ELSEVIER

K-band ESR spectra of calcite stalagmites from southeast and south Brazil

Angela Kinoshita[a,b,*], Ivo Karmann[c], Francisco William da Cruz Jr.[c], Carlos F.O. Graeff[a], Oswaldo Baffa[a]

[a]*Departamento de Física e Matemática, Ffclrp-Usp, 14040-901 Ribeirão Preto, Sp, Brazil*
[b]*Universidade do Sagrado Coração, 17011-160 Bauru, SP, Brazil*
[c]*Instituto de Geociências, USP, São Paulo, SP, Brazil*

Abstract

Samples of calcite stalagmites from Caverna Santana (São Paulo State) and Caverna Botuvera (Santa Catarina State), southeastern and southern Brazil, respectively, were studied by electron spin resonance (ESR). The more common microwave frequency (X-Band, 9.5 GHz) as well as higher frequency K-band, 24 GHz were employed for the determination of the age of the samples. Even after extensive signal averaging, the dosimetric signal is not very well defined in the X-band (9.5 GHz). Using the K-band spectrometer it was possible to clearly identify the 6 hyperfine lines of Mn^{2+} and other paramagnetic centers in the $g = 2$ region: SO_2^- and CO_2^- radicals. The use of high microwave frequency gives better S/N and spectral resolution making the identification of the dosimetric signal easier. The total dose (TD) or equivalent dose (ED) deposited in the samples was 2.3 ± 0.3 Gy and 1.7 ± 0.4 Gy for Caverna Botuvera samples and 2.6 ± 0.7 Gy for the sample of Caverna Santana, giving an age of 2.9 ± 0.7 ky, 2.1 ± 0.8 ky and 3 ± 1 ky, respectively. These first results are compatible with U/Th analysis. Due to the low S/N precision, measurements were possible only with the use of secondary standard composed on Mn^{2+} lines, naturally present in this sample.
© 2004 Elsevier Ltd. All rights reserved.

Keywords: K-band ESR; Dating; Calcite; Stalagmites; Caves; Speleothemes

1. Introduction

Ikeya (1975) published the pioneering work on dating of stalagmites by ESR in Akiyoshi-dô Cave. After that, several works have been published as Ikeya et al. (1993), Perrette et al. (2000), and others cited in Rink (1997) relating the effectiveness of this dating technique. The dating of stalagmites is important in order to support paleoenvironmental studies based on the stalagmite growth rate and oxygen and carbon stable isotope variations with time.

Karst areas are developed by dissolution of limestone ($CaCO_3$) by water containing carbon dioxide (CO_2). The reaction of carbonate dissolution and the back reaction of its deposition are written as

$$CaCO_3 + H_2O + CO_2 \leftrightarrow Ca(HCO_3)_2. \qquad (1)$$
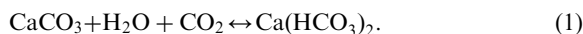
Stable free radicals are generated in calcite and in impurities incorporated when ionizing radiation interacts with speleothemes. The most important paramagnetic species present in the ESR spectra are CO_3, CO_2, SO_3 and SO_2 radicals, usually associated with Mn^{2+}

*Corresponding author.
E-mail address:* angelak@dfm.ffclrp.usp.br (A. Kinoshita).

sextet . The equivalent dose (ED) deposited by natural environmental radiation is determined by the additive dose method, usually measured by the increase in the signal at $g = 2.0007$, attributed to freely rotating CO_2^-, due to irradiation.

2. Experimental

Samples of calcite stalagmites from Caverna Santana (coordinates of 24° 31′ 51″S/48° 43′ 36″W, São Paulo State) and Caverna Botuvera (coordinates of 27° 13′ 24″S/49° 09′ 20″W, Santa Catarina State), southeastern and southern Brazil, respectively, were selected for ESR studies. These samples were drilled out along the growth axis of each stalagmite using a water-cooled drilling system. Samples were divided into two parts: one of them was used for ESR measurements and the other sent for U/Th analysis. At present, U/Th dating is available only for the Caverna Botuverá stalagmite.

For ESR measurements, the samples were ground manually to a powder with grain size approximately 0.2 mm to assure that the sample is isotropic. The material obtained was divided into aliquots of about 20 mg each and placed inside plastic tubes. All tubes, except one, were irradiated in the laboratory with gamma rays, using teleradiotherapy source (Gammatron-S Siemens) in air, at room temperature with a dose rate of 1.2 Gy/min using 0.4 g/mm^2 thick Lucite build-up cap over the samples. The doses given to the samples were 0.5, 1.0, 1.5, 2.0, 3.0, 4.0, 6.0, 10.0 and 15 Gy. After irradiation, the samples were transferred to ESR quartz tubes.

