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INTERCOMPARISONS OF RED TL AND ESR SIGNALS FROM HEATED QUARTZ GRAINS

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Abstract—Red thermoluminescence (TL) and electron-spin-resonance (ESR) measurements were made on identically prepared quartz grains, which had been zeroed by a lava flow of the Gravenoire volcano (Clermont-Ferrand, France) during the last glacial period (Würm glaciation). Samples from two different sites were studied. The additive technique was used in order to evaluate the palaeodoses and the corresponding dose response curves (DRC), approximating saturating exponentials, were fitted on the basis of DRC obtained with laboratory reset samples. Using this technique of regression, results derived from Al and Ti ESR signals and red TL signals converged better than when only the additive DRC were taken into account in a simple exponential fit. Annealing experiments indicated that the traps involved in red TL, Al and Ti ESR centres had different stabilities vs time and temperature; thus the agreement of the palaeodoses derived from the three signals, within error limits, strengthened confidence in the results for each sample. The ages obtained for the two sites agreed with each other, although the palaeodoses and natural radiation dose rates were significantly different: 62.2 ± 9.0 and 61.3 ± 9.0 ka.

1. INTRODUCTION

SINCE THE FIRST observations on the red TL of quartz were published by Hashimoto *et al.* (1987), several trials indicated that this signal could be useful for dating ancient volcanoes (Hashimoto *et al.*, 1991; Pilleyre, 1991; Pilleyre *et al.*, 1992; Montret *et al.*, 1992). Meanwhile, the first dates were obtained, in similar geological contexts, using the Al and Ti ESR signals of heated quartz grains (e.g. Yokoyama *et al.*, 1985; Imai *et al.*, 1992; Toyoda and Ikeya, 1991; Buhay *et al.*, 1992). In the present work, the two techniques were tested on identical aliquots of quartz grains. This was particularly intended to compare, under the same conditions, the dose responses and the calculated palaeodoses of the different signals, in order to check the validity of the techniques employed and identify possible problems.

Two different samples were studied; they came from baked sediments taken at two different locations, situated at around 2500 m from each other, under lava flows produced by the Gravenoire volcano (Clermont-Ferrand, France). Previous analysis of the local geomorphology and of the available dates suggested that the eruption probably happened at the beginning of the last glacial period; it was clear that there had been only one volcanic event, thus the samples to be dated were expected to give the same age (De Goër *et al.*, 1993). Both samples were sandy clay, which had acquired the colour and aspect of brick at the contact of the lava. The two sampling sites will be referred to as C215 (lotissement du Mirondet, Aubière) and C213 (rue de la Veyre, la Chataigneraie, Beaumont).

Inclusions of quartz, in the size range 200–315 μm were prepared using the usual techniques (e.g. Fleming, 1970; Aitken, 1985), including hydrofluoric acid etching (1.5 h in 1/1 diluted HF). Laboratory irradiations were made at a rate of 3.72 mGy s^{-1} in a ^{137}Cs gamma source, the geometry of which allows the dosing of 250–300 mg of powder contained in an aluminium tube in a single irradiation.

2. TECHNIQUES

2.1. *Experimental*

The TL measurements were made at a heating rate of 5°C s^{-1} in a nitrogen atmosphere, with an RG 610 Schott long-pass filter with a sharp cutoff (50% at 610 nm) and a bi-alkali EMI 9635 QA photomultiplier tube. The TL of each dose/sample was measured on at least eight different aliquots, of around 9 mg each, of quartz grains, normalized for volume; the blackbody background signal was individually subtracted.

ESR measurements were performed on aliquots of around 200 mg each of quartz grains contained in

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an artificial silica tube (suprasyl). They were carried out with an ESR spectrometer Varian E109 using a microwave frequency of 9 GHz (X band). The ESR signals were observed at a low cavity temperature (93 K) in order to reduce dipolar magnetic interactions. The intensity of the signal was normalized for weight and height of the powder inside the tubes. Due to the limited quantity of prepared quartz available, it was not possible to make repeated measurements for each dose. Uncertainty and corresponding error bars quoted on the dose response curves (DRC) for ESR were thus derived from repeated measurements (at least 3) on the same powder on different days with—and without—emptying the tubes in between. In fact, "little is known about the intrinsic error of an ESR measurement" (Grün and Rhodes, 1992) and, as will be seen, this is a drawback in the correct interpretation of ESR dose response curves.

2.2. Measurements

Usually, the red TL peak of quartz shifts towards low temperatures with increasing accrued radiation dose (Miallier et al., 1991; Pilleyre et al., 1992). This can be interpreted in terms of kinetics and, therefore, for utilizing the glow-curves, the peaks corresponding to the different doses are brought into alignment before plotting the DRC for intensity at various temperatures—which are then related to the peak temperature taken as a reference. This procedure of re-alignment was suggested, on a theoretical basis, by Chen et al. (1983) and put into application by Berger (1985). Although the second order kinetics TL theory used by Chen et al. does not explain all of the TL features of natural minerals, it is able to explain

qualitatively a certain number of experimental observations, including peak shifts with dose. On this basis, it was verified theoretically and experimentally (Ousmoï, 1989; Sanzelle, unpublished) that the peak re-alignment resulted in fairly reproducible and simple (i.e. at least monotonic) DRC, while the DRC shape varied rapidly (being sinuous in certain cases) with temperature when no realignment was performed. Thereafter the plateaus plotted to check the validity of the age evaluation (Aitken, 1985) were significantly improved; the ratio-plateau was smoothed, and so was the age-plateau.

