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Florence Pirouelle, Jean-Jacques Bahain, Christophe Falguères, Jean-Michel Dolo. Study of the effect of a thermal treatment on the DE determination in ESR dating of speleothems. *Quaternary Geochronology*, 2007, 2 (1-4), pp.386-391. 10.1016/j.quageo.2006.05.030 . hal-04714941

**HAL Id: hal-04714941**

**<https://hal.science/hal-04714941v1>**

Submitted on 2 Jan 2025

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# Study of the effect of a thermal treatment on the $D_E$ determination in ESR dating of speleothems

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## Abstract

The choice of the ESR signal in the dating of speleothems is still debated. Among the peaks observed in speleothem ESR spectra, the most frequently signals used for the determination of the palaeodoses are the peaks at  $g=2.0007$  (h3 line),  $g=2.0040$  (Broad Line) and  $g=2.0057$  (h1 line).

In order to determine the better analytical way to obtain reproducible  $D_E$  values from these three ESR signals, successive additional annealing treatments ranging from 60–300°C were performed on several samples of a stalagmitic floor from the Mousterian site of the Caverna delle Fate (Liguria, Italy), also dated by *U*-series between 90 and 130 ka. The results confirm that  $D_E$  values can be obtained from h3 and BL signals without annealing, while the h1 signal requires a thermal pre-treatment, to obtain the maximum intensity of this line. Then, on our samples, the  $D_E$  values derived for the three lines are equivalent. It gives, hence, the opportunity to obtain data when the  $g=2.0007$  line cannot be used.

## Keywords

Carbonates, Speleothems, ESR, Equivalent dose, Thermal treatment

## 1. Introduction

Speleothems are frequently found in caves, often in relation to paleolithic materials. The dating of such carbonates takes a great importance in Quaternary research, especially for palaeoclimatical and archaeological considerations. Among the possible dating methods, the electron spin resonance (ESR) allows the determination of the palaeodose or equivalent dose ( $D_E$ ) by several signals.

The present methodological study performed on several samples of stalagmitic floors from the Mousterian site of the 'Caverna delle Fate' (Liguria, Italy), tries to improve the analytical way to obtain  $D_E$  values from the various ESR peaks.

## 2. ESR signals from calcite

ESR spectra of natural carbonates generally show two peaks at  $g=2.0007$  (h3) and  $g=2.0057$  (h1) (Yokoyama et al., 1983; Grün, 1989) (Fig. 1). A third peak at  $g=2.0040$ , named broad line (BL), superposed on h1 and h3, has also been observed (e.g. Apers et al., 1981) (Fig. 2). The ESR spectra can be complicated by the occurrence of other peaks due e.g. to paramagnetic impurities ( $Mn^{2+}$  and/or  $Fe^{3+}$ ) (Fig. 1).

