ESR dating of quartz from quaternary sediments: First attempt

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ESR DATING OF QUARTZ FROM QUATERNARY SEDIMENTS: FIRST ATTEMPT

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Abstract--Wind-blown sand from Arago cave at Tautavel and beach sand from Terra Amata at Nice are studied for the dating by a quartz large grain technique using electron spin resonance (ESR). The signal intensity of AI center increased with artificial y-ray dose, and total equivalent doses of 2030 + 109 Gy and
1795 + 103 Gy are obtained for Arago and Terra Amata samples respectively.
A preliminary UV experiment shows that the AI center signal initially decreased under UV irradiation but approached a residual strength. 'Zero age" quartz samples taken from present beach sand near Terra Amata show a signal intensity corresponding to 18% of the saturated intensity of Terra Amata sample (this same proportion is 30% for the 'zero age' Arago samples). After the subtraction of this residual strength, paleodoses of 1010 + 149 Gy and 750 + 147 Gy and ages of 430 + 85 kyr and 380 4- 80 kyr are deduced for Arago cave and Terra Amata, respectively. These ages are in good agreement with those estimated from the faunal studies of these sites.

1. INTRODUCTION

Application of the electron spin resonance (ESR) to the dating of sunlight bleached sediment has not yet been reported, while the thermoluminescence (TL) dating of such samples is widely developed. Wintle and Huntley (1982) reviewed the latter field. We have attempted ESR study of quartz from Palaeolithic sediments (Quaegebeur and Yokoyama, 1981). The present paper reports our preliminary results on the ESR dating of sunlight bleached quartz from Palaeolithic sediments.

2. EXPERIMENTAL

2.1. Questions on experimental technique

Following questions can be asked for the choice of experimental procedure:

(1) Crude sediment or mineral separate? Some radiation-induced ESR signals were observed in crude sediments, but the use of mineral separate is preferable, because of the high concentration of Mn :+ and Fe 3+ in crude sediments.

(2) Polymineral mixture or monomineral separate?
The use of polymineral mixture may be possible. In this preliminary experiment, we ,have worked on monomineral separates.

(3) Feldspars o.r quartz? Some TL investigators prefer feldspars which are more easily bleached by sunlight. Unfortunately no ESR signals were observed in feldspars in our study. We have therefore worked on quartz.

(4) Fine grain technique or large grain one? The use of fine grain technique may be possible. We have, however, applied large grain technique because of the HF treatment used for the preparation of quartz.

(5) 3 mg sample or 300 mg? TL measurements are often done on 3 mg sample. It seems not impossible to use also such a small sample for ESR study with the digital accumulation device (Quaegebeur and Yokoyama, 1981), but sample of 100-300 mg is preferable for currently used instruments.

(6) Which centers? Existence of several different radiation-induced centers in quartz is known: E' center, Ge center, Ti center, radiation damage center, oxygen hole center, AI center and so on. For the identification of these centers, a pioneering paper by McMorris (1971) is very useful. Also a paper by Griffiths *et al.* (1983) on chert is useful because similar centers exist in chert.

We have studied E' center and A1 center, but finally adopted AI center (see Section 3). The A1 center can be detected at an ESR cavity temperature less than 100°K. Our measurements were carried out at 88-93°K by a cooling system using nitrogen gas cooled by liquid nitrogen. The signal intensity depends on the ESR cavity temperature. It is therefore necessary to keep a constant temperature for the quantitative measurements. The signal to noise ratio at this temperature is typically 100 in our experimental conditions for these samples.

2.2. *Palaeolithic sites studied*

We have studied two french Acheulean sites: Arago cave at Tautavel and Terra Amata at Nice. Arago cave is known by the discovery of famous Tautavel Man (Lumley artd Lumley, 1971).

