Densities of Modern and Fossil Dental Tissues: Significance to ESR Dating of Tooth Enamel

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Abstract. *We measured the density of enamel, dentine and cementum from teeth that range in age from 0-450 ka. We found that the density of dentine and cementum is significantly higher in samples of Palaeolithic age or older relative to young archaeological teeth and modern teeth from an abbatoir. These density changes occur within the first 50,000 years of burial. This density change is important for new calculations of beta attenuation in tooth enamel based on One-Group Theory, which requires density input data in order to calculate energy transport across interfaces between enamel and adjacent sediment, cementum or dentine. Enamel densities were unchanged over the time interval between 0 and 450 ka.*

Introduction

Electron spin resonance (ESR) dating of tooth enamel has now been used to establish the ages of many Palaeolithic archaeological sites as well as sites of importance to Quaternary geology (Rink, 1997). Though still experimental in some regards, the technique as originally proposed by Grün et al. (1987) is still in use, and has shown good agreement with other independent dating methods (Rink *et al.*, 1996a, Monigal *et al.*, 1998).

Horse, cow and deer teeth are characterized by layered arrangements of three different dental tissues: cementum, dentine and enamel (Fig. 1). In horse molars, the outer layer of cementum can be quite thick (2-3 mm) near the top of the tooth (chewing end), and generally thins to less than 0.5 mm toward the base of the tooth. The same is true for teeth of wild ass (*Equus hydrontinus*). The outer cementum layer on fossil cow and deer teeth is rarely as well preserved as it is in horse and wild ass teeth, but thicknesses approaching that seen in modern cow samples (up to 0.5 - 1 mm) are seen in some exceptional cases, and also in cases where deer teeth are heavily worn. It is usually easy to avoid areas covered with thin layers of fossil cementum on cow teeth, but this is more difficult in cases where relatively thinner layers occur on well-preserved, unworn cervid teeth. For cases where enamel, dentine or cementum are strong beta dose sources, or where a large fraction of the total dose is transmitted from sediment through a low U-content cementum layer, the ESR ages are strongly dependent upon calculations of beta dose attenuation in teeth.

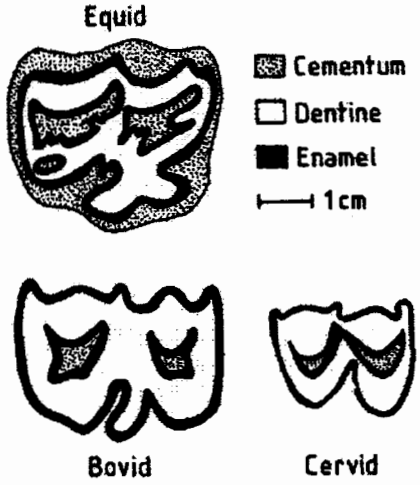

Figure 1.

Occlusal surface view (chewing surface) of fossil molar teeth commonly used for ESR dating. The outer enamel in equid (horse) teeth is covered by cementum, while in bovid (cow) and cervid (deer) teeth, the outer enamel layer is exposed to sediment at positions near the occlusal surface (in some cases thin layers of cementum are preserved on cervid and bovid teeth).

Beta particles are strongly attenuated by dental tissues. Beta attenuation in tooth enamel must be accounted for in ESR dating (Grün, 1986). The

gradient of beta attenuation in the enamel depends, amongst other things, on the density of the enamel.

The fraction of beta dose emitted by dentine is also controlled by the density-dependent self-absorption of the beta particles in the dentine. Moreover, in some teeth enamel is partly covered by a layer of cementum (up to 3 mm thick) which may act both as a source of beta rays and as an absorber of beta radiation during transmission of sediment-sourced beta radiation. The beta attenuation is dependent on the density of the cementum. For all these reasons it is necessary to know the density of cementum, dentine and enamel, and the present work was dedicated to determining densities of these tissues.

Since 1987, the McMaster ESR dating group has been using the computer software DATA (provided graciously by R. Grün of Australian National University) to calculate ESR dates. This program assumes that infinite matrix beta doses from uranium in the cementum and dentine elements are absorbed by the enamel. In order to use this software, the actual layers of cementum and dentine on the tooth must be about 2 mm thick, which satisfies the assumption that these dose sources are an infinite matrix with respect to the maximum range of the beta particles (about 2 mm). In this approach, ages calculated by DATA are assumed to be independent of the actual density of the cementum and dentine. However, many teeth have cementum and dentine layers which are too thin to satisfy the infinite matrix assumption. At McMaster Geology, we developed an ESR dating software called ROSY, which allows us to date teeth with any thickness of dentine or cementum (Brennan et al, 1997), now that we have measured their densities (and that of enamel) in fossil teeth. This program utilizes One-Group Theory (O'Brien *et al.*, 1964, Prestwich *et al.*, 1997) to model the beta radiation fluxes across the boundaries between sediment, cementum, enamel and dentine. We can incorporate a value for the fractional water content of these materials, which of course modifies their density in the actual calculation. The One-Group beta attenuation calculation yields considerably lower beta doses to enamel (Brennan *et al.*, 1997) than the beta attenuation calculation of Grün (1986).

Gilda (1951) reports densities for rat and hamster dental tissues, but we are not aware of reported densities for horse or cow dental tissues. Differences in density among the dental tissues of a given species are related to their degree of mineralization (Fig. 2). The mineral phase of these materials is widely regarded to be the mineral dahllite (Lowenstam and Weiner, 1989) which is a carbonate hydroxyapatite with the formula

$$Ca_5 [(PO_4)_3 - B (CO_3)_B] [(OH)_1 - A (CO_3)_A],$$

where the carbonate can substitute at either the PO_4 site (B) or the OH site (A).

Experimental Methods and Samples

Table 1 lists the origin, taxa and approximate burial age of the samples we have used. Enamel, dentine and cementum samples were separated from one another using a dental drill followed by visual inspection at 15-40 x magnification to insure purity.

Sample density, D_S, determinations were made using a pycnnometer flask, electronic balance and the following equation:

$$D_s = \{M_S / [(M_1 - M_2) - (M_3 - M_4)]\} \{D_{isop}/D_{water}\} \quad (1)$$

where M_S is the dry sample mass, M_1 is the mass of the flask filled with isopropyl alcohol, M_2 is the mass of the flask, M_3 is the mass of the flask filled with isopropyl alcohol and containing the sample, M_4 is the mass of the flask plus the dry sample, D_{isop} is the density of isopropyl alcohol (0.785) and D_{water} is the density of water (water was used as the fluid for some of the enamels, thus the last term of the equation was not used). This calculation is based on the buoyancy of the sample in a fluid (Archimedes principle), where the sample density is given by its (weight in air)/ (weight in air - weight in fluid of known density). Bubbling occurred for tens of minutes during the wetting of the cementum and dentine, as isopropyl alcohol filled the pore spaces. Measurements had to wait until bubbling ceased. Replicate analyses were made by partial emptying and refilling of the flask with isopropyl alcohol, but using the same dry weight for the sample (the sample was wet with isopropyl only one time).

The values that have been measured are the pure mineral density (without pore space) based on the assumption that the bubbling has caused all of

the pore space to be filled with fluid before the density value was determined. For the purposes of the age calculation by ROSY, this value is the "dry density" of the tissue, which is modified by an additional input value for the fractional water content, which is used to modify the dry density for the beta dose calculation.

Accuracy of the pycnometer was checked using a quartz density standard. The expected values are 2.65 - 2.67 g cm^{-3} for quartz. We interspersed measurements of the standard with those of the dental tissues. For the three enamels measured in water (92050, 91182 and 2060), we measured the quartz standard 11 times on the same day as all three enamel densities were determined. The value was 2.69 +/- .03 (1s). All of the remaining samples were measured in isopropyl alcohol over a period of 27 days. During that time the quartz standard was measured a total of 5 times on three different measurement days. This yielded a value of 2.66 +/- .03 (1s).

Results

The density values of enamel, dentine and cementum are given in Table 1. Our values for relatively modern cementum and dentine are slightly higher than, but similar to densities of human cementum and dentine of 2.03 and 2.14 g cm^{-3} respectively (Rowles 1967). Enamel values are in excellent agreement with published values of 2.9-3.0 g cm^{-3} for human enamel (Rowles, 1967). Table 1 shows that consistently higher values for fossil cementum and dentine were found relative to modern or young archaeological material. The fossil cementum was more variable and less dense than the fossil dentine in our sample set. A significant difference between dentine and cementum was found for the only tooth (95072) where both tissues were measured. Since the youngest true fossil sample studied thus far is about 40 ka, the increase in density of the cementum over modern values has been shown to occur within the time interval between 0.2 and 40 ka, and for dentine the increase has clearly occurred within the first 100 ka or so, but more likely within the first 50 ka (see sample 95072, Table 2).

Table 2 shows that beta doses to enamel based on One-Group theory are significantly reduced as a function of density of the dental tissues involved. ROSY ESR ages calculated using fossil cementum and dentine densities of 2.8 g cm^{-3} were as much as 10% higher than those calculated using modern densities of 2.1-2.2 g cm^{-3}, whenever the cementum and enamel thicknesses are about 0.5 mm and the dominant source of dose in the sediment is potassium (because of its larger contribution of beta radiation relative to gamma). If the sediment dose arises mainly from U or Th, the age difference was lower, in the range of only 2- 5%. The density dependence on ESR age was negligible ($\leq$ 2%) whenever the thicknesses of these same tissues approach 1-2 mm, and also when U uptake into dentine, cementum or enamel has occurred. Age calculations assume that density changes have occurred early in the burial history, and changes that occur later would make these effects less severe. Thus these results provide a worst-case scenario for the effects of density change on ESR ages.

Discussion

The higher densities of cementum and dentine in fossil material do not appear to be related to rapid post-mortem dehydration because the densities of modern and 100-200 year old archaeological samples are similar to those of the modern human samples studied by Rowles (1967). However, dehydration on a longer timescale does seem to be involved in density increases. Using the values in Fig. 2, we can compute the increased density of these tissues with complete dehydration or total loss of the organic fraction, making the assumption that a commensurate volume reduction also occurs. Cementum and dentine densities would increase to 2.51 and 2.62 g cm^{-3} respectively after dehydration, but only increase to 2.26 and 2.33 g cm^{-3} respectively for total loss of organics. Complete dehydration could explain the increases to the fossil cementum values in Table 1, but this could not explain the increase in dentine values, which require loss of water and organic components to reach values as high as 2.89. Significant loss of organics in dentine and bone are known to occur within the first 40 ka of burial, based on yields of collagen from dentine and bone in routine radiocarbon dating. Therefore it is logical to assume that both dehydration and loss of organics are active processes during burial, and that both contribute to the increase in density of cementum and dentine.