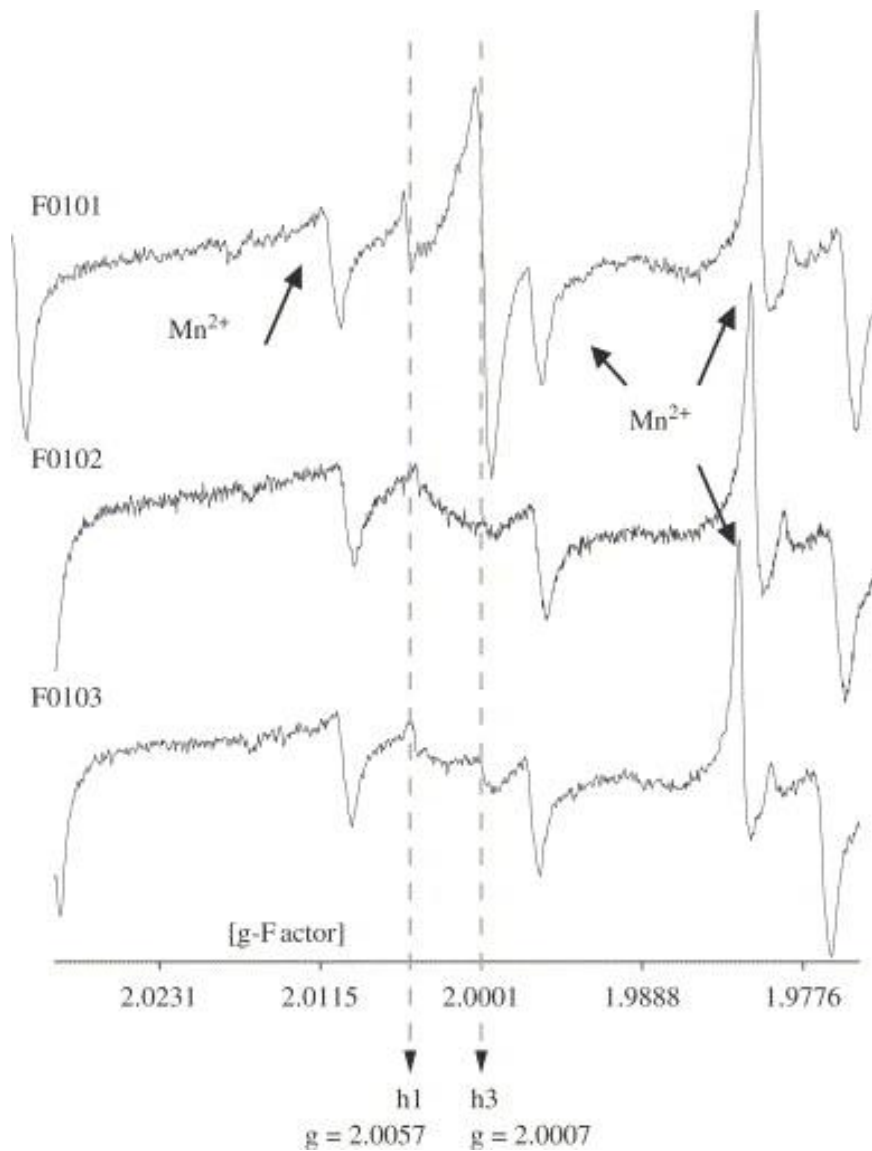


Fig. 1. ESR signals at  $g=2.0057$  and  $2.0007$  from the three natural speleothem samples.

The choice of the useful ESR signals for dating was strongly debated for relatively old samples (more than 300 ka) (Smith et al., 1985; Bahain, 1993). However, for samples younger than 300 ka, the  $D_E$  and the ages obtained from the different lines are equivalent (Bahain et al., 1994a). Most researchers use the  $g=2.0007$  line, corresponding to a tumbling  $\text{CO}_2^-$  radical (Debuyst et al., 1993), at room temperature or after thermal treatment (Grün, 1989). Sometimes, the natural intensity of this signal is too weak for measurement. In others cases, a parasite line at  $g=2.0001$ , related to the crushing of the sample, can interfere with the measurement. Additionally, some doubts have been expressed concerning the geological stability of the associated trap (Yokoyama et al., 1983, Yokoyama et al., 1981). It has therefore been proposed to use  $g=2.0040$  or  $2.0057$  lines, which correspond to an organic radical and to a rotating  $\text{SO}_2^-$  radical respectively (Barabas, 1992). However, BL intensity measurements can be interfered with the presence of h3 (Fig. 2) and the use of h1 line necessitates a thermal pre-treatment.

