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THERMAL BEHAVIOUR OF ESR SIGNALS OBSERVED IN VARIOUS NATURAL CARBONATES

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The thermal behaviour of the five main ESR lines observed in Quaternary carbonates ($g=2.0057$, $g=2.0031$, $g=2.0018$, $g=2.0006$ and $g=1.9972$) was studied through isochron annealing experiments. As the general rule, ESR lines are more stable in calcitic samples than in aragonitic ones and in speleothems than in marine carbonates. In all the studied carbonates, the most stable signals are $g=2.0057$ and $g=2.0031$, then $g=2.0006$.

INTRODUCTION

Since the first attempt to date a stalactite by ESR (Ikeya, 1975), natural carbonates have been the object of many studies. Indeed these minerals are very common in Quaternary deposits in various forms (speleothems, travertines, corals, foraminifera, mollusc shells, etc.) and may contain important information about palaeoclimatology, palaeogeography or archaeological chronology. Today, the nature of the most paramagnetic species observed in Quaternary carbonates is known with respect to structure, ESR features, dose-response, thermal behaviour, stability etc. (see for example Grün, 1989; Barabas *et al.*, 1992a, b; Bahain, 1993), but it is rather difficult to compare results obtained in different works, because, on the one hand, they have been generally focused on a specific kind of carbonates (often calcitic speleothems or aragonitic corals), and, on the other hand, experimental procedures may vary greatly from one study to another, especially concerning annealing experiments.

The main purpose of the present work is to observe and compare the evolution of ESR spectra for different carbonates during cumulated annealing experiments, in order to measure the effect of the nature, the mineralogy, the origin or the geological history of the samples on the thermal behaviour of the main ESR lines.

ESR SPECTRA OF CARBONATES

Six types of fossil carbonates have been studied: calcitic and aragonitic speleothems, aragonitic and calcitic (recrystallised) corals and aragonitic and calcitic (non-recrystallised) mollusc shells. The natural ESR spectra of these different carbonates are shown in Fig. 1.

ESR spectra of calcitic speleothems can change considerably from one sample to another (see for example Grün, 1989), but they show generally several isotropic lines at $g=2.0057$, $g=2.0040$, $g=2.0031$ and

$g=2.0006$, and a big rhombic signal at $g_{xx}=2.0030$, $g_{zz}=2.0015$, $g_{yy}=1.9972$. Spectra can be complicated by peaks due to paramagnetic impurities (Mn^{2+} and/or Fe^{3+}), irradiation (short-living signal, $g=2.0023$) or grinding (crushing signal, $g=2.0001$). Several lines have been used for dating ($g=2.0057$, $g=2.0040$ and $g=2.0006$) but even today the choice of the dating signal is the subject of controversy. On the other hand, relatively little is known about aragonitic speleothems. The ESR spectrum of the sample used in this study is nearly similar to the calcitic one, except for a very poor peak resolution. Lines at $g=2.0057$ and 2.0006 are present as well as the rhombic signal. This latter one has been used for dating (see Grün, 1989).