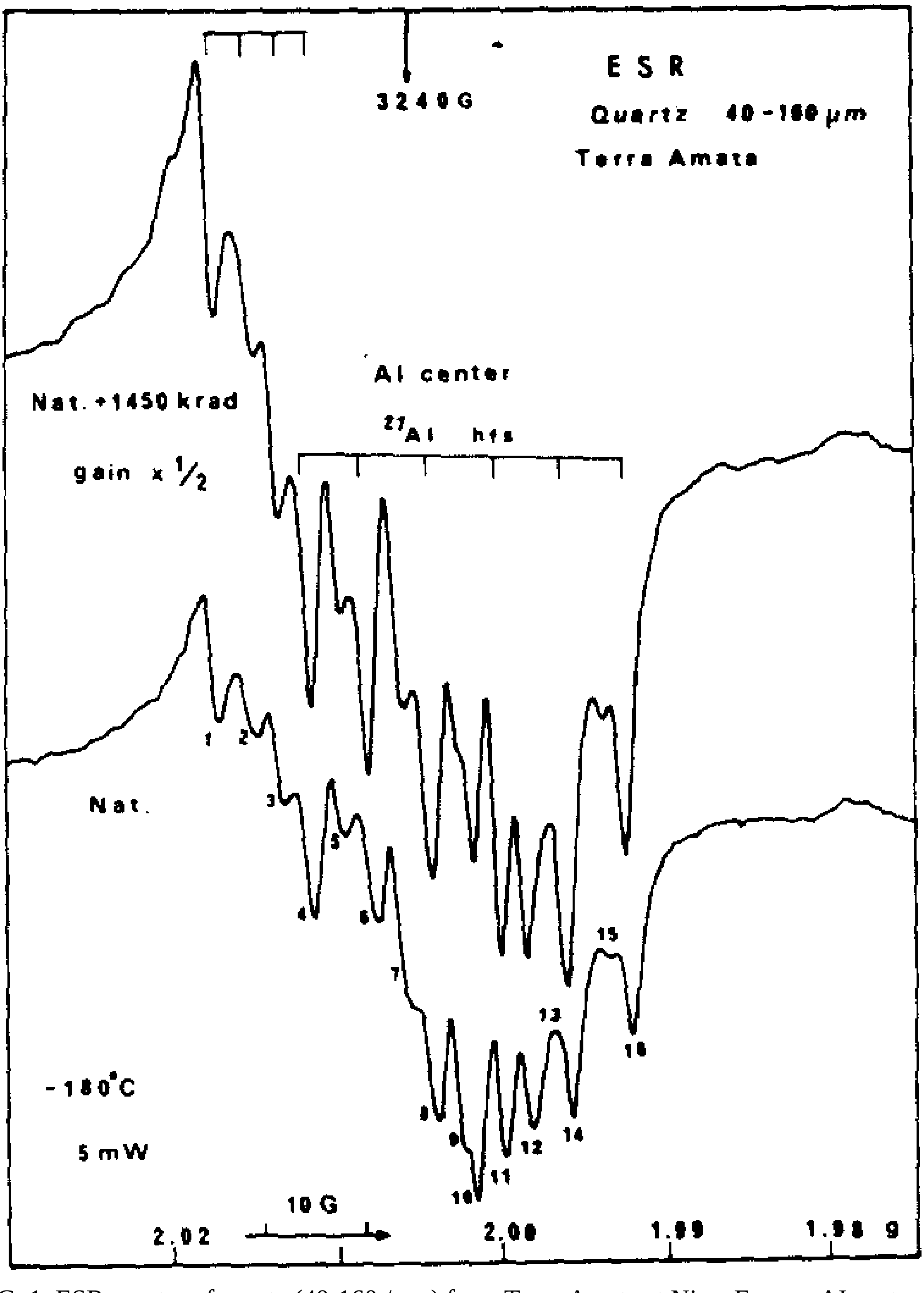

FIG. 1. ESR spectra of quartz (40-160 /z m) from Terra Amata at Nice, France. AI center signals are detected at an ESR cavity temperature of 93~'K. The signals are composed of six ^{27}A1 hyperfine structure lines, of which each is quadrupled (indicated at the top left of the figure). These lines are numbered from I to 16.

Sediment sample (43) was taken between sol E and sol F of Unit III at the least altered zone (I-18). The sediment in this unit is essentially composed of wind-blown sand.

Terra Amata is a seaside camping site of Acheulean hunters (Lumley, 1967). They used fire. (On the contrary Tautavel Man seems ignorant of the use of fire, which suggests a great antiquity of Arago cave).
Sediment sample from Terra Amata (No. 3155) was taken at an ancient coast line of Unit C la (zone F-19). It is beach sand.

