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RADIATION-INDUCED PARAMAGNETIC SPECIES IN NATURAL CALCITE
SPELEOTHEMS*

by

A.M. ROSSI^{1,2} and G. POUPEAU²

¹Centro Brasileiro de Pesquisas Físicas - CBPF/CNPq
Rua Dr. Xavier Sigaud, 150
22290 - Rio de Janeiro, RJ - Brasil

²URA 69/CNRS and Institut Dolomieu
Université Joseph Fourier
Rue Maurice Gignoux, 38031 Grenoble Cedex, France

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ABSTRACT

The ESR natural spectrum of humic-free speleothem calcite single crystals in the region of $g = 2.0000$ is a composite of lines from 4 radiogenic species, in addition to Mn^{++} lines. Laboratory irradiation causes appearance of three more species. Use of isotropic F species ($g = 2.0003$) for dating is possible if specific cautions are followed.

1. INTRODUCTION

In 1975, Ikeya presented the first attempt to date speleothems calcites by ESR. Since then, as many other speleothem dating attempts have been published, it was progressively realized that both the natural ESR spectra of calcites and the thermal stability of the dating paramagnetic species might vary from sample to sample (e.g. Hennig and Grün 1983, Rossi 1987).

The lines most generally used in ESR dating of speleothems are characterized by g factors of 2.0007 (Skinner 1983, Smith et al 1985, Wieser et al. 1985) and 2.0056 (Yokoyama et al. 1981, 1983). These two lines, dubbed respectively h_3 and h_1 by Yokoyama, were chosen because of their thermal stability, with mean lifes of the order of $10^6 - 10^7$ yr for h_3 (Hennig and Grün, 1983) and $> 10^6$ yr for h_1 (Yokoyama et al. 1983). Second, h_3 , with a high sensitivity to radiation dose, presents a linear increase of line intensity up to gamma-ray doses of ≈ 1 kGy. However, the nature, formation mechanisms and thermal redistribution of paramagnetic species responsible for these lines are yet not well elucidated.

In a previous work on irradiated speleothems monocrystals of calcite (Rossi et al. 1985) we studied the behaviour of four species A, B, C, and D, induced by beta- and gamma-ray doses higher than 1 kGy. The presence of these centres, probably $\text{CO}_3^{\cdot-}$ and $\text{CO}_2^{\cdot-}$ groups (Marshall et al. 1964, Serway and Marshall 1967), was later recognized in powder spectra of the same samples. At that time no information could be obtained on the nature of h_1 and h_3 lines.

In the present article we discuss results and interpretations of single crystal and powder spectra of unirradiated speleothem

calcites and describe the characteristics of lines associated with three paramagnetic species present in natural ESR spectra, C, F, and G.

2. ESR NATURAL SPECTRA OF SPELEOTHEM CALCITE

2.1. Single-crystal studies: Matozinho (MT) cave monocrystals

Speleothems single crystals of calcite from the Matozinho cave (Bahia, Brazil) were cut into several slices following the (111) plane or perpendicular to it and were observed in an X-band ESR spectrometer, between 300°K and 90°K. At the ambient temperature, three paramagnetic species C, F and G (Fig.1) were identified from angular variation studies. Species F ($g = 2.0003$) and G ($g = 2.0053$) are characterized by an isotropic singlet (Fig.2). Their linewidth at 300°K are respectively 1.5 G and 0.9 G; saturation of the signal occurs with klystron power of 60 mW and 20 mW respectively. Single-crystal species F and G therefore exhibit the same behaviors as lines h_3 and h_1 of speleothems powder spectra.

Species C is constituted of two lines with a linewidth of 0.6 G which saturate at a klystron power of 0.5 mW. The angular variation of these lines in planes perpendicular and parallel to the [111] direction is shown on Fig.2. This species presents an axial symmetry in the plane perpendicular to [111]. The g factor principal values are $g_{\perp} = 2.0029$ and $g_{\parallel} = 1.9990$.

Upon cooling from 300°K to 90°K the intensities of the C, F and G lines decrease; meanwhile from 200°K downwards there appear

and increase three lines belonging to another species, E, presenting an orthorhombic symmetry. The E species spectra present a symmetry about the [111] axis and correspond to three magnetically unequivalent orientations of the defect centers relative to the calcite coordinate system. At 90°K, the linewidth of E species is 0.5 G and saturation of the signal occurs at a klystron power of 0.5 mW. The principal values of the E species factor g are: $g_{xx} = 2.0028$, $g_{yy} = 2.0010$ and $g_{zz} = 1.9966$, the x axis being parallel to the [111] direction (Table 1).

Species C and E have also been observed in the natural spectrum of irradiated single crystals of other speleothems, as samples SB (Bahia, Brazil) and SP1 (Sao Paulo, Brazil), with remarkably similar g values.

From single crystals studies, it thus appears that, in the dating region of the natural ESR spectrum of calcite speleothems, only two paramagnetic species, F and G, have in our samples, isotropic g factors. All other species we observed, A, B, C, D, and E, present axial or orthorhombic symmetries relative to the [111] direction. This suggests that these species might be located, within the calcite lattice, on the same crystalline planes as the CO_3^{2-} groups. The g factors and linewidth values of these species, as well as their saturation curves versus microwave power, are identical to those measured by Marshall et al. (1964) and Serway and Marshall (1967) for CO_2^- and CO_3^{2-} groups. The F and G species, with a larger linewidth, higher saturation level with microwave power than the above species and an isotropic g factor, could be associated with punctual defects in interstitial position in the calcite lattice.

2.2. Powder Spectra

Matozinho calcite crystals were gently crushed in a mortar and the 177-250 μm grain-size fraction was selected for ESR powder spectra studies. A typical powder spectrum is shown in Fig.3b, with the identification of species C, F and G. One can observe that, in the vicinity of the F line, the spectrum is rather complex with the presence of the C species (Table 1) and Mn^{++} lines and possibly a small component, very subdued at 300°K, due to the E lines.