The ESR signals of the original samples (before irradiation in the laboratory) were measured in a computer interfaced Varian E-4 X-Band spectrometer. The spectrometer parameters used were: central field 338 mT, modulation amplitude 0.16 mT, modulation frequency 100 kHz, and microwave power 20 mW. About 100 mg of sample was used placed in a 4 mm quartz tube.

The K-band spectrometer employed was assembled in our laboratory with a 12 inch electromagnet (Varian), a magnetic field controller, a microwave bridge and cylindrical cavity (Bruker), a microwave digital frequency counter (HP), and a lock-in amplifier (EG&G). The cylindrical cavity has 2 cm height and allows measurements of samples with approximately 1–2 mm diameter and 4 mm length. This equipment is controlled by a microcomputer via a GPIB card. The data acquisition is made by software written in HP-VEE platform. The spectrometer parameters used were central field 854 mT, scanning field 20 mT, modulation amplitude 0.2 mT, microwave power 0.63 mW, modulation frequency 50 kHz, and microwave frequency

23.9 GHz. The K-band quartz tube has a diameter of 3 mm and ~10 mg of sample was used. The amplitude of the signal at $g = 2.0008$ and a linear and exponential fitting were used for ED determination.

3. Results

The ESR spectrum using the X-band of a sample of stalagmite from Caverna Santana before artificial irradiation is reported in Fig. 1. Even after 200 scans, the dosimetric signal cannot be adequately identified and quantified due to the low S/N ratio in this spectrum. Fig. 2 shows the spectrum of stalagmite from Caverna Botuvera recorded in the K-band. The dosimetric signal is at the center of the six lines of Mn^{2+}. Comparing Fig. 2 with Fig. 3, showing the spectrum of the sample from Caverna Santana, we can notice that the concentration of Mn^{2+} present in the samples is different. The signals identified by A, B and C in Figs. 2 and 3 are tentatively ascribed to the radicals described in Table 1.

Fig. 4 shows the dose–response curve for the sample from Caverna Botuvera, normalized by the Mn^{2+} signal amplitude and by mass. The ED values obtained are 2.3 ± 0.3 Gy and 1.7 ± 0.4 Gy. The ED of the sample from Caverna Santana is 1.1 ± 0.4 Gy, extrapolated from the curve in Fig. 5. For this sample, only amplitude normalized by mass was used since the Mn^{2+} signal intensity is very weak precluding its use as an internal standard. The linear and exponential fitting gave the same results for the Botuvera sample (Fig. 4). An exponential function gave the best fit with data for the Santana sample (Fig. 5).
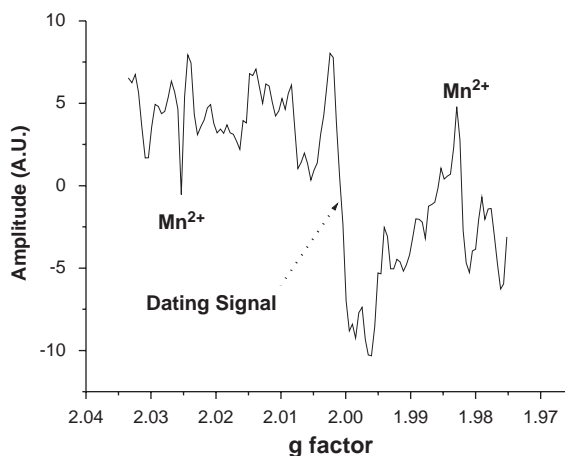