2.3. *Sample preparation*
The method used for the sample preparation is similar to that used by TL investigators. For Arago sample, a 40-80 #m fraction was sieved, washed by water, treated by conc HC1 to dissolve carbonate, washed by water, by aceton, then etched by HF (40%) for 5 min, washed again by water, by aceton and dried at 60°C. For Terra Amata sample, a fraction of 40-160/~m was prepared with the same procedure. For these two samples, it was not necessary to use any further purification methods, because the ESR signals due to impurities such as Fe, Mn and fluoride are not detected. However, for some other samples such as heated sediments, it was necessary to use a magnetic separator to eliminate heavy minerals.

3. RESULTS AND DISCUSSIONS

3.1. E' *center* (g = 2.0005)
The intensity of E' center decreased after ^{60}Co γ-ray irradiations of 100 to 2000 Gy, in regard to that of the natural samples. This indicates that the E' center is already saturated in the natural samples. In addition, the microwave saturation of E’ center occurs at very small microwave field. A power of 0.005 mW we used is a limit of our apparatus. From these reasons, we excluded the use of E' center.

3.2. AI *center* (g = 2.01)
Figure 1 shows the ESR spectra of AI center in the natural sample and that irradiated by ^{60}Co γ--ray. The A1 center signal is characterized by a hyperfine structure, that we have provisionally numbered from 1 to 16. The superposition of intense signals due to other centers than A1 one such those detected in the Al center in chert (cf. Fig. 6 of the paper by Grifliths *et*

al) was not observed in the spectra of our samples. However, a comparison of the growth curves of each hyperfine line showed a superposition of other centers in lines No. 9 and No.