Laboratory-irradiated powders exhibit even more complex spectra, as in samples SB and SP1, because of the formation of species A and B, Fig.3a. In the Matozinho sample, irradiation with a 2.5 kGy gamma-dose results also in the appearance of a new species, which is presently under study.

The shape of the absorption lines associated to species C, F and G is best defined within 250°K and 350°K (cf. Matozinho sample, Fig.4). For instance, the intensity of species C line decreases in this temperature interval, while its linewidth keeps constant. Species F intensity increases with cooling between 350°K and 260°K and decreases progressively below this temperature (Fig.5). The width of this line, 1.5 Gauss, remains constant from 350°K to 270°K and then reduces to 1.1 Gauss at 230°K. This behavior was observed with four other samples SB, SP1, YCP36 (Caune de l'Arago, France) and ALD1 (Aldène Cave, France). The best temperature range for the observation of species F is between 250°K and 270°K, where it presents the largest peak-to-peak amplitude, the narrowest linewidth and therefore the most limited superposition with the C species

lines. Under these conditions, the F line appears as perfectly Lorentzian (Fig.4). Species G presents the same behavior as species F between 350°K and 250°K with the restriction of a constant linewidth.

Close comparisons between powder and single-crystal spectra of the same sample thus show that the F and G species, identified in single crystal studies, do correspond to the $g=2.0007$ (" h_3 ") and $g=2.0056$ (" h_1 ") lines generally used for dating with powder spectra. Moreover, the F species present a perfectly Lorentzian line. The " h_2 " line of Yokoyama et al. (1981) results, in fact, of a superposition of lines of species A, B and C, as already pointed out by Rossi et al. (1985). We would like to underline that if the F species line is to be used in ESR dating, utmost care must be given to minimize superposition effects from other lines, such as those related to the A, B, C and E species. From our experience, best observation conditions are obtained with klystron power around 5-10 mW and resonance cavity temperatures between 273°K and 260°K.

3. THERMAL ANNEALING EXPERIMENTS: BEHAVIOUR OF F AND G SPECIES

Several years ago, it was suggested that the unpaired radiogenic electrons giving rise to the h_3 line (our F species) in speleothem powder spectra, could be quantitatively redistributed over the site responsible of the h_1 line (G species), under the influence of temperature, and that this phenomenon could be used in ESR dating (Yokoyama et al. 1981). We studied the relative behavior of the F and G species against thermal annealing in the 177-250 μm size fraction of speleothems YC18, YC62 (Caune de l'Arago, Yokoyama

et al. 1981) and various samples, MT7, CP7, FC and SP2 from caves in Bahia and Sao Paulo states, Brazil (Rossi, 1987).

The spectra shown in Fig.6 illustrate the variability of response to isothermal annealing between different samples. For instance, in sample MT and SP2, the rate of decrease with time of F signal is faster than for G (Fig.6a). In sample FC, the natural ESR spectrum presents only the C and F lines (Fig.6c); thermal annealing results in a F-line intensity decrease without the appearance of the G line. On the other hand, in CP7, only the G line is present in the natural ESR spectrum (Fig.6b). Upon heating in 10-minute steps, this line increases approximately exponentially up to 200 minutes. Thus, thermal redistribution of F electrons appears to be more complex in our samples than was previously suggested.

This kinetics behavior was studied from a series of isothermal annealing experiments on SP2 at 189.8°C, 202.2°C and 213.5°C (temperatures stable to within 0.2°C) for times between 5 minutes and 4 hours. In the 189.8°C experiment, for instance, the G-line intensity increased during the first 30 minutes and then stabilized, while the decrease of the F line was pronounced during the first hours of heating (Fig.7).

Isothermal annealing kinetics were fitted with functional characteristics of processes of first order, second order and order 3/2. The simulation which approximates most our experimental results, whatever the isothermal annealing temperature, was of second order, i.e. of the type: $1/I=1/I_0 + Kt$ where I and t are respectively, the residual intensity after heating time, t, I_0 being the initial line intensity, and K the reaction rate constant.

On the basis of the decrease of F-line species following the

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Arrhenius law, $1/\kappa = \mathcal{V} e^{-E/kT}$, where k is the Boltzman constant and T the temperature ($^{\circ}\text{K}$), we find an activation energy $E = 1.54 \pm 0.02$ eV and a pre-exponential factor $6.3 \times 10^{10} \text{ s}^{-1}$. The resulting value for the mean life for thermal annealing at 15°C is of 5×10^4 yr.

The same isothermal experiments were conducted with YC62 for temperatures of 193.05°C , 201.8°C , 208.3°C and 213.5°C and heating times between 5 minutes and 450 minutes. Experimental results were also fitted with kinetics of orders 1, 2 and $3/2$. Best fitting with experimental results were obtained with a process of order $3/2$. Using the Arrhenius law we computed E and \mathcal{V} values of respectively 1.48 ± 0.02 eV and $5.8 \times 10^{11} \text{ s}^{-1}$ and a mean life at 15°C of 4.7×10^6 yr. With first order kinetics, we would have, respectively, arrived at $E = 1.41$ eV, and $\mathcal{V} = 1.38 \times 10^{11} \text{ sec}^{-1}$ and a mean life at 15°C of 1.3×10^6 yr (Rossi 1987). This last value is of the same order as was found for other speleothems by Hennig and Grün (1983) and Grün (1985). It is, however, at variance with the Yokoyama et al. (1983) value of 2.2×10^5 yr for the YC62 sample. The nature of the difference between these two YC62 samples is not known. It may be pointed out that, although from the same speleothem, our ESR sample was taken from a different fragment than that of Yokoyama et al (1981). We would like to point out that, although our activation energy for the F electrons is in the same range as has been found by other authors for the $g = 2.0007$ line, we observed that (i) the thermal redistribution of F electrons may be described by a kinetic function of an order different from one and that (ii), according to the sample studied, the extrapolated mean life time of F electrons against thermal annealing of calcite speleothems may be found to vary by at least two orders of magnitude.

