ESR-DATING OF A FLOWSTONE CORE FROM COVA DE SA BASSA BLANCA (Mallorca, Spain)

by Rainer GRÜN *

Abstract

A flowstone core from the Cova de Sa Basa Blanca (SBB), Mallorca, was dated by means of ESR. This systematic investigation shows that the precipitation of this flowstone took place in several time-periods. It began at about 700,000 a and finished at the end of the penultimate interglaciation at about 200,000 a.

Resumen

Una muestra de material estalagmítico parietal procedente de la Cova de Sa Bassa Blanca (testigo n.° 21/campaña de muestreo de marzo-81) ha sido datada mediante la técnica de Resonancia de Spin Electrónico (E.S.R.). Las investigaciones realizadas sistemáticamente sobre dicha muestra han puesto de manifiesto que la precipitación de esta secuencia de espeleotemas tuvo lugar en varios períodos de tiempo; habiendo comenzado en torno a los 700.000 años y acabando hacia el final del penúltimo interglacial, hace alrededor de 200.000 años.

A flowstone core of about 190 cm from the Cova de Sa Bassa Blanca (SBB) was dated by means of ESR. This core (N.° 21) was taken during a campaign in this cave (MAROTO & FONT, 1981) in order to investigate the paleoclimate of the Western Mediterranean. The Cova de Sa Bassa Blanca is connected with the Mediterranean Sea and typical cauliflower-like speleothems, which grew subaquatically (POMAR et al., 1976, 1979), document paleo-sealevels (GINÉS & GINÉS, 1974; GINÉS et al., 1975, 1981 a & b). First U-series dating on these speleothems were carried by HENNIG et al. (1981). The subaquatic speleothems show various states of crystallization and a so called fibrous aragonite is very conspicuous (POMAR et al. 1976).

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ESR-dating

ESR-spectroscopy allows the detection of unpaired, paramagnetic, quasi free electrons in the crystal lattice. These free electrons are produced by the natural radiation (alpha-, beta-, gamma-, and cosmic rays) and can be stabilized by various traps (see MARFUNIN, 1979; HENNIG & GRÜN, 1983; HOROWITZ, 1984). Along with continuous natural radiation the number of trapped electrons is increasing and so does the ESR-signal, which is proportional to the population of captured electrons. An ESR-age is calculated according the simple formula:

$$\text{Age (Ma)} = \frac{\text{accumulated dose (AD) [krad]}}{\text{annual dose } (D_0) \text{ [mrad/ka]}}$$

The accumulated dose (AD), a sample received since the time of its formation is determined by

ESR-spectroscopy via the so called additive dose method (Fig. 1): Homogeneous aliquots of the sample are irradiated stepwise with artificial gamma-doses, the extrapolation towards zero-ESR-intensity allows the determination of the AD. The annual dose (D_0) results from the analysis of the radioactive elements (U, Th, K) of the sample (internal dose rate) and its surroundings (external dose rate). For details of the method see IKEYA (1978), HENNIG & GRÜN (1983) and GRÜN (1985).

Experimental

For the ESR-age determination of the SBB-samples two ESR-signals were used: fibrous aragonite showed an ESR-signal with g = 2.0021 (Fig. 2) and the calcitic samples displayed an ESR-signal with g = 2.0007 (Fig. 3), which was also used for ESR-dating in other publications (e.g. GRÜN, 1985; SIEGELE & MANGINI, 1985). The samples were crushed in a mortar and the sieve-fraction 100-400 microns was used for the ESR-measurement. In order to avoid interferences from surface defects due to crushing (GRÜN & DECANNIERE, 1984) the samples were etched with 0.5N CH_3COOH for 4 minutes. Both signals showed no decrease upon sun-