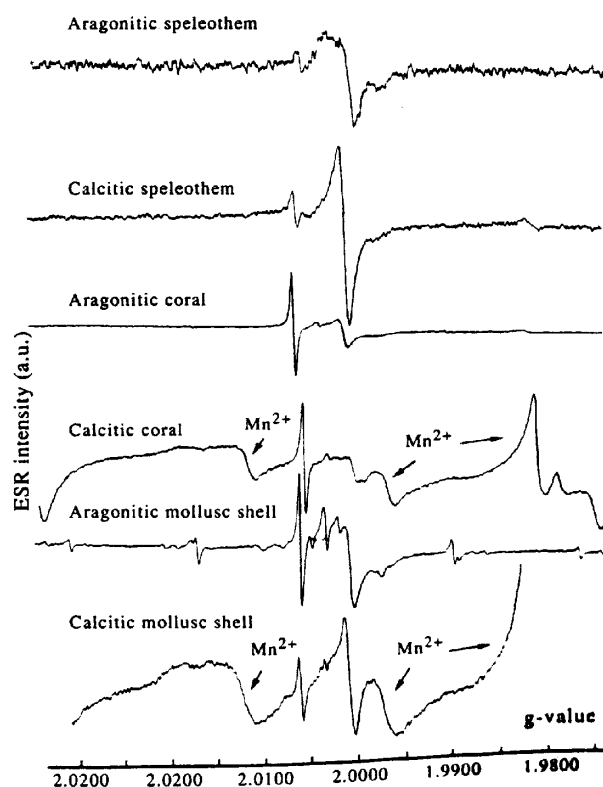


FIG. 1. Natural ESR spectra of several Quaternary carbonates.

ESR spectra of aragonitic corals display three peaks at $g=2.0057$, $g=2.0031$ and $g=2.0006$ (the latter is the dating signal). In the sample used in this study, the rhombic signal with a gap at $g=1.9972$ and an isotropic line at $g=2.0018$ appear with irradiation. These signals are also present in recrystallised corals as well as parasitic peaks (crushing signal and/or Mn^{2+} lines).

Mollusc shells show complex ESR spectra and five main lines ($g=2.0057$, $g=2.0018$, $g=2.0006$, and the rhombic one) and additionally paramagnetic impurities signals. At present, there is no consensus about the choice of a useful dating signal.

The main ESR features of signals observed in Quaternary carbonates are summarized in Barabas (1992).

Five signals are often present in natural carbonates: $g=2.0057$ (called *h-1* by Yokoyama *et al.*, 1981); $g=2.0031$ (or $g_{\perp}=2.0036$ and $g_{\parallel}=2.0021$) (*b*, Ikeya and Ohmura, 1981); $g=2.0018$ (*g-3*, Molodkov, 1988); $g=2.0006$ (*h-3*, Yokoyama *et al.*, 1981); $g=1.9972$ ($g_{xx}=2.0030$, $g_{zz}=2.0015$, $g_{yy}=1.9972$) (*A-complex*, Barabas *et al.*, 1992a). The thermal behaviour of these five lines are studied in this work.

EXPERIMENTAL

The resolution of the ESR spectrum of the aragonitic speleothem sample is not very good because of its

young age. On the other hand, some ESR signals appear only after irradiation. So, for each sample, five aliquots were irradiated with a ^{60}Co -source (at 42.5, 97.5, 172.5, 380 and 570 Gy). The thermal evolution was studied from a mean value of the ESR intensities, which corresponds to the non-irradiated and the five irradiated aliquots' intensities.

Powders (100–200 μm size) were filled in Suprasil tubes (3 mm inner diameter) and ESR measurements were carried out at room temperature using a Varian E-109 X-band spectrometer. The experimental parameters were: microwave power—5 mW, modulation amplitude—0.05 mT, scan range— 331 ± 5 mT, time constant—0.128 sec, modulation frequency—100 kHz. The peak-to-peak amplitudes of each signal were measured for each step of temperature, except for the line at $g=1.9972$ for which the distance from the peak to the baseline was used, then the intensities were normalized for weight and height of the powder inside the tube.

The thermal experiments consist of isochron annealings of 16 hr from 80°C to 220°C with steps of 20°C, performed with an Adamel T-2 electrical oven. A long annealing time was preferred because the equivalent short annealing at a higher temperature could cause an effect due to the relative thermal instability of the samples. The effective temperature during annealing was measured continuously and, except for fluctuations at the beginning of the experiments, temperature