4. RESPONSE TO DOSE

The intensity of lines A, B, C, D, F and G increases with laboratory gamma-doses. The relative behavior of F and G species was studied on the most recently formed part of SP1, assumed to be very young, as deduced from speleothem geometry and water inflow rate. In the natural ESR spectrum of SP1, the only species present is F, which, due to its low peak-to-peak amplitude, could only be observed with a high gain. The intensity-versus-dose curves for F and G species are displayed in Fig.8. We can observe that the G species is induced by gamma-rays but saturates with doses of 0.15 kGy and that the growth of the F line, although monotonous on this dose range, is, however, not linear. This is at variance with the usual observations of a linear increase up to ≈ 1 kGy (Hennig and Grün 1983, Rossi 1987).

5. SUMMARY

The ESR study of humic acid-free speleothem calcite monocrystals show that:

- 1) at room temperature, the variability of the natural powder spectra is due to variable mixtures of three paramagnetic species; three more species may appear through gamma-ray laboratory irradiation and complicate further the use of powder spectra for ESR dating with the conventional "additive-dose method";
- 2) The most widely used line in ESR dating is due to the

isotropic species F characterized by a $g = 2.0003$. Using this line however, requires utmost caution, because of (i) its variable lifetime upon thermal annealing, ranging from sample-to-sample up to a factor 100; (ii) amplitude and linewidth temperature dependence between $\approx 250^\circ\text{K}$ and 350°K ; (iii) its sometimes sublinear increase with gamma-dose even at low (<1 kGy) dose values.

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FIGURES CAPTIONS

Fig.1: Natural ESR spectra of single crystal of Matozinho (MT) cave speleothem:

- a) static magnetic field H perpendicular to $[111]$ calcite direction, $T = 20^{\circ}\text{C}$;
- b) and c) spectra taken in a plane containing the $[111]$ direction, with $[111]$ respectively parallel and perpendicular to H , $T = 20^{\circ}\text{C}$;
- d) same as a), in a position of maximum symmetry, $T = -180^{\circ}\text{C}$.

Fig.2: Angular variation of the ESR lines in one unirradiated single crystal of the MT calcite speleothem:

- angular variation in planes perpendicular to $[111]$ calcite direction;
- angular variation in planes parallel to $[111]$.

Fig.3: ESR calcite speleothem powder spectra:

- a) laboratory irradiated SB sample ($\cong 1$, 50 kGy gamma-ray dose);
- b) natural spectrum of MT sample.

Fig.4: ESR spectra of C and F lines at various temperatures in sample MT. Microwave power, 1mW:

- a) $T = 20^{\circ}\text{C}$
- b) $T = -15^{\circ}\text{C}$
- c) $T = -50^{\circ}\text{C}$

Fig.5: Lines behavior of the C, F and G species with the ESR spectrometer cavity temperature.

Fig.6: Isothermal annealing behavior of F and G species in different calcites speleothems:

- a) MT sample annealed at 178°C;
- b) CP7 sample annealed at 205°C;
- c) FC sample annealed at 220°C.

Fig.7: Isothermal annealing on SP 2 sample at a temperature of 189.8°C:

- F line intensity, experimental values;
- F line, first order fitting;
- F line, 3/2 order fitting;
- F line, fitting of order 2;
- x G line experimental values.

Fig.8: F and G lines intensity variation with laboratory gamma-ray dose in SP1 sample.

