Ancient TL

www.ancienttl.org · ISSN: 2693-0935

Rhodes, E. and Grün, R., 1991. *ESR behaviour of the paramagnetic centre at g=2.0018 in tooth enamel.* Ancient TL 9(2): 14-18. https://doi.org/10.26034/la.atl.1991.175

ESR behaviour of the paramagnetic centre at g=2.0018 in tooth enamel

Edward J. Rhodes and Rainer Grün
Subdept. of Quaternary Research, Cambridge University, Free School Lane, Cambridge CB2 3RS, U.K.

Introduction

The dating of mammal teeth from archaeological and geological sites has played an important role in both the field of human evolution (Grün and Stringer, 1991) and in assigning oxygen isotope stages to Quaternary terrestrial sequences (eg Zymela et al., 1988). Although many ESR age estimates have been published using the signal at g=2.0018 in tooth enamel, no systematic study has been carried out with respect to optimizing the measurement conditions for AD determination.

One problem of using the signal at g=2.0018 for AD determination is the correct definition of the signal. In many cases this signal, which has a line width of about 0.35 mT, is superimposed by narrower signals which have been attributed to various organic substances (Ikeya, 1982; Grün, 1985; Grün et al., 1987; Bouchez et al., 1988; see figure 1). Based on some coarse plateau-tests, Grün et al., (1987) suggested recording the signal with a modulation amplitude of 0.5 mTpp (see figure 2a).

Hoshi et al. (1985) studied the saturation characteristics of tooth enamel at room temperature, showing that microwave saturation occurs at powers of greater than about 1 mW. However, no study of the influence of measurement power on the size of systematic or random deviations in the AD determination has been undertaken.

In this study measurements have been conducted to test the influence of modulation amplitude, temperature and microwave power on the AD determination. The aims of this study were to (i) confirm the validity of previously measured dates and (ii) determine the optimum conditions for AD measurement.

We selected two enamel samples (529a and 533a, horse) that had been previously used in a dating study of Border Cave (Grün et al. 1990). Sample 529a shows very strong interferences by organic radicals whereas these are almost invisible in the ESR spectrum of sample 533a (see figure 1). The ESR measurements for this study were carried out approximately 2 years after the initial measurements of Grün et al. (1990) who used the measurement parameters as recommended by Grün (1989a,b): 2 mW microwave power, 0.5 mTpp modulation amplitude, room temperature. The AD values were determined by exponential fitting using a jackknifing procedure for error estimation (Grün & Macdonald 1989). The previously published AD values were: 68.3 ± 11.8 Gy (529a) and 74.5 ± 4.9 Gy (533a).

All measurements included in this study were performed on a JEOL JES RE1X ESR spectrometer equipped with a ES DVT2 variable temperature unit.

Results

The organic radicals can be suppressed by using a large modulation amplitude (figure 2a), increasing microwave power (figure 2b), or lower temperatures (figure 2c). Using lowered temperatures (in 10 ± 0.5 °C steps) we observed that the sharp organic interferences disappear at about -80 °C. We therefore decided to study the influence of microwave power on AD determination at room temperature and at -100 °C.

Figure 3 and table 1 summarize the results of this study. The first column of figure 3 shows that the samples show microwave saturation effects above 1 mW under any set of measurement conditions. This agrees with the observation of Hoshi et al. (1985) and seems to be intrinsically characteristic for the paramagnetic centre at g=2.0018. Note, that the background increases significantly above 10 mW.

The second and third columns of figure 3 show that the AD determination does not seem to be systematically influenced by microwave saturation. Only the AD determination for sample 529a, measured with a low modulation amplitude of 0.05 mTpp at room temperature shows a trend towards smaller AD values with increasing microwave power. However, this is more likely due to the poor signal definition under these measurement conditions than the effect of microwave power. Some scattering in the mean AD value can be observed in the results of sample 529a at -100 °C with 0.05 mTpp, although there is no systematic trend. All other determinations of the mean AD value seem to be completely independent of temperature, microwave saturation and modulation amplitude.