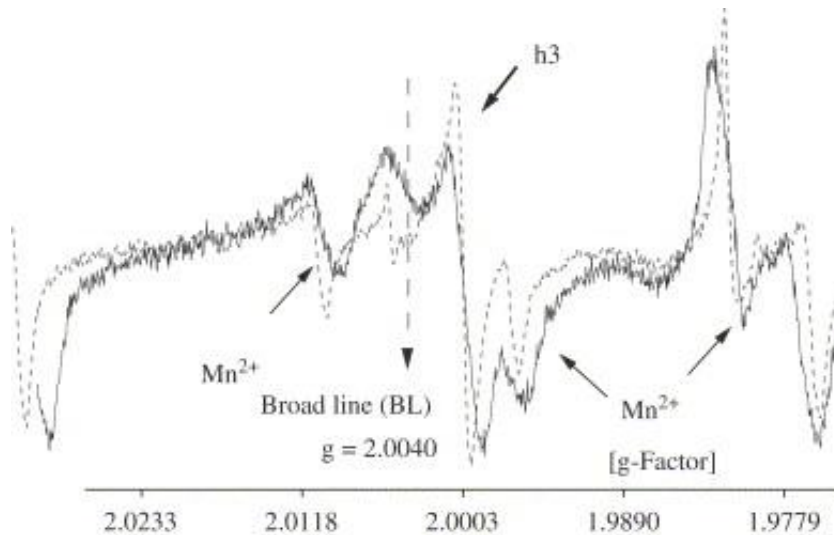


Fig. 2. ESR signal at  $g=2.0040$  (broad line (BL)) from F0101 natural sample.

To estimate the stability of these three signals, experiments using annealing were carried out (Yokoyama et al., 1983, Yokoyama et al., 1981; Smith et al., 1985; Grün, 1989; Barabas et al., 1992a; Bahain et al., 1994b). These studies showed, that all natural signals rapidly decrease with annealing time or with increasing temperature, except  $g=2.0057$  (h1) which increases at first. Yokoyama et al., 1988, Yokoyama et al., 1981 concluded that the initial increase of this line was a consequence of a complex electronic transfer from h3 to h1-traps, and they proposed to use h1 after a thermal treatment at 180–190°C during 16 h for  $D_E$  calculations. Martinez et al. (2001) developed an analytical model to explain this phenomenon and also suggested that the h1 signal can be applied for  $D_E$  determination after heating. They recommended an annealing temperature of 200°C for 3 days, but their study concerned corals, not speleothems, and this theory should be checked before its application on continental carbonates.

Firstly, it is necessary to find the best analytical conditions for ESR measurements, of the h1 and/or BL signals when it is impossible to measure the  $g=2.0007$  (h3) line.

### 3. Samples and experimental conditions

Three carbonate samples (F0101, F0102 and F0103) extracted from stalagmitic floors interstratified in the Mousterian layers of the ‘Caverna delle Fate’ (Liguria, Italy) were studied. The excavations of this site have provided a large amount of animal bones, lithic materials and Neanderthal fossil remains (Giacobini and de Lumley, 1984). The speleothems have been independently dated by U-series between 90 and 130 ka (Table 1).

Sample		F0101	F0102	F0103				
U content (ppm)		0.022	0.061	0.029				
U-series age (ka)		117±21	105±11	92±28				
<b>ESR analyses</b>								
ESR Line	Annealing conditions	$T$ (°C)	$D_E$ (Gy)	Age (ka)	$D_E$ (Gy)	Age (ka)	$D_E$ (Gy)	Age (ka)
h3		RT	78.24±4.63	130±20	ND	ND	38.66±4.03	65±10
h1		RT	1286.93±31.46	2139±321	94.71±6.34	155±23	175.72±15.95	291±44
	Martinez et al.	>200° (3)	214.03±24.42	356±53	89.67±10.33	146±22	80.05±9.43	134±20

	(2001)	days)						
	Max. intensity	<sup>a</sup>	78.73±5.10	<b>131±20</b>	40.50±2.87	<b>67±10</b>	45.57±2.58	<b>76±11</b>
BL		RT	83.29±4.46	<b>139±21</b>	40.86±7.58	<b>67±10</b>	41.72±12.71	<b>70±11</b>
	Yokoyama et al. (1983)	140	103.66±9.97	173±26	59.11±4.20	97±15	56.76±9.06	95±14

A  $k$ -value of 0.05 was used for all calculations (Lyons and Brennan, 1991). Gamma-ray spectrometry was used to measure the radioelement contents of the surrounding sediment ( $^{238}\text{U}=2.426$  ppm;  $^{232}\text{Th}=5.050$  ppm;  $^{40}\text{K}=0.818\%$ ). The gamma attenuation factor was calculated using the equation of Falguères et al. (1990):  $A=0.5[e^{-(mD)}-mDEi(-mD)]$ , where  $A$  is the fraction of the external gamma rays received at a distance  $D$  ( $\text{g}/\text{cm}^2$ ) of the sediment,  $m$  is the attenuation coefficient of the gamma rays ( $m=0.065$   $\text{cm}^2/\text{g}$ ),  $Ei$  is the exponential integration function and 0.5 the  $2\pi$  geometric factor.