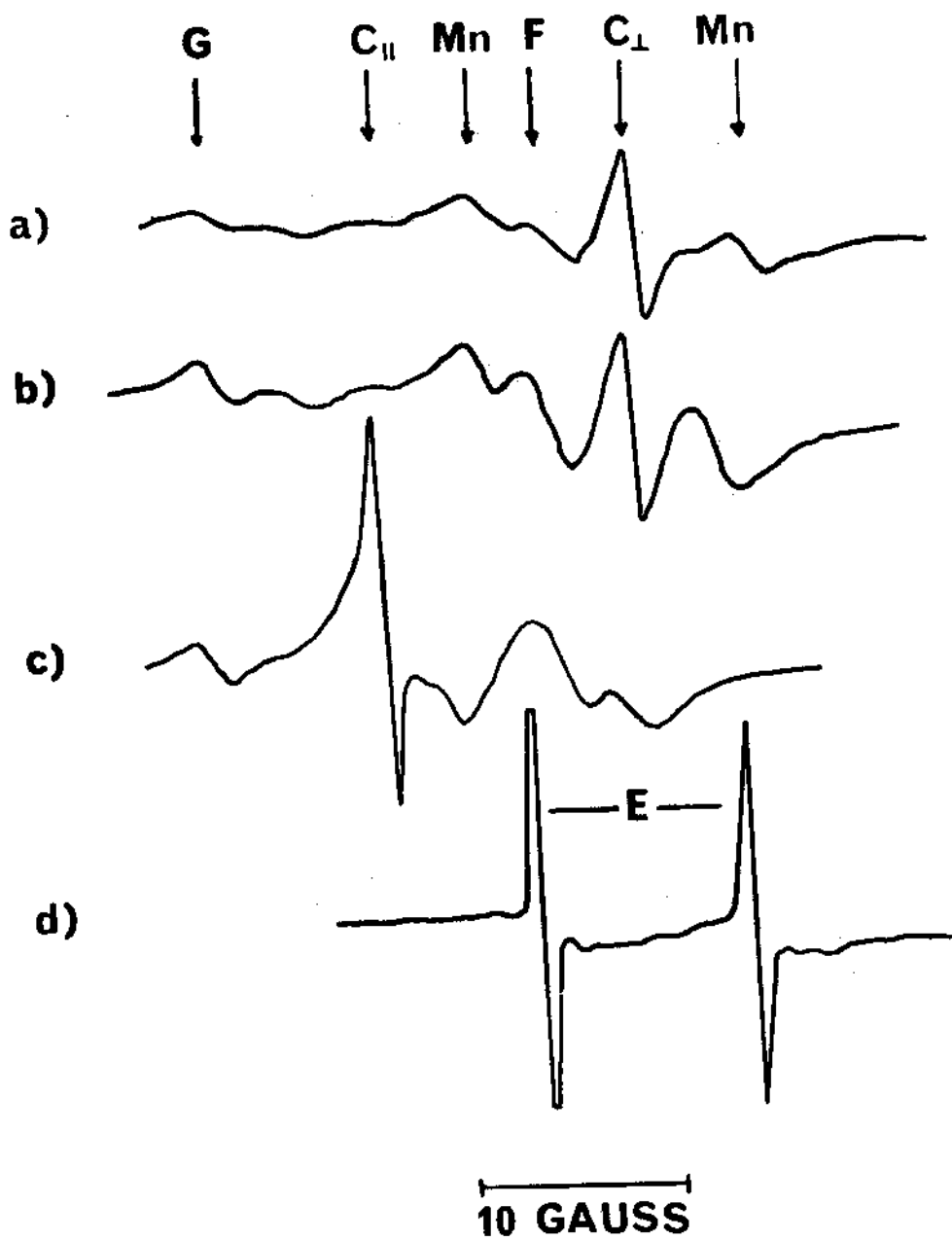


Fig. 1

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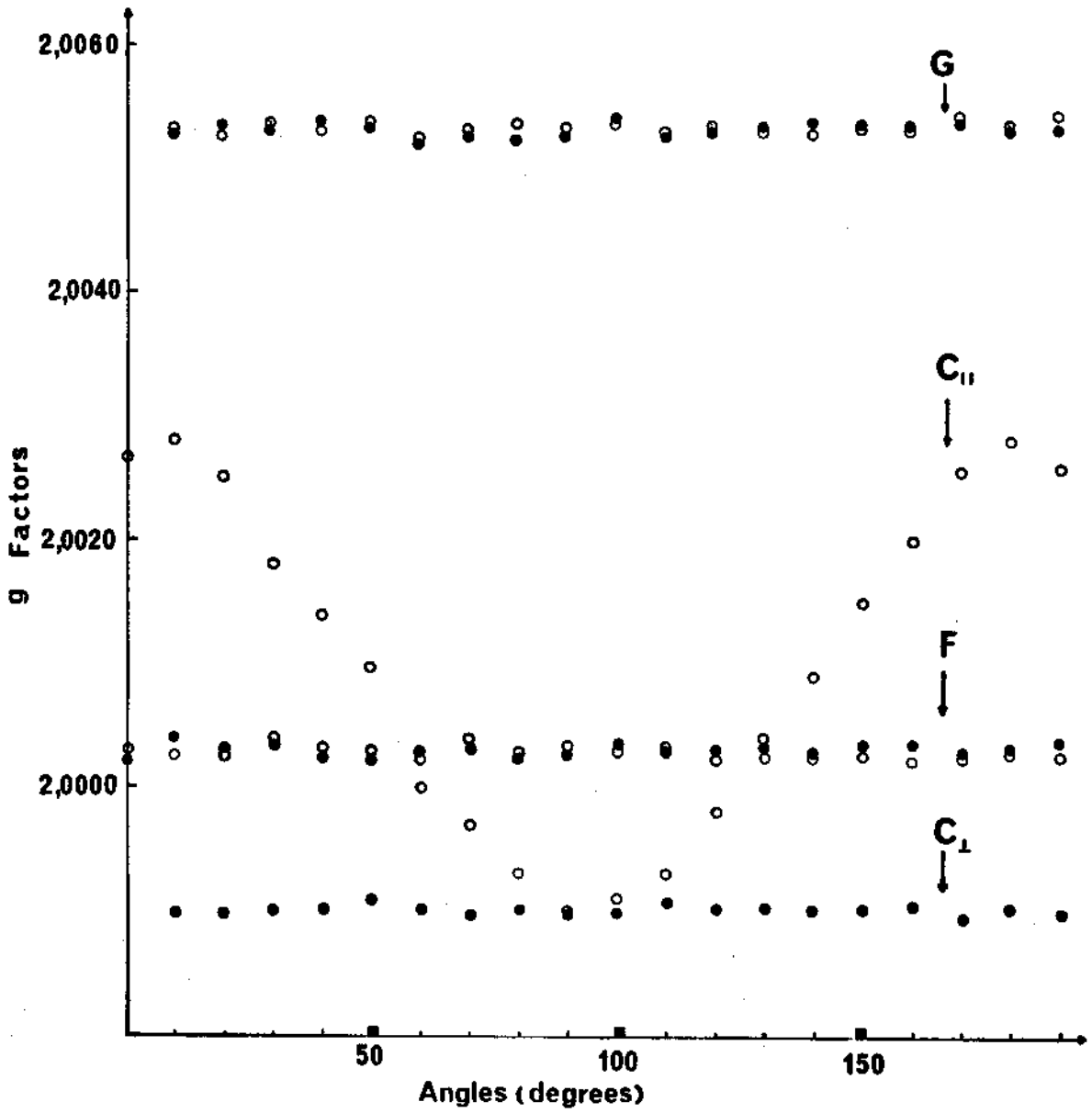