Figure 4 shows a plot of the signal-to-noise (s/n) ratio versus the error in AD estimation. The s/n ratio is highest in the region of 10 mW. However, the minimum fractional error does not consistently coincide with the optimum s/n ratio; best results in AD determination seem to be obtainable for microwave powers in the range of 1 to 10 mW.

Although the low temperature measurements suppress the organic signals very effectively, the size of the errors do not systematically decrease.

Discussion

Figure 2 shows that the organic interferences of the signal at g=2.0018 can in principle be suppressed either with large modulation amplitudes, increasing microwave powers or measurement at lower temperatures. Measurements at very high microwave powers have the disadvantage of increasing the error in the AD determination which seems to result from a worse s/n ratio.

The basic improvement for sample 529a, which contains the organic interferences, is the measurement with a 0.5 mTpp modulation amplitude.

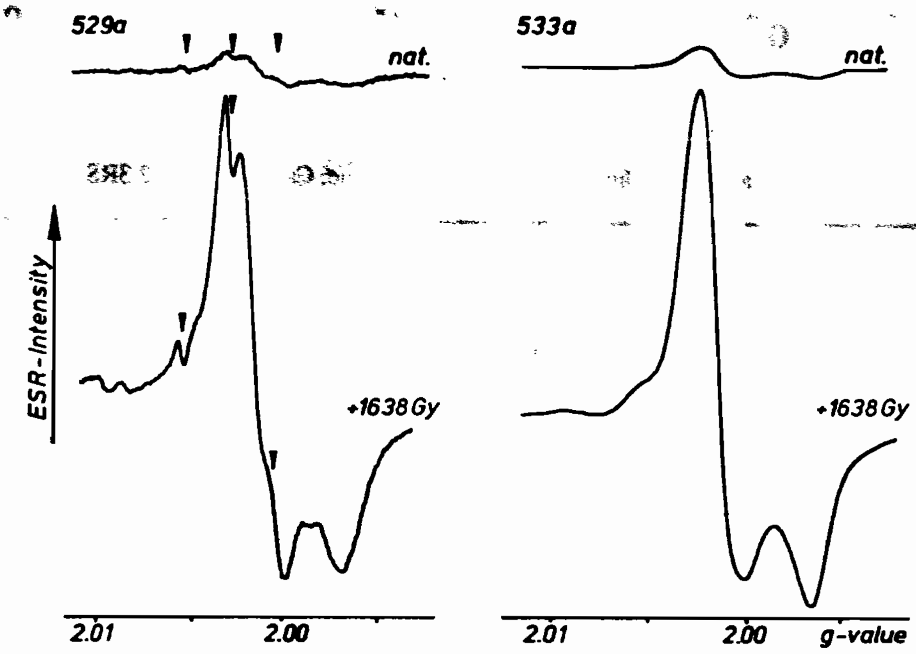

Figure 1.
ESR spectra of samples 529a and 533a (0.05 mTpp, 2 mW, 20 °C). Upper spectrum: natural sample; lower spectrum: +1638 Gy. The arrows indicate the interferences by organic radicals.