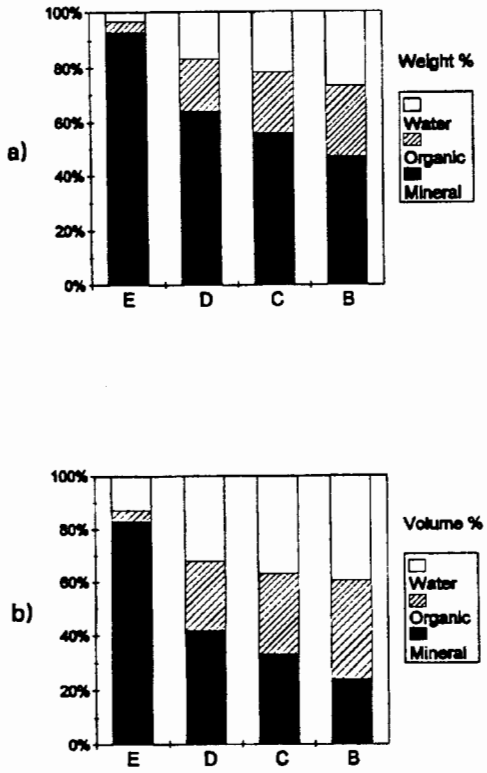

Figure 2.
Comparison of the relative proportions of mineral, organic and water components in human teeth. a) by weight %, b) by volume %.. (E) - enamel, (D) - dentine, (C) - cementum and (B) - bone, after Trautz (1967)

Before the ROSY ESR age calculation program was available, we applied fossil cementum density results to ESR dating of horse teeth from Mousterian layers at El Castillo Cave (Rink *et al.*, 1997). Here the teeth have a sediment/cementum/enamel/dentine irradiation geometry in which the cementum layer acts primarily as an absorber of sediment beta dose, without being a significant dose source itself (the cementum is virtually uranium free). The fraction, F, of infinite matrix sediment beta dose D_S transmitted through a cementum of thickness t can be approximated by:

$$F = [D_S \{\exp (-\mu_R tp)\}] * 0.5 \quad (2)$$

where μ_R is the linear absorption coefficient (per micrometer) in aluminium and p is the ratio of the density of aluminum to the cementum density.

We used equation 2 to calculate the fraction of infinite matrix beta dose reaching the enamel. The ages were calculated using the software program DATA (mentioned above), but we reduced the input concentration values for U, Th and K in the sediment as follows: input value = F * measured U, Th or K concentration. Without correction for the intervening cementum absorber, ESR ages were about 10% too low, since the sediment beta dose rates were erroneously high.

Experimental studies which used powdered tooth enamel as a detector of beta attenuation are in close agreement with One-Group Theory calculations of beta attenuation in solid enamel. (Rink *et al.*, submitted) Thus, we expect that future use of the density values will mainly be for applications of One-Group theory to beta attenuation in ESR dating.

Conclusions

Density values for fossilized dental tissues are important to One-Group theory-based beta attenuation calculations for teeth with thin (ca. 0.5 mm) dental tissues. Use of values for modern teeth of 2.1-2.2 g cm^{-3} for cementum and dentine could lead to ESR age underestimates in the range of 2-10% when the dominant source of beta dose is the sediment. The mean values of 2.54 ± 0.22 for fossil cementum and 2.82 ± 0.07 g cm^{-3} for fossil dentine represent the best values available for use in One-Group Theory beta dose attenuation calculations for samples in the age range of >40 ka. A combination of dehydration and loss of organics within the first 40 ka of burial leads to increases in density of dentine and cementum, but no changes in enamel density are found for the first 450 ka of burial for the sample set studied.

Acknowledgements

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Table 1. Densities of Modern and Fossil Dental Tissues

Tooth Number	Site	Taxa	Age (ka)	Density[6] Cementum ($g\ cm^{-3}$)	Density[6] Dentine ($g\ cm^{-3}$)	Density[6] Enamel ($g\ cm^{-3}$)
92050	Tobermory, Canada	Horse	< 0.2	2.14 ± <.01 (n=2)		2.94 ± .04 (n=4)
92315	Kings Lynn, UK	Cow	Modern	2.12 ± .07 (n=3)		
94810	Williamstown, Canada	Cow	<0.2		2.22 ± .02 (n=4)	
Mean[7]	Young or Modern			2.13 ± .01		
94141	Starosele, Crimea	Wild Ass	40-45[1]	2.79 ± .08 (n=4)		3.02 ± .17 (n=2)
95072	El Pendo, Spain	Cow	<50[2]	2.39 ± .02 (n=4)	2.89 ± .03 (n=4)	
2060	Karain, Turkey	Cow	100 - 120[3]		2.76 ± .04 (n=4)	3.02 ± .05 (n=4)
91182	Krapina, Croatia	Rhinoceros	120 - 130[4]		2.80 ± .07 (n=4)	2.96 ± .08 (n=4)
989	West Runton, UK	Elephant	380 - 540[5]	2.44 ± .05 (n=4)		
Mean[7]	Fossil			2.54 ± .22	2.82 ± .07	3.00 ± .03

Footnotes:

1. Monigal et al. (1998)
2. Preliminary ESR age, Volterra (in prep).
3. Rink et al., 1994
4. Rink et al., 1995
5. Rink et al., 1996b
6. The reported density value for a given tooth number is the average value and standard deviation (precision) of n repeated measurements.
7. The mean value is the average and standard deviation of the density measurements for the different teeth in the column directly above the quoted mean.

Table 2. One-Group Theory-based ESR age calculations for a hypothetical tooth enamel

Cementum			Dentine			Enamel		Beta Dose (EU) (μGy a^{-1})	EU ESR Age (ka)	Beta Dose (LU) (μGy a^{-1})	LU ESR Age (ka)	EU Age % Difference Low vs. High ρ
U (ppm)	ρ (g cm^{-3})	T (mm)	U (ppm)	ρ (g cm^{-3})	T (mm)	U (ppm)	T (mm)					
0 0	2.1 2.8	0.5 0.5	0 0	2.2 2.8	0.5 0.5	0 0	0.5 0.5	236 167	124 136	236 167	*	10
0 0	2.1 2.8	0.5 0.5	0 0	2.2 2.8	0.5 0.5	0 0	0.5 0.5	46 33	163 166	46 33	*	2
0 0	2.1 2.8	0.5 0.5	0 0	2.2 2.8	0.5 0.5	0 0	0.5 0.5	124 95	144 151	124 95	*	5
0 0	2.1 2.8	1.0 1.0	0 0	2.2 2.8	1.0 1.0	0 0	1.0 1.0	34 21	166 170	34 21	*	2
0 0	2.1 2.8	2.0 2.0	0 0	2.2 2.8	2.0 2.0	0 0	1.0 1.0	7 3	174 175	7 3	*	1
1 1	2.1 2.8	1.0 1.0	1 1	2.2 2.8	1.0 1.0	0 0	1.0 1.0	60 49	159 162	46 33	163 166	2
5 5	2.1 2.8	1.0 1.0	5 5	2.2 2.8	1.0 1.0	0 0	1.0 1.0	160 157	137 138	92 83	152 153	2
20 20	2.1 2.8	1.0 1.0	20 20	2.2 2.8	1.0 1.0	20 20	1.0 1.0	1242 1262	21 21	652 656	37 36	0

Footnotes:

Row 1: Sediment radioactivity: U=0.5 ppm, Th = 2.01 ppm, K=1.65 wt. % (gamma dose = 568 μGy a^{-1})

Row 2: Sediment radioactivity: U=0 ppm, Th = 10.9 ppm, K = 0 wt. % (gamma dose = 568 μGy a^{-1})

All other rows: Sediment radioactivity: U= 5 ppm, Th = 0 ppm, K = 0 wt. % (gamma dose = 568 μGy a^{-1})

For all the calculations above: equivalent dose = 100 Gy, cosmic dose = 0 μGy a^{-1}, moisture in dentine = 5%, moisture in sediment = 0%, alpha efficiency = 0.15, $^{234}U/^{238}U$ = 1.4, density of sediment = 2.0 g cm^{-3}, radon loss = 0%, enamel stripped from cementum side and from dentine side of enamel = 0.05 mm.

* LU ages omitted because they are the same as EU for U concentrations of 0.

Reviewer
Gunther A. Wagner

Comments

This work deals with the influence of the sample's density on the beta microdosimetry in teeth. The fact that the density of the cementum and the dentine increases within the first 40 ka leads to an age underestimate if not taken into account. Although it is shown that the ultimate effect on the ESR age is in the worst case around 10% - which seems relatively little in view of errors introduced by the model assumptions on early or late uranium uptake - it is good to see a quantitative assessment of this effect.

A proposal for dealing with anomalous fading

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This proposal was inspired by variations in the scatter observed during measurements pertaining to anomalous fading. The anomalous fading results themselves are reported in Huntley and Clague (1996); some relevant details are given at the end of this note.

The basic idea is that the feldspar grains on a planchet are a highly inhomogeneous bunch with most of the luminescence arising from only a small fraction of the grains, these grains exhibiting differing amounts of anomalous fading. The proposal then is to make an equivalent dose determination with a very large number of planchets, say 200, using 20 or more planchets for each point. After this, anomalous fading measurements would be made on all the planchets, allowing the planchets then to be grouped by differing degrees of anomalous fading. The grouping would be somewhat arbitrary, but supposing that four groups were chosen then from the equivalent dose measurements four equivalent doses would be obtained. A plot would then be made of "equivalent dose" vs amount of fading, and extrapolated to zero fading to obtain the best estimate of the actual equivalent dose, as illustrated in Figure 1.

Apart from the labour involved there are two obvious difficulties. The spread in the amount of fading may be rather small, in which case the points shown in the figure would be rather clustered, thus precluding a usable fit and extrapolation; putting fewer grains on the planchets may help here. A second difficulty is that this may only deal with some of the fading; if there is a component which is unobservable on a time scale of weeks, but significant over the life of the sediment, this would not be allowed for in this method.

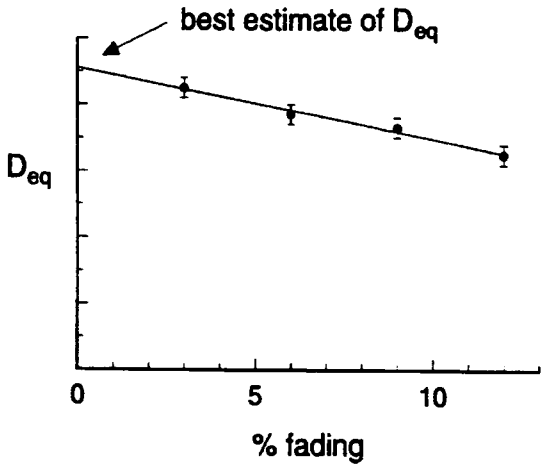

Figure 1.

This hypothetical result shows four equivalent doses, each one being obtained from a different group of planchets. The groups are formed on the basis of the amount of anomalous fading each planchet exhibits, the fading being made after the equivalent dose measurements. For the samples listed in the table there were not sufficient numbers of planchets to make such a graph.

The principal data that inspired the above were obtained as follows. For each sample twenty 8 mg planchets of separated "K-feldspar" grains were prepared. A short-shine measurement of each was made for later normalization. Two planchets were kept untreated and the remaining 18 given an infrared bleach. The latter were then given irradiation doses in 3 groups of 6 at different times, together given a 16 h 120°C preheat and the luminescence caused by 1.4 eV (IR) excitation measured. The delays between irradiation and measurement for the 3 groups were 3 days, 18 days and 7 months.

The 18 were then bleached, dosed, preheated and measured again, this time all

together. The delay between irradiation and measurement was 3 days. These data were taken for use as an alternative normalization.