Non-kinetic effects, namely: (i) fading; and (ii) occurrence of overlying peaks can also explain the shift of a TL peak with dose (Aitken, 1985, pp. 52–53), but they can be ruled out in the case of the red TL peak of quartz. Fading (i) would result in an apparent shift of the natural peak (NTL) towards high temperatures (as a result of loss in its lower temperature part) in comparison with the NTL + dose peaks, but no shift would be observed for glow-curves obtained with samples annealed and irradiated in the laboratory ("second glow-curves"); the contrary is generally observed, the amount of shift of the red TL peak of quartz being roughly the same for additive and second glow-curves (e.g. in the present work). In the event of (ii), if two overlying peaks have different sensitivities to radiation, there would be an apparent peak shift with dose; however, the shape of the peak—and especially the width—would change also; this is not observed for the red TL of quartz.

An incidental effect of re-alignment of the peaks is reduction of the standard deviation, S.D., of the mean TL intensity because the scattering of the peak temperature owing to instrumentation alone will be
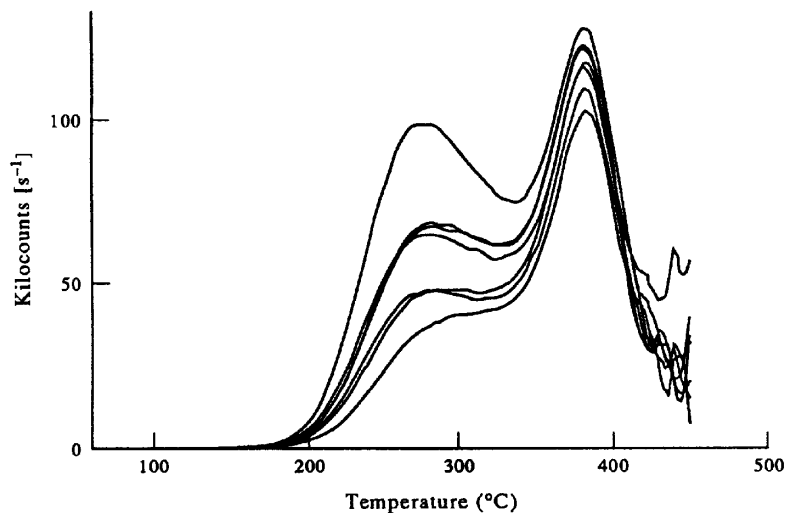

Fig. 1. Natural TL glow-curves of 9 mg aliquots of quartz C213, backgrounds individually subtracted. Conditions: red filter RG610, PM tube bi-alkali EMI 9635 QA, 5°C s^{-1} heating rate, nitrogen atmosphere. The useful peak at 380°C is accompanied by a scattered peak around 270°C.

corrected. As outlined by Berger and Huntley (1989), this S.D. should be roughly constant, in percentage terms, for a given set of glow-curves because, if the sample is homogeneous in composition, scattering is mainly due to variations of quantity and sensitivity. Therefore, the error on the calculated palaeodose will also be reduced.

The way in which the plateau test is used in the evaluation of the palaeodose may depend on (i) occurrence of poorly defined peaks and plateaus; or (ii) the contrary. In the first case, the mean value of the palaeodose plateau will be used, with a careful estimation of associated errors (e.g. Berger and Huntley, 1989); but, when the peak is sharp and the S.D. not important (ii), which is the case for the red TL peak of quartz, it is more judicious to use the palaeodose corresponding to the peak only—after having verified the existence of good plateau. This procedure renders the evaluation of the S.D. easier; at the same time, the calculated palaeodose will be more accurate, because the measurement of TL intensity at the top of the peak is less subject to variations than on its rather steep slopes, and because errors due to blackbody background subtraction
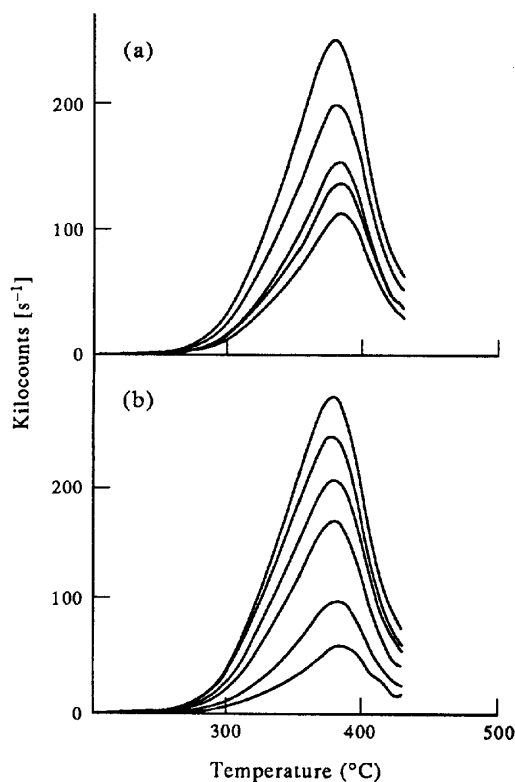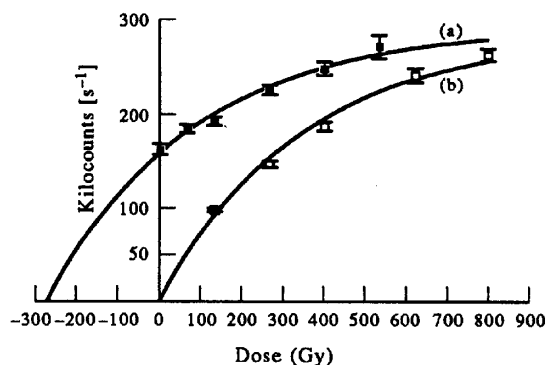