Fig. 1. ESR X-band spectrum (plotted in a *g*-scale) of stalagmite (natural) from Caverna Santana. The 3rd and 4th manganese ESR lines: field scan 10 mT and central field 338 mT.
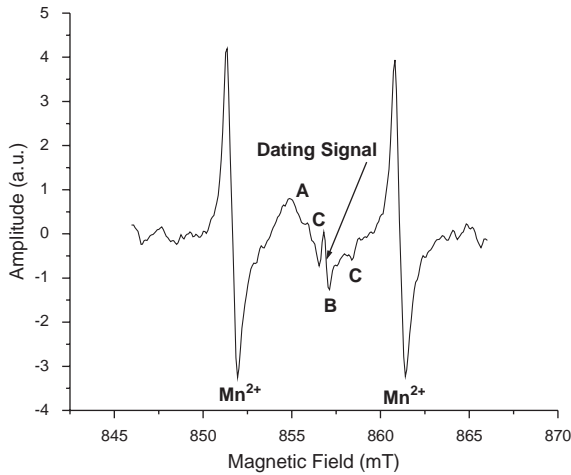
Fig. 2. K-band ESR spectrum of stalagmite from Caverna Botuvera, irradiated with a dose of 15 Gy. The central field is 856 mT and the field scan is 20 mT. The dating signal (B) has g-factor 2.0008. The radicals A, B and C are listed in Table 1.
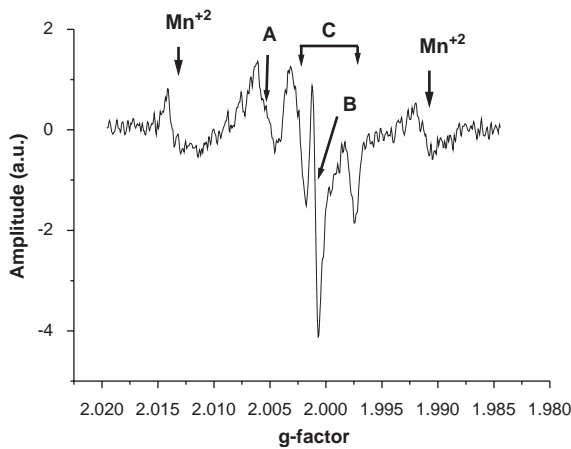
Table 1
List of radicals present in the ESR spectrum of the stalagmite in the $g = 2$ region from both caves

	g-factor	Radical
A	2.0057	SO_2^-
B	2.0008	CO_2^- (isotropic)
C	1.9974	$(g_\parallel)$ CO_2^-
	2.0022	$(g_\perp)$

Fig. 3. K-band ESR spectrum of stalagmite from Caverna Santana irradiated with 15 Gy. The radicals identified with A, B and C are listed in Table 1.
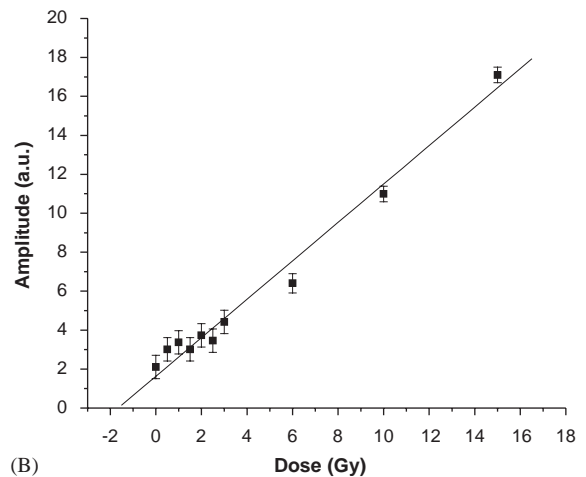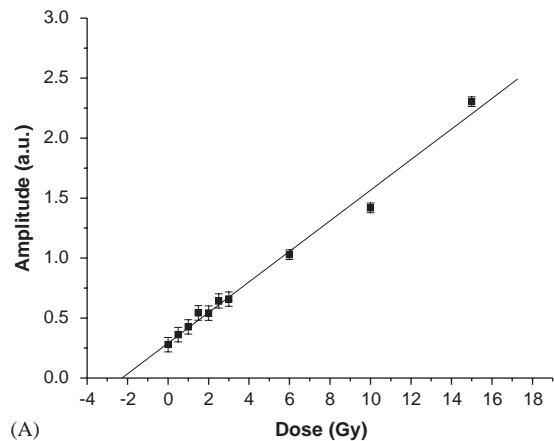

Fig. 4. Dose–response curve for sample from Caverna Botuvera normalized by: (A) Mn signal intensity and (B) normalized by mass.