Use of the second set of normalization data resulted in much less scatter and the figures below were obtained using it. For the groups of 6 planchets the scatter, expressed as a standard deviation, was as follows:

	Sample CBTS2	TTS3
Delay	Scatter	Scatter
3 days	1.3%	0.8%
18 days	2.4%	1.1%
7 months	6.4%	2.0%
	Fading ratio	Fading ratio
18 days/ 3 days	0.959 ± 0.013	0.967 ± 0.006
7 months/ 3 days	0.935 ± 0.028	0.890 ± 0.009

As can be seen the scatter systematically increases with the delay. There would appear to be enough data to rule this out as a statistical effect and the obvious explanation is that it is associated with variations in the extent of anomalous fading. For completeness the actual fading ratios are also shown in the table.

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Reviewer
M. J. Aitken

Dispersive decay kinetics and dose responses of isotropic radicals in natural carbonates

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Abstract *: The isotropic signals at g = 2.0006 and g = 2.0057 in marine carbonates are due to freely rotating CO^-_2 and SO^-_2 radicals respectively. We have investigated the kinetics of these signals by selecting a fossil coral exhibiting a simple ESR spectrum. Various kinetic approaches were considered, including diffusion-controlled mechanisms and dispersive kinetics with time-dependent rate constant. The best decay description was found to be the second-order equal concentrations dispersive equation. Some dose response curves of modern coral and mollusc shell obtained by Çetin et al (1993) could be fitted with a single dispersive model with a time-dependent radical-creation efficiency. These dispersive models allow satisfactory fittings over the entire ranges of doses or time, with a minimum number of parameters.*

Introduction

Kinetics

The isotropic ESR signals at g = 2.0006 and g = 2.0057, due to rapidly rotating CO^-_2 and SO^-_2 radicals, are potential dating signals (Ikeya, 1993; Brumby and Yoshida, 1994; Martinez-Walter, 1994). They are thought to be located in the occluded water surroundings of the constituent crystallites of the material (Callens *et al.*, 1994; Idrissi *et al.*, 1996).Their thermal stability at room temperature is normally estimated by extrapolating Arrhenius plots from higher temperature isothermal annealing data. These isothermal annealing curves have been described in the literature by different mechanisms : first-order, two or three first-order reactions occurring simultaneously and independently of each other with different rates, 1.5 - or second-order or even third-order reactions (Debuyst *et al.*, 1995 and references therein). The purpose of the present work is to look at this problem by adding other kinetic descriptions and to try to fit the annealing curves with a minimum of parameters. Therefore, good quality experimental data are necessary. This is not a trivial problem for the following reasons. First, the concentration of the radicals should be measured by the double integral of the ESR signal, but the results are doubtful because of the overlapping of Lorentzian lines and contribution of anisotropic signals. Spectrum deconvolution is a tedious and not always unambiguous procedure. The ESR intensity is usually estimated by the peak to peak height of the signal but the line width should then be checked to be a constant during the thermal annealing or irradiation. Secondly, when a natural sample is irradiated with a γ source, anisotropic signals with variable thermal stabilities are also produced, which again perturb the isotropic signals ("shoulders and dips" appear) and alter line shape, line width and height. The annealing time needed to get rid of these perturbations varies from sample to sample. Thirdly, after laboratory irradiation, the ESR intensity often decreases only after an initial increase of the signal, revealing the presence of a precursor feeding the isotropic signals (see also Lyons, 1996). In the case of the SO^-_2 radical, this "initial" increase is sometimes the only feature observed even after a long time period (Martinez-Walter, 1994; Brumby and Yoshida, 1995). Finally, the decay kinetics should be performed over a long annealing time period, which is not frequently encountered in the literature. We tried to avoid some of these difficulties by selecting a fossil coral sample from the Barbados (Kendal Hill) (given to us by U. Radtke, with an approximate age of 2.10^5 years) exhibiting an apparently simple ESR spectrum consisting principally of the two isotropic lines of CO^-_2 and

SO^-_2 with a small contribution of a signal at g = 2.0032 due to SO^-_3 (Barabas, 1992) whose decay has not been studied. The derivative ESR spectrum with a small dip at g = 1.9972 around 3490 Gauss and the corresponding integrated spectrum reveal the presence of anisotropic CO^-_2 species and show the long wings of the isotropic Lorentzian line shapes (Fig. 1). The signals were sufficiently high so that no laboratory irradiation was needed and no initial increase observed. Furthermore, the line width of the two species were found to be constant during the annealing time : 1.65 ± 0.05 Gauss for CO^-_2 and 0.72 ± 0.01 Gauss for SO^-_2 so that we used the peak-to-peak height for estimating the radical concentration. In doing so, the values of the CO^-_2 signal at the end of the thermal annealing are slightly overestimated because of the presence of a small anisotropic CO^-_2 residue.

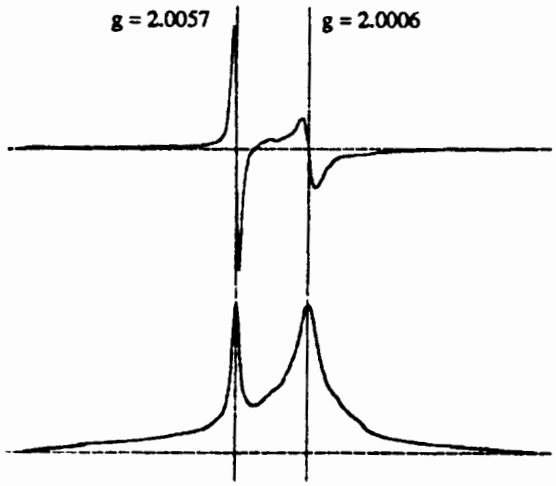

Figure 1.
First-derivative and absorbtion ESR spectra of the fossil coral showing the SO^-_2 signal at g= 2.0057 on the left and the CO^-_2 signal at g = 2.0006 on the right.

Dose response
It is well known that a single saturation curve is not able to fit dose response curves at high doses (> 10^3 Gy). Several models have been suggested in order to improve the fittings : linear or exponential creation of additional traps by irradiation , decrease of the radical-creation efficiency, combination of two or three single exponential saturation functions (Çetin *et al.*, 1993 and references therein). Because our kinetic results are in favour of a time-dependent rate constant, we tried to reproduce the dose response data of Çetin *et al.* (1993) with analogous time-dependence of the radical-creation efficiency.

Experimental
ESR spectra have been recorded at room temperature with a Bruker ER 200tt X-band spectrometer, connected to a Stelar computer system, at a power of 20 mW and a modulation amplitude of 0.5 Gauss. The spectrum of an independent Mn^{++} sample was taken as a reference before and after each annealing experiment. The temperature at which the sample has to be annealed should be neither too high (the radicals are surrounded by water molecules whose departure must be avoided) nor too low (for evident duration considerations). A temperature of 160°C has been chosen. The annealings were performed by putting the sample into an oven and regularly removing it for ESR measurement. The CO^-_2 radicals disappeared completely after approximately 10 days annealing (Fig. 2), whereas the SO^-_2 radicals were still present after 40 days (Fig. 3).

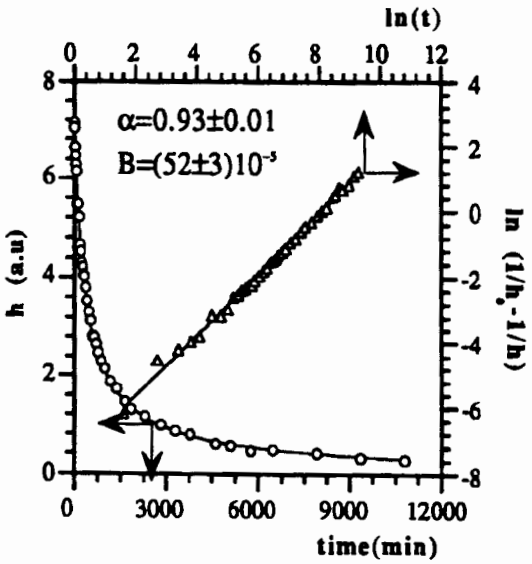

Figure 2.
Decay of CO^-_2 at 160°C in fossil coral, fitting equation (1) in normal (height versus time) and linearized (logarithmic) forms. The arrows indicate the relevant axes.

Results and discussions

Kinetics

For a rapid checking of the relevance of the various kinetic models, linearized forms were used for both CO^-_2 and SO^-_2 decays. Plots of $\ln(I_o/I)$, where I is the ESR intensity (height) and I_o the initial intensity, I_o/I , $(I_o/I)^2$, $(I_o/I)^{0.5}$ versus t (time) allow to eliminate the classical first-, second-, third- and 1.5- order reactions. A second-order reaction with a non-decaying fraction has been investigated by plotting $t/(I_o-I)$ versus t (Dole, 1988). A mixture of first- and second-order reactions has been tested by plotting $\ln((I/I_o + I_o\lambda\tau)/(1 + I_o\lambda\tau))$ versus t (τ and λ are the first-order decay time and the second-order rate constant respectively) (Ikeya, 1992). Diffusion-controlled reactions need plots of $\ln(I_o/I)$ versus $t^{0.5}$ (first-order) and $(1/I - 1/I_o)t^{-0.5}$ versus $t^{0.5}$ (second-order) (Kantoglu *et al.*, 1995). Plots of I versus ln(t) have also been proposed by Brumby and Yoshida (1995). Finally, non-classical, inhomogeneous or dispersive kinetics with a time-dependent rate constant ($k(t) = Bt^{\alpha-1}$, B and α are constants, $0 < \alpha \leq 1$) (Plonka, 1991a) have been investigated with $\ln(\ln(I_o/I))$ versus ln(t) (first-order) and $\ln(I_o/I)$ versus ln(t) (second-order equal concentrations). The decay of both radicals was found to be best described with the latter model (Fig. 2 and 3) involving the following equation :

$$c^{-1} - c_o^{-1} = B\alpha^{-1} t^{\alpha} \qquad (1)$$

where c and c_o are the radical concentrations at t and $t_o = 0$. With a non-decaying fraction A, the equation becomes

$$(c-A)^{-1} - (c_o-A)^{-1} = B\alpha^{-1}t^{\alpha} \quad (2),$$

which can be rewritten as

$$(c_o-c)^{-1} = (c_o-A)^{-1} + \alpha/(Bt^{\alpha}(c_o-A)^2) \quad (3).$$

The parameter values indicated in the figures were obtained from the linearized forms. In dispersive kinetics, the activation energy increases with time and the parameter α is interpreted as a measure of the dispersion of the activation energy in these disordered systems.

In the case of SO^-_2 , the fitting was optimized by taking account of a non-decaying fraction A, corresponding to the existence of a plateau. Such plateaus were observed by Martinez-Walter (1994), who used them for dating purposes. The dispersive second-order model has been already found convenient for isotropic CO^-_3 and CO^-_2 radicals in laboratory irradiated synthetic monohydrate and biocarbonates where activation energies could be calculated (Debuyst *et al.*, 1995). It implies only 2 parameters : B and α, eventually 3 if A is unknown.

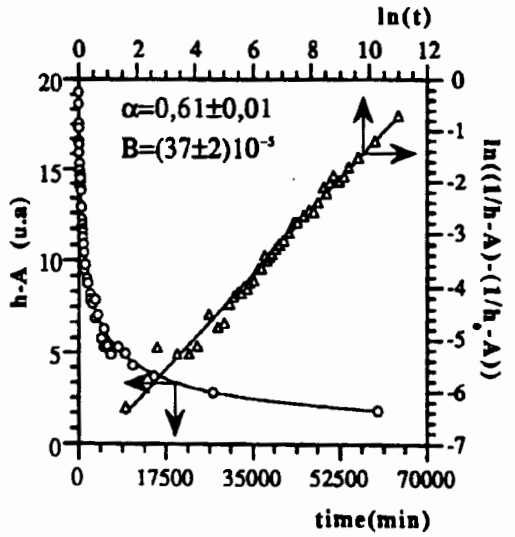

Figure 3.
Decay of SO^-_2 at 160°C in fossil coral, fitting equation (2) in normal (h-A versus time) and linearized (logarithmic) forms. Here A= 5 a.u.

