Anais da Academia Brasileira de Ciências (2016) 88(4): 2137-2142
(Annals of the Brazilian Academy of Sciences)
Printed version ISSN 0001-3765 / Online version ISSN 1678-2690
http://dx.doi.org/10.1590/0001-3765201620150755
www.scielo.br/aabc

Dating stalagmite from Caverna do Diabo (Devil´S Cave) by TL and EPR techniques

SHIGUEO WATANABE[1], NILO F. CANO[2], T.K. GUNDU RAO[1], BETZABEL N. SILVA-CARRERA[1], LUCAS S. CARMO[3], ANTONIO J.A. QUINA[3], ROSELI F. GENNARI[1], CASIMIRO S. MUNITA[3], JORGE S. AYALA-ARENAS[4] and BRUNO G. FERNANDES[5]

[1]Instituto de Física, Universidade de São Paulo, Rua do Matão, Travessa R,
187, Cidade Universitária, 05508-090 São Paulo, SP, Brazil
[2]Departamento de Ciências do Mar, Universidade Federal de São Paulo, Rua Doutor
Carvalho de Mendonça, 144, 11070-100 Santos, SP, Brazil
[3]Instituto de Pesquisas Energéticas e Nucleares, IPEN-CNEN/SP, Av. Prof. Lineu
Prestes, 2242, Cidade Universitária, 05508-000 São Paulo, SP, Brazil
[4]Escuela Profesional de Física, Facultad de Ciencias Naturales y Formales, Universidad
Nacional de San Agustín/UNSA, Av. Independencia, s/n, Arequipa, Peru
[5]Departamento de Engenharia Metalúrgica e Materiais, Escola Politécnica, Universidade de
São Paulo, Av. Prof. Mello Moraes, 2463, 05508-030 São Paulo, SP, Brazil

Manuscript received on October 19, 2015; accepted for publication on June 18, 2016

ABSTRACT

A cylindrical fragment of stalagmite from Caverna do Diabo, State of São Paulo, Brazil, has been studied and dated by thermoluminescence and electron paramagnetic resonance techniques. The thermoluminescence glow curves of stalagmite samples and subsequently gamma irradiated, have shown rise of three peaks at 135, 180 and 265 °C. From electron paramagnetic resonance spectra of stalagmite was possible to clearly identify three paramagnetic centers in the g = 2.0 region: Centers I, II and III are due to CO_2^-, CO_3^- and CO_3^{3-}, respectively. The additive method was applied to calculate the accumulated dose using thermoluminescence peak at 265 °C and the electron paramagnetic resonance signal at g = 1.9973 of CO^-_2 radical. The ages of the different slices of stalagmite were determined from the D_{ac}- values and D_{an}- value, obtaining an average of 86410 for central slice, 53421 for second slice, 31490 for third slice and 46390 years B.P. for the central region of upper end.

Key words: stalagmite, Caverna do Diabo, dating, TL, EPR.

INTRODUCTION

Many caves in nature are characterized by speleothems such as stalagmite, stalactite, dolomite, etc. Some of them may have originated more than millions years ago.

The use of cave deposits, such as speleothems, mainly stalagmites, is a powerful tool for the study of past climatic and environmental evolution (Gascoyne 1992, Lauritzen and Lundberg 1999). The stalagmites generally contain brown rings; the brown rings in a stalagmite may be markers of the same age (Ikeya 1993). The origin of such brown rings in cave deposits may be considered due to

---

Correspondence to: Nilo Francisco Cano
E-mail: nilocano@if.usp.br

flooding or to an extraordinarily high precipitation that brought a large amount of small clay particles as inclusions into the stalagmite (Ikeya 1980, Arakawa and Hori 1989). Brown rings can be used as an indicator of the paleoclimate, like an age indicator in dendrochronology (tree ring counting), at the local level. These brown rings or clay sediments might have occurred at the time of a global change in the climate, or due to changes in the groundwater level related to sea-level changes (Ikeya 1993). The study of stalagmite is thus a powerful tool for the high-resolution reconstruction of past climate changes and the period of each change. Through the dating of stalagmite it is possible to support the paleoenvironmental studies based on the stalagmite growth with the time. Therefore, the study of stalagmites is a powerful tool for reconstruction and determination of the period of the past climate changes.