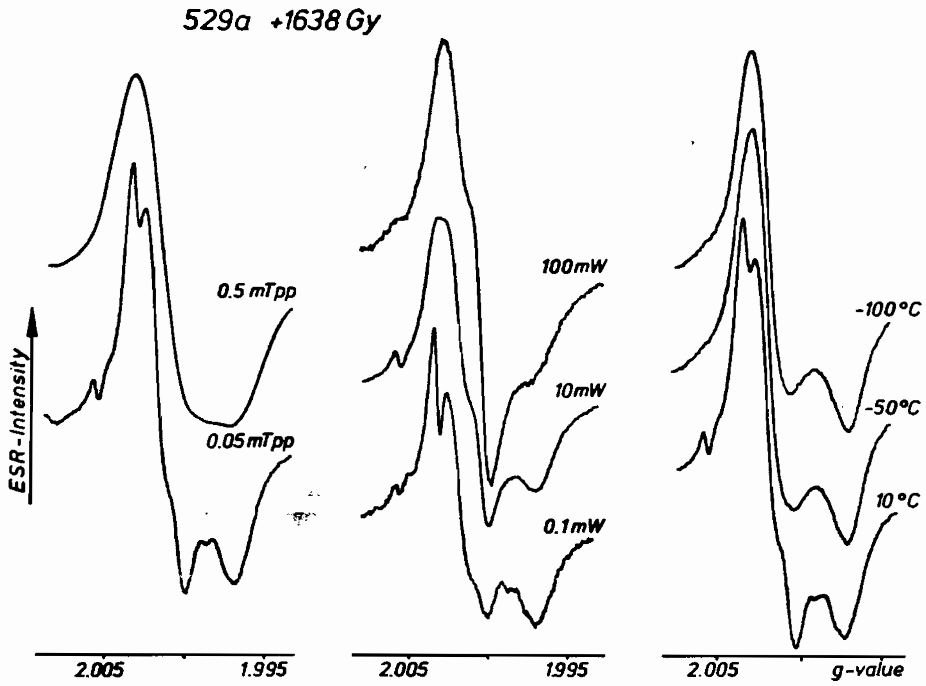

Figure 2.
(a) influence of modulation amplitude (+1638 Gy, 2 mW, 20 °C); (b) influence of microwave power (0.05 mTpp, 20 °C, +1638 Gy); (c) influence of temperature (0.05 mTpp, 2 mW, +1638 Gy).