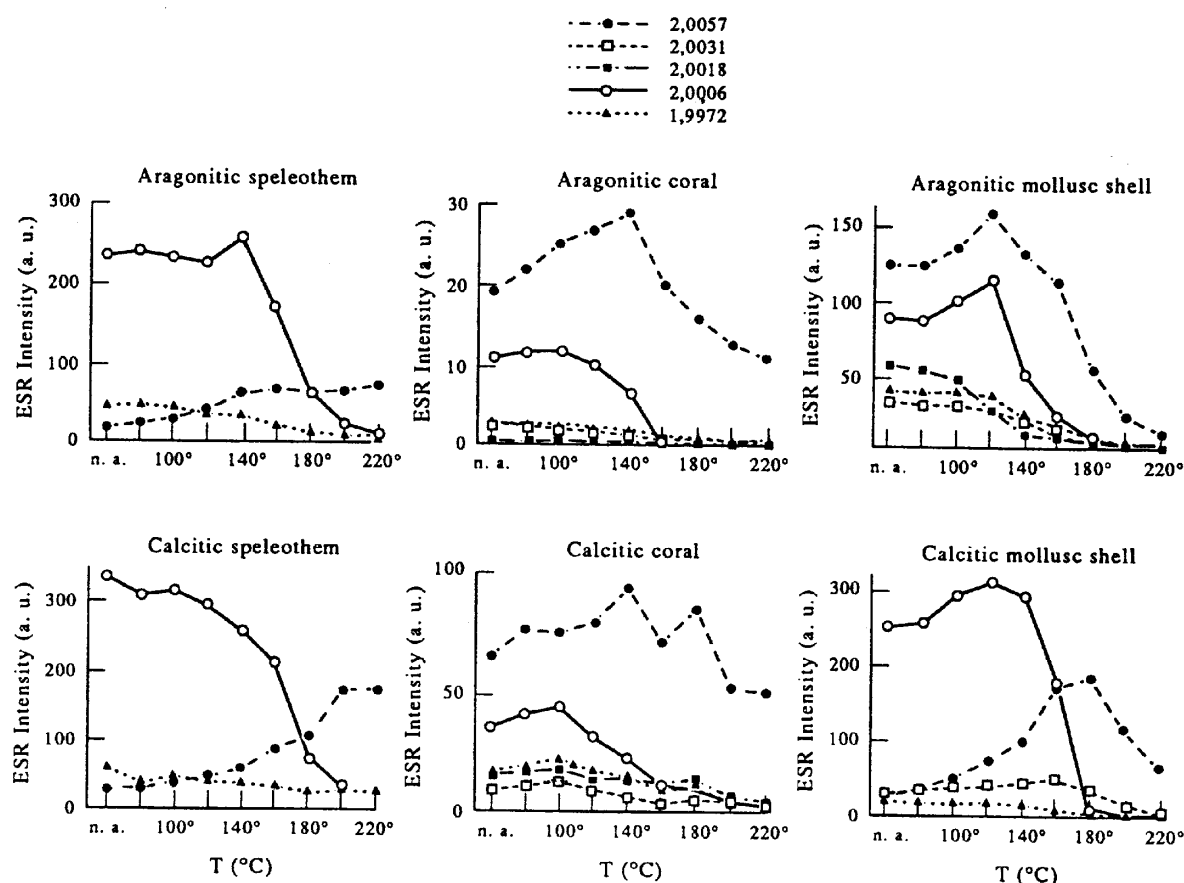


FIG. 2. Effect of cumulated isochron annealing experiments of 16 hr on ESR signals for different carbonates.

variations did not exceed $\pm 1^\circ\text{C}$. As samples were annealed directly inside ESR tubes, in order to reduce differences between two steps of thermal treatment, annealing effects are cumulated.

RESULTS

Isochron curves obtained for the various carbonates are shown in Fig. 2. In each diagram of this figure, the ratio of the intensities between the different ESR lines observed have been represented. Some interesting observations can be made about these curves.

(1) As a general rule, ESR signals are more stable in calcitic samples than in aragonitic ones.

(2) The general thermal behaviour of the main ESR signals does not change significantly with the mineralogy for speleothems and corals, when curves obtained for mollusc shells are very different according to whether the shell is calcite or aragonite.