ND: not determined; RT: room temperature

<sup>a</sup> The temperatures corresponding to the maximum intensity are different from each sample: 220°C for F0101, between 160 and 180°C for F0102 and between 180 and 190°C for F0103.

Table 1.  $D_E$  variations and ages comparison for the three samples of the Caverna delle Fate

For ESR analyses, the samples were crushed, the grain size 100–200  $\mu\text{m}$  selected and each sample were divided in ten aliquots. Nine of them were irradiated with a  $^{60}\text{Co}$  gamma ray source (with doses ranging from 63–1500 Gy) of the LNHB laboratory (CEA/Saclay). ESR measurements were performed at room temperature using an EMX Bruker X-band spectrometer. The following experimental conditions were used (see also Yokoyama et al., 1985a): a modulation frequency of 100 kHz, a microwave power of 0.1 (BL) or 5 mW (h1–h3), a sweep width of 8 mT and a modulation amplitude of 0.05 (h1–h3) and 0.5 mT (BL).

Successive annealing treatments ranging from 60–300°C were performed, using a UE-200 drying oven. For each sample, at each temperature step, the ESR intensities of the h1, h3 and BL lines were measured and the associated  $D_E$  values determined.

#### 4. Effect of the thermal treatment on the peaks intensity

The intensity variations of the three signals are shown in Fig. 3, Fig. 4, Fig. 5.

- $g=2.0007$  (h3) line (Fig. 3): For F0102 sample, no intensity measurement was possible for  $g=2.0007$  line. There is a great difference of intensity of this line between the two other samples but a similar behaviour: after a relative stability up to a temperature of 120°C, the h3 peak intensity rapidly decreases and finally the line disappears. It is probably related both to a thermal release of the center but also to its destruction by the annealing (Barabas et al., 1992b). However, the complete disappearance takes place at different temperatures for each sample (200°C for F0101 and 180°C for F0103) and this difference must be in relation with the fact that the corresponding  $\text{CO}_2^-$  radical is associated into the crystal to a  $\text{H}_2\text{O}$  molecule (Debuyst et al., 1993).

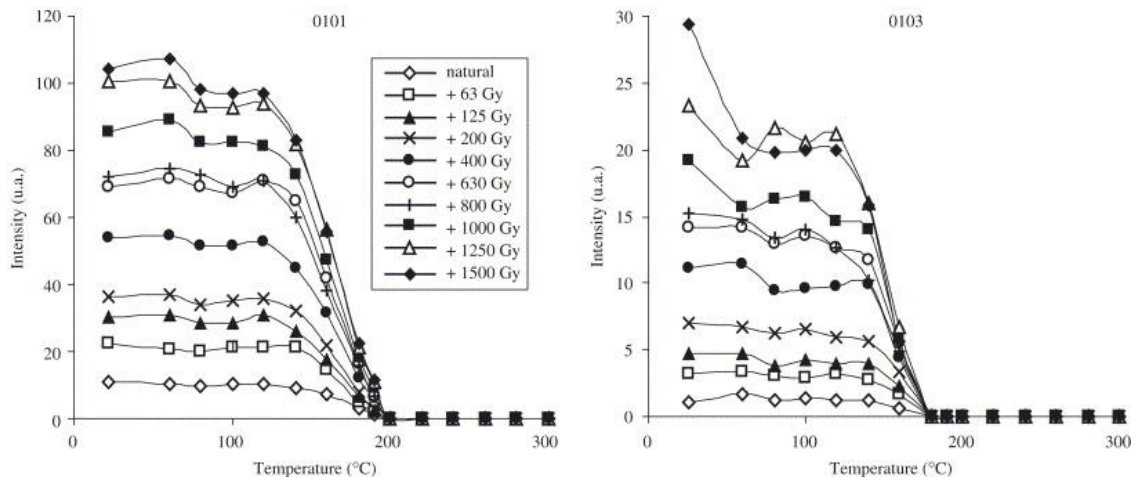


Fig. 3. Effect of thermal treatment on ESR signal intensity at  $g=2.0007$  ( $h_3$ ) from the carbonates samples F0101 and F0103.