Caverna do Diabo (Devil´s Cave) is an extensive cave located in southeast of the São Paulo State, Brazil (24°38’0”S and 48°24’0”W) (see Fig. 1), with 6340 m of galleries already identified and unevenness of the order 175 m. It is well known due to a large number of huge stalagmites and stalactites. The wall of the cave is mainly composed of dolomite, but, calcite is also part of the wall in many parts.

Dating by TL and/or EPR techniques is a particular application of dosimetry using natural minerals such as carbonates (in this work stalagmite), as dosimeters of environmental radiation arising

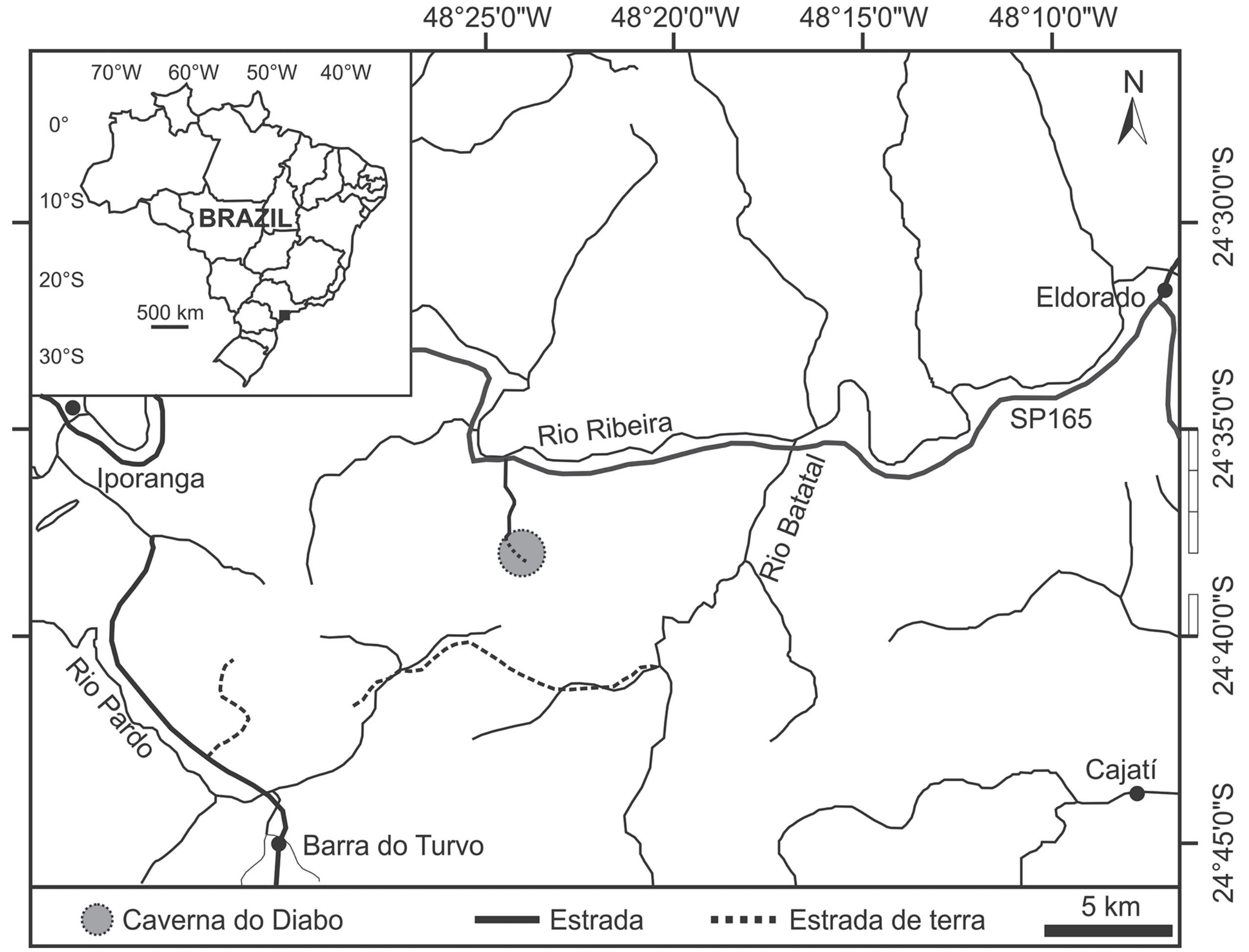

Figure 1 - Location map of the study area (Adapted from the work of Cordeiro (2013)).

from the decay of naturally occurring U, Th and K. The TL or EPR intensity of natural samples is proportional to the absorbed dose up to dating. Both dating techniques are radiogenic methods that can be used to determine the amount of radiation damage stored in a solid material. These techniques are based on the measurement of radiation-sensitive TL or EPR signals which begin to form after crystallization or can grow after being reset to zero or reduced to a residual level by exposure during depositional processes (McKeever 1985, Wintle 1997, Ikeya 1993, Bartoll and Ikeya 1997, Aitken 1985, Grün 1989).

A study of the thermoluminescent and EPR response of the stalagmite sample from Devil´s Cave with gamma irradiation is reported in this work in order to find an alternative material for dating by TL and EPR techniques. Furthermore, we present the first results of dating of a stalagmite from the Devil´s Cave, São Paulo State, Brazil. There is no evidence in the literature about dating of stalagmite using both techniques for this cave.

MATERIALS AND METHODS