Fig. 3. DRC plotted for height of the TL peak, sample C215. (a) First DRC; full line: fitting curve using parameters of the second DRC ("2 + 1, rel." technique); (b) second DRC (annealing temperature: 400°C); full line: exponential fitting.

and, to some extent, to spurious TL, will be relatively less important.

As regards ESR, the structures of the Al and Ti centres were recently reconfirmed (Falguères et al., 1991); for each signal, the height was measured between the indicating arrows shown on Fig. 5. The g-values were checked by use of a standard of DPPH (1-1-diphenyl-2-picrylhydrozyl) at a g-value of 2.0036.

3. RESULTS

3.1. Additive measurements (first growth)

The red TL of the two quartz samples showed low temperature peaks which are strong enough to have a weak component superimposed on the TL peak of interest at around 380°C (Fig. 1). Using a red filter, such peaks often appear at high doses and grow more rapidly than the 380°C peak. In order to eliminate this unwanted component, all samples were pre-heated at 295°C for 10 s prior to glowing

Fig. 2. Glow-curves of quartz C213. Conditions as on Fig. 1, with preheating. Each curve was averaged over 8-10 curves for each dose. Gamma irradiations were performed with a ^{137}Cs gamma source. (a) Additive glow-curves; doses are, from the lowest one, 0, 6, 134, 268 and 536 Gy. (b) Sample annealed at 400°C; doses are 67, 138, 268, 388, 536 and 670 Gy.
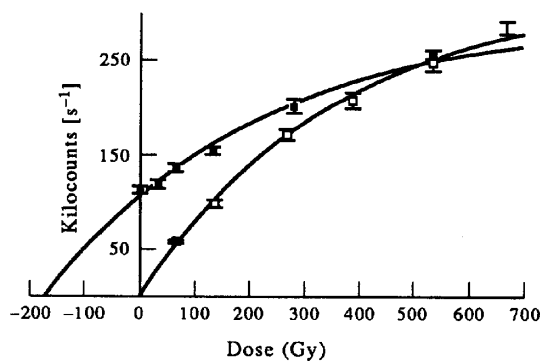
Fig. 4. Sample C213. DRC plotted for height of the TL peak. (a) First DRC; full line: fitting curve using parameters of the second DRC ("2 + 1, rel." technique); (b) second DRC (annealing temperature: 400°C); full line: exponential fitting.

Fig. 5. ESR spectrum of Al and Ti centres of quartz from irradiated C213 sample (693.1 Gy); conditions: cavity temperature 93 K, microwave power of 5 mW, field set is 3300 ± 200 G. The g-value of DPPH is 2.0036.

Fig. 6. DRC of the Al and Ti paramagnetic centres for sample C213; explanations: as for Fig. 3.

Fig. 7. As Fig. 6, but for sample C215.