- $g=2.0057$  ( $h_1$ ) line (Fig. 4): For the three samples, the  $h_1$ -intensities increase with temperature up to a maximum value, then decrease to a plateau. The temperatures corresponding to the maximum intensity are different from each sample (220°C for F0101, between 160 and 180°C for F0102 and between 180 and 190°C for F0103). Hence, for F0101 sample, the thermal pre-treatment temperature of 180–190°C as proposed by Yokoyama et al. (1983) does not seem optimal. Besides, for the F0101 and F0103 samples, a relationship between the disappearance temperature of the  $h_3$  line and the maximum intensity of the  $h_1$  signal can effectively be suspected.

The experimental procedure recommended by Martinez et al. (2001) was also applied. “Steady state” was reached after several hours at 300°C. However, for two of the three samples (F0102 and F0103), the final intensity of the line is similar to the initial one (before thermal treatment) while for F0101, the steady state is reached at 50% of maximum intensity.

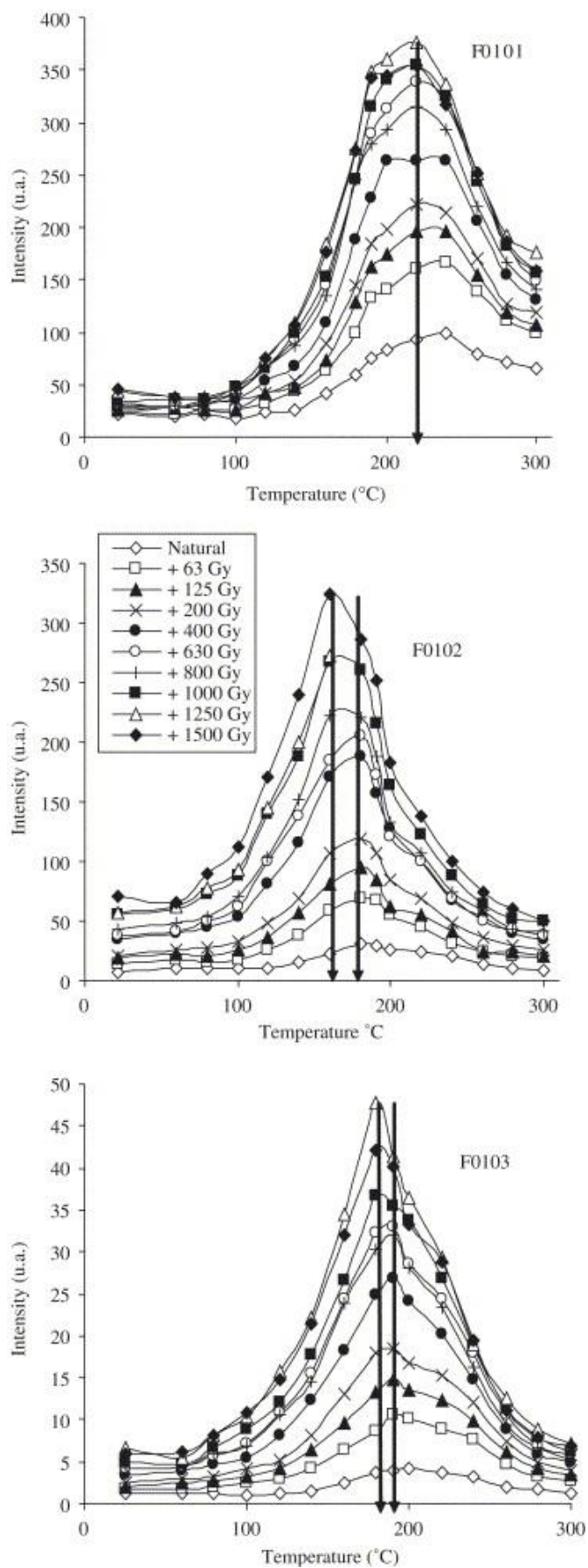


Fig. 4. Effect of thermal treatment on ESR signal intensity at  $g=2.0057$  (h1) for the three carbonates samples.