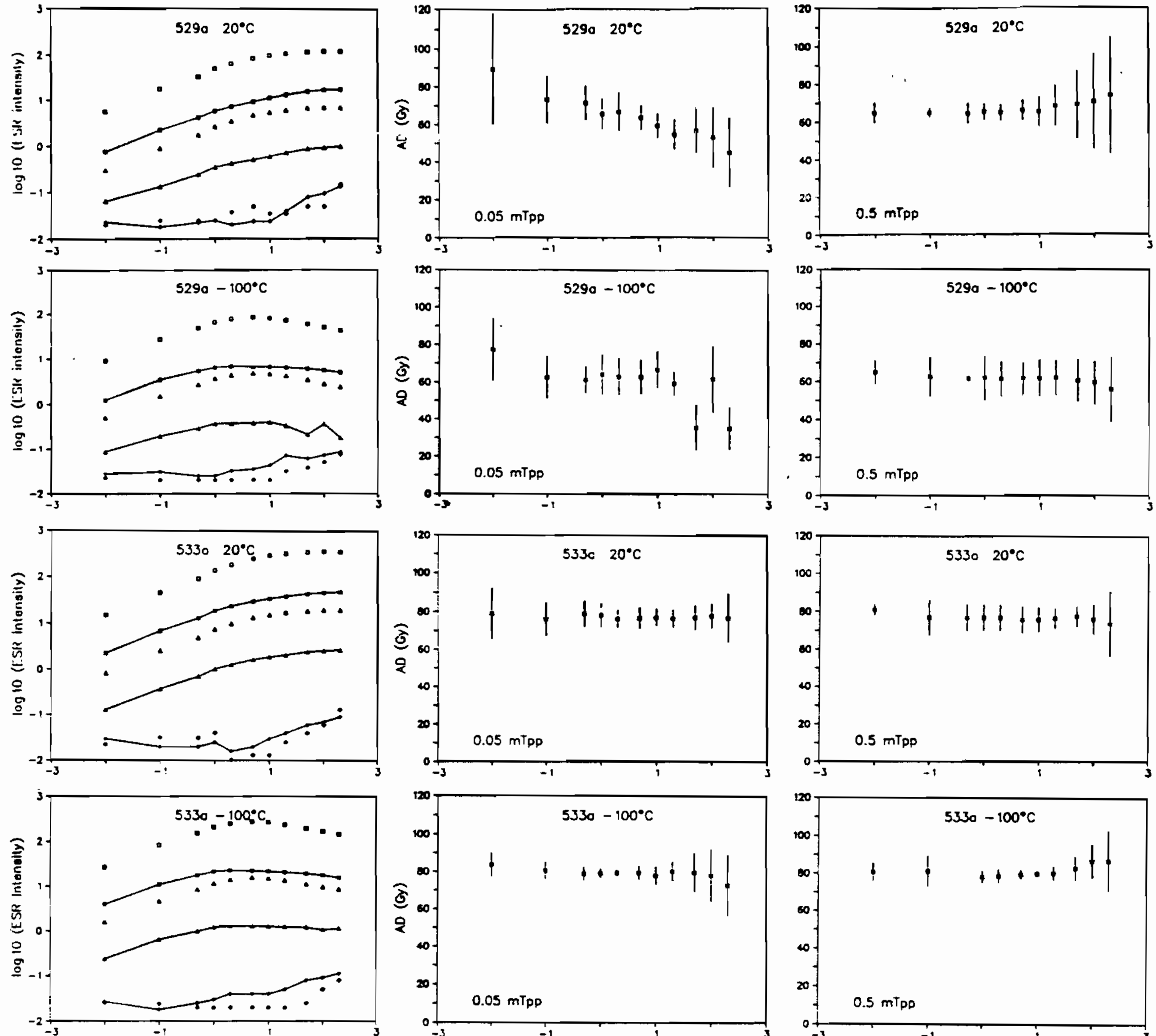

Figure 3.
Left column: signal and noise intensities versus microwave power.
Open symbols: 0.5 mTpp; closed symbols (joined by lines): 0.05 mTpp. Diamonds: background; triangles: natural sample; squares: +1638 Gy. Middle column: AD versus microwave power (0.05 mTpp modulation amplitude). Right column: AD versus microwave power (0.5 mTpp modulation amplitude).

Measurements at low temperatures do not seem beneficial for the AD determination of sample 529a, but show some improvement for sample 533a. Although it seems desirable to measure at temperatures around -100 °C, most ESR spectrometers are not equipped with a temperature unit that can keep this temperature very stable and the measurements take a considerably longer time since the equipment has to get into thermal equilibrium for each measurement.
A side-effect of this study is that we cannot observe anomalous fading of the signal at g=2.0018 after two years.

Conclusion

The optimal ESR measurement conditions for AD determination using the paramagnetic centre at g=2.0018 in tooth enamel are at room temperature at around 1 to 10 mW microwave power and a modulation amplitude of 0.5 mTpp. Measurements at -100 °C, which suppresses the organic signals very effectively, do not seem to provide significant advantages. We cannot observe an anomalous fading component after about two years.
Our results confirm the validity of the measurement conditions (and age estimates) that have been suggested by Grün (1989a,b).