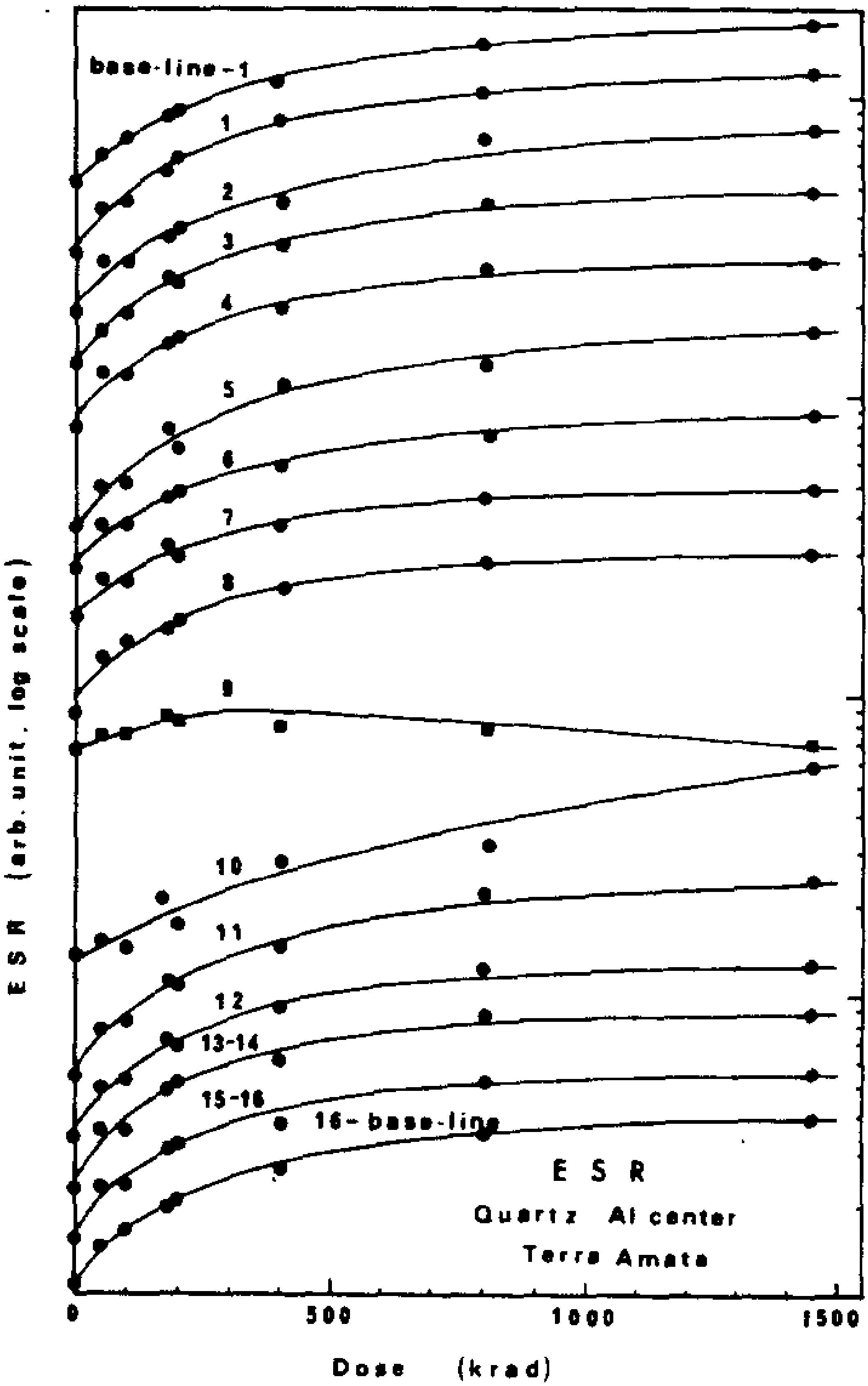

FIG. 2, Growth curves (in log scale) of each hyperfine lines of A1 center in quartz from Terra Amata at Nice. Line numbers are indicated in Fig. 1. Parallel growth curves of these lines except Nos. 9 and 10 indicate the purity of spectra. Nos. 9 and 10 are disturbed by other signals, probably Fe 3+ signals.

10 of the hyperfine structure: all lines except No. 9 (g =2.0031) and No. 10(g =2.0019) parallelly grow with gamma-ray irradiation (Fig. 2). Line No. 9 (g =2.0031) may be attributed to Fe 3+. Line No. 10 (g = 2.0019) is disturbed by this line. For these Arago and Terra Amata samples, the signals due to Ge center (g = 1.996) are not detected. However, some quartz samples taken from other sites show a strong interference of Ge center signal (g = 1.996) on Line No. 14 (g = 1.996), after γ-ray irradiations. The Ge center signal is more easily detected at 200°K or at room temperature.
Natural samples don't generally show Ge center signal. Use of lines between Nos. 9-14 is therefore not preferable. The test of supra (or infra) linearity of the growth curve is under way. Griffiths *et al.* (1983) showed no supra (nor infra) linearity for the AI center in chert.