(3) Aragonitic corals and aragonitic shells show approximately the same thermal behaviour: a small growth of intensities of the lines at $g=2.0057$ and $g=2.0006$ in the first steps of the thermal treatment, then a quick decrease. These two signals are more stable in aragonitic speleothem.

(4) The diagram obtained for calcitic speleothem is similar to that reported by Hennig and Grün (1983) or Smith *et al.* (1985). After a relative stability up to 120°C , the intensity of the line at $g=2.0006$ decreases rapidly, when, in the same time, the signal

at $g=2.0057$ is increasing. These features were also observed by Yokoyama *et al.* (1983), who explained these phenomena by a transfer of electrons from $g=2.0006$ to $g=2.0057$. This theory was, however, much criticized in the past (see for example Hennig and Grün, 1983 or Grün, 1989). In the present work, a similar thermal behaviour is also observed for the calcitic mollusc shell while the secondary calcite of recrystallised corals shows thermal features which are nearest to those observed in the aragonitic samples than in the other calcitic carbonates. In this latter case, the nature of the carbonate seems to play a more prominent part on the thermal behaviour than the mineralogy.

(5) ESR signals can be classified in terms of thermal stability:

$$g=2.0057 > g=2.0031 \geq g=2.0006 > g=2.0018 \approx g=1.9972$$

This classification is observed in all the studied samples, but the stability of the ESR centres may change with the nature and the mineralogy of the carbonates.

Figure 3 shows the thermal behaviour of a given ESR signal in the different carbonates. Here, the real sizes of the signals are not respected and only the shape of the isochron curves should be taken into consideration. The following observations can be noted.

(1) The isochron curves of $g=2.0018$, $g=2.0006$ and $g=1.9972$ are approximately the same for all samples. The intensities of these signals decrease quickly from the very first steps of annealing. The line at $g=2.0006$