Dose response

Çetin *et al.* (1993) described their dose response curves for the isotropic CO^-_2 in modern aragonitic coral and shell samples by a combination of three single exponential saturation functions. They also described their isothermal decay curves by the combination of three first order decay functions. We tried to fit their dose response data (table 1, p. 676 in Çetin *et al.*, 1993) with models implying less parameters . The possibility of a linear creation of traps yields the following function :

$$I = (K_o - b/a)\,(1 - \exp(-aDt)) + bDt \qquad (4),$$

where K_o is the number of traps before the irradiation , D the dose rate, a (and b) the radical - (and trap-) creation efficiency (Levy, 1989). By analogy with the dispersive kinetic model, we consider a time-dependent radical-creation efficiency $a = a't^{\alpha-1}$ $(0 < \alpha \leq 1)$. The following function is then derived by integration :

$$I = K(1-\exp(-a'Dt^{\alpha}/\alpha)) \qquad (5).$$

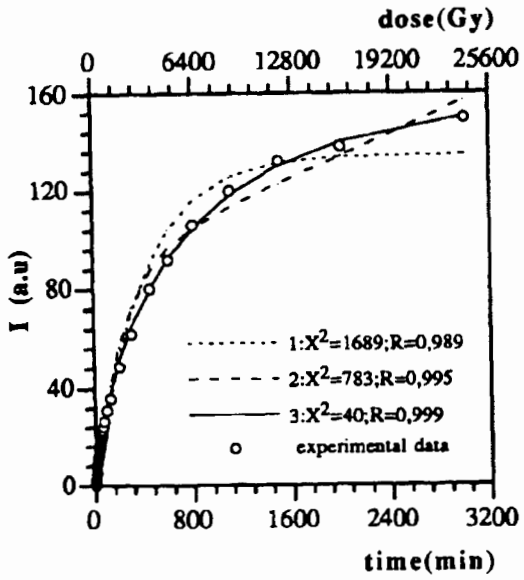

Figure 4.
Dose response of a modern shell (data of Cetin et al., 1993). Model 1 : single exponential saturation function ; model 2 : equation (4) ; model 3 : equation (5).

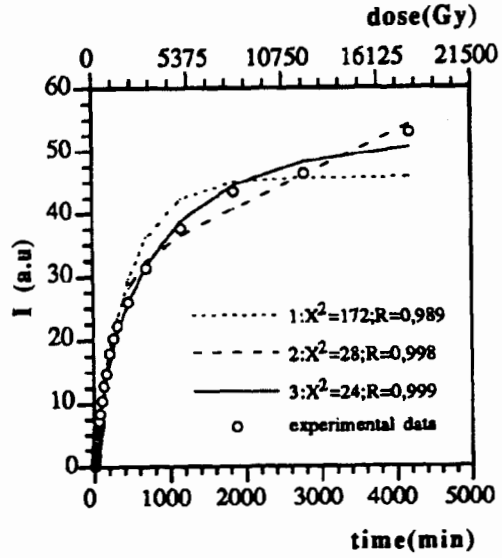

Figure 5.
Dose response of a modern coral (data of Cetin et al., 1993). Same models as in figure 4.

This equation is equivalent to that of Grün and McDonald (1989) with their phenomenological exponent Γ. Indeed, as pointed out by Barabas *et al.* (1992) and Walther *et al.* (1992), the latter equation assumes $a = a'(Dt)^{\Gamma-1}$ which yields by integration $I = K(1-\exp(-a'(Dt)^{\Gamma}/\Gamma))$. Time-dependent radical-creation efficiencies were also considered by Çetin *et al.* (1993) and Martinez-Walter (1994). Figures 4 and 5 show the fitting with a normal exponential saturation function and the two aforementioned functions. The dispersive model yields the fitting with the best statistical characteristics (χ^2 and R with the KaleidaGraph program). Çetin *et al.* (1993) found also good results with an equivalent model but they prefered globally the combination of three exponential saturation functions. The data of Grün (1990) were best described with the model including a production of defects by irradiation. The model with the exponent Γ was rejected because Γ was found to decrease as more data were added in the fittings (Γ =1 for ~ 200 Gy compared to Γ=0.85 for ~ 700 Gy, the maximum dose used in this study). The dose interval in Çetin's data is much higher ($0\text{-}2.10^4$ Gy). As also stressed by Martinez-Walter (1994), the exponent α allows a quite satisfactory fitting of the curvature at higher doses (here, around 5-6000 Gy). In the case of modern mollusc shell (see Fig. 4) which offers the broadest dose interval and number of aliquots (59), the fitted parameters are K = 160 ± 1 a.u., a = 0.736 ± 0.005 and $a' = (136 \pm 3)10^{-5}$ $Gy^{-1}min^{1-\alpha}$

If data are removed one by one from the high to the low dose region, the same set of values is able to fit the experimental data, provided that this set is introduced as guessed values in KaleidaGraph. The value of a remains 0.74 ± 0.04 from 21000 to ~250 Gy. Below ~250 Gy, it tends to increase progressively and reaches 0.88 at ~ 100 Gy, but the role of α in this region is weak and the errors in K and a' are tremendous (100% around 350 Gy). So, in our opinion, dispersive dose response should be reconsidered all the more as dispersive kinetics yield satisfactory results.

Conclusions

Decay kinetic and dose response curves over long time periods could be fitted with models implying time-dependent rate constant and radical-creation efficiency : the probability for radical decay or creation is supposed to decrease with time. The transition from classical to dispersive models implies the replacement of time by $(time)^{\alpha}$. In dispersive kinetics, the increase in activation energy with time is due either to depletion from the system of more reactive species or to local matrix relaxation making all species progressively less reactive. (Plonka, 1991b). In dose response, the creation of radicals could decrease with irradiation time due to the creation of more and more competitive species. The dispersive models which are able to fit the data of the isotropic radicals (CO^-_2, CO^-_3, SO^-_2) in natural and synthetic carbonates should be considered in ESR dating.

Acknowledgements
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Reviewer
R. Grün

Comments : We can be grateful to Debuyst *et al.* to present a comprehensive model for the thermal decay and dose response of the paramagnetic centre at g=2.0007 in corals. Although the time

dependent radical creation model seems best suited to describe the overall dose response of this centre, there are some problems in the lower dose range (< ~ 250Gy) where the exponent α changes. However, for dating purposes, this dose range has to be exactly known as most samples (<250,000 years) will have dose values of < 250 Gy.

A new technique (foil technique) for measuring the natural dose in TL dating and its application in the dating of a mortar containing ceramic fragments

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Abstract *A modification of the fine grain TL dating technique for measuring the natural dose is presented. In this technique (foil technique) we tried to make very thin samples and with the necessary plasticity, in order to achieve the best heating contact between sample and heater plate. Because the so prepared samples have not the same amount of powder a suitable new normalization technique is also proposed. The advantages of the proposed foil technique are such that make it quite suitable for samples with low levels of natural TL and also for authenticity testing. This technique was tested using artificially irradiated samples with known doses and applied to the dating of a mortar containing ceramic grains.*

Introduction

One of the most important steps in thermoluminescence dating is sample preparation for which two main techniques have been established: the classical fine grain technique (Zimmerman, 1971) and the quartz inclusion technique (Fleming, 1970). The present paper describes a modification of the fine grain technique (foil technique), which was mainly developed in order to overcome the spurious TL problem of samples with a relatively low level of natural TL (low natural dose or sensitivity) and also to simplify the sample preparation process.

By this technique a very good heating contact between sample and heater plate is achieved, making the use of a heat conducting gas unnecessary. This has two main advantages: a) Measurements can be made in vacuum (better than 10^{-1} mbar) which avoids the use of very pure nitrogen, making the procedure cheaper and resulting in a significant reduction of spurious TL mainly in cases where the N_2 purity is insufficient. The use of N_2 is based on the assumption that spurious TL is usually the result of oxidation. However in some cases, spurious TL seems to have other sources such as phase changes in carbonates due to heating. In this case the presence of spurious TL can be detected by the plateau test and must be eliminated by acid treatment. b) A possible shift of the glow curve due to a delay in heating is avoided, thus giving the possibility of using higher heating rates. This results in an increased TL signal making the technique suitable for samples with low levels of natural TL (as will be described in a future paper). This technique is quicker than the classical fine grain method and also has the advantage of avoiding the use of toxic acetone.

Sample preparation

In order to achieve very good heating contact between sample and heater plate we tried to make very thin samples and with the necessary plasticity, so that they can follow the possible lack of perfect flatness of the heater plate surface. This lack is also possible for the hard aluminium disks (0.5 mm thick) usually used. Thus the samples prepared have a near monolayer cover of pottery powder (grains smaller than 8 ìm). The grains are well adhered to aluminium foil disks, of 1 cm diameter and 10 ìm thick, by using silicone grease (silicone DC high vacuum grease

from Riedel - de Haën). Details of the preparation procedure are given in the Appendix.

It is possible to handle these sample disks using tweezers (Fig. 1) in order to place them on the heater plate, for measuring the TL, or taken to the irradiation sources, without affecting the sample. The heater plate is pre-covered with a thin layer of silicone grease and the sample then adhered by pressing it gently with a rice-paper. In some cases, in order to eliminate the possible spurious TL from the silicone grease, it is better to take a first measurement (glow it) before the sample is added.

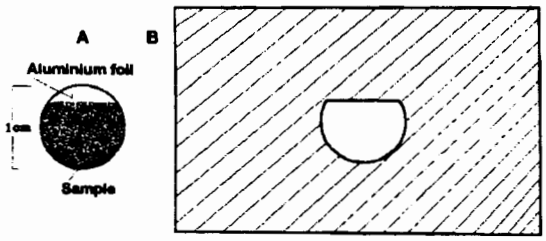

Figure 1.
A schematic presentation of the sample prepared by the proposed technique (A) and the aluminium foil square with the central hole (B), see Appendix. It can be seen that the upper part of the foil disk is left uncovered in order to be able to handle this by tweezers without affecting the ceramic powder

Ceramic powder with grains smaller than 8 μm is prepared by crushing the sample in a vice and using the settlement technique. In order to avoid toxic acetone, ethylalcohol is used. Because the viscosity coefficient of the ethylalcohol is about 4 times higher than that of acetone the settling period must be increased to 8 min for a 60 mm column. This technique is quicker than the classical fine grain technique because we avoid the procedure of resuspending the separated fine grains in acetone for the deposition of pottery powder on aluminium disks, followed by evaporation of the acetone, which is the usual procedure in fine-grain technique.