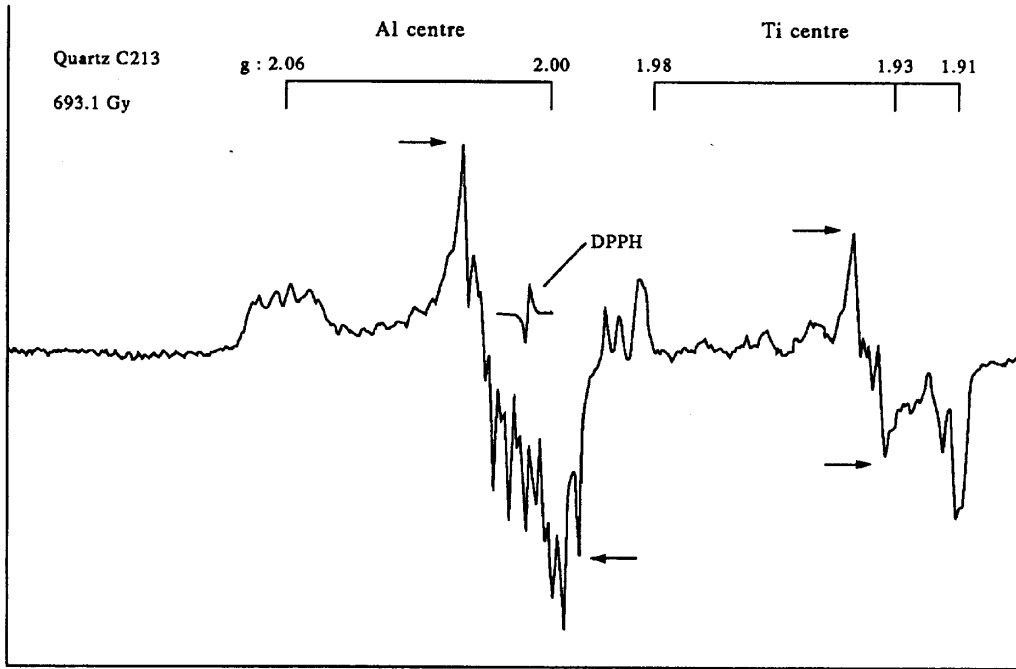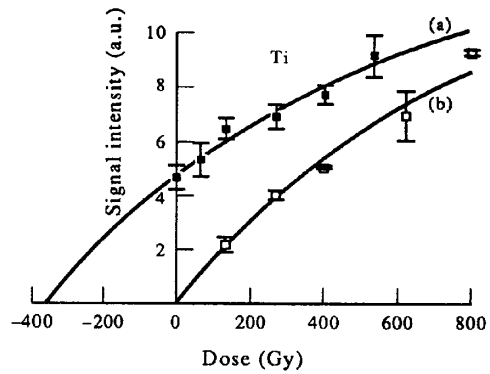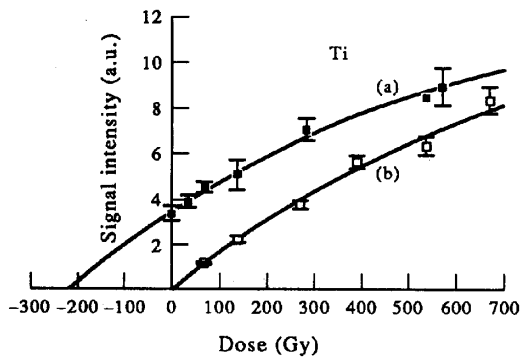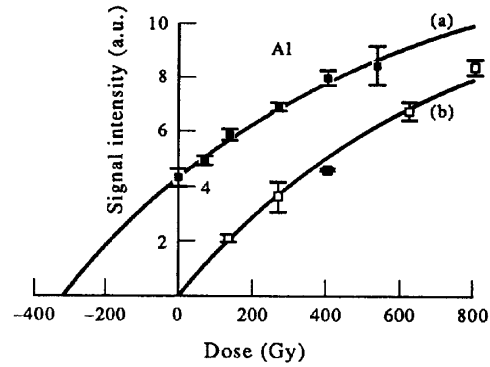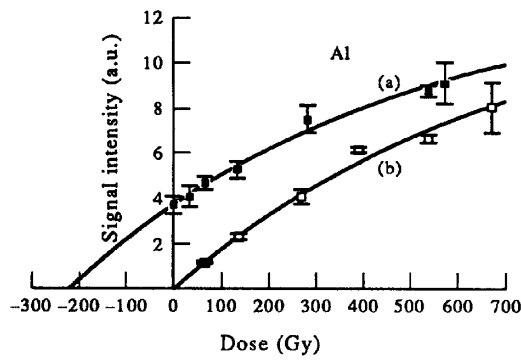from 50 to 450°C. The "standard" red TL peak was then obtained.

As usual the peak shifted slightly towards low temperatures when the radiation dose was increased: from 382 to 378°C for C213 (Fig. 2(a)) and 380 to 378°C for C215, from NTL to NTL + 536 Gy. For both samples the dose response curves appear to be saturating exponentials (Figs 3 and 4).

On the ESR spectra the hyperfine structure of Al and Ti signals were not superimposed, so that a comparative study was possible (Fig. 5). The DRC obtained for the Al and Ti ESR signals had a similar shape, looking like saturating exponentials, although they were not identical (Figs 6 and 7).

(Hereafter, the additive DRC will be referred to as "first DRC" and the curves obtained with laboratory reset samples as "second DRC".)

3.2. Laboratory reset samples (second growth)

Unmeasured aliquots of quartz C213 were annealed in the laboratory, in air, at various temperatures and for various durations: 197°C/185 h, 255°C/16 h, 400°C/16 h and 470°C/17 h. These aliquots were then irradiated and measured for TL and ESR, under the same experimental conditions as before. This was intended to check on the effect of the annealing conditions on the results. An aliquot of C215, also unmeasured, was annealed at 350°C for 3 days.

The resulting TL glow-curves were similar to the previous additive curves for both samples and the amount of shift vs accrued dose was comparable: from 382°C at 67 Gy to 377–378°C at 670 Gy for C213 (Fig. 2(b)), and 380°C at 134 Gy to 378°C at 803 Gy for C215. For C213, the four different annealing treatments resulted in DRC rather similar to each other, nearly equal within error limits; however, a slight evolution with annealing temperature could be detected: the sensitivity of the red peak to radiation increased by around 10% from the least heated sample (197°C) to the most heated one (470°C).

As concerns ESR, for both samples the DRC for laboratory reset samples were also very comparable to the additive ones. For C213, the four annealing treatments gave four DRC which were not significantly different from each other.