Fig. 2

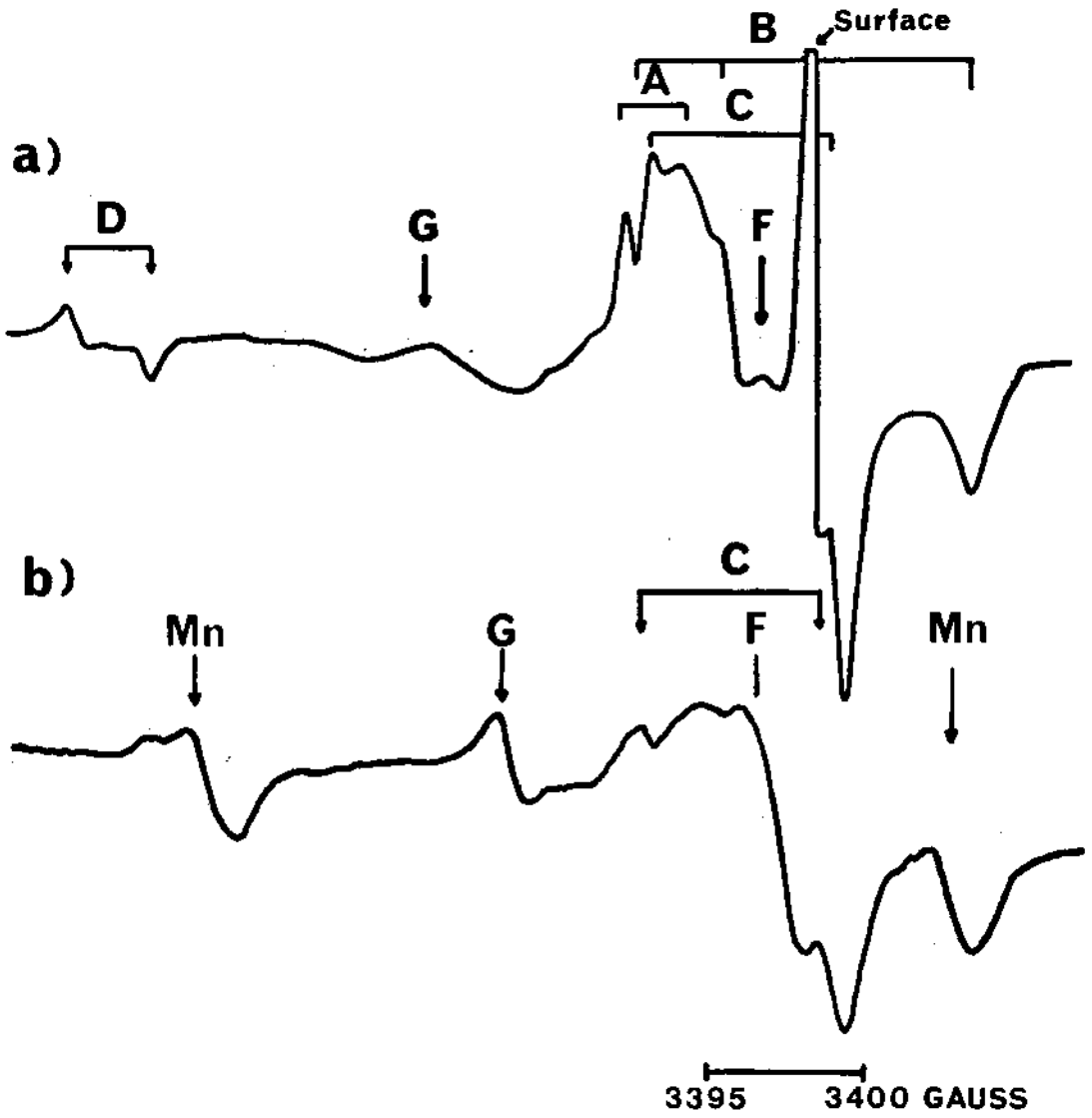
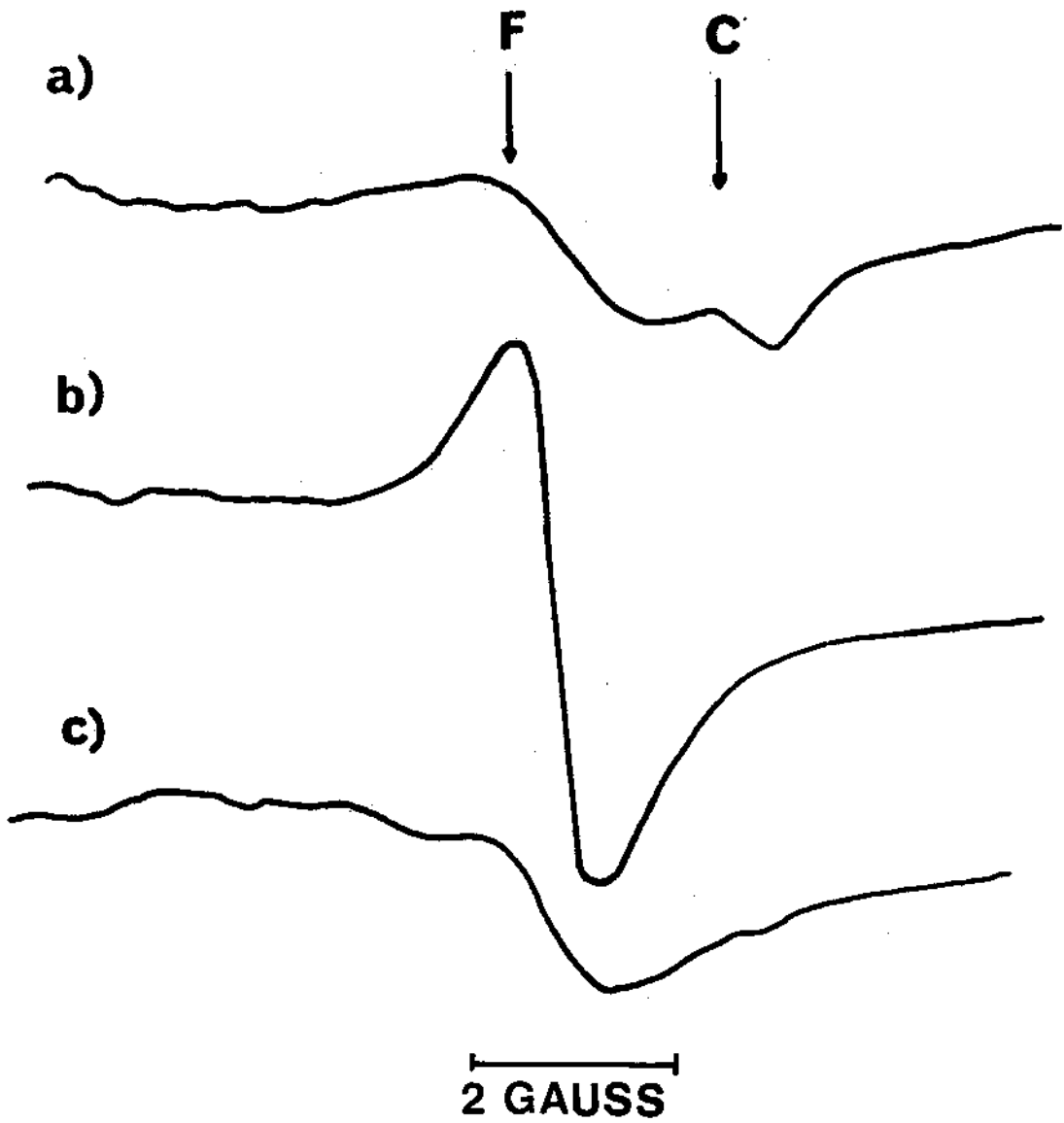