Figure 2, shows glow curves of two samples of the same sherd prepared by the proposed technique. One of the samples was measured in vacuum (a) and the other in N_2 atmosphere (b). In order to normalise the two samples we take the second glow for each sample by giving a monitor dose (4.2 Gy). Sample (a) shows near coincidence of the first and second glow curves, but not sample (b). This is because the level of spurious TL is higher in a N_2 atmosphere than in a vacuum. It is apparent from many experimental results that for measurements in vacuum, even if the level of Natural TL is very low, the percentage of chemiluminescence in most cases is practically eliminated (Michael *et al.* 1985). This was checked especially in the case of very low natural TL (ceramic vase two years old) as will be explicitly described in a future paper. In Figure 3, glow curves of five samples of the same sherd are shown: one prepared by the foil technique measured in vacuum, the other four prepared by the classical fine grain technique measured in a N_2 atmosphere. The peak positions of the samples prepared by the classical technique show a shift as compared with the peak positions of the sample prepared by the foil technique.

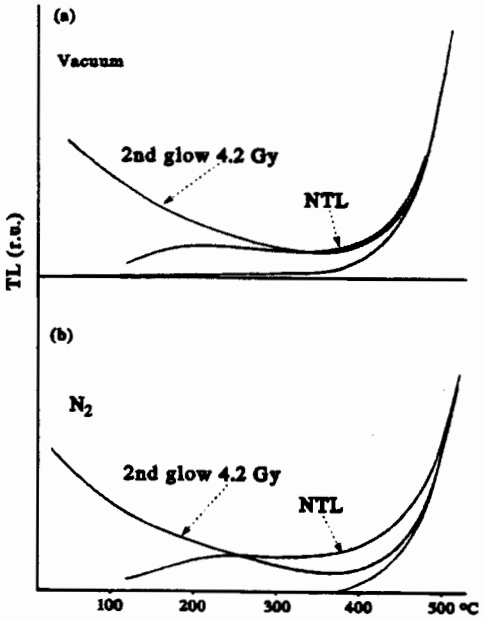

Figure 2.
Glow curves of two samples of the same sherd prepared by the proposed technique. One of these samples was measured in vacuum (a) and the other in N_2 atmosphere (b). For normalisation the second glow for each sample was taken by giving a monitor dose (4.2 Gy).

This shift increases with sample thickness (amount of powder), although it is not exactly the same for samples of the same batch (the shift of the two thin samples is not exactly the same). It is clear that this shift is due to a delay in heating of the upper grains of the classically prepared samples with respect to the heater plate, which increases with the raising of the heating rate. On the other hand, for samples made by the foil technique, because of the immediate contact, the peaks are always at the same temperature as shown in Figure 4. The differences in the height of the glow-curves of the two samples are due to the differences in the quantity of pottery powder.

Normalisation of the samples and calculations

Since the quantity of pottery powder in the samples is not the same, a normalisation of the samples is necessary (a procedure followed usually in inclusion dating). This can be achieved by giving all samples a monitor dose. However, because the samples have received different doses in producing the growth curves, there is the problem of the sensitivity change due to the pre-dose effect. Various techniques have been proposed to overcome the problem in the case of inclusion dating, which may be applicable in the proposed technique. The possibility of improving the accuracy of dating results by using hyperbolic or polynomial regressions on the normalised points of growth curves for materials exhibiting significant pre-dose effects was proposed by Mejdahl (1985). Also, the possibility of linear regression for materials not exhibiting significant pre-dose effect, when the initial part of the normalised growth curve is approximately linear was proposed by Michael et al. (1985).

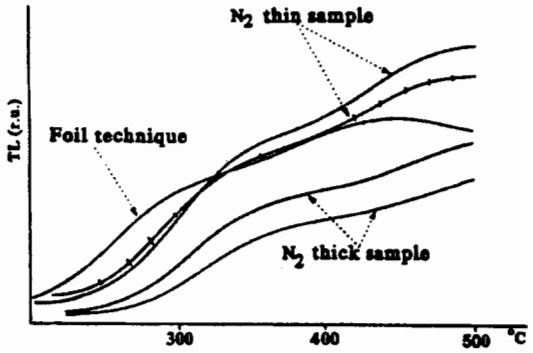

Figure 3.
Glow curves of samples of the same sherd. One prepared by the proposed technique measured in vacuum and four prepared by the classical fine grain method measured in N_2 atmosphere (heating rate 14 °C/s).

The application of a small monitor dose and measurement of a low-temperature peak prior to measuring the high temperature peak (zero-glow monitoring) was proposed and applied to calcite by Aitken *et al.* (1979), to quartz by Bowman (1977) and Liritzis (1980) and to fine-grain sediments by Debenham (1985). G. A. Wagner has also proposed the equal pre-dose technique which is described by Mejdahl (1985) and Aitken (1985). An alternative normalisation technique suitable for foil technique is proposed below, which can also be applied to inclusion dating. By this technique we have a quantitative estimation of the pre-dose effect by calculating the value of k (see below - Equation 1), which can be useful for some applications such as the dating of a mortar described below.

According to this, after the sample preparation with the foil technique, the normalized growth curve is produced as follows: for a mean value of zero point r_o (normalised natural TL) of this curve several samples are used (usually 3 to 5) for measuring their natural TL (first glow). These samples are then irradiated with a monitor dose and the second glow measured. For the other points the same procedure is repeated with samples having the natural dose plus a laboratory dose (natural + D_1 , natural + D_2, etc.). Each point of the normalised growth curve represents a mean value of the ratio r_D of the TL of the first glow to the second glow (Fig. 4) at the same temperature of the plateau region, as a function of the laboratory dose D. Figure 5 illustrates a characteristic normalised growth curve.

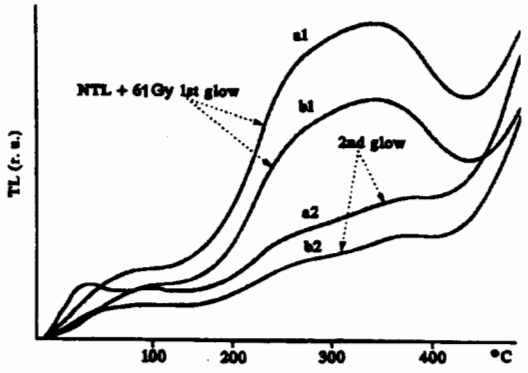

Figure 4.
Glow curves (1st and 2nd glows) of samples a, b of sherd 16003 (prehistoric from Macedonia) for the calculation of r_D (see in the text below) for ρ = 30.95 Gy (monitor dose).

The calculation for the estimate of the natural dose is based on the assumption that the degree of sensitivity enhancement (pre-dose effect) is a linear function of the pre-dose applied (Aitken and Fleming, 1972). This assumption can be tested experimentally for every sherd and is given by the following equation (Aitken, personal communication)

$$S' = S\left[1 + k\,(P + D)\right] \qquad (1)$$

which is the mathematical expression of Figure 6 in case where P = 0. Where S' is the TL sensitivity of the second glow, S is the TL sensitivity of the first glow, k is a specific sensitivity enhancement factor and P is the natural dose (paleodose).

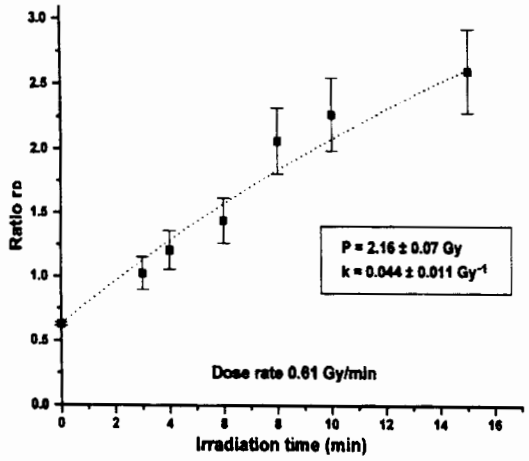

Figure 5.
Normalised growth curve, for samples made by the 300 μm ceramic grains, existed in a cistern mortar from Heraklion Crete.

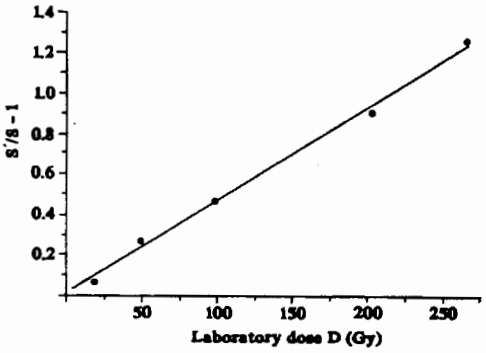

Figure 6.
The second glow TL sensitivity (S') enhancement for the glow curve temperature 415°C versus D of sherd 3120 annealed from its NTL at 1000°C for 2 hours, so that it can be considered recently fired pottery (P = 0).

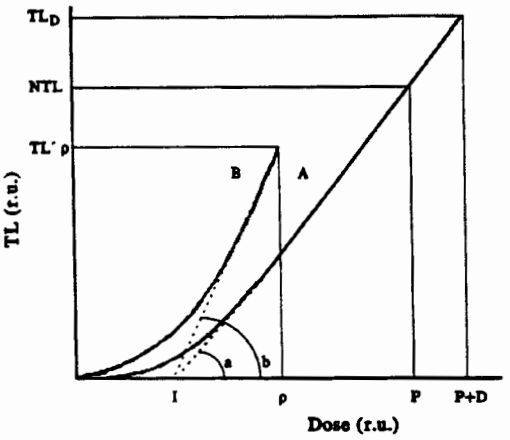

Figure 7.
First (A) and second (B) glow growth characteristic curves. NTL is the level of natural TL.

In Figure 7, TL_D is the TL for the sample which has been given a laboratory dose D (first glow) and TL ' ρ (second glow) is the TL of the same sample after the monitor dose ρ. This figure gives:

$TL_D = S(P+D-I)$ and
$TL'_\rho = S'(\rho-I)t$

where S = tan a, S ' = tan b and I is the supralinearity correction. Hence, taking into account Equation 1 and because $r_D = \frac{TL_D}{TL'\rho}$ we take:

$r_D = (P + D - I)/[(\rho - I)(1 + k(P + D))]$ (2)

and for D=0 we have the value of

$$r_0 = \frac{P-I}{(\rho-I)(1+kP)} \qquad (3)$$

From the Equations 2 and 3 it is possible to determine the values of P and k given by the equations (4) and (5):

$$P = -\frac{D-I}{2} + \sqrt{\left(\frac{D-I}{2}\right)^2 + \frac{r_D r_0 D(\rho-I) + r_D I D}{r_D - r_0}}$$

$$k = \frac{P-I-r_0(\rho-I)}{P r_0(\rho-I)}$$

It is also possible to estimate the values of P and k with better accuracy using a software program in which we insert Equation 2 substituting ρ and I with their values and the values of r_D and D for each point of the normalised growth curve.

The value of I can be determined by producing the normalised second glow growth curve. For the normalisation of the samples the natural TL is used. Each point of the normalised growth curve represents the ratio of the TL of second glow to the first glow (natural TL). It is obvious that in this case the growth curve after the first supralinear part is normally linear, in contrast with the normalised first glow growth curve which is linear only when k = 0 (Equation 2).