4. EVALUATION OF THE PALAEODOSES AND AGES

4.1. Palaeodoses

The palaeodoses were evaluated by extrapolation of the first DRC towards the dose-axes. The regression technique used in the present work (hereafter noted "2 + 1") has been described by Sanzelle et al. (1993). It is discussed below.

Several techniques for exponential regression of the additive DRC have been published (e.g. Mejdahl,

1985; Debenham, 1985; Berger et al., 1987; Poljakov and Hütt, 1990), for TL (mostly for unburnt sediments) and for ESR. These techniques do not take into account the shape of the second DRC although, in practice, the latter are often plotted; rather they try to make a best fit to the available first growth data points. Yet it has been demonstrated that large errors in palaeodose can result from fitting to data sets taken from a fragment of a calculated test-curve having a shape which is not purely exponential (Li, 1991; Sanzelle et al., 1993). This effect applies to experimental curves, which are rarely strictly saturating exponential, neither in TL (e.g. comments of McKeever in Bulur and Özer, 1992) nor in ESR, where Grün (1991) remarked that "in many cases the dose response cannot be described by a simple saturation function". In order to overcome this source of enormous and unpredictable errors, in the "2 + 1" technique (Sanzelle et al., 1993), the first DRC is extrapolated by an exponential function in which the exponential factor is derived from the second DRC.

Two peculiar features of the "2 + 1" technique are worth stressing: in the regression, minimization usually concerns the sum of the square of relative differences between the experimental points and the calculated curve and not of the aboslute ones; both approaches were used in the present work for comparison (corresponding regressions are denoted "rel" or "abs"). The S.D. of the calculated palaeodoses are derived from a Monte Carlo draw, having a Gaussian distribution within the error limits. The consequences will be discussed later.

The TL palaeodoses were calculated from the red peak height only, as mentioned above. An example of a plateau test is given in Fig. 8 for sample C215.

Tables 1 and 2 list the palaeodose results obtained for samples C213 and C215, respectively, and with various techniques of extrapolation. In the left-hand part of the tables are given the results obtained with
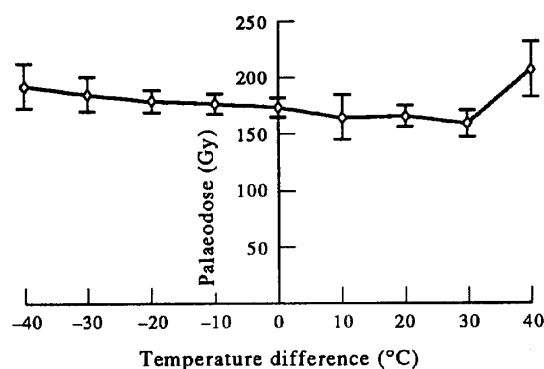

Fig. 8. Palaeodose plateau test for sample C213. Temperatures are related to the peak temperature rather than given in absolute terms because of the adoption of peak shifting as explained in text; regression technique: "2 + 1, rel".

Table 3. Dose rate data and age results with various regression techniques (see Tables 1 and 2). Quoted errors correspond to the quadratic sum of the S.D. on the palaeodose and the overall error on the annual dose rate. Only two different annual dose rates have to be taken into account, one for C213 and one for C215. For C213, the mean of the four palaeodose values, obtained with four different pre-heats was used

Technique	Sample	Palaeodose (Gy)	In situ gamma dose (Gy/ka)	Cosmic dose (Gy/ka)	K$_2$O (%)	Alpha activity (α/cm²d)	In situ water content (%)	Annual beta Equivalent dose (Gy/ka)	Age (ka)	Sample	Regression technique	Technique
TL	C213	267 ± 36	1.21	0.13	2.74	43.5	27	2.94 ± 0.29	90.8 ± 15	C213	(1, rel)	TL
	C215	463 ± 101	1.90	0.13	3.63	108 ± 12	10	4.92 ± 0.49	94.1 ± 23	C213	
	C213	457 ± 5	1.21	0.13	2.74	43.5	27	2.94 ± 0.29	53.4 ± 6	C213	(2 + 1, rel)
	C215	275 ± 14	1.90	0.13	3.63	108 ± 12	10	4.92 ± 0.49	55.9 ± 6	C215	
ESR Ti	C213	190 ± 70	1.21	0.13	2.74	43.5	27	2.94 ± 0.29	64.6 ± 25	C213	(1, rel)	ESR Ti
	C215	356 ± 181	1.90	0.13	3.63	108 ± 12	10	4.92 ± 0.49	72.4 ± 37	C215	
	C213	192 ± 25	1.90	0.13	2.74	43.5	27	2.94 ± 0.29	73.1 ± 11	C213	(2 + 1, rel)
	C215	87	1.90	0.13	3.63	108 ± 12	10	4.92 ± 0.49	74.5 ± 19	C215	
ESR Al	C213	179 ± 72	1.90	0.13	2.74	43.5	27	2.94 ± 0.29	60.9 ± 25	C213	(1, rel)	ESR Al
	C215	258 ± 81	1.90	0.13	3.63	108 ± 12	10	4.92 ± 0.49	52.4 ± 17	C215	
	C213	203 ± 20	1.90	0.13	2.74	43.5	27	2.94 ± 0.29	69 ± 10	C213	(2 + 1, ref)
	C215	205 ± 61	1.90	0.13	3.63	108 ± 12	10	2.94 ± 0.29	63 ± 14	C215	

extrapolation technique are very similar to each other, thus confirming the contemporaneity of the two samples.