A cylindrical fragment of stalagmite was collected from Devil's Cave, State of São Paulo, Brazil (see Fig. 1). Fig. 2a shows a picture of a piece of stalagmite that has a diameter of about 15 cm and 37 cm length. From lower end of the stalagmite cylinder, about five grams around central axis, another five grams from 2 cm to 4 cm cylindrical layer from the central axis and another five grams from 4 cm to 6 cm cylindrical layer from the central axis were extracted, which were labeled as 1, 2 and 3 (See Fig. 2b).

The samples labeled as 1, 2 and 3 were first crushed and then sieved, retaining grains between 0.080 and 0.180 mm in size. These powders were irradiated with gamma-rays at doses in the range of tens of Gy up to 600 Gy. The additive dose method was used to determine the accumulated dose (D_{ac}) in TL as well as in EPR measurements.

The crystal structure of stalagmite sample was examined by X-ray diffraction (XRD) analysis; utilizing a Rigaku diffractometer with Cu-k_{α} radiation and using a 10 - 70° scan range.

Concentrations of U, Th and K in the stalagmite samples were determined by means of Instrumental Neutron Activation Analysis (INAA) analysis.

The TL measurements were performed in a nitrogen atmosphere using a model 4500 Harshaw TL reader equipped with two photomultiplier tubes, which could record luminescence signals independently. The reader was controlled by WinREMS Software, which was supplied with the

Figure 2 - Picture of a piece of stalagmite.

spectrometer and was run on a Windows computer. The heating rate used in the TL measurements was 4 °C/s. Each point in the glow curve represents an average of six readings.

EPR measurements were carried out with a Bruker EMX EPR spectrometer operating at X-band frequency with 100 kHz modulation frequency. One hundred milligrams of powdered sample were used for each measurement.

RESULTS AND DISCUSSION

Fig. 3 shows the XRD pattern of the stalagmite sample of this work and the pure standard calcite. The result of XRD was analyzed using computer software and compared with the standard spectrum of calcite cataloged by JCPDS (Joint Committee Powder Diffraction Standards). The XRD spectra show that all the peaks are of calcite.