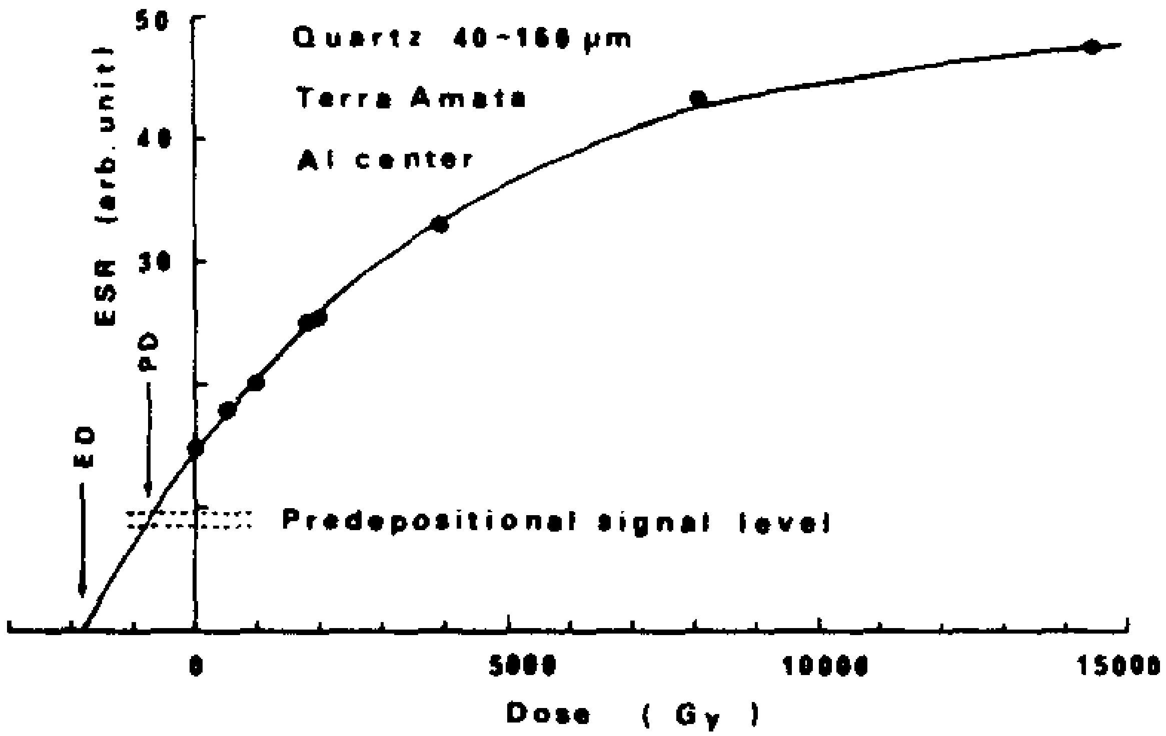

FIG. 3. Growth curve of A] center signal of quartz from Terra Amata at Nice. Peak to peak height (the maximum of line No. I to the minimum of line No. 16) is used. For the line Nos,, see Fig. 1. ED is determined by the least square method using equation (I). Details are given in the text. A value of 1795 _+ 103 Gy was obtained. Dashed lines indicate the predepositional signal intensity deduced from 'zero age' quartz taken from present beach sands near Terra Amata. Paleodose PD of 750 +/- 147 Gy is obtained from the extrapolation of the growth curve to this predepositional signal level.

On the other hand, the A1 center is one of the most thermally stable radiation induced centers in SiO_2 (McMorris, 1971; Griffiths *et al.*, 1983; McKeever *et al.*, 1985). Thermal annealing studies of our samples are under way.

3.3. *Determination of equivalent dose (El))*

The AI center of Terra Amata sample with additional γ-ray doses up to 2000 Gy showed a nearly linear growth curve (Fig. 3). An ED value of 2680 +/- 190 Gy was obtained by the usual linear extrapolation method. However the growth curve is somewhat curved and suggests a slight tendence of saturation. Therefore v-ray irradiations of longer times were then performed. It showed that the saturation occurs at about 15 kGy (Fig. 3). The observed growth curves are well represented by the exponentialequation of first order kinetics (Apers *et al.*, 1981; Ikeya, 1981):

$$I = Is\ (1 - e^{-\mu(D+ED\sim)})\ (1)$$

where I is the signal intensity at a y-ray dose D, Is is the saturation intensity, μ is the sensitivity coefficient, ED is the equivalent dose. The ED is determined by a down-hill least square method.

Equation (1) is transformed to equation (2):