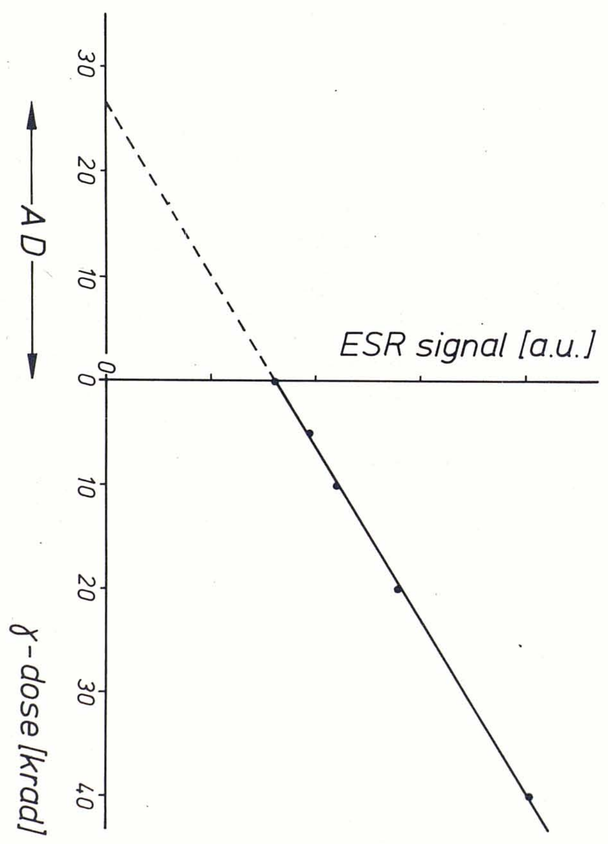

Fig. 1. Determination of AD by means of additive artificial irradiation.

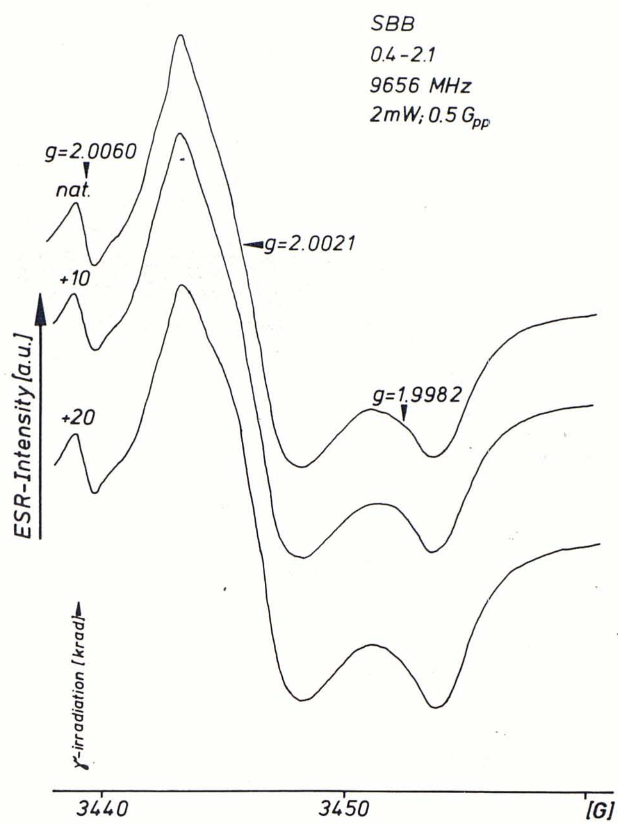

Fig. 2. ESR spectra of an aragonitic speleothem of the SBB.

light exposure. The thermal stability is in the range of some 10^6 a (at 10° C; HENNIG & GRÜN, 1983; HENNIG et al., 1985) and, hence, this signal should be stable enough to date in the range up to a million years. Unfortunately, there are no detailed annealing results available for the aragonitic ESR signal with g = 2.0021, but prior preliminary annealing tests indicated, that this signal is rather stable. The measurement conditions are given in Fig. 2 & 3. The internal U-content was measured by fission-track powder preparations.