Experimental test of the technique

To test the accuracy of the proposed technique it was applied to prehistoric sherds from Macedonia (sample codes: 3120 and 1022) artificially irradiated with known doses. These sherds did not exhibit supralinearity or sublinearity in the range of our measurements. The following experimental steps were applied: a) a piece of sherd 3120 and of sherd 1022 were heated at about 1000°C for two hours, b) the sherds were crushed and c) samples of them prepared by the foil technique were irradiated with γ-dose. The artificial doses were 51 Gy for a group of samples of sherd 3120 and a group of samples of sherd 1022 and 101 Gy for another group of samples of sherd 3120. The procedure for the calculation of the natural dose was then applied to these three groups of artificially irradiated samples. Figure 8 illustrates the glow curves for the calculation of r_0 (sample α) and r_D (sample β for D=100 Gy) for samples from the group of sherd 3120 for which the exposure time was 101 Gy. The values of P and k were calculated from Equations 4 and 5 for each of the three groups for three temperatures within the plateau region (324, 360 and 387 °C).

The TL glow curves were recorded with conventional Littlemore, 711 TL equipment and a 9635QA photomultiplier with a Corning 7-59 blue filter. All TL measurements were performed with a heating rate of 14 °C/s and the irradiations were administered with a multi-KiloCurie Co-60 source (dose rate 10 Gy/min).

From the results shown in Tables 1, 2 and 3 it can be seen that the variations between the calculated values of P and artificially given doses are below 2.5% for all calculated values except for the value 5.28 min in Table 1 for which the variation is about 3.5%. From these Tables it can also be seen that the values of k increase as the temperature increases. This is the reason why the values of ro and r_D are not the same for the three temperatures, and thus there is no plateau between the first and second glow curves, and also between second glow curves for different values of D, as is evident by comparing curves $\alpha 2$ and $\beta 2$ (Fig. 8). This is a general observation for most sherds studied until now (see also Fig. 4).

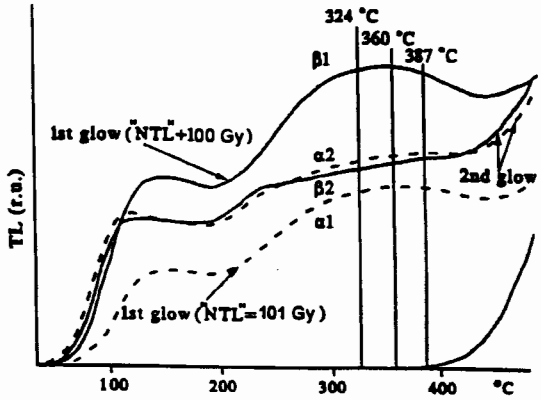

Figure 8.
Glow curves (1st and 2nd glows) for the calculation of r_0 (sample α) and r_D (sample β). These samples are from the group of sherd 3120.

Dating of a mortar containing ceramic fragments

To date the mortar from a cistern excavated in Heraklion Crete, its ceramic fragments were used. The size of these fragments ranged from a few microns to 4-5 mm. After the removal of a 2 mm external layer, the mortar was crushed in a vice. The rubble produced was then treated with hydrochloric acid so that the calcitic matter was removed. In order to be able to calculate the internal beta dose-rate received by the sample, grains of size larger than 4 mm in diameter must be used. This is necessary because a 2 mm layer from each ceramic fragment must be removed. In this layer the beta dosage is transitional between that corresponding to the ceramic radioactivity and that corresponding to the surrounding material of the mortar which is lower than that of the ceramic. Since the fragment of that size available in our mortar sample were very few (about 10) we used the following technique: First we prepared 5 samples from these fragments, using the foil technique, from which the external layer of 2 mm had been removed by hydrofluoric acid (37%) treatment for 4 min. Then the mean value of r_0 was estimated as described above.

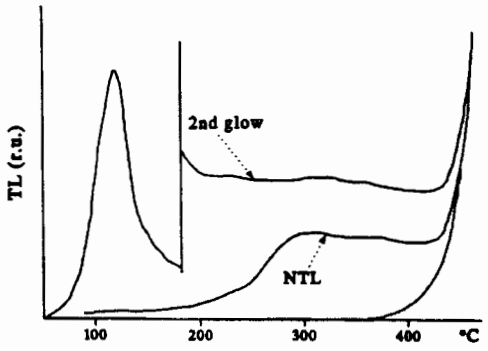

Figure 9.
The natural TL (first glow) and the 2nd glow (ρ = 3.05 Gy) of the ceramic grains (300 ìm), from Heraklion Crete.

From Equation 3 we can calculate the value of P, when we know r_o, given by:

$$P = \frac{r_o(\rho - I) + I}{1 - kr_o(\rho - I)} \qquad (6)$$

This equation involves the corrections due to the pre-dose effect and supralinearity (values k and I). As the values of k and I are dependent only on the material (independent of the fragment size), fragments of smaller size (about 300 μm) may be used for these estimations. These fragments are much more abundant in our material and can be selected by hand, using a suitable microscope. By applying the foil technique to pottery powder from these fragments (Figure 9) and using the software program mentioned above we found P=2.16 ± 0.07 Gy and k=0,044 ±0,011 Gy^{-1}, I = 0.209 ± 0.15 Gy. The corresponding normalised growth curve is illustrated in Figure 5. By substituting in Equation 6 the value of r_0 = 0.72 found for fragments larger than 4 mm which is 14.6% higher than that found for the 300 ìm fragments and the values of k and I found above, we calculate the paleodose corresponding to the core of the larger grains which is 2.48 ± 0.15 Gy. The higher value of P for the larger fragments results from the fact that the whole beta dose-rate comes from the fragment itself. This is not the case for the 300 ìm fragments, for which a part of the beta dose-rate comes from outside.

For the estimation of the a-value we also used samples made by the 300 μm fragments and the estimated value is: 0.115 ± 0.02. The U, Th and K concentrations were measured using all the separated ceramic fragments independently of their size, and their concentrations were found to be: 4.96 ± 0.43 ppm and 7.72 ± 1.22 ppm for U and Th respectively (α-counting) and 1.46 ± 0.15 % for K (AAS). The resulting dose rates from these concentrations are: For alpha particles 16.10 ± 0.52, for beta particles from U and Th 0.94 ± 0.04 and for beta particles from K 1.20 ± 0.12, all values in mGy/year (Liritzis *et al.*, 1992). The environmental dose rate was recorded with a portable NaI scintillator. Its value is 0.406 ± 0.08 mGy/year. Taking into account the reduction due to the water content (saturation content 0.25 and fraction of saturation 0.5 ± 0.3) the total dose rate is 3.82 mGy/year. Finally the age of the cistern was found to be 650 ± 95 years BP which is in agreement with the historical date (Venetian period 1206 - 1669 AD, A. Karetsou personal communication).

Conclusions

The foil technique was tested by the use of artificially irradiated samples with known doses and the accuracy found to be satisfactory. Also, this technique allows the dating of the mortar, which is not possible using any of the other TL dating techniques because there were too few ceramic fragments of sufficient size in our mortar sample.

Acknowledgements

The authors are indebted to Dr. J. Tomlinson and Dr. Y. Facorellis for help in the preparation of the text and figures.

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Tables

Table 1: Values of r_D, ro, P and k for sherd 3120.
D= 150 Gy, ρ= 151 Gy,
P= 51 Gy (Artificial irradiation).

T (°C)	r_D	r_0	P (Gy)	k (Gy^{-1})
324	1.106	0.314	49.7	0.00098
360	1.089	0.323	51.6	0.00112
387	1.060	0.327	52.8	0.00131

Table 2: Values of r_D, r_0, P and k for sherd 3120.
D= 100 Gy, ρ= 101 Gy,
P= 101 Gy (Artificial irradiation).

T (°C)	r_D	r_0	P (Gy)	k (Gy^{-1})
324	1.492	0.857	101.1	0.00166
360	1.453	0.853	102.8	0.00180
387	1.381	0.828	102.8	0.00224

Table 3: Values of r_D, r_0, P and k for sherd 1022.
D= 61 Gy, ρ= 101 Gy,
P= 51 Gy (Artificial irradiation).

T (°C)	r_D	r_0	P (Gy)	k (Gy^{-1})
445	0.902	0.453	50.35	0.00199
463	0.885	0.455	51.35	0.00228
481	0.859	0.453	52.17	0.00269

APPENDIX

Samples are made by first covering a glass plate with a thin layer of silicone grease, and then placing an aluminium foil disk on it. The disk is pressed using rice-paper until its surface becomes flat and smooth (all ripples disappear), and the disk and glass surface are then cleaned with a paper tissue. After that, a 50 μm thick aluminium foil square 5x5 cm having a central hole of 1.1 cm diameter is used to cover the glass surface around the disk leaving the disk uncovered. Next, a rice paper is covered with silicone grease using a small wire, and the disk covered with a thin layer of the grease by pressing it with the paper. The use of the aluminium foil square is essential in order to avoid silicone grease remaining on the glass around the disk and thus to avoid a loss of pottery powder on the glass plate (see below). This is necessary in case of authenticity testing where the amount of pottery powder is usually very small.

After removing the aluminium foil square, pottery powder of grain-size less than 8 ìm is spread on the aluminium disk using a small paintbrush. In order to check whether the surface of the disk is completely covered with powder a rice-paper is pressed on the disk. If the paper shows no traces of silicon grease or pottery grains the sample is ready for measuring, otherwise a small amount of powder is added and the sample rechecked. The disk is loosened from the glass plate with the help of a sharp thin blade.

Reviewer
Gunther A. Wagner

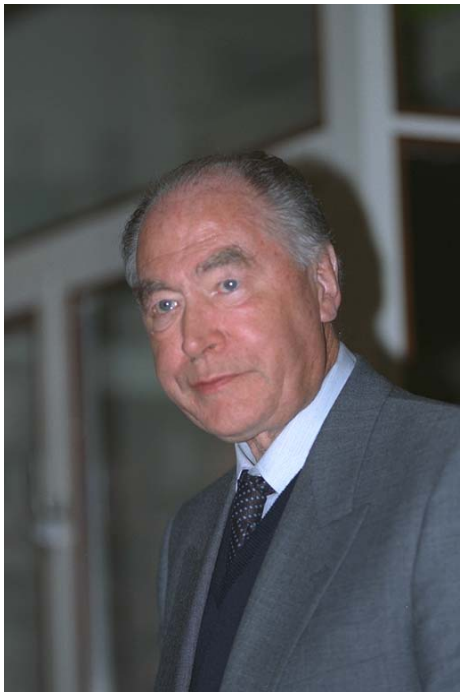
Obituary

Vagn Mejdahl (1928-1997)

Vagn Mejdahl, founder and leader of the Nordic Laboratory for Luminescence Dating at Risø, Denmark, died on the 21st August 1997, after a brief illness. He had been left partly disabled by a stroke some years ago, but continued to be very active until late July, when he suffered another stroke.

Vagn was from a rural community in western Jutland, and left school when he was 10 years old. Despite this, he acquired an education and graduated in physics from the University of Copenhagen in 1955. In 1958 he was recruited by the then Danish Atomic Energy Commission's Research Establishment at Risø. He was a pioneer in the field of solid state dosimetry, and introduced TL techniques in personnel monitoring with the aim of replacing film dosimeters. Some years later, Vagn was inspired by Martin Aitken's early work at Oxford using TL to date archaeological materials, and he started his own dating research in close collaboration with Risø's health physics group. Visits to Oxford and to the National Museum in Edinburgh in the mid 1970s further stimulated his interest in luminescence dating and after much hard work he was able to obtain results of sufficient promise to convince the Danish authorities to raise funds for the establishment of a Nordic Laboratory for TL Dating in 1983. He led the laboratory at Risø until his death, at first with funding from recurrent grants and later as a permanent lecturer in the Geological Institute of the University of Aarhus. For some years, Vagn had been concerned about the future of his laboratory after his retirement, which was due next year. He was very pleased when the University approved last year the appointment of a successor to take over the direction of the Nordic Laboratory.