$$\ln(l - 1/Is) = -\mu\ (D + ED)\ (2)$$

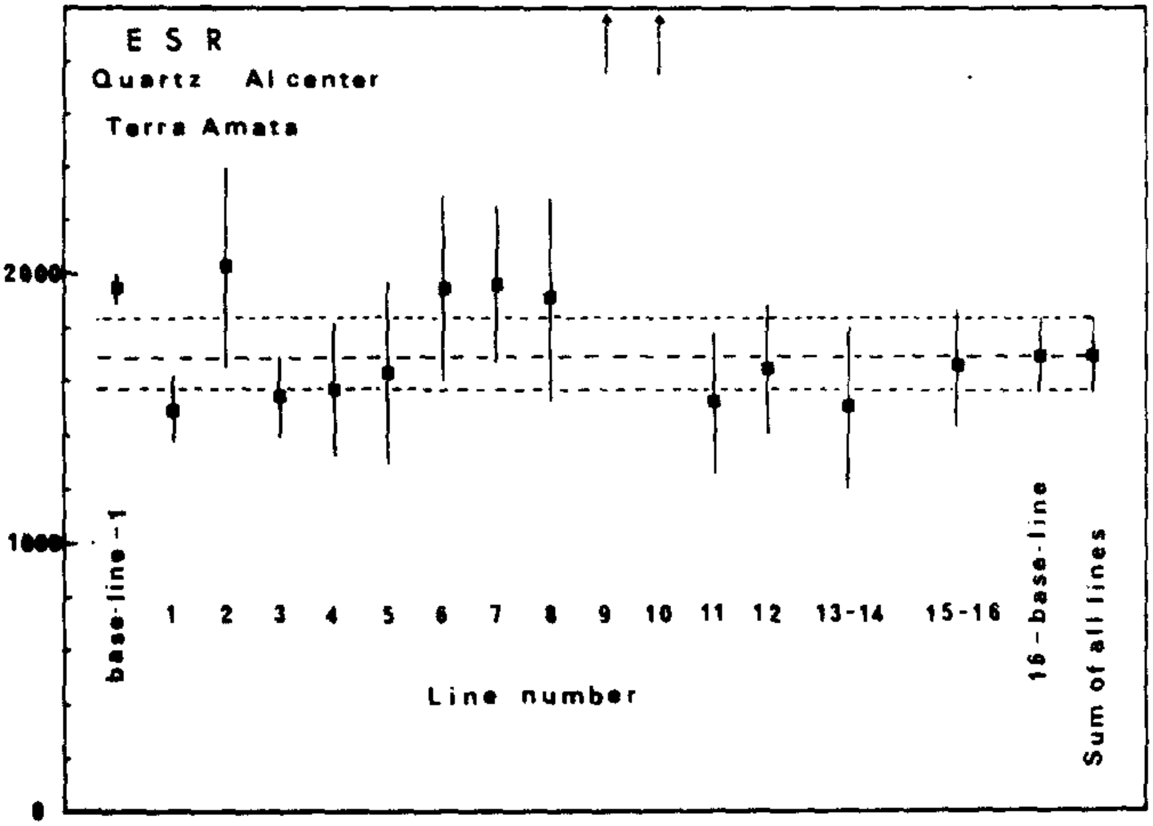

FIG. 4. A plateau test of ED determination. EDs are determined for each hyperfine line and compared. From the sum of peak heights of all lines except Nos. 9 and 10, an ED value of 1700 +/- 140 Gy is obtained: dashed lines.

μ and ED are obtained by the simple least square method supposing 19 in equation (2). This process is repeated by modifying Is until the least square in the sum of (I_{the} - I_{obs})^2 is obtained (I_{the} is theoretical value of I in equation (1) using Is, μ, D and ED). The uncertainty ΔED in the estimation of ED by this procedure can be approximately evaluated by

ΔED = exp((μED) /μIs) x square root ((I_{the} - I_{obs})^2/ *(n-3)) (3)*

where n is the number of measurements, 3 is the number of unknown variables in equation (l) and hence n - 3 is the degree of freedom. The first term of right hand of equation (3) represents the inverse of slope, Δ(D+ ED)/ΔI at D =0. If μED is small, exp(μED) can be approximated by 1. The second term is the standard deviation ΔI for each measure point. The product of these two terms therefore gives ΔED.

This procedure was applied to different methods of the determination of signal intensity:
(i) Peak to peak height in differential spectrum, from top of line No. l (g = 2.018) to bottom of line No. 16 (g = 1.992), after verification that the g = 2.00region doesn't contain interfering signals.
(ii) Integrated area in absorption line.
(iii) Plateau method (Ikeya *et al.,* 1985) applied to each hyperfine line height (Fig. 4). A good agreement is obtained in EDs determinedby (i) and (iii) 1795+/- 103 and 1700 +/-140 Gy respectively (Terra Amata). The integrated area (ii), however, shows a slightly large value, 2055 +/- 120 Gy. The methods (i) and (iii) don't include the effect of nongrowth peaks No. 9-10, but the method (ii) integrates all peaks. We adopted the method (i) because of its simplicity. The method (iii) can be used to check the non-existence of other superposed signals.

Two ED determinations of Terra Amata sample, the one 1 week after the γ-ray irradiation the other 7 months after that and both by method (i), give ED values in good agreement: 1710+/-90 and 1795 +/- 103 Gy respectively. This agreement shows that the fading after γ-ray irradiation isn't significant.

For Arago cave sample (Fig. 5), ED values of 2060 +/- 140 and 2030 +/- t09 Gy are obtained after a week and 10 months storages respectively.