The ESR results are on the whole less sensitive to the technique of extrapolation; this can be explained by the fact that the ESR dose response curve can be rather well described by saturating exponential equations. This was confirmed by a low scatter of the calculated exponential factors. The worst case concerns the palaeodoses from Al and Ti with the fit "1, abs" of C215 (Table 2) but the corresponding S.D. is very large. In the other cases, the dispersion of the results is smaller than expected from the calculated errors. This could be due to coincidence or to an overestimation of the errors on the ESR measurements; however, the scatter of the points around the fitting curves (Figs 6 and 7) does not suggest an important overestimation of those errors.

As concerns TL, the extrapolations of the first DRC give much higher results than for the "2 + 1" technique. This can be explained by the fact that the shapes of the DRC are rather different from a simple exponential form and the need for the second DRC, as in the "2 + 1" technique, is thus emphasized. Another possible explanation could be that there is a change in the shape of the DRC after annealing in the oven. There is no indication of an important effect, which would probably result in a significant variation of the exponential parameter with the annealing temperature; however, a slight one, not visible because of uncertainties, could affect the results. The corresponding palaeodose results ("2 + 1") agree with the ESR results, given the error limits (Table 3).

The results of the "2 + 1" technique with various temperatures of annealing (bottom right of Table 1) do not indicate important systematic effects; the four calculated palaeodoses agree within error limits. It seems that annealing at around 400°C gives the most coherent results; this annealing temperature is routinely used in our laboratory for dating using the red TL of quartz.

5. ANNEALING EXPERIMENTS

In the analysis of the results, it is important to know whether or not the three signals which were measured are related to each other. The paramagnetic centres are well known (e.g. Weil, 1984) and correspond evidently to two individual defects; this is not the case for the red TL of quartz, for which the origin has not yet been firmly established. However possible correlations might show up in the study of the behaviour of the signals vs annealing.

From a previous annealing experiment (Falguères et al., 1991), it was suspected that the red TL peak of quartz resists heating more strongly than the Al and Ti ESR centres: for the same sample of quartz

of anomalous fading would have been much reduced.

A possible cause of the discrepancy between the ESR and TL palaeodose results lies in the alpha efficiency; in fact the internal alpha dose rate that was used takes into account an alpha particle efficiency (compared with beta particles) of around 0.06, which was once measured for the red TL but never for ESR. An elimination of the difference between TL and ESR would need a surprisingly high alpha efficiency of at least one for ESR

Another radiation effect that could result in different palaeodoses is linked to dose rates; it should be verified that the height of a signal for a given dose does not depend on the dose rate at which the dose was delivered, because the laboratory dose rate is around 4×10^8 times higher than the natural one. For the red TL of quartz, preliminary experiments suggested that dose rate effects, if any, were weak (Miallier et al., 1991); this was also supported by the agreement between red TL ages and known ages (Montret et al., 1992). In a new experiment, we compared the signals obtained with the same dose (25.3 Gy) delivered by two different ^{137}Cs gamma sources, with a dose rate ratio of 80,000 (i.e. 37.2 Gy ks^{-1}, 683 s of irradiation and 0.465 mGy ks^{-1}, 620 days, account being taken of the decay of the weak source during 620 days), on two sets of the same sample of quartz (ref. C94) initially zeroed in an oven. TL measurements were made simultaneously for the two sets immediately at the end of the long irradiation with the weak source, the day of irradiation with the strong source. The red TL glow-curves (Fig. 11) corresponding to the two sets had the same shape above ~280°C and their ratio was 1.072 ± 0.033 confirming the

weak variation of dose rate sensitivity within this span of rates (the error on the ratio of activities of the two sources is unknown, but probably around 1%). But the ESR signals were too low to be accurately measured. Thus dose rate effects are also still to be studied in ESR of quartz. Unfortunately, the corresponding experiments need very long irradiations (i.e. years) when high ratios between the different sources are required.

There is no doubt that the regression techniques have to be improved for a better evaluation of the palaeodoses: in fact, as was already outlined, a saturating exponential curve cannot perfectly reproduce the DRC of the three different signals studied here and three different regression algorithms would be needed. Development of regression techniques may include various approaches such as: (i) test of empirical functions without taking into account any physical models; (ii) mathematical functions based on physical models, like the spatial correlation model, which may explain some of the peculiar features of the red TL peak of quartz (Faïn et al., 1990); and (iii) systematic investigation of the effects of sensitization of quartz by annealing in order to improve the use of the second DRC in the regression.

In order to propose an age for each of the two samples it was considered, to a first approximation, that for each sample the three results were compatible within error limits. As discussed above, only the "2 + 1, rel" regression technique was used. Thereafter it was necessary to average the calculated palaeodoses obtained with the three methods. However, questions arose concerning the averaging method and evaluation of associated errors.