- $g=2.0040$  (BL) line (Fig. 5): For the three samples, the BL intensities present an anarchical variation up to 180°C, then a decrease to a steady state. The interferences on the intensity measurements, firstly of the h3 line between 25 and 160°C, then of the h1 line between 120 and 240°C, might explain these variations. The size  $D_E$  determination at 140°C, as proposed by Yokoyama et al. (1983), does not seem appropriate.

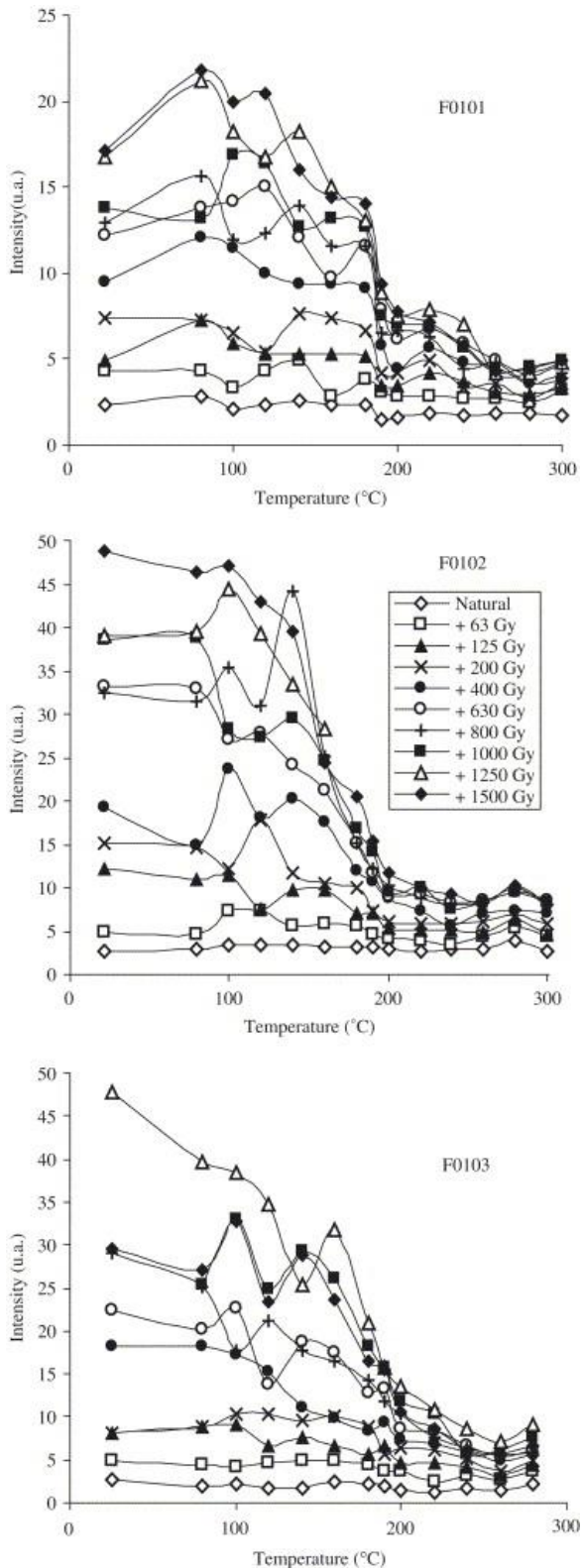


Fig. 5. Effect of thermal treatment on ESR signal intensity at  $g=2.0040$  (h1) for F0101, F0102 and F0103 samples.