Fig. 3



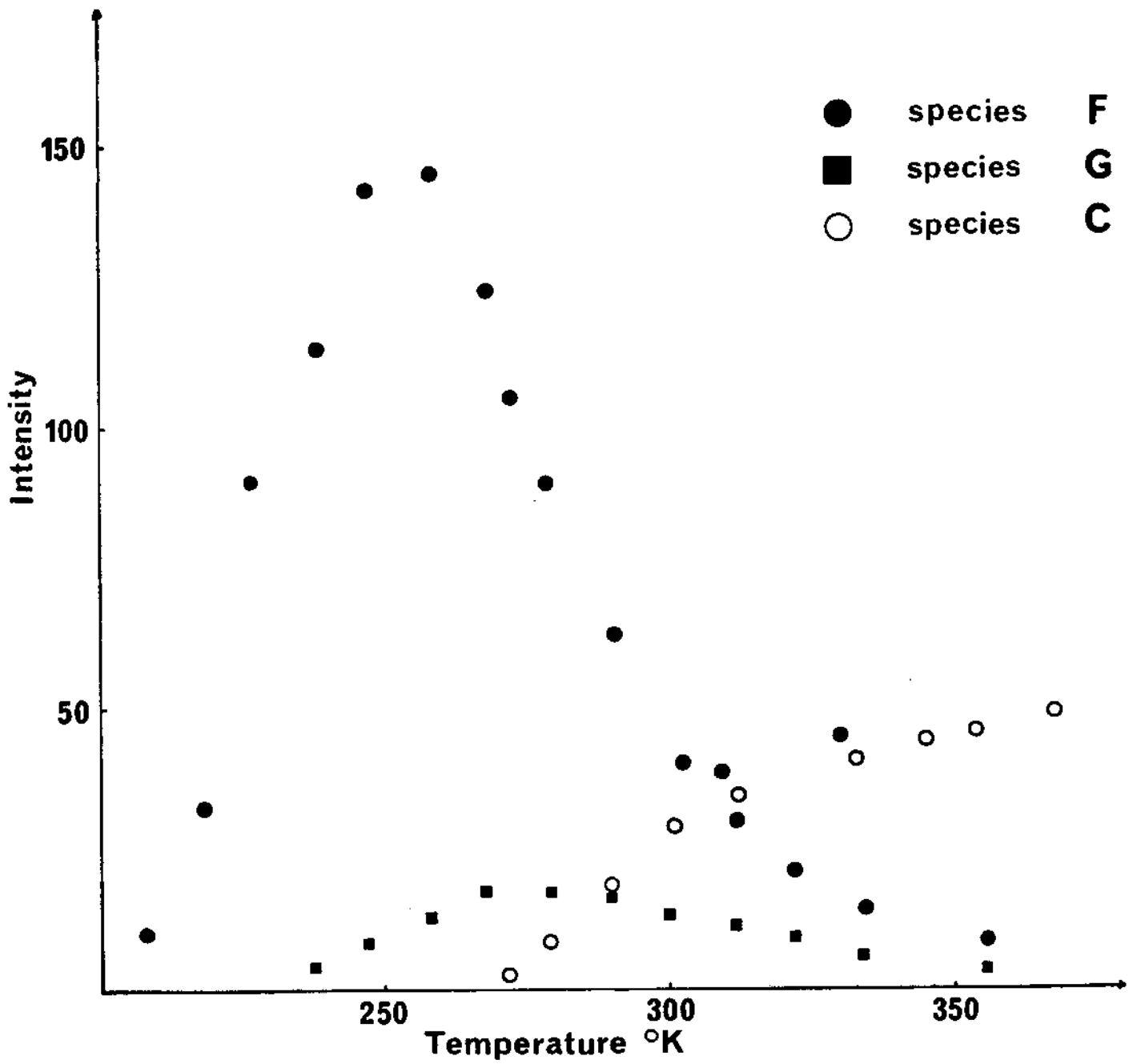


Fig. 5

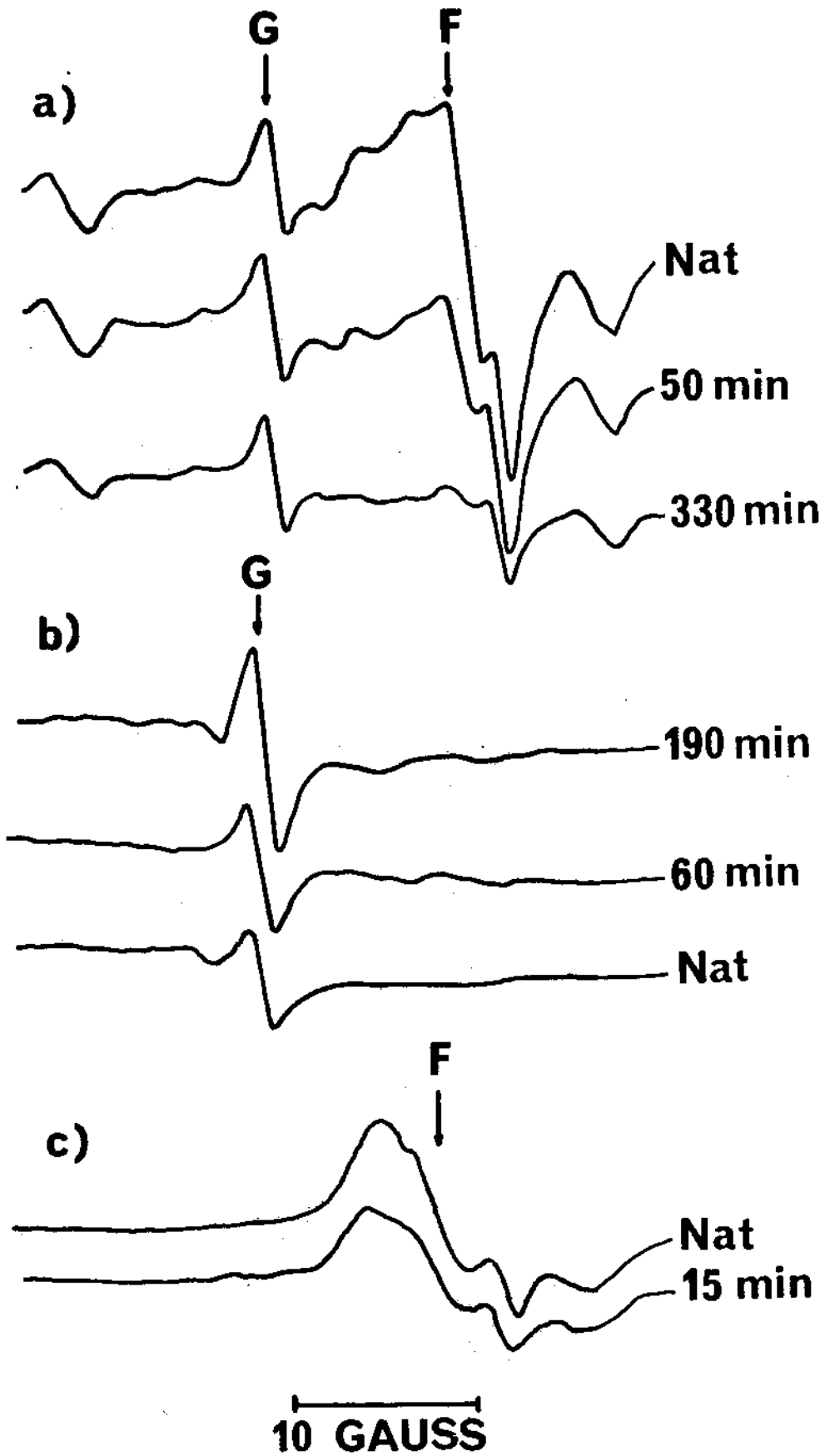


Fig. 6

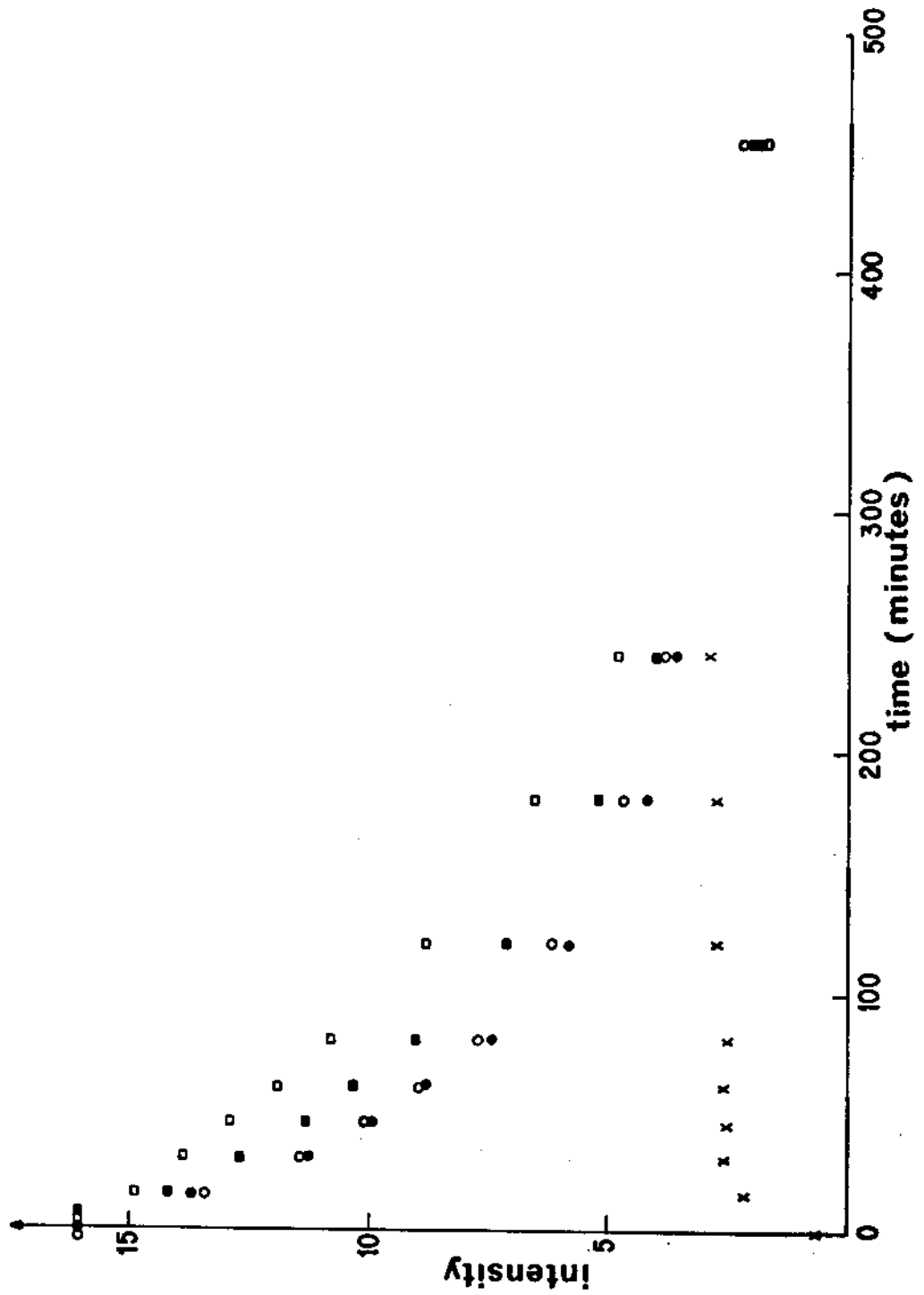


Fig. 7

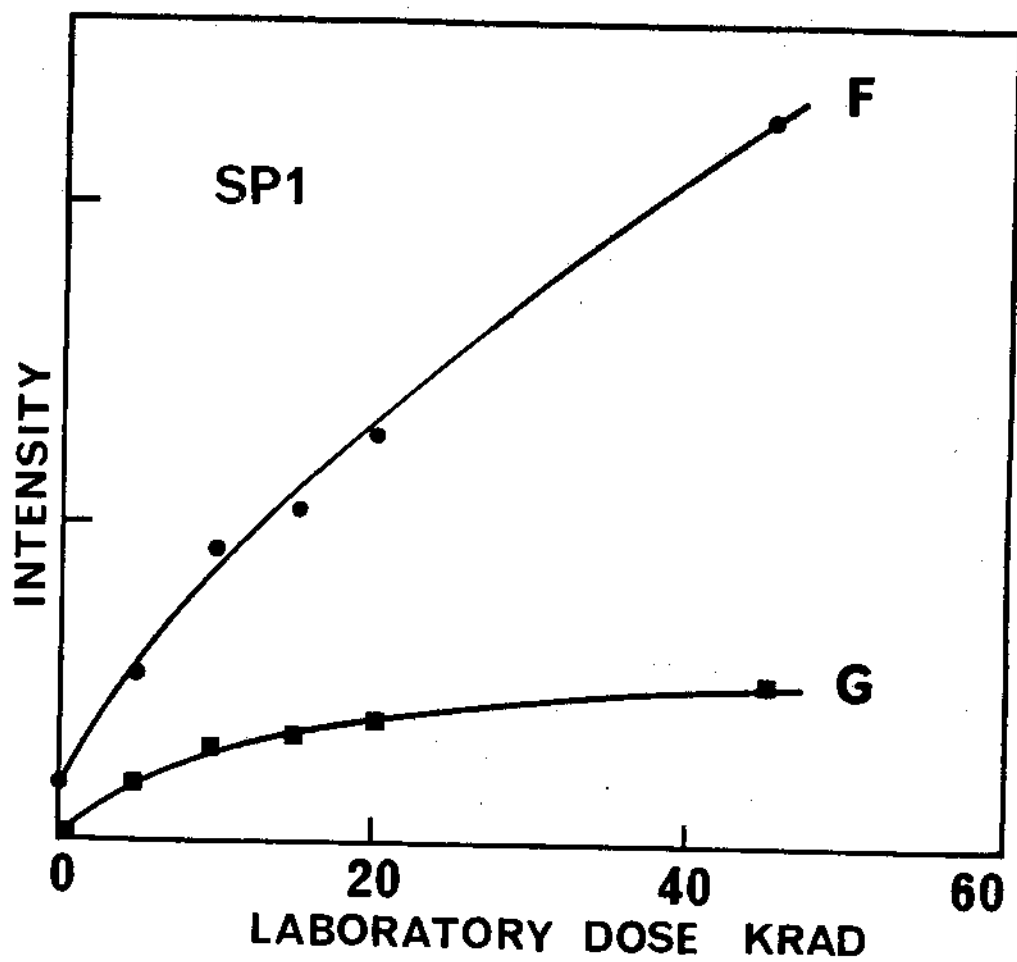


Fig. 8

TABLE 1

Paramagnetic species identified in the ESR spectrum of speleothem calcites

| SPECIES | SAMPLE | g_{xx}° | g_{yy} | g_{zz} | REMARKS | REFERENCES |
|---------|--------|------------------|----------|----------|---|------------|
| A | SB | 2.0018 | 2.0034 | 2.0034 | Axial symmetry about [111] calcite direction observed at ambient temperature | a |