It should be noted that even if the two ESR centres are independent, the measurements of the centres
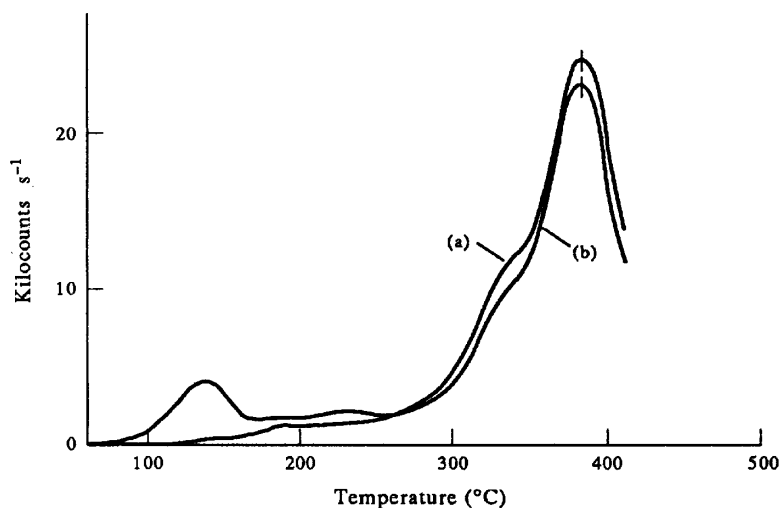

Fig. 11. TL glow-curves of two identical quartz aliquots (C94) irradiated at the same dose (25.3 Gy) with two dose rates different from each other by a factor of 80,000. Each of the curves was an average of 10 measurements. Error bars (one S.D.) are given at the peak. Conditions as in Fig. 1(a): low dose rate, 0.465 mGy ks^{-1}; (b) high dose rate, 37.2 Gy ks^{-1}.

are not. This can be verified by looking at the DRC
e.g. Fig. 6(a) and (b), or Fig. 7(a) and (b); the
distribution of the points around the curves and the
error bars are very similar for the Al and Ti signals.
This occurs because the two signals were measured
simultaneously, on the same aliquot of quartz, for a
given dose; therefore, random errors due to cali-
bration and/or adjustments of the ESR spectrometer
were the same. Thus it would not be correct to give
equal weights to the three signals in the calculation of
the mean. On the other hand, weighting by the overall
errors would in practice result in emphasizing TL
whilst almost neglecting the ESR; this calls into
question the observation of the weak dispersion of
the ESR results.

Instead, a mean ESR value was calculated and then
simply averaged with the TL age for the two samples:
the two following ages were obtained $A(C213) =
62.2 \pm 9.0$ ka and $A(C215) = 61.3 \pm 9.0$ ka. This
procedure is not completely satisfactory and the
need for a better evaluation of errors in ESR
measurements is once more clear.

7. CONCLUSION

Thermoluminescence and electron spin resonance
techniques, applied to the red TL peak and to the Al
and Ti paramagnetic centres, respectively, have given
realistic ages for quartz grains heated during the last
60,000 years; no major malign effect that could lead
to completely erroneous results was suspected. How-
ever, with current methodology, it would be illusory
to expect an accuracy, on a single sample, better than
12–15% of the age, one of the greatest source of
errors and uncertainties being the evaluation of the
palaeodose by regression of the first dose response
curve.

In spite of this mediocre precision, the present
practical application of the two dating techniques
illustrates their importance in the domain of quater-
nary volcanism provided that heated quartz grains
can be found.

REFERENCES

Aitken M. J. (1985) *Thermoluminescence Dating.* Academic Press, New York.
Berger G. W. (1985) Thermoluminescence dating studies of rapidly deposited silts from south–central British Columbia. *Can. J. Earth Sci.* **22**, 704–710.
Berger G. W. and Huntley D. J. (1989) Treatment of error in plateau values—caveat emptor. *Ancient TL* **7**, 27–29.
Berger G. W., Lockhart R. A. and Kuo J. (1987) Regression and error analysis applied to the dose-response curves in thermoluminescence dating. *Nucl. Tracks Radiat. Meas.* **13**, 177–184.
Buhay W. M., Clifford P. M. and Schwarcz H. P. (1992) ESR dating of the Rotoiti breccia in the Taupo volcanic zone, New Zealand. *Quat. Sci. Rev.* **11**, 267–271.