Fig. 4 shows the glow curves corresponding to the TL from a natural sample and the artificial TL following gamma irradiation with dose from 10 Gy up to 1240 Gy for the slice 1. The sample exhibits three TL peaks, one around 125 °C, other at 180 °C and another broad peak centered at 265 °C. This last peak has been used to obtain D_{ac}-values by additive method. The inset of Fig. 4 shows the increase in the intensity of the 265 °C TL peak with γ dose for the slice 1.

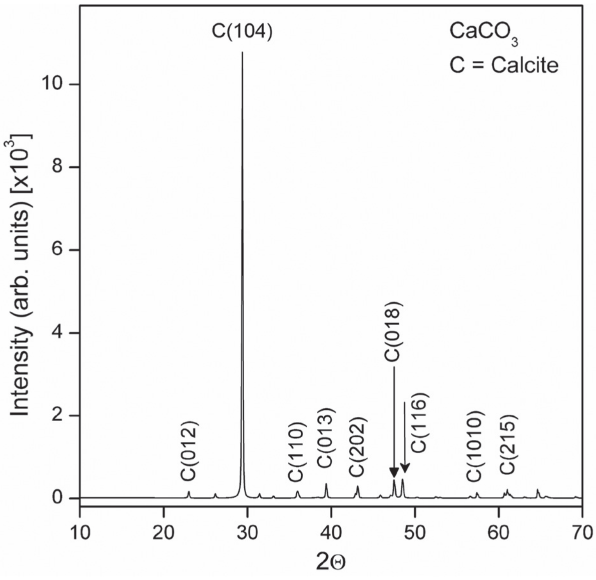

Figure 3 - The powder X-ray diffraction of stalagmite sample.

For the determination of the accumulated dose by additive method, the dose-response curves of the TL peak and the EPR signal of the samples were fitted using an exponential function. This fitting function is:

$$I(D) = I_0\left(1 + e^{-\frac{D+D_{ac}}{SD}}\right) \qquad (1)$$

where I is the measured TL or EPR intensity, D is the gamma dose, I_0 is the saturation intensity, SD is the saturation dose and D_{ac} is the accumulated dose. An accumulated dose of 89.4 ± 6.7 Gy has been obtained from the TL dose response curve (inset of Fig. 4). Similar measurements yield D_{ac}-values for slice 2 and 3, as well as for the central part of the stalagmite from the other end.

The room temperature EPR signal of irradiated stalagmite (Dose: 600 Gy) is shown in Fig. 5.

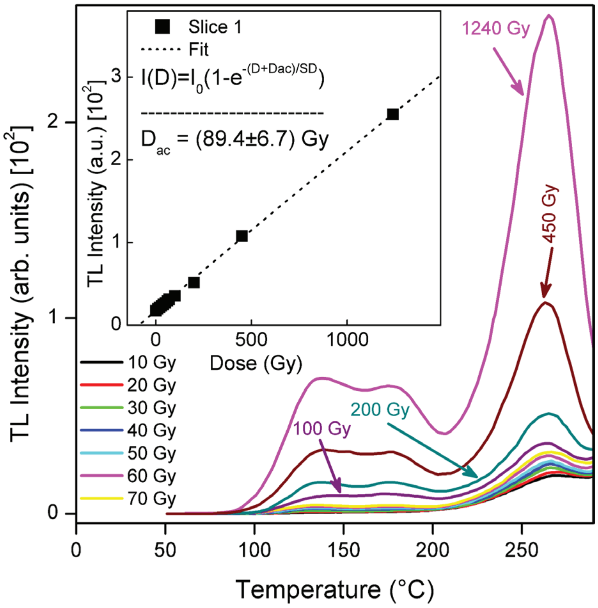

Figure 4 - TL glow curves of stalagmite samples plus additional gamma-doses up to 1420 Gy. Inset of the figure shows the TL intensity of the 265 °C peak as a function of the dose given to stalagmite from slice 1 for the determination to D_{ac}.

