THE NATURE AND THERMAL STABILITY OF TRAPPING CENTRES IN NATURAL CALCITE

A.M. ROSSI AND G. POUPEAU

URA 69/CNRS and Institut Dolomieu, Université Joseph Fourier
Rue Maurice Gignoux, Grenoble 38031 cedex, France
and
Centro Brasileiro de Pesquisas Fisicas
Rua Xavier Sigaud 150, Rio de Janeiro, Brasil.

In the g=2.0000 region of the ESR spectrum of natural calcites, many lines belonging to at least 5 paramagnetic species are sensible to radiation dose (Henning and Grün 1983, Rossi et al. 1985). It was proposed long ago (Zeller et al. 1967) to use the most stable of these species for natural sites dosimetry and dating. Among these, the F species of Rossi (1987), characterized by an isotropic line at g= 2.0003, appeared as the most interesting and is presently the most widely used in ESR dating. Previous studies suggested that the thermal redistribution of F electrons followed a first order kinetics. However, there were disagreements between different groups about the mean life of the F radiogenic species in stalagmitic calcites as deduced from laboratory thermal annealing experiments. In the present work, we re-investigated (i) the number and nature of radiogenic paramagnetic species in stalagmitic calcites and (ii) the thermal stability of these species.

Calcite cm-sized monocrystals were sampled from various stalagmites of brazilian caves. Calcite purity was checked by X-ray diffraction and trace-element contents determined by atomic absorption analysis. These crystals were cut into small (mm-sized) fragments following directions parallel or perpendicular to the crystallographic plane (111), i.e. the plane of CO_3^{2-} groups. ESR measurements on single fragments were there led at 9.5 GHz and 35 GHz, with (111) plane perpendicular or parallel to the static magnetic field of the spectrometer. Our results are presented in table 1 : up to three species, C, F and G, could be observed in the natural ESR spectrum of pure calcite. While the F and G species are isotrope, species C presents and axial symmetry about the [111] direction.

Upon gamma irradiation (^{60}Co source delivering 0.17 Gy/mn), the intensity of lines related to the C, F and G species was found to increase and four additionnal anisotropic species A, B, D and E appear. Of all the lines present in the spectrum, the isotropic line associated to species F is the most sensible to dose. Based on our and Marshall and associates (1964, 1967) earlier observations, we suggest centre A is related to a CO_3^{3-} group; D, to a CO_3^- group; and B, C and E to CO_2^- groups in different environements. The C centre could be a rotating CO_2^- group. The nature of the F and G centres is yet unknown.

Thermal annealing between 150°C and 250°C of single crystal fragments show that species F is by far the most stable radiogenic species of calcite. A detailed study of the F species was led with the isothermal decay method on two samples where the F line was the only or the most prominent signal in the g=2.000 region of the ESR spectrum. The samples were prepared as powders (grain size range 177-250 µm). As the F linewidth does not change with line annealing, its intensity was measured as the peak-to-peak amplitude. Isothermal annealing experiments were led in air, between 180°C and 220°C, within an especially designed oven, with temperature controlled to within ±0.2°C. Heating times were beween 5 minutes and 8 hours. Experimental results were fitted with equations corresponding to redistribution kinetics of various orders. Our experimental results at the annealing temperature of 213°C are shown in Fig.1, together with calculated points for annealing kinetics of order 1, 3/2 and 2.In

TABLE 1

Paramagnetic species identified in the ESR spectrum of speleothem calcites

SPECIES	SAMPLE	g_{xx}°	g_{yy}	g_{zz}	REMARKS	REF.
A	SB SP1	2.0018 2.0021	2.0034 2.0035	2.0034 2.0035	Axial symmetry about [111] calcite direction observed at ambient temperature	a
B	SB SP1	2.0026 n.o.[£]	2.0018 n.o.	1.9972 n.o.	Orthorhombic symmetry about [111] calcite direction observed at ambient temp.	a
C*	SB SP1 MT	2.0028 2.0031 2.0029	1.9991 1.9994 1.9990	1.9991 1.9994 1.9990	Axial symmetry about [111] calcite direction observed at ambient temperature	a a c
D	SB SP1	2.0164 2.0163	2.0142 2.0143	2.0126 2.0128	Orthorhombic symmetry about [111] calcite direction observed at ambient temp.	a
E	SB SP1 MT	2.0032 n.o. 2.0028	2.0016 n.o. 2.0010	1.9971 n.o. 1.9966	Orthorhombic symmetry about [111] calcite direction observed at low temperature	b
F*	MT		2.0003		Isotropic, observed at ambient temperature	c
G*	MT		2.0053		Isotropic, 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) Rossi and Poupeau (1989).
°The X direction is parallel to [111].
£not observed

sample SP2, the best fitting was obtained with a second order decay function, giving an activation energy of 1.54 eV and a pre-exponential factor of 6.3 x 10^{10} s^{-1}. The decay process of the second sample, YC62, was better represented by a function of order 3/2, an activation energy of 1.48 eV and a pre-exponential factor of 5.8 x 10^{11} s^{-1}. The corresponding extrapolated meanlives at 15°C of the F species are of the order of 5 x 10^4 yr and 5 x 10^6 yr respectively.