| | SP1 | 2.0021 | 2.0035 | 2.0035 | | |
| B | SB | 2.0026 | 2.0018 | 1.9972 | Orthorhombic symmetry about [111] calcite direction observed at ambient temperature | a |
| | SP1 | - | - | - | | |
| C* | SB | 2.0028 | 1.9991 | 1.9991 | Axial symmetry about [111] calcite direction observed at ambient temperature | a |
| | SP1 | 2.0031 | 1.9994 | 1.9994 | | a |
| | MT | 2.0029 | 1.9990 | 1.9990 | | c |
| D | SB | 2.0164 | 2.0142 | 2.0126 | Orthorhombic symmetry about [111] calcite direction observed at ambient temperature | a |
| | SP1 | 2.0163 | 2.0143 | 2.0128 | | |
| E | SB | 2.0032 | 2.0016 | 1.9971 | Orthorhombic symmetry about [111] calcite direction observed at low temperature | b |
| | SP1 | - | - | - | | |
| | MT | 2.0028 | 2.0010 | 1.9966 | | |
| F* | MT | | 2.0003 | | Isotropic symmetry observed at ambient temperature | c |
| G* | MT | | 2.0053 | | Isotropic symmetry observed at ambient temperature | c |

*Species generally present in natural ESR spectra. Others are induced by laboratory irradiation. References: (a) Rossi et al., (1985); (b) to be published elsewhere; (c) this work.

^oThe x direction is parallel to [111].

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