## 5. $D_E$ determination

For each sample, at each step of temperature,  $D_E$ -values were calculated from h1, h3 and BL lines using an exponential extrapolation (Yokoyama et al., 1985b) with weighting by the natural point. The obtained data and their variations are shown in Fig. 6.

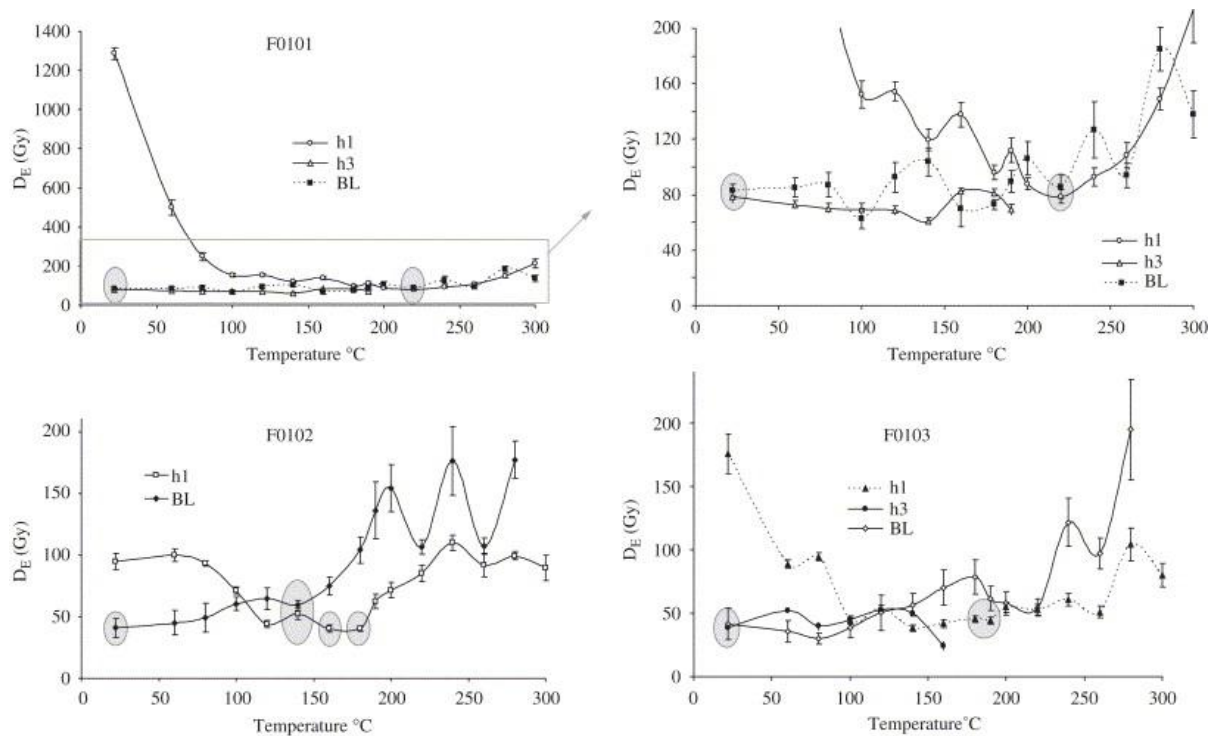


Fig. 6.  $D_E$ s variations with temperature for the three samples of stalagmitic floors of the Caverna delle Fate.

$D_E$  values calculated from  $g=2.0007$  line (h3) show little variations with temperature up to  $120^\circ\text{C}$  (e.g. ranging between 68 and 78 Gy for F0101). In contrast, those derived from  $g=2.0040$  line (LR) (ranging between 63 and 93 Gy for the same sample) or from  $g=2.0057$  line (h1) (decreasing from 1287–155 Gy). After  $120^\circ\text{C}$ , in spite of a great decrease of the h3 intensity,  $D_E$ -values obtained from this line show small variations before a sudden drop. On the other hand, palaeodoses derived from BL continually increase, but show anarchical variations similar to those observed for the corresponding intensities. At the same time, the decrease of the  $D_E$ -values calculated from h1 line continues, but with less significant variations, until a minimal value corresponding to temperature for which the maximal ESR intensities are obtained. For higher temperatures, the  $D_E$ -values increase again.