The thermal behaviour of species F was investigated in four others samples. Preliminary results indicate again variability of response to temperature. The thermal redistribution process of F electrons in natural calcites thus appear to be specific of the sample considered and its particular crystallochemistry. As a result, calculated mean lifetimes of these electrons at ambiant temperatures may be found to vary, according to the sample measured, by more than two orders of magnitude. Our results show that, if the F species appeared as one of the most promising signals for ESR dating of calcites, because of its high sensitivity to dose and high saturation level, its effective use requieres utmost cautions. First, because of the emergence of nearby lines upon laboratory irradiation (table 1), and second due to its sample-to-sample variable mean life. It is suggested that some control of thermal stability be made before dating

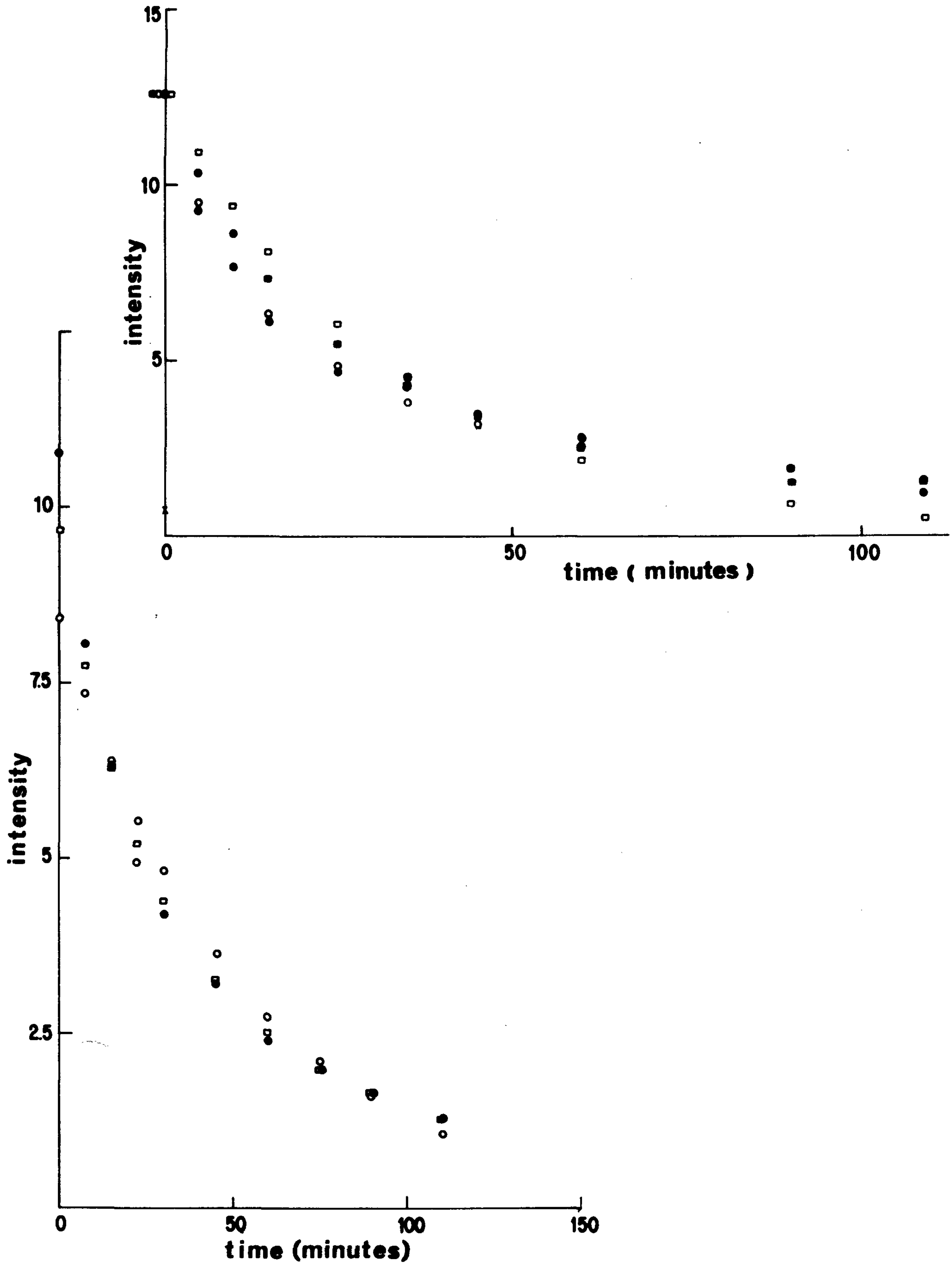

Fig. 1: Decrease with heating time of the F species intensity in stalagmitic calcites.
Top: Sample SP2 at 213.5°C; bottom, sample YC 62 at 213.8°C.
Symbols: closed circles, experimental values; open squares, closed squares and open circles, respectively first order, 3/2 order and second order fittings.

attempts of any sample. In addition, not mentionned above, grinding of calcite for ESR dating on powdered material has often for consequence the appearance of an intense tribo-related very nearby line after gamma-irradiation with g=2.0001 (Hennig and Grün 1983,Rossi et al. 1985). This problem can however be easily eliminated by a chemical etching treatment before irradiation (Rossi 1987). Finally, it results from our annealing data that the thermal fading of F species does not necessarily follow a first order kinetics as assumed previously.

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