Throughout his working life Vagn was internationally respected for his pioneering work. His fertile career has given us publications from the late 1950s, up to the papers he co-authored for the international Specialist Seminar "Luminescence Dating: Methods and Applications", held at the University of Aarhus in May of this year. This very successful meeting was organised specifically to celebrate his great contributions to luminescence dating.



The close collaboration between the Laboratory and the health physics group at Risø resulted in some outstanding research and development in luminescence dating methods, instrumentation and protocols. Many of Vagn's articles will continue to be cited frequently by workers around the world: examples cover the attenuation of beta rays in coarse-grain samples, the use of $CaSO_4$:Mn as TL dosimeter for determining the internal beta dose-rate of feldspar samples, and his more recent work on the SARA technique for estimating the burial dose. He also played an active role as a member of several programme and editorial committees for international conferences on both solid-state dosimetry and luminescence dating. He was much valued as a referee by many scientific journals and research councils.

Vagn was not put off by controversy. In the late 1970s, he was intrigued by the mystery of the inscribed clay tiles found at Glozel in France. He visited the site many times and published TL results that demonstrated that the artefacts were not modern forgeries, as was then firmly believed by archaeologists. He remained involved in the Glozel controversy until his death.

We have lost not only a highly respected colleague but a wise counsellor and a loyal friend. He is widely missed.

Lars Bøtter-Jensen

Risø National Laboratory
Roskilde, Denmark

Thesis Abstracts

Thesis title : Quaternary geology of the Fraser Valley area, Big Bar Creek to Pavilion, Southcentral British Columbia

Author : Olav B. Lian

Submitted to : the Faculty of Graduate Studies, The University of Western Ontario, London, Ontario for the degree of Doctor of Philosophy, March, 1997.

A detailed glacial geological investigation of late Wisconsinan ($\delta^{18}O$ stage 2) till, and associated sediments, in conjunction with a lithostratigraphic study, was conducted in south-central British Columbia between Pavilion and Big Bar Creek, near the centre of the Cordilleran Ice Sheet. In addition, the utility of optical dating using 1.4 eV excitation was tested on sediments from depositional environments most common to the region.

Till was characterised by the strength and shape of pebble fabric, the orientation of stoss-lee features on stones, the shape of stones, the nature and orientation of surface striae, and by nature of structures in the till matrix and in the substrate. It was generally found that on the mountain plateaux, and within a mountain valley, that sub glacial deposition generally involved a series of superimposed processes and till rheologies.

Ice that arrived first into this region appears to have been cold-based, and it may have been coupled to the substrate. Evidence of this includes glacially-fractured bedrock and sediment. However, it is clear that a glaciation proceeded warm-based conditions ensued and motion at the ice-substrate interface resulted in the deposition of lodgement till. There is also evidence from several sites that indicates that as the till thickened, and as pore-water increased, the till experienced viscous deformation. During this time till would have moved (flowed) as a thick slurry, thus contributing to the forward motion of the ice. In places there is evidence that periodic (?) drainage resulted in brittle deformation. Ice-flow indicators show that flow direction was generally controlled by topography.

The existence of a deformable bed implies that ice in this region moved rapidly, possible streamed, over plateaux and through mountain valleys. If these conditions were widespread, then the centre of Cordilleran Ice Sheet probably consisted of localised accumulation zones and divides, with ice issuing from them. This conjecture is supported by previous studies of regional ice-flow patterns.

Evidence of the last (Fraser) and penultimate (Okanagan Centre) glaciations have been found in the Fraser Valley, and evidence of an older glaciation has been found near Pavilion. In the Fraser Valley, Okanagan Centre Drift occurs at the base of the valley fill, which in turn indicated complete incision during the last interglaciation ($\delta^{18}O$ stage 5).

Ice flow on the plateaux and in a mountain valleys, between Pavilion and Jesmond, appears to have been to the north. This together with data from previous studies suggests that a major ice divide may have occurred between 50°50.4'N and 50°40.5'N.

Optical dating studies were performed on poorly-bleached glaciolacustrine sediments from the Fraser Valley fill. The results indicate that the apparent optical ages can be valuable in establishing age-ranges, at least at the $d^{18}O$ time scale. Holocene-aged loess from the Fraser Plateau, adjacent to the eastern edge of the Marble Range, yielded incorrect and inconsistent optical ages, and further study indicated that some of the sediment grains had remained shielded from sunlight during transport; it is thought that this effect was due to the presence of carbonate-cemented grain clusters. On the other hand, loess from the western edge of the Fraser Valley produced optical ages which were in excellent agreement with the known age of the deposit.

Thesis title: The development of luminescence methods to measure thermal exposure in lithic and ceramic materials

Author: Joel Q. Spencer*, Scottish Universities Research and Reactor Centre, East Kilbride, Scotland, UK.

Submitted to : the University of Glasgow for the degree of Doctor of Philosophy, September 1996.

Thermometric analyses provide extremely useful information about heated archaeological materials and fire-damaged modern structures. A number of non-luminescence thermometry methods have been developed for analysing pottery firing temperatures. However, many of these methods are limited in analysis range and accuracy, or are time consuming, expensive and complex. In addition to these techniques there are a number of thermoluminescence (TL) thermometry methods but they are also limited in analysis range and the majority have been developed for specific thermometry problems. The aim of this study was to investigate the use of TL and photostimulated luminescence (PSL) methods to develop rapid, precise, inexpensive thermometry techniques that were applicable to a wide range of thermal events and materials from archaeological and modern contexts.

A basic theoretical treatment of luminescence kinetics in silicate systems was undertaken to develop an understanding of TL glow curve alterations arising from thermal exposure. Kinetic studies showed that a combination of temperature and duration parameters is expected for single trap systems. Kinetic theory was developed to produce a new first order multi-trap system which provides a theoretical means of separating temperature and time components, which may be applicable to synthetic phosphors. Additionally heat transfer solutions were investigated to examine the temperature distribution in heated solids and TL instrumentation.

Isothermal annealing experiments on IAEA F-1 potassium feldspar showed a highly precise progressive thermal exposure monitor, whereby the position of the first rise of an annealed TL glow curve is characterised by a linear increase in temperature and a logarithmic increase in time. First order kinetic simulations and initial rise measurements demonstrated a continuous linear distribution of traps in IAEA F-1 feldspar. Using a high temperature TL system (maximum temperature 700°C) the progressive thermometry method was successfully applied to separated feldspar minerals and polymineral samples from archaeological (ceramics, burnt stones and hearthstones) and modern (fire damaged concrete) materials.

PSL excitation spectroscopy showed potential thermometric behaviour but for some samples the sensitivity of the system was too low. Pulsed infra-red PSL showed there may be a limited trap distribution over which a small range of thermal exposures will operate. Combined TL/PSL measurements showed it may be possible to separate temperature and time parameters.

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The age of the Diring Yuriakh archaeological site

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The question of the age of the Diring Yuriakh paleolithic archaeological site in Siberia has been a difficult one to answer ever since the site was discovered in 1982. It is thus with great interest we read that Waters *et al.* (1997) have pinned it down to between 260 and 370 ka on the basis of thermoluminescence ages obtained from sediments overlying and underlying the artifact layer. The purpose of this letter is to give cause to readers to think about this result. We have several questions.

1. The event being dated using thermoluminescence is the last exposure of the mineral grains to sufficient daylight to empty the relevant electron traps. Can Waters *et al.* convince us that sufficient daylight exposure occurred before burial of the sediments they measured?

With regard to the sediment overlying the artifacts, Mochanov (1988) and Alekseev *et al.* (1990) conclude it to be alluvial whereas Waters *et al.* show the grains to have aeolian characteristics, observations that are not necessarily conflicting. Whether or not the grains were exposed to daylight before burial depends on the environmental process, which, at present remains unknown. If we suppose the sediments to be aeolian, since they are now at the top of a ~ 100 m cliff above the Lena River it is possible that their source is the banks and river bottom of the Lena and that they were transported upwards by strong winds during a storm. During such a process, even if it were to occur in the daytime, very little daylight exposure to the grains is to be expected. In fact examples of cases in which cliff-top aeolian sediments did not receive adequate daylight exposure for thermo-luminescence dating or optical dating to yield the correct ages exist; three can be found in Huntley *et al.* (1983, site Hark-1) Lamothe and Auclair (1997, sample MR3) and Huntley and Lian (in press).

2. The equivalent doses reported by Waters *et al.* of the order of 1000 grays are usually obtained for samples close to TL saturation, and the information provided shows this to be the case here. It is well known that such equivalent doses are not necessarily the correct ones for the ages, but can result from a dynamic equilibrium between trap filling and trap emptying. Example data given by Mejdahl (1988) are very similar to the data described by Waters *et al.*; the dose rate was 2.73 Gy/ka the extrapolated dose axis intercept was 1120 Gy, and a laboratory dose of 2500 Gy increased the thermoluminescence by 50%. If an age had been calculated it would have been 410 ka yet the sample was actually of tertiary age (> 1.6 Ma). It thus appears that the ages of 240 ka or more obtained by Waters *et al.* should be regarded as lower limits, and that they do not preclude the possibility that the archaeological material is well over 1 million years old as suggested by Mochanov. Can Waters *et al.* argue to the contrary?

3. Waters *et al.* are quoted as having obtained an age of 500 ka (Morell, 1994). Why the difference between this and ~300 ka now?

4. Mochanov (1988) and Alekseev *et al.* (1990) report some sediments above the artifact layer to be reversely magnetized. This is strong evidence that the site is older than 780,000 years. How do Waters *et al.* discount this?

We thus conclude that the ages quoted should be regarded with caution, and not representing the actual ages of the deposits until satisfactory answers to these questions are obtained.

We have been independently pursuing the same objective, and have conducted thermoluminescence dating and optical dating studies on sediments above and below the artifact layer. Included among these is optical dating on inclusions within quartz grains as suggested by Rink (Holden, 1997). The results of these will be presented for publication in due course, but we do not consider them to be useful indicators of the age of the artifact layer for the reasons given in points 1 and 2 above (one preliminary result can be found in Hu, 1994). Our main effort has been directed at quartzite pebbles from the layer that includes the artifacts. The evidence presented by Mochanov (1988) leads us to expect that these

pebbles were lying on the surface for some time, during which they would be exposed to daylight. We have devoted a considerable effort aimed at developing techniques for determining how far sunlight effectively penetrates the surface and for determining equivalent doses for the surface layers (Richards, 1994). We have shown that there can be sufficient light penetration for optical dating to be used on a surface layer. However, for most samples the quartz gave so little luminescence in response to optical stimulation that our attempts to obtain reliable equivalent doses have so far been defeated. One indicative result was obtained, however, optical dating measurements on single aliquots from the upper and lower surfaces of a pebble from the artifact layer where it was covered by Mochanov's stratum 6 (Unit III of Waters *et al.*) were similar and indicative of saturation (Richards, 1994). While we are unwilling to draw any firm conclusions about the age of the site from these data we consider them to be much better evidence of significant antiquity for Diring Yuriakh than that provided by Waters *et al.* We feel that this approach is more likely to yield a believable age for Diring Yuriakh, or perhaps a lower limit to it, than are measurements on the sediments. If both together can be used to form a coherent picture that would be better still.

