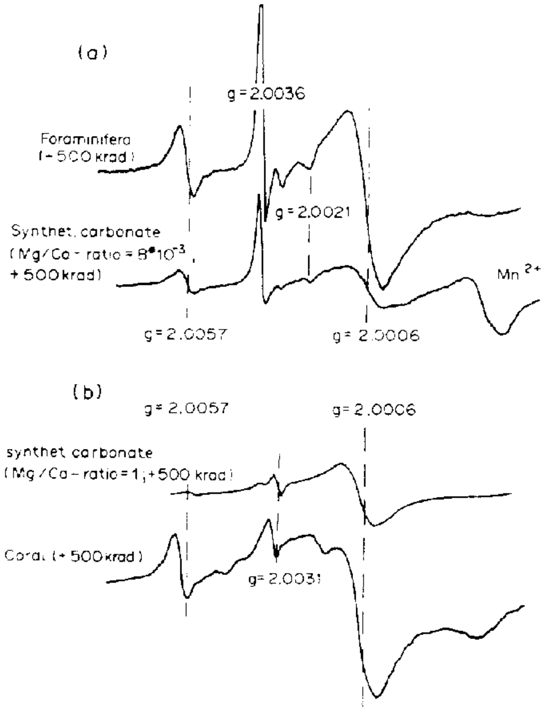

Fig. 4. Comparison of irradiated spectra of (a) synthetic crystals with low Mg-content (calcite) with foraminifera and (b) synthetic crystals with high Mg-content (mainly aragonite) with corals. The concordance in both cases in relation to g-values and signal-widths is good.

ESR-spectra of irradiated crystals doped with high Mg-concentration (Mg/Ca ratio = 1 in the solution) and spectra of aragonitic coral [Fig. 4(b)]. The only difference is the symmetric signal at $g = 2.0031$ which was not present previously (and no signal at $g = 2.0036$).

The signals show the same characteristics relative to microwave-power than natural samples: while the signals at $g = 2.0057$ and $g = 2.0006$ are not saturated up to 20 mW, those at $g = 2.0036$ and $g = 2.0031$ saturate at low power (about 2 and 10 mW respectively).

This concordance of g-values and microwave dependency suggest that the growing conditions have been of such a kind that paramagnetic centers have been created that are very similar to those in natural material. This concordance was not observed for any of the crystals grown in the absence of Mg^{2+} (Fig. 2). One important point to emphasize is the existence of the signal at $g = 2.0057$ in artificial samples: although we cannot definitely exclude the presence of any organic material in the synthetic crystals, it seems unlikely that organic matter is the origin of this signal.

3.3. Characteristics of the signals in synthetic carbonates

(i) Sensitivity on irradiation. The γ-ray irradiations were carried out in 4 steps (0.5/1/3/5 kGy). Shortly after irradiation the crystals displayed large signals in the region of $g = 2.002$. This was attributed to the unstable signal at $g = 2.0023$ (meanlife: 2 y at 10°C, Hennig and Grün, 1983) which is well known from natural carbonates. This signal was sufficiently reduced after heating for 1 h at 160°C, so that it did not disturb mesurements of the signal at $g = 2.0006$.

All signals (except at $g = 2.0057$) grow with the absorbed dose and display a noticeable saturation behavior*. The measured signals were then fitted to a saturation function (Barabas *et al.*, 1988) to determine its saturation value and saturation dose (assuming zero signal for non-irradiated samples). For the signal at $g = 2.0006$ the saturation dose D_e† was 1.3 ± 0.25 kGy for all samples except those three with the highest magnesium content. In these samples D_e was about a factor of 2 larger. These values agree well with values in the region of 1.0 kGy observed in foraminifera (own data).

For the signal at $g = 2.0036$ the observed D_e was 3 ± 1 kGy and thus larger than the values for foraminifera ($D_e = 0.8$ kGy). The signal at $g = 2.0031$ in comparison saturated very fast: its D_e was distinctly less than 1 kGy. It exhibits a similar saturation behavior in corals (Grün, 1988), whereas in molluscs usually it is not increased by irradiation (Radtke *et al.*, 1985).