For the calculation of the ESR-ages the following assumptions were made:

- the alpha-efficiency (k-factor) was assumed to be 0.34 throughout. Measurements of 9 speleothem samples yield a value of 0.34 ± 0.08. This result is in agreement with TL-investigations (DEBENHAM & AITKEN, 1984), where the alpha-efficiency of speleothem samples varied between 0.11 and 0.6
- the U-234/U-238 ratio was assumed to be 1.2 based on the alpha-spectrometric measurements done for U-series study.
- the influence of K-40 and Th-232 is negligible.
- the influence of cosmic rays is negligible.

Unfortunately, it was not possible to determine the external gamma-irradiation in the core yet, because the detector of a portable gamma-spectrometer had a larger diameter than the holes

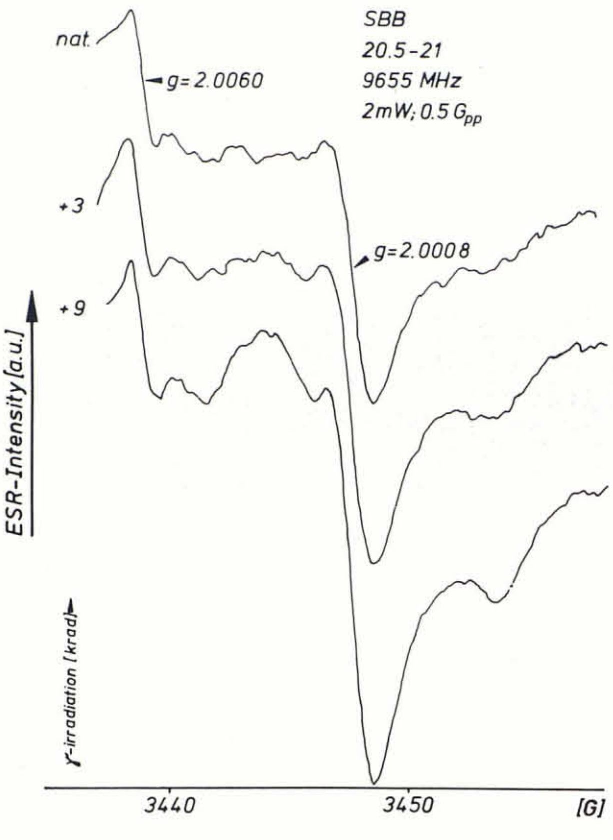

Fig. 3. ESR spectra of a calcitic speleothem of the SBB.