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The age of the Diring Yuriakh archaeological site: reply to Huntley and Richards

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USA

Huntley and Richards have raised several issues concerning the stratigraphy and age of Diring Yuriakh, Siberia. Most importantly, they suggest that our TL measurements may be in error and the site significantly older than we suggested in our article in *Science* (Waters, Forman, and Pierson, 1997). We address the points raised by Huntley and Richards, and offer additional insights into problems they may encounter in measuring TL from gravels collected from the artifact-bearing deflation surface.

Point 1: There is unequivocal evidence for the eolian origin of the sediments at Diring Yuriakh. The sedimentologic succession, granulometry, and SEM surface textures all indicate eolian transport. The eolian sands are not cliff edge sands, but reflect deposition of a regional sand sheet. Sand sheets form with the migration of low angle bedforms across the landscape and not just during "storm events." Sand grains can receive repeated light exposure over many days with movement and deposition in a sand sheet (e.g., Dijkmans, J. W. A., 1990). However, we dated the fine-grained (4-11 μm) polymineral extract from these eolian sediments which received greater light exposure, than sand grains, during suspension settling onto the landscape. This finer fraction is primary because the presence of permafrost prevents secondary translocation of fines.

We differ with the comment of Huntley and Richards that "the environmental processes . .. at present remains unknown..." for deposition of eolian sands. There is a long and rich literature on the physics of eolian transport and deposition starting with Bagnold (1941) to more recent treatment by Pye and Tsoar (1990), that clearly provides specific processes for eolian sand transport and deposition, that yields sediments with a low TL residual.

TL emissions from sediments from Diring Yuriakh were rapidly reduced with exposure to sunlight, with >84% reduction remaining after exposure to 16 hours sunlight and more rigorous treatment with exposure to UV-dominated light from a 275-watt sunlight bulb. It is also important to note that minerals with different susceptibilities to solar resetting, quartz and polymineral extracts, yielded statistically similar ages; a testament to the solar resetting of TL.

The majority of ages for the older sediments are not on eolian sand, but on overlying loess of Unit IIIe. This loess is a regional deposit and received prolonged (days) light exposure with exposure on a floodplain source area, atmospheric entrainment, and deposition on the paleolandscape, similar to processes identified in the Loess Plateau of China (e.g., Liu et al., 1981).

Point 2. It is poor practice to compare the TL ingrowth between a Tertiary (10s Ma and not >1.6 Ma) feldspar and a Late Quaternary unconsolidated eolian sediment, unearthed from permafrost. The Tertiary sediment during burial may have been exposed to elevated temperatures (>200° C) and the sediment may have been diagenetically altered, disrupting traps and elemental composition, effecting dose rate calculations.

None-the-less, we agree that the ages reported in Waters *et al.* (1997) are at the upper limit of luminescence geochronology and should be viewed as minimums. However, we weigh the analysis of Unit IIIe loess that yielded ages of 240 ± 19 (OTL538), 251 ± 21 (OTL487Q2), 264 ± 22 (OTL487), and 267 ± 22 (OTL507) ka, which are not saturated and provide a minimum limiting age on the artifact bearing horizon. There is no indication of a considerable diastem (1000s ka) between Unit IIIe and the artifact bearing surface covered by Unit IIIa, thus the two ages bounding the artifact bearing horizon of 267 ± 24 ka (OTL471) and 366 ± 32 (OTL472) are apparently

consistent. A conservative treatment of these data place the age of Diring Yuriakh at >260 ka as stated in Waters *et al.* (1997).

Point 3: The TL age reported by Morell (1994) in her news column was based on incomplete analysis of one of the bracketing samples. Morell reported that this was a preliminary, approximate age and that this represented a maximum age for the site. It was further reported that this age would be refined once the analysis was completed.

Point 4: A paleomagnetic stratigraphy was developed for Diring (Mochanov, 1993). However, we feel that a paleomagnetic reversal stratigraphy is inaccurate given that the site has been subjected to cryoturbation and solifluction processes. The Russian scientists reported that care was taken not to sample sediments that were obviously disturbed by secondary processes. However, this selection appears flawed. Many magnetic reversals were obtained from the most disturbed deposits (Units IIIa-d). Both reverse and normal signals were obtained from the large intrusive sand wedges (Unit II), a cryogenic feature. Because of the geological context of these samples, the reliability of the magnetic signals is highly suspect.

Finally, we have a few additional comments concerning Huntley's and Richards' attempt to date the occupation surface at Diring by luminescence response of quartz grains from artifacts found on a deflation surface. It is critical to note that many of the clasts on the deflation surface have been sand-blasted, sometime(s) after deposition. Thus, the artifact surface does not correspond to the last period of use, but a later process of sand blasting. It is important that Huntley and Richards specify where the clasts were collected at Diring. If they collected their samples from the re-exposed deflation surface near the front of the terrace, then these samples would have been re-exposed to sunlight for an unknown period of time prior to reburial as dune migration occurred during the late Pleistocene. Indeed, the Russian archaeologist who helped Huntley collect samples at Diring showed Waters some of the exact locations where "Huntley collected samples." One of these locations is directly under the younger dune sands (15 ka old). Hopefully, additional clast samples were collected from deeper sections that were not reworked.

We stand by our original ages for Diring Yuriakh and fully recognized they may be minimum estimates. We welcome other efforts to date this site. We wish Huntley and Richards success in this endeavor.

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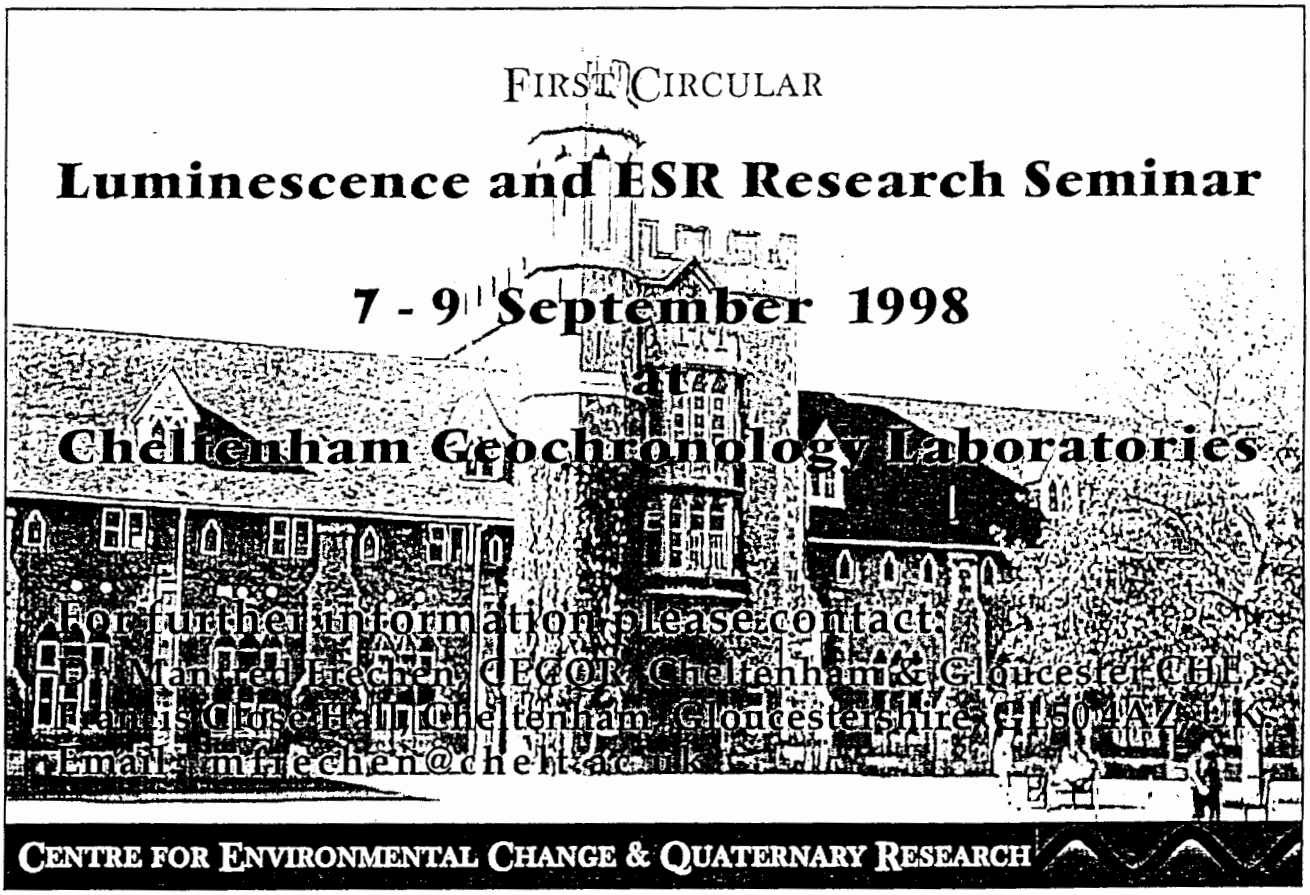

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Forthcoming Postdoctoral Position : Wollongong, Australia

The School of Geosciences in the University of Wollongong, Australia, is soon to advertise a 3 year postdoctoral position. The successful applicant will be required to establish and operate an OSL laboratory which will function in conjunction with the existing TL facility. The unit will operate closely with members of the Quaternary Environmental Research Centre (QERC) whose interests include tsunami, aeolian, fluvial, marine and lacustrine sediments as well as having archaeological applications.
For further detail please contact David Price, e.mail address: david_price@uow.edu.au

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Postdoctoral Research Fellowship : Oxford, Great Britain

Applications are invited for a postdoctoral research fellow in luminescence dating at the Research Laboratory for Archaeology and the History of Art at the University of Oxford. The position is offered for a two year period in the first instance, but may be renewable for a third year.

The primary role of the successful applicant will be to initiate applied and/or fundamental research into the luminescence dating of archaeological and geological samples, and to assist in the supervision of DPhil students. In addition, the person appointed will be expected to undertake some luminescence dating, principally, of archaeological sediments and pottery. The person appointed will be encouraged to seek alternative funding, in order to enable the appointment to continue beyond the initial two or three year period.

The person appointed will have access to a wide range of luminescence and radiation dosimetry equipment, including automated Riso sets, a laser for optically stimulated luminescence and a high resolution gamma spectrometer. Some technical assistance in the maintenance and development of equipment will be available, and there is the possibility of limited technician support for the luminescence dating of archaeological materials. In addition, interaction and collaboration with the luminescence group in the Department of Geography will be encouraged. There is also the possibility of limited teaching experience in geochronology and related areas for suitably qualified applicants.

Applicants should have an honours degree, and should have completed a PhD or have equivalent research experience in luminescence dating. Preference will be given to candidates whose previous research has involved the study of the luminescence properties of quartz. The appointment will be to academically-related research staff grade 1A at a salary in the range £15,159 to £22,785, depending on age and qualifications.

Applications, including a cv, a brief outline of proposed research, and the names and addresses of two academic referees, should be sent to Professor M S Tite, Research Laboratory for Archaeology and the History of Art, 6 Keble Road, Oxford OX1 3QJ. Enquiries about this post can be made to Professor Tite on (01865) 515211. The closing date for applications is 28 February 1998.