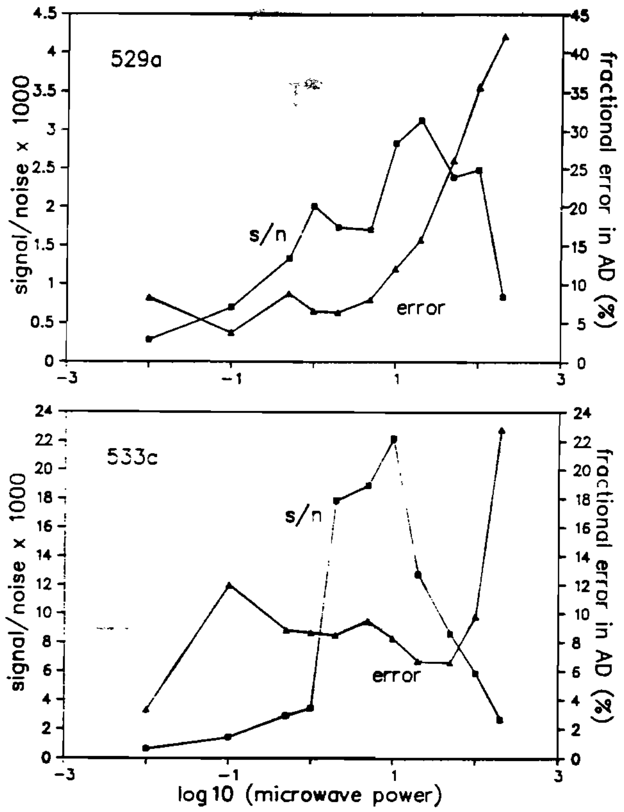

Figure 4.
Signal-to-noise (s/n) ratio and fractional error versus microwave power for 529 and 533 (20 °C, 0.5 mTpp).

Table 1.

i) sample 529a

microwave power(mW)	20 °C 0.05 mTpp	-100 °C 0.05 mTpp	20 °C 0.5 mTpp	-100 °C 0.5 mTpp	Grün et al. (1990)
200	44.9 ± 18.0	34.8 ± 10.8	73.7 ± 31.1	55.9 ± 16.8	
100	52.9 ± 15.7	61.4 ± 17.5	70.4 ± 25.1	59.5 ± 11.3	
50	56.2 ± 11.1	35.2 ± 12.2	68.6 ± 17.9	60.5 ± 11.0	
20	54.4 ± 8.2	59.0 ± 6.3	68.0 ± 10.8	62.1 ± 9.0	
10	59.1 ± 6.3	66.4 ± 9.5	65.0 ± 7.8	61.8 ± 9.3	
5	63.6 ± 6.4	62.6 ± 9.0	65.8 ± 5.3	61.7 ± 8.2	
2	66.8 ± 10.0	62.8 ± 9.6	64.8 ± 4.1	61.6 ± 9.1	68.3 ± 11.8
1	65.7 ± 8.3	64.1 ± 10.5	65.0 ± 4.2	62.0 ± 11.3	
0.5	71.6 ± 9.0	61.2 ± 7.0	64.3 ± 5.6	61.4 ± 1.3	
0.1	73.2 ± 12.2	62.2 ± 11.0	64.9 ± 2.4	62.3 ± 10.0	
0.01	89.3 ± 28.7	77.1 ± 16.5	65.3 ± 5.4	64.8 ± 6.1	
means	63.4	58.8	66.9	61.2	
scatter in means	12.1	12.7	3.0	2.2	

ii) sample 533a

microwave power(mW)	20 °C 0.05 mTpp	-100 °C 0.05 mTpp	20 °C 0.5 mTpp	-100 °C 0.5 mTpp	Grün et al. (1990)
200	76.7 ± 12.5	72.7 ± 16.0	73.5 ± 16.8	86.9 ± 15.7	
100	77.8 ± 6.0	78.1 ± 13.8	75.8 ± 7.4	86.9 ± 8.7	
50	76.9 ± 6.3	79.7 ± 10.2	77.4 ± 5.1	82.9 ± 6.4	
20	76.5 ± 4.5	80.1 ± 4.9	76.4 ± 5.1	80.4 ± 3.3	
10	77.1 ± 4.4	78.1 ± 4.6	75.8 ± 6.3	80.1 ± 1.2	
5	76.7 ± 5.4	79.4 ± 3.6	75.8 ± 7.2	79.6 ± 2.3	
2	76.3 ± 4.6	79.4 ± 2.0	76.8 ± 6.5	78.7 ± 3.2	74.5 ± 4.9
1	78.2 ± 6.4	79.2 ± 2.7	76.8 ± 6.7	78.3 ± 3.2	
0.5	79.0 ± 6.7	79.0 ± 3.5	76.8 ± 6.8	80.3 ± 7.9	
0.1	76.2 ± 8.6	80.5 ± 4.4	76.8 ± 9.2	81.3 ± 8.1	
0.01	78.8 ± 13.2	83.7 ± 6.1	80.9 ± 2.7	80.8 ± 4.6	
means	77.3	79.1	76.6	81.5	
scatter in means	1.0	2.6	1.8	3.0	

Acknowledgement
This study was partly funded by a SERC grant to N. Shackleton and by a NERC research fellowship to EJR.