Three distinct centers could be identified which are labeled as center I, center II and center III. Center I is the CO^-_2 ion with principal g-values: $g_1 = 2.0028$, $g_2 = 2.0020$ and $g_3 = 1.9973$. The natural and irradiated EPR spectra of the samples labeled as 1, 2 and 3 were found to be similar. The EPR signal of the calcite crystal at $g = 1.9973$ is most suitable signal for dating due to radiation-sensitive, stable over geological times and gives more realistic age estimates (Ikeya 1993, Barabas et al. 1992, Engin et al. 1999, Smith et al. 1985). The EPR signal of CO^-_2 ion was used in the present dating experiments.

Fig. 6 shows the behavior of the intensity of the EPR signal at $g = 1.9973$ as a function of gamma dose. Applying the additive method, the accumulated dose D_{ac} was estimated to be about 95±9 Gy for slice 1, comparable to the value obtained by TL measurements. The determined D_{ac} for another two samples are given in Table I.

Table I shows the D_{an} and the age of the stalagmite sample obtained by TL and EPR techniques respectively. The annual dose rate determination was carried out by measuring the concentrations of ^{238}U, ^{232}Th and ^{40}K in the stalagmite using the INAA method. The concentration of the uranium, thorium and potassium did not significantly change from center and the external layer of the studied stalagmite materials. The calculated annual dose rate $D_{an} = 1.067 \pm 0.107$ mGy. The dose of cosmic rays can also be assumed to be negligible in underground environments like caves.

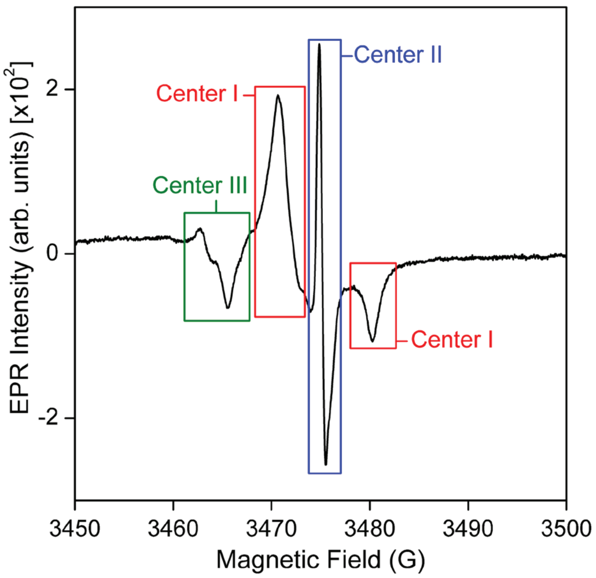

Figure 5 - Room temperature EPR spectrum of irradiated stalagmite (Dose: 600 Gy).

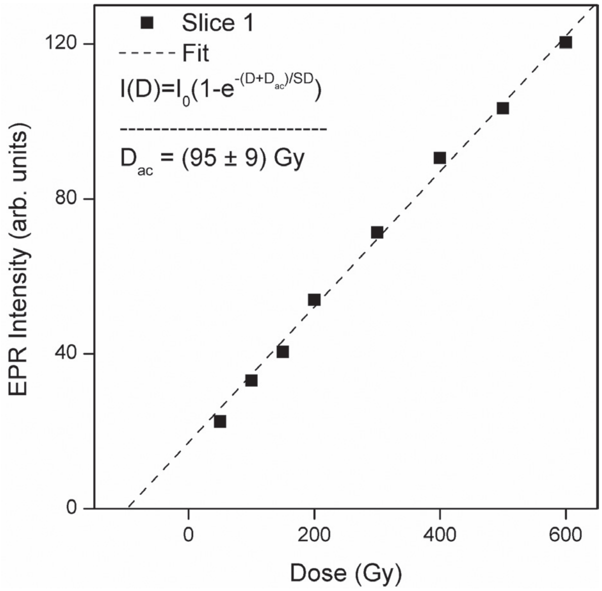

Figure 6 - EPR intensity versus gamma dose of the EPR signal at $g = 1.9973$ due to CO^-_2.