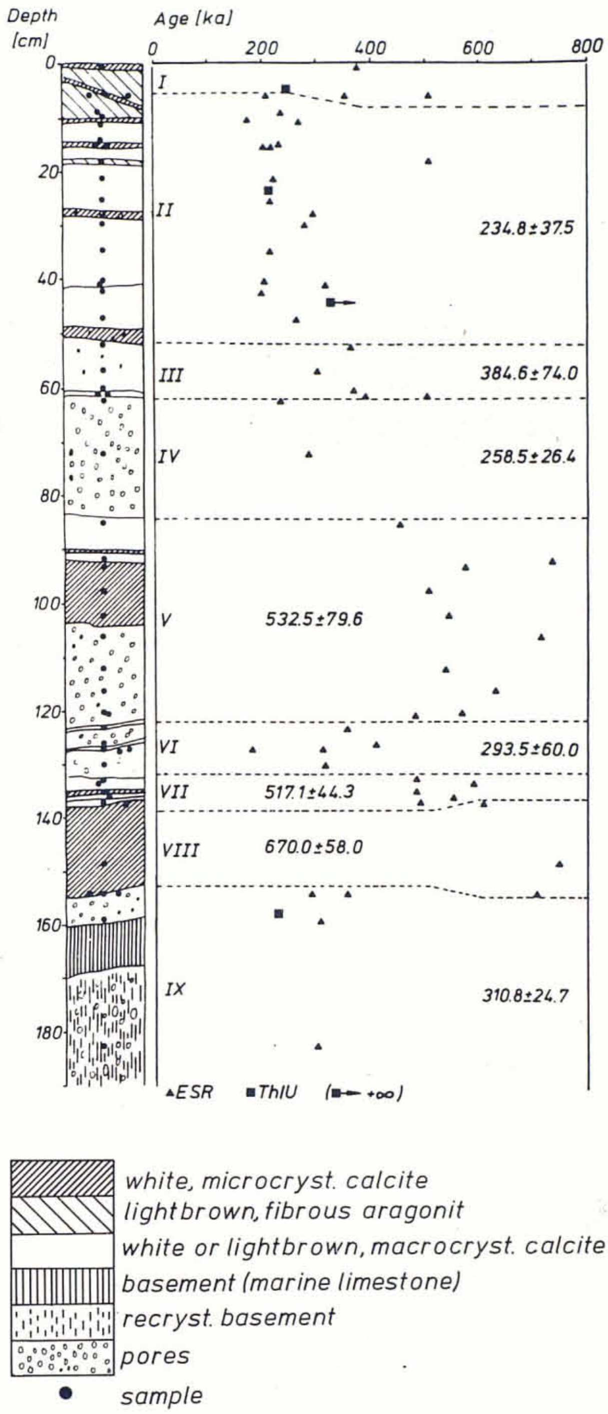

Fig. 4. ESR and U-series age data of the SBB-core.
Left: Schematic profile.
Right: The roman Numbers (I-IX) label the age-units according to the ESR-results, the arabic numbers give the average age with the standard deviation.

of the cores. Therefore, the external gamma-dose rate was assumed to be equal to the internal except for those samples lying between U-rich aragonite layers. Here, the gamma-dose was extrapolated from the aragonite layers (see Tab. 1, Nr. 6, 11-15, 17). Tab. 1 shows, that the fibrous aragonite contains much more uranium (up to 7 ppm) than sea-water (about 0.3 ppm, KAUFMAN et al. 1971). It cannot be decided here, whether this U-uptake is syn- or postsedimentary, but U-accumulation in aragonitic corals has been attributed to a synsedimentary uptake by SWART & HUBBART (1982). For the ESR-age calculation of these samples a short time U-uptake during or shortly after precipitation was assumed.

The Th-230/U-234 and Pa-231/U-235 disequilibria were iteratively taken into account.

In addition to the ESR-investigations, four U-series age determinations were carried out by the Niedersächsisches Landesamt für Bodenforschung, Hannover.

Results

Tab. 1 shows the results of the ESR- and U-series age determinations. The ESR-results can be grouped into 9 age units (see Fig. 4). The outer few cm yield very high ages. This might be due to a plate-out effect of the daughter products of Rn-222 (see HENNIG & GRÜN, 1983), which might increase the ADs of samples near the surface. This effect might especially occur at this site, for there is nearly no air-circulation in the cave. A similar ob-