3.4. *UV irradiation*

UV irradiation was carried out by Prolabo 4-W black UV lamp at a distance of 5 cm. The radiation of black UV lamp, having a broad emission spectrum in a wave length range of 300-400 nm, was thought to be a good approximation of shortwave sunlight (Jungner, 1982). A preliminary experiment showed the decrease in the intensity of A1 center for etched sample, while the intensity increased after UV irradiation in non-etched sample (Fig. 6). The result of non-etched sample can be interpreted with a following mechanism:

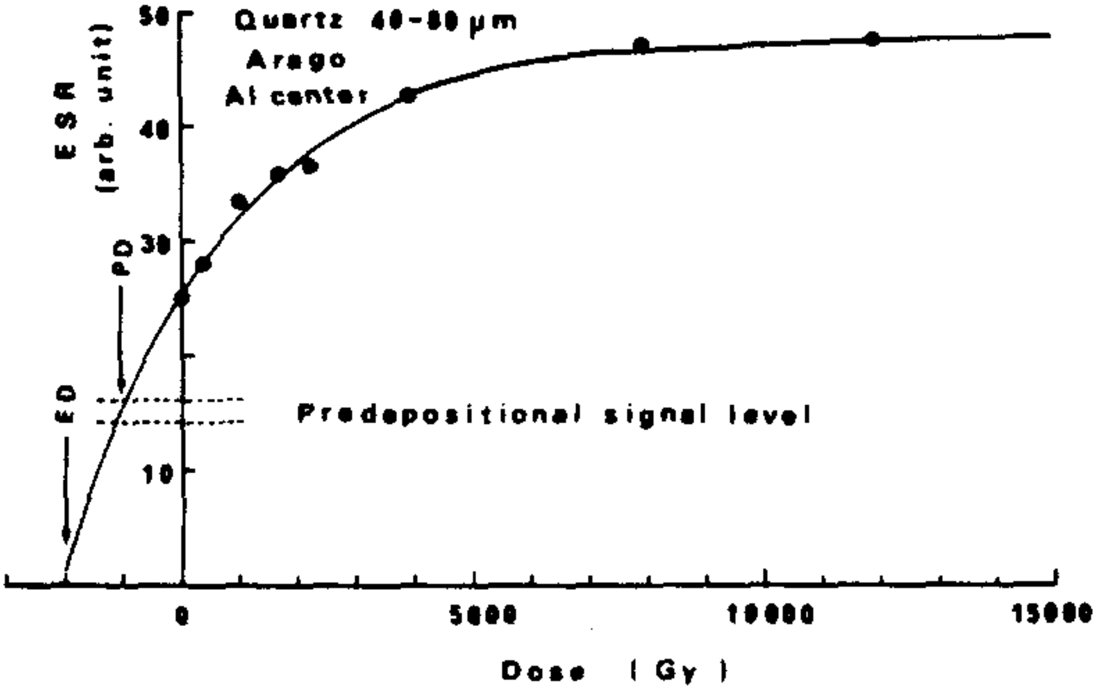

FIG. 5. Growth curve of AI center signal of quartz from Arago cave at Tautavel. The same procedure as that in Fig. 3 is used to the determination of ED: a value of 2030± 109Gy was obtained. Dashed line indicates the predepositional signal intensity deduced from 'zero age' quartz taken from present surface soils at Tautavel Plain near Arago cave. Paleodose PD of 1010 +/- 149Gy is obtained from the extrapolation of the growth curve to this predepositional signal level.

The quartz grains were covered with a thin film of oxide or carbonate. This film doesn't pass UV and consequently there is no drain of AI centers by UV. However, electron-hole pairs are formed by UV in this film, and these pairs are migrated into the quartz grain and trapped by impurity centers. The formation of electron-hole pairs by UV may occur also in the etched quartz. If so, the residual intensity after UV irradiation in etched samples can be due to an equilibrium between the formation of electron-hole pairs by UV and the drain of AI center by UV. The residual signal in this preliminary UV experiment is very high: about 80% of the intensity in the natural sample. It is possible that the UV lamp used in this preliminary experiment was not sufficiently powerful. Bleaching experiment using natural sunlight is under way, but it suggests the necessity of a long exposure, in agreement with the result of similar experiment by TL: Murray *et al.*, 1983) reported that more than 500h of daylight would be needed.