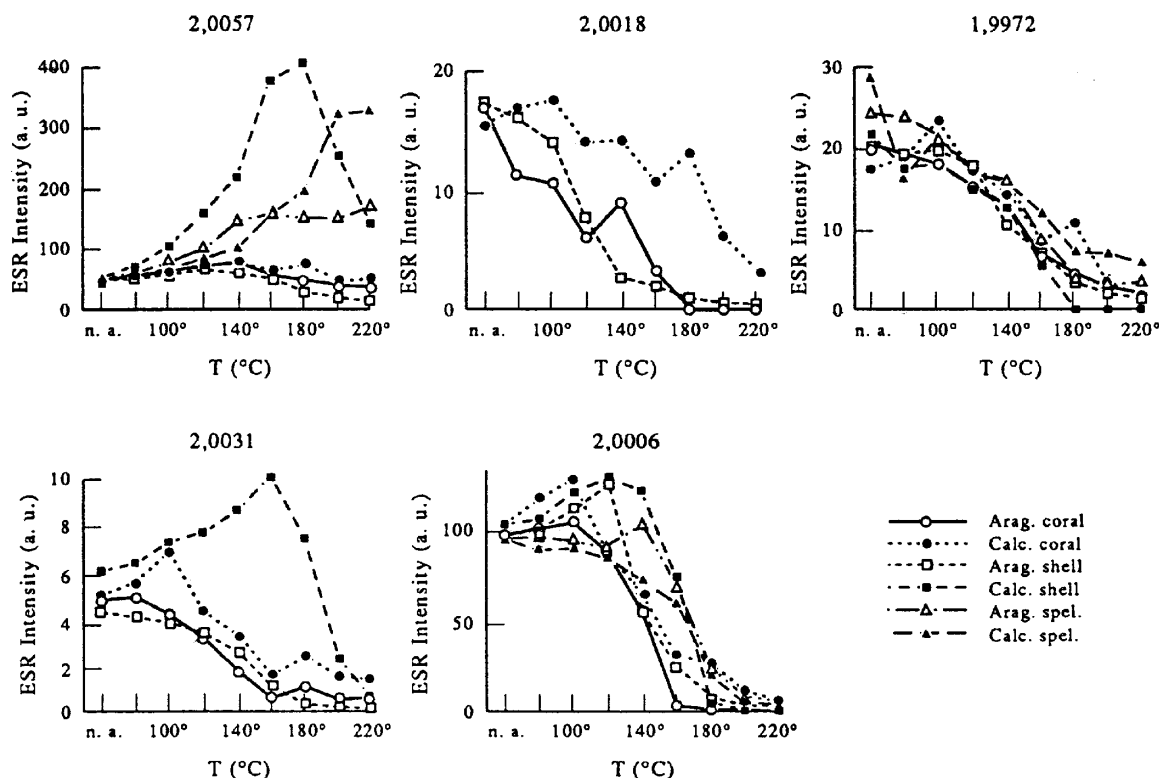


FIG. 3. Effect of cumulated isochron annealing experiments of 16 hr on main ESR signals according to the nature and the mineralogy of the studied carbonates.

is more stable up to 120–140°C, then it decreases rapidly and disappears about 180–200°C.

(2) The thermal behaviour of the signal at $g=2.0031$ seems to be very dependent on the nature and the mineralogy of the studied carbonate. In calcitic marine carbonates, this line shows a low thermal stability, when in calcitic ones, its intensity increases in the first steps of annealing. In calcitic mollusc shell, this initial growth is particularly important and continues up to 160°C, then intensity decreases quickly.

(3) Two kinds of isochron curves can be distinguished for the line at $g=2.0057$ according to the nature of the carbonates. In corals and in aragonitic mollusc shell, the signal is stable or grows slightly up to 120–140°C then decreases. On the other hand, in speleothems and in calcitic shell, the intensity of $g=2.0057$ strongly increases up to 160–200°C up to maximum values, which can be 8–10 times higher than the initial intensity. The mineralogy and the biological or geological nature of the carbonates have therefore a considerable importance on the stability of the paramagnetic centre responsible for this line.

CONCLUSION

Isochron annealing experiments show that the thermal behaviour of the main ESR signals observed in natural carbonates greatly changes with the nature and the mineralogy of the samples. As a general rule, signals are more stable in calcitic samples than in aragonitic ones and in speleothems than in marine carbonates. It is also possible to classify ESR signals in terms of thermal stability: the lines at $g=2.0057$ and $g=2.0031$ are the most stable, then $g=2.0006$.

The relative instability of the line at $g=2.0006$ is probably related to the fact that the CO_2^- radicals responsible for this signal are associated with water molecules (Barabas *et al.*, 1992a; Debuyst *et al.*, 1993). Moreover, intensity measurements of this line are often difficult because of the presence of the very unstable A-complex signal. The low thermal stability of the line at $g=2.0006$ was already discussed (Yokoyama *et al.*, 1983; Barabas *et al.*, 1992b).

The signal at $g=2.0031$ shows a good thermal stability in calcitic mollusc shell. This fact can be put together with the works of Barabas *et al.* (1988) and Mudelsee *et al.* (1992), in which this signal is used to date calcitic foraminifera. On the other hand, in aragonitic marine carbonates, this line displays a very poor thermal stability and its use for dating does not seem possible.

The use of the line at $g=2.0057$ to date speleothems is a subject of controversy, on account of the non- γ -sensitivity of this signal and to its growth during thermal treatments (see, for example Grün, 1989; Bahain, 1993). An increase of the signal intensity is also observed during the thermal treatment of the calcitic mollusc shell, but not in aragonitic or recrystallized samples. This phenomenon could be related to a

structural feature of the calcite rather than to the nature of the paramagnetic centre responsible for the signal. However, the present study confirms that this line is the most stable signal observed in Quaternary natural carbonates.

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