References

Bouchez, R., Cox, R., Herve, A., Lopez-Carranza, E., Ma, J. L., Piboule, M., Poupeau, G. and Rey, P., 1988, Q-band ESR studies of fossil teeth, consequences for ESR dating. *Quaternary Science Reviews* **7**, 497-501.

Grün, R. (1985) Beiträge zur ESR-Datierung. Sonderverffentlichungen des Geologischen Instituts der Universität zu Köln **59**, 1-157.

Grün, R. (1989a) Electron spin resonance (ESR) dating. *Quaternary International* **1**, 65-109.

Grün, R. (1989b) *Die ESR-Altersbestimmungsmethode*. 132 p., Springer, Berlin - Heidelberg.

Grün, R., Beaumont, P. & Stringer, C. B. (1990) ESR dating evidence for early modern humans at Border Cave in South Africa. *Nature* **344**, 537-539.

Grün, R. & Macdonald, P. D. M. (1989) Non-linear fitting of TL/ESR dose response curves. *Applied Radiation and Isotopes* **40(10-12)**, 1077-1080.

Grün, R., Schwarcz, H. P. & Zymela, S. (1987) ESR dating of tooth enamel. *Canadian Journal of Earth Sciences* **24**, 1022-1037.

Grün, R. & Stringer, C. B. (1991) ESR dating and the evolution of modern humans. *Archaeometry* (in press).

Hoshi,M., Sawada, S., Ikeya, M. and Miki, T., 1985, ESR dosimetry for Hiroshima A-bomb survivors, in *ESR Dating and Dosimetry* (eds. M. Ikeya and T. Miki), pp. 407-414, Tokyo, Ionics Press.

Ikeya, M., 1982, A model of linear uranium accumulation for ESR age of Heidelberg, Mauer, and Tautavel bones. *Japanese Journal of Applied Physics* **21**, L690-L692.

Zymela, S., Schwarcz, H. P., Grün, R., Stalker, A. M. and Churcher, C. S. (1988) ESR dating of Pleistocene fossil teeth from Alberta and Saskatchewan. *Canadian Journal of Earth Sciences* **25**, 235-245.

PI Reviewers Comments (Anne Skinner)

I am strongly in favour of this type of work. It is a pity that the constant pressure to produce "useful" results (ie dates) limits the opportunities to go back and check (and recheck) fundamental assumptions about the nature of the phenomenon being used. Therefore I would rate this contribution as both interesting and a constructive addition to the literature. There is one minor comment. One would expect the relatively sharp peaks of the radical species to vanish when the modulation amplitude is increased. This is simply an artefact of the measurement process. It is not clear that they are "suppressed", in the sense of no longer contributing to the spectrum. Rather, the intensity of these peaks may be contained within the envelope of the larger peak. In contrast, when the temperature of the sample is lowered, the relaxation time of the radical may be such that it cannot respond to the magnetic field. In that case, the effect from these radicals has truly been removed from the spectrum. In the example shown in this paper it does not seem to matter what technique is used, which suggests that the contribution by the radical peak to the overall intensity is insignificant.

The apparent decrease of AD with increasing power at low modulation amplitude, shown by sample 529, is initially of some concern. However, the use of sample 533 as a "control" suggests that the variability is indeed a function of difficulty in interpreting a complex spectrum, rather than a real problem. The authors were fortunate to have a sample which was free of radicals.

Perhaps the most useful information is that on low temperature behaviour. As the authors point out, low temperature work is not practicable in many laboratories. It is a comfort to see that it is not necessary.