TABLE I

The accumulated dose (D_{ac}) and ages (by EPR and TL dating) of four position of the stalagmite.

Position of stalagmite	EPR		TL	
	D_{ac} (Gy)	Age (years B.P)	D_{ac} (Gy)	Age (years B.P)
Slice 1	95 ± 9	89034 ± 10520	89.4 ± 6.7	83786 ± 8850
Slice 2	56 ± 5	52484 ± 7250	58 ± 5	54358 ± 6530
Slice 3	33.8 ± 3.6	31677 ± 3425	33.4 ± 3.5	31302 ± 3860
Upper end	53 ± 5.0	49671 ± 5946	46.0 ± 5.0	43110 ± 5324

The age of the samples (labeled as slices 1, 2 and 3) obtained by EPR method are comparable to the value obtained by TL measurements. These results confirm the geological interpretation on the formation of Devil´s Cave.

CONCLUSIONS

Ages of different positions of stalagmite by EPR and TL are close to each other within experimental error. The average age of the central part of stalagmite is in the order of 86410 years. The coherence of the dating by TL and EPR techniques and the presence of rings show that this stalagmite can be used as a high-resolution climatic record. The growth rate from lower and to upper end along the axis is about 0.82 cm per 1000 years, a slow process. Horizontally the growth rate is much slower; 0.09 cm per year.

ACKNOWLEDGMENTS

The authors wish to thank Ms. E. Somessari and Mr. C. Gaia, Instituto de Pesquisas Energeticas e Nucleares (IPEN), Brazil, for kindly carrying out the irradiation of the samples. To Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP, Process number 2014/03085-0) for partial financial support and to Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES, Process number BEX-9612130) for fellowship to T.K. Gundu Rao.

REFERENCES

AITKEN MJ. 1985. Thermoluminescence Dating. Academic Press, London.

ARAKAWA T AND HORI N. 1989. ESR dating of carbonate speleothem rings and late quaternary climatic changes in the Ryukyu Islands, Japan. Appl Radiat Isotopes 40: 1143-1146.

BARABAS M, BACH A, MUDELSEE M AND MANGINI A. 1992. General properties of the paramagnetic centre at g=2.0006 in carbonates. Quaternary Sci Rev 11: 165-171.

BARTOLL J AND IKEYA M. 1997. Dating of Pottery: a Trial. Appl Radiat Isotopes 48: 981-984.

CORDEIRO BM. 2013. Planalto Carbonático do André Lopes (SP): Geomorfologia Cárstica e Geoespeleologia da Gruta da Tapagem (Caverna do Diabo), Instituto de Geociências, Universidade de São Paulo, Brazil, p. 4.

ENGIN B, GÜVEN O AND KÖKSAL F. 1999. Electron spin resonance age determination of a travertine sample from the southwestern part of Turkey. Appl Radiat Isotopes 51: 689-699.

GASCOYNE M. 1992. Paleoclimate determination from cave calcite deposits. Quaternary Sci Rev 11: 609-632.

GRÜN R. 1989. Electron spin resonance (ESR) dating. Quatern Int 1: 65-109.

IKEYA M. 1980. ESR dating of carbonates at Petralona Cave. Anthropos 7: 143-50.

IKEYA M. 1993. New Applications of Electron Spin Resonance: Dating, Dosimetry and Microscopy. World Scientific, Singapore.

LAURITZEN SE AND LUNDBERG J. 1999. Speleothems and climate: a special issues of the Holocene. Holocene 9: 643-647.

MCKEEVER SWS. 1985. Thermoluminescence of Solids. Cambridge University Press, Cambridge, UK.

SMITH BW, SMART PL AND SYMONS MCR. 1985. ESR signals in a variety of speleothem calcites and their suitability for dating. Nucl Tracks 10: 837-844.

WINTLE AG. 1997. Luminescence dating: laboratory procedures and protocols. Radiat Meas 27: 769-817.