The signal at $g = 2.0057$ displayed a small increase (about 10%) after each irradiation step. This enlarge-

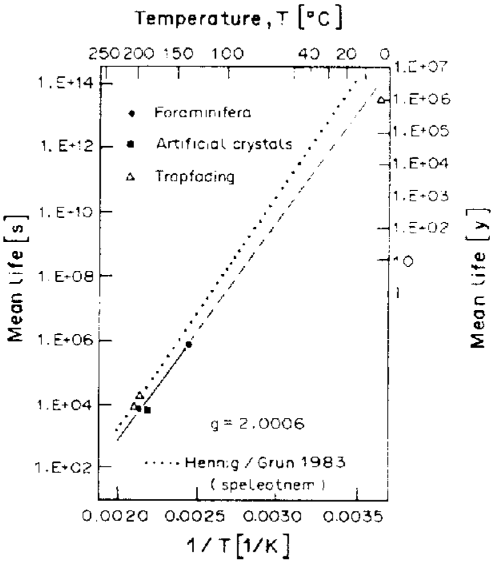

Fig. 5. Arrhenius plot of the signal at $g = 2.0006$ in forminifera. For comparison the lifetime of the signal at $g = 2.0006$ in synthetic crystals at 184°C is shown. Additionally we have plotted the lifetimes of the traps responsible for this signal as derived from deep-sea foraminifera.

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*For low Mg-concentrations the signal seems to decrease a little for the last irradiation step.

†The saturation dose D_e is defined as the dose required to reach the saturation level multiplied by $(1 - 1/e)$.

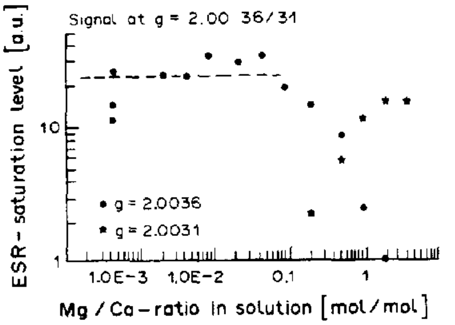

Fig. 6. Saturation values of the signals at $g = 2.0036$ and $g = 2.0031$ respectively vs the Mg/Ca-ratio of the $CaCl_2$-solution. The change between these signals goes parallel to the phase change from calcite to aragonite.

ment was attributed to the heat-treatment after irradiation (see next section).

(ii) Thermal stability. To check the thermal stability of the signals and to compare it with natural values, the samples were heated at 184°C for 1 h. Results for $g = 2.0006$ are shown in an Arrhenius plot (Fig. 5) together with new measurements from foraminifera. They exhibit almost identical values (lifetimes of the signal at $g = 2.0036$ of natural and synthetic samples are both in the same range).

The signals at $g = 2.0057$ of all crystals increased with this heat treatment by a factor of 1.9 ± 0.4. This increase is usually observed in natural carbonates (e.g. Yokoyama *et al.*, 1983).

Summarizing, the ESR-signals of synthetic carbonates show the same behavior upon irradiation, and similar thermal stabilities, as natural carbonates.

3.4. Dependency of the signals upon Mg^{2+}-concentration

To compare the amount of traps in the samples responsible for a certain signal, we assumed that the number of these traps is constant and that all of them can be filled upon (sufficient) irradiation. From the parameters of the fitted irradiation curve we can thus deduce relative values for the number of traps, i.e. the respective saturation level S_m (Barabas *et al.*, 1988). These values were normalized to the specific density of the sample. The quotient S_m/D_e gives the irradiation sensitivity of a specific signal.

(i) Signals at $g = 2.0036$ and $g = 2.0031$. In Fig. 6 the saturation values S_m of the signals at $g = 2.0036$ and $g = 2.0031$ are plotted together vs the Mg/Ca-ratio of the solution. Our results indicate that the value of the signal at $g = 2.0036$ is virtually uninfluenced by the growing Mg-concentration up to a Mg/Ca ratio of 0.1. Therefore we conclude that the Mg-concentration does not influence the amount of traps responsible for the signal at $g = 2.0036$. At further increasing Mg-concentratons in the solution the signal at $g = 2.0036$ diminishes and disappears totally at a Mg/Ca-ratio of more than 1.

While the signal at $g = 2.0036$ decreases, the signal at $g = 2.0031$ is not present at low Mg concentrations and increases for high Mg-concentrations.

It is most probable that the described behavior of these signals corresponds to an observed phase change of the synthetic crystals from calcite to aragonite. This is also characteristic for natural calcitic samples (foraminifera) where the signal at $g = 2.0036$ is present while natural aragonitic samples (corals) display the signal at $g = 2.0031$.

As reported by Rossi *et al.* (1986) the signal at $g = 2.0036$ is the g-perpendicular of a paramagnetic site with g-parallel $= 2.0021$. We came to similar conclusions for our natural and synthetic samples. The CO_3^{3-}-center is most probably responsible for this signal (Servay and Marshall, 1967). Thus we deduce that this center, which displays axial symmetry in calcite, changes to cubic symmetry in aragonite exhibiting a g-factor $\frac{1}{3}(2 \times 2.0036^2 + 2.0021^2)^{1/2} \approx 2.0031$ which agrees with the observed value. This may be due to larger inter-atomic distance in aragonite resulting in less interaction with the crystalline field (Plato and Schneider, 1971; Goldsmith and Graf, 1958). So, one and the same paramagnetic center could be responsible for the signals at $g = 2.0036$ and at $g = 2.0031$.