4. Discussion

The subject of signal/noise dependence on the frequency in ESR measurements is a topic that has been seldom studied in the past. There is a well-accepted quotation from Poole's book (Poole, 1996) that the minimum number of detected spins will depend on ω_0^{-2}, in other words S/N $\propto \omega_0^2$. However more recent work carefully done by Rinard et al. (1999, 2002) at frequencies from 250 MHz to 9.1 GHz shows that S/N depends on several factors and that Poole's expression is incorrect. For the present case where the sample size is constant, S/N will scale with microwave frequency as $\omega_0^{11/4}$. Thus the use of K-band (24 GHz) microwave

frequency potentially produces an important increase in signal sensitivity together with improvements in spectral resolution when compared to the X-band, for the same sample size. Where sample size is limited, as is often the case in dating and dosimetry, investigators may find the best experimental conditions in the K-band.
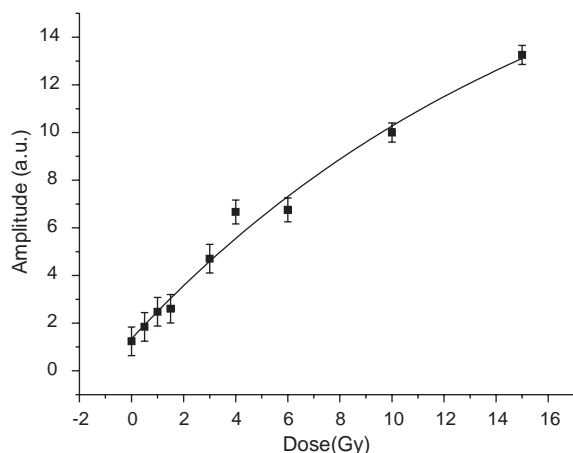
Fig. 5. Dose–response curve for sample from Caverna Santana normalized by mass.

Measurements in the K-band are also crucial to determine signals not detectable in the X-band.

Comparing the ED results for the sample from Caverna Botuvera, one observes that the normalization of the dosimetric signal by the amplitude of the Mn^{2+} signal results in a smaller dispersion of experimental data and in the ED. The intensity of the signal of Mn^{2+} is proportional to the sample mass and at the same time it is used to correct the variations that may occur in the tuning of the resonant cavity when samples are exchanged. It was not possible to perform this procedure for the sample from Caverna Santana because the signal of Mn^{2+} has low intensity and poor S/N. Using an external dose rate of 0.8 ± 0.1 mGy/year, determined by Baffa et al. (2000) for another limestone cave in southeastern Brazil, ages of 2.9 ± 0.8 ky and 2.1 ± 0.8 ky were estimated for the Caverna Botuvera sample and 1.4 ± 0.7 ky for the Caverna Santana sample. Sample thickness is less than 20 cm; thus the external gamma attenuation was not considered in age estimation. The concentrations of uranium and thorium in the samples are low (< 0.2 ppm and $< 10^{-3}$ ppm, respectively); thus the contribution of these nuclides are insignificant to internal dose rate. The estimated ages for the Caverna Botuvera sample are compatible with U/Th dating for the Caverna Botuvera sample, 2.3 ± 0.13 ky. The possibility of dating techniques else than U/Th for speleothems is fundamental in order to get the chronology for stalagmite paleoenvironmental records which are not suitable for U/Th dating due to detrital Th or very low U concentration.

References

Baffa, O., Brunetti, A., Karmann, I., Dias Neto, C.M., 2000. ESR dating of toxodon from Brazilian karstic cave. Appl. Rad. Isot. 52, 1345–1349.

Ikeya, M., 1975. Dating a stalactite by electron paramagnetic resonance. Nature 255, 48–50.

Ikeya, M., Baffa, F.O., Mascarenhas, S., 1993. ESR dating of cave deposits from Akyoshi-dô Cave in Japan and Diabo Cavern in Brazil. J. Speleol. Soc., Japan 9, 58–67.

Perrette, Y., Delannoy, J., Bolvin, H., Cordonnier, M., Destombes, J., Zhilinskaya, E.A., Aboukais, A., 2000. Comparative study of stalagmite sample by statigraphy, laser induced fluorescence spectroscopy, EPR spectrometry amd reflectance imaging. Chem. Geol. 152, 221–243.

Poole, C.P., 1996. Electron spin resonance, A comprehensive treatise on experimental technique. Dover publications, New York.

Rinard, G.A., Quine, R.W., Hartbridge, J.R., Song, R., Eaton, G.R., Eaton, S.S., 1999. Frequency dependence of EPR signal-to-noise. J. Mag. Res. 140, 218–227.

Rinard, G.A., Quine, R.W., Eaton, S.S., Eaton, G.R., 2002. Frequency dependence of EPR signal intensity, 250 MHz to 9.1 GHz. J. Mag. Res. 156, 113–121.

Rink, W.J., 1997. Electron Spin Resonance (ESR) dating and ESR applications in Quaternary Science and Arhaeometry. Rad. Meas. 27 (5–6), 975–1025.