For each sample, the  $D_E$ -values calculated for the  $g=2.0007$  (h3) and at  $g=2.0040$  (BL) lines at room temperature are practically identical. Besides, these values are in good agreement with the  $D_E$  obtained for the  $g=2.0057$  (h1) signal, calculated for the temperature corresponding to the maximum intensity (Fig. 7). Then, the ages derived from these  $D_E$  are coherent with those obtained by U-series (Table 1). On the other hand,  $D_E$  calculated for h1 using the Martinez conditions (Fig. 6) are severely overestimated. Then, it seems that the thermal pre-treatment they proposed for  $D_E$  determination by h1 signal in corals is not adapted to our speleothems samples.

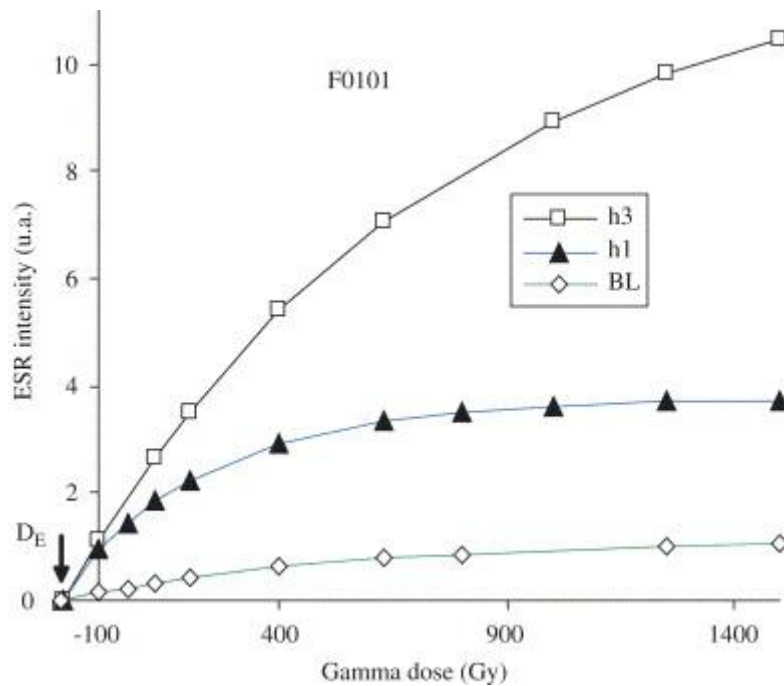


Fig. 7. Dose-response curves obtained from the three ESR lines observed in the F0101 speleothem sample.  $D_E$ -values are determined using exponential extrapolation (Yokoyama et al., 1985b) at room temperature for  $g=2.0007$  (h3) line ( $D_E=78.24\pm 4.63$  Gy) and  $g=2.0040$  (BL) one ( $D_E=83.29\pm 4.46$  Gy) and after a thermal pre-treatment of  $220^\circ\text{C}$  during 16 h for  $g=2.0057$  (h1) line ( $D_E=78.73\pm 5.10$  Gy).

## 6. Conclusion

Three ESR signals, at  $g=2.0007$  (h3),  $g=2.0057$  (h1) and  $g=2.0040$  (BL), are commonly used for  $D_E$  determination of speleothems. The effect of a thermal treatment (from room temperature to  $300^\circ\text{C}$ ) on the  $D_E$  determination has been studied on several samples recovered from the stalagmitic floors of 'Caverna delle Fate' dated by U-series of 90–130 ka.

The results show that:

- 1) h3 and BL signals will be used without pre-annealing while h1 signal requires a thermal pre-treatment;
- 2)  $D_E$ -values for h1 line should be determined at an annealing temperature corresponding to the maximum ESR intensities;
- 3) This one is different for each sample but occurs between 160 and  $220^\circ\text{C}$ ;
- 4) The  $D_E$ -values obtained from the different lines—and the derived ESR ages—are in agreement for the three analysed samples.

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