However, it is not yet clear which anion plays the role of stabilization of the center.

(ii) Signal at $g = 2.0006$. The saturation level of the signal at $g = 2.0006$ displays a quite different behavior with Mg-increase [Fig. 7(a)]. Up to a Mg/Ca ratio of 0.005 the signal seems to be unaffected by the Mg concentration but for higher concentrations it increases on a straight line with a slope between 0.5 (square-root) and 1 (linear). For a Mg/Ca ratio >0.5 it displays a nearly constant value*.

The situation is similar if we look at the saturation values as a function of the Mg-content in the crystals [Fig. 7(b)]. We find a nearly proportional increase of signal and Mg-content, starting at a Mg/Ca-ratio of 0.001 to a ratio of about 0.02 (about 6000 ppm), which is the highest Mg-content observed in the synthetic crystals. At higher Mg-concentration of the solution, the Mg-content of the crystals decreases by about a factor of 10 and the signal height remains constant. The decrease of Mg in the crystals goes along with the observed phase change from calcite to aragonite.

Another important feature of this signal was described in detail by Barabas *et al.* (1988), the decrease of the saturation value by heating. Preliminary annealing experiments with our synthetic crystals confirm that the traps responsible for the signal at $g = 2.0006$ disappear by heating, i.e. the saturation level S_m decreases with heating time, although the effect could not be quantified up to the present time. The same effect was observed for the saturation

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*The signal at $g = 2.0057$ also increases with Mg-concentration by a factor of 5.

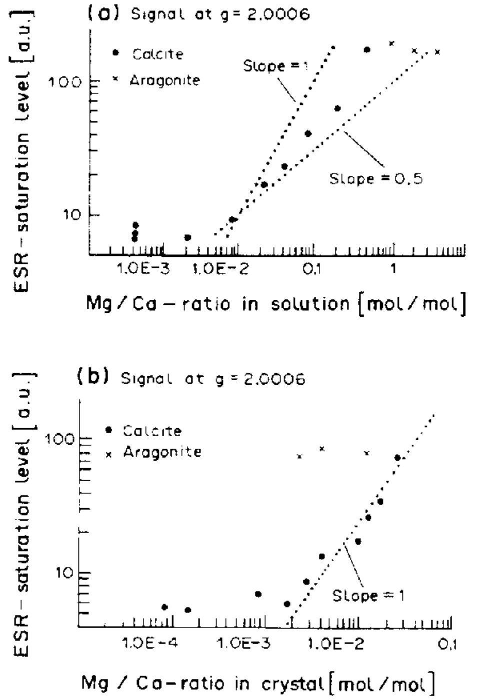

Fig. 7. Saturation values of the signal at $g = 2.0006$ in synthetic crystal (a) as a function of Mg/Ca-ratio in the solution and (b) as a function of the Mg/Ca-ratio in the crystals.

levels of the signals at $g = 2.0006$ in a deep-sea core (Barabas, 1989). The saturation levels of foraminifera —i.e. trap concentrations—decreased with the edge of the core, resulting in a lifetime of about 10^6 years (at 2°C; Fig. 6), even though the Mg concentration remains constant.

Although we do not yet know how the Mg^{2+}-ions change the properties of the carbonate crystals our results indicate that it is the Mg-content which is responsible for the signal at $g = 2.0006$ observed in synthetic and natural carbonates.

4. Conclusions

We observe in synthetic carbonate crystals doped with Mg^{2+}:

(i) ESR-spectra which display signals at the same g-factors, and with same properties as in natural carbonates.
(ii) An increase of the signal at $g = 2.0006$ with Mg-concentration in the doping solution.
(iii) Change from the signal at $g = 2.0036$ to $g = 2.0031$ parallel to the phase change from calcite to aragonite.

Additionally the presence of the signals at $g = 2.0057$ and $g = 2.0031$ indicates that it is most probable that none of these signals originates from organic matter.

Post scriptum

Latest experiments show that it is indeed the Mg^{2+}-presence and not the growing by gel-diffusion which influences the ESR-signal at $g = 2.0006$. Carbonate crystals grown with the precipitation method (according to De Keyser and Degueldre, 1950) display the characteristic ESR-signals in the presence of Mg^{2+}-ions as well.

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