Bulur E. and Özer A. M. (1992) comment on: A cautionary note: apparent sensitivity change resulting from curve fitting. *Ancient TL* **10**, 12–14.
Chen R., Huntley D. J. and Berger G. W. (1983) Analysis of thermoluminescence data dominated by second order kinetics. *Physica Status Solidi A: Appl. Res.* **79**, 251–261.
Debenham N. C. (1985) Comments on extrapolation methods of dating sediments by TL. *Ancient TL* **3**, 17–20.
De Goër de Hervé A., Camus G., Miallier D., Sanzelle S., Falguères C., Faïn J., Montret M. and Pilleyre Th. (1993) Le puy de Gravenoire et ses coulées dans l'agglomération de Clermont-Ferrand: un modèle inhabituel d'avalanche de débris déclenchée par une éruption strombolienne en climat périglaciare. *Bull. Soc. Geol. France* **164(6)**, 783–793.
Faïn J., Sanzelle S., Miallier D., Montret M., Pilleyre Th. and Ousmoï M. (1990) Incidence of mechanisms taking place in the heating stage of TL output. *6th Int. Specialist Seminar on TL and ESR Dating*, Clermont-Ferrand, 2–6 July.
Falguères C., Yokoyama Y. and Miallier D. (1991) Stability of some centres in quartz. *Nucl. Tracks Radiat. Meas.* **18**, 155–161.
Fleming S. J. (1970) Thermoluminescence dating. Refine-ment of the quartz inclusion method. *Archaeometry* **12**, 133–147.
Grün R. (1991) Potential and problems of ESR dating. *Nucl. Tracks Radiat. Meas.* **18**, 143–153.
Grün R. and Rhodes E. J. (1992) Simulations of saturating exponential ESR/TL dose response curves—weighting of intensity values by inverse variance. *Ancient TL* **10**, 50–56.
Hashimoto T., Kojima M. and Sakai T. (1991) Age deter-mination of prehistorical sites in Japan using red-thermoluminescence measurements from quartz grains. *Archaeol. Nat. Sci.* **23**, 13–25 (in Japanese, abstract in English).
Hashimoto T., Yokosaka K. and Habuki H. (1987) Emis-sion properties of thermoluminescence from natural quartz. Blue and red response to absorbed dose. *Nucl. Tracks Radiat. Meas.* **13**, 57–66.
Imai N., Shimokawa K., Sakaguchi K. and Takada M. (1992) ESR dates and thermal behaviour of Al and Ti centers in quartz for the tephra and welded tuff in Japan. *Quat. Sci. Rev.* **11**, 257–265.
Li. S. H. (1991) A cautionary note: apparent sensitivity change resulting from curve fitting. *Ancient TL* **9**, 12–13.
Mejdahl V. (1985) Further comments on extrapolation methods of dating sediments. *Ancient TL* **3**, 21–26.
Miallier D., Faïn J., Montret M., Pilleyre Th., Sanzelle S. and Soumana S. (1991) Properties of the red TL peak of quartz relevant to thermoluminescence dating. *Nucl. Tracks Radiat. Meas.* **18**, 89–94.
Montret M., Miallier D., Sanzelle S., Faïn J., Pilleyre Th. and Soumana S. (1992) TL dating in the holocene using the red TL of heated quartz grains. *Ancient TL* **10**, 33–36.
Ousmoï M. (1989) Application de la datation par thermo-luminescence au néolithique marocain. Thesis, Univ. Clermont-Ferrand, France, 122 pp.
Pilleyre Th. (1991) Datation par thermoluminescence. Application à la chronologie des retombées vol-caniques. Thesis, Univ. Blaise Pascal, Clermont-Ferrand, France, 170 pp.
Pilleyre Th., Montret M., Faïn J., Maillier D. and Sanzelle S. (1992) Attempts at dating ancient volcanoes using the red TL of quartz. *Quat. Sci. Rev.* **11**, 13–17.
Poljakov V. and Hütt G. (1990) Regression analysis of exponential palaeodose growth curves. *Ancient TL* **8**, 1–2.

Prescott, J. R. and Hutton J. T. (1988) Cosmic and gamma ray dosimetry for TL and ESR. *Nucl. Tracks Radiat. Meas.* **14,** 223–227.

Prescott J. R. and Stephan L. G. (1982) The contribution of cosmic radiation to the environmental dose for thermoluminescence dating. Lattitude, altitude and depth dependences. *PACT J* **6,** 17–25.

Sanzelle S., Erramli H., Faïn J. and Miallier D. (1987) The assessment of gamma dose-rate by gamma-ray field spectrometer. *Nucl. Tracks Radiat. Meas.* **14,** 209–213.

Sanzelle S., Faïn J., Miallier D., Montret M. and Pilleyre Th. (1993). On the use of regenerated dose response curves from laboratory reset samples for exponential regressions in TL/ESR dating minerals which have been zeroed by heat. *Ancient TL* **11,** 6–14.

Shimokawa K. and Imai N. (1985) ESR dating of quartz in tuff and tephra. In *ESR Dating and Dosimetry*, pp. 181–185. IONICS, Tokyo.

Shimokawa K., Imai N. and Moriyama A. (1988) ESR dating of volcanic and baked rocks. *Quat. Sci. Rev.* **7,** 529–532.

Toyoda S. and Ikeya M. (1991) ESR dating of quartz and plagioclase from volcanic ashes using E'1, Al and Ti centres. *Nucl. Tracks Radiat. Meas.* **18,** 179–184.

Yokoyama Y., Falguères C. and Quaegebeur J. P. (1985) ESR dating of sediment baked by lava-flows: comparison of paleodoses for Al and Ti centers. In *ESR Dating and Dosimetry*, pp. 197–204. IONICS, Tokyo.

Weil J. A. (1984) A review of electron spin spectroscopy and its application to the study of paramagnetic defects in crystalline quartz. *Phys. Chem. Miner.* **10,** 149–165.