N.°	Depth [cm]	U-Content [ppb]	AD [krad]	int. Do [mrad/a]	ext. Do [mrad/a]	ESR-Age [a]	U-series Age [a]
1	0-1	5350	236.0	630.3	—	374 400	
2	5-6a	5474	347.5	685.5	—	506 900	
3	5-6b	596	45.6	69.4	60	352 400	244 300
4	5-6c	7057	147.8	698.9	—	211 500	
5	8.5-9	4991	123.6	515.9	—	239 600	
6	10	337	9.0	31.4	20	175 100	
7	10.5	334	15.0	35.8	20	268 800	
8	14-15	338	12.6	34.4	20	231 600	
9	15a	546	15.0	53.6	20	203 800	
10	15b	417	13.4	41.6	20	217 500	
11	17-18	3684	233.0	460.9	—	505 500	
12	21	464	15.0	47.0	20	223 900	216 500
13	25	410	8.9	41.1	—	216 500	
14	27-28	317	10.3	35.0	—	294 300	
15	29-30	198	5.8	21.3	—	272 300	
16	34-35	235	5.1	23.6	—	216 100	
17	40	300	6.0	29.4	—	204 100	
18	40-41	145	5.2	16.3	—	319 000	
19	42	338	6.6	33.1	—	199 400	326 000
20	47	262	7.4	28.0	—	264 300	
21	52	136	5.8	15.9	—	364 800	
22	56-57	149	5.0	16.6	—	301 200	
23	60	113	4.9	13.3	—	368 400	
24	61d2	103	6.5	12.9	—	503 900	
25	61d3	110	5.1	13.1	—	389 300	
26	62	231	5.5	23.7	—	232 100	
27	72	479	14.9	52.3	—	284 900	
28	85	153	8.5	18.8	—	452 100	
29	92	57	5.6	7.6	—	736 800	
30	93	68	5.0	8.7	—	574 700	
31	97-98	89	5.6	11.1	—	504 500	
32	102	95	6.5	12.0	—	541 700	
33	106	66	6.2	8.7	—	712 600	
34	112	77	4.6	9.5	—	484 200	
35	116	65	4.8	8.3	—	578 300	
36	120	100	6.5	12.6	—	515 900	
37	120-121	115	6.0	14.0	—	428 600	
38	123h	154	5.2	17.1	—	304 100	
39	126	139	5.8	16.2	—	358 000	
40	127r	360	6.1	33.8	—	180 500	
41	127d	257	8.9	28.7	—	310 100	
42	130	284	10.1	32.0	—	315 000	
43	132.5	133	7.9	16.5	—	478 800	
44	133-134	123	9.3	15.8	—	588 600	
45	135	121	7.2	15.0	—	480 000	
46	136	103	7.2	13.1	—	549 600	
47	137rl	140	8.5	17.4	—	488 500	
48	137w	116	9.1	15.0	—	606 700	
49	148-149	110	10.9	14.6	—	746 600	
50	154h	120	9.9	15.1	—	655 600	
51	154r	774	24.3	84.8	—	288 300	
52	154d	284	11.6	32.9	—	352 600	225 000
53	159	344	11.6	38.3	—	302 900	
54	182-183	1330	44.2	147.6	—	299 500	

Tab. I: ESR and U-series results

servation was made during the investigation of a German speleothem profile (GRÜN, 1985).

The upper 50 cm of the profile give ESR-ages of about 230,000 a, which are independent of the U-content. The ESR-results are in a good agreement with the U-series data and allow a classification of this part of the core into the penultimate interglaciation (stage 7 of the $\delta^{18}O$ deep sea record V28-238. SHACKLETON & OPDYKE, 1973). The next section with an average value of 380,000 seems to represent an older interglaciation (stage 9 and/or 11). The deeper sections imply that the growth of the speleothem began at about 700,000 a (unit VIII). Some units (IX, VI and IV) display recrystallization processes.

Discussion

The four U-series results seem to show, that this speleothem core grew throughout during the last interglaciation. The ESR-investigations show, however, that the speleothem growth in the Cova de Sa Bassa Blanca is more complex and began about 700,000 a ago. It must be mentioned, that the average data of the age-units are based in some cases on only a few results. For a more precise classification of these units more ESR-investigations have to be carried out (up to about 10 per unit). A comparison of the ESR-results with the geological settings and mineralogical investigations will be carried out in collaboration with the Department of Geology, University of Palma de Mallorca. Nevertheless, a preliminary comparison (POMAR, pers. comm.) showed rather promising aspects. Additionally, it is planned to carry out a comparison with $\delta^{13}C$- and $\delta^{18}O$- data as determined by the Niedersächsisches Landesamt für Bodenforschung, Hannover. For future work, paleomagnetic investigations seem also to be very promising, because the ESR-results do not exclude a paleomagnetic reversal.

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