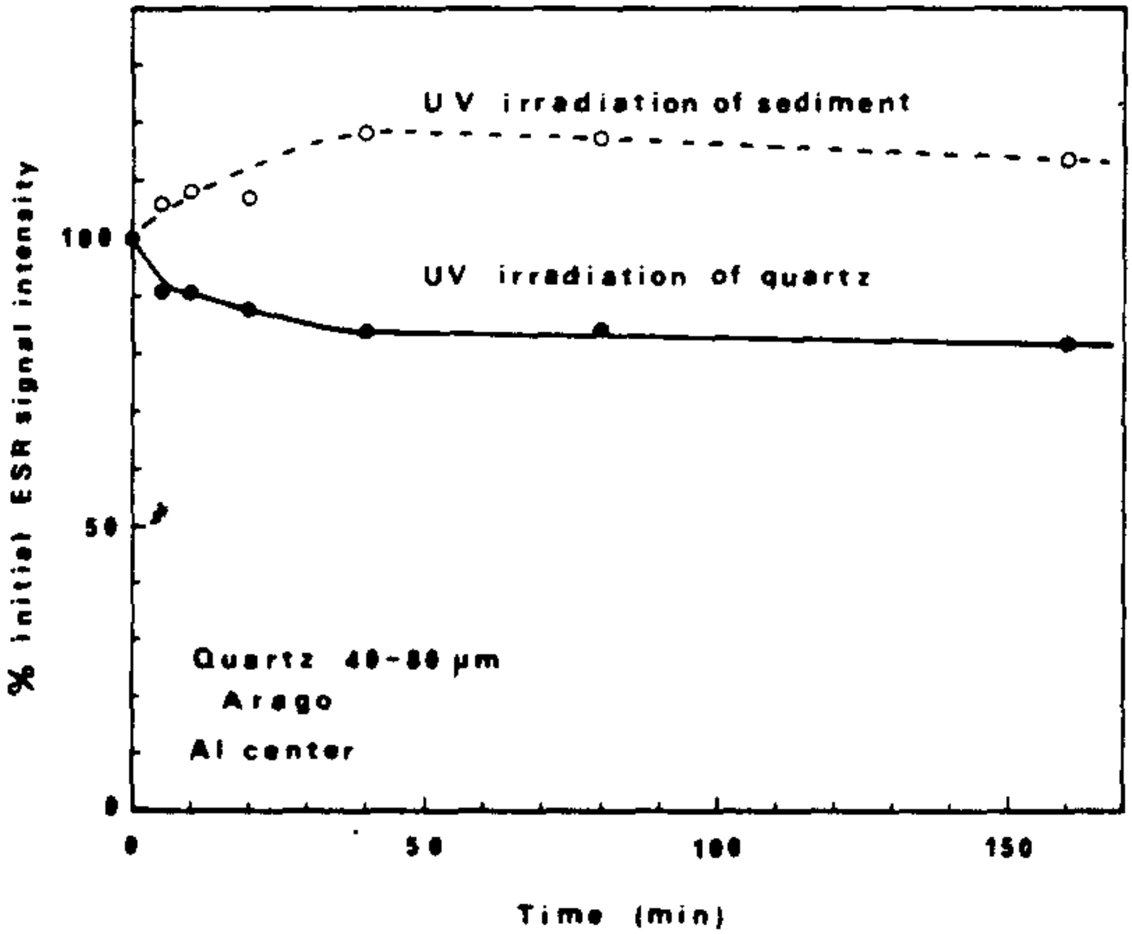

Fig. 6. UV bleaching experiment of quartz from Arago cave. The natural sample was irradiated for a black UV lamp of 4 W. The UV irradiation before etching (upper curve) show the growth of signal intensity with the UV irradiation. The explication for this growth is given in the text. The lower curve is for the UV irradiation after etching. The residual signal intensity in this preliminary experiment was about 80% of the natural intensity for 160min UV irradiation.

3.5. *Signal intensity in 'zero age" samples*

In order to estimate the predepositional ESR signal intensity, quartz grains are extracted from present beach sands near Terra Amata and from surface soils on the alluvion of Tautavel Plain near the Arago cave. These samples can be considered as 'zero age' ones. AI center signal intensities of the present beach sands correspond to 60 + 5% of the intensity of Terra Amata natural sample and to 18% of the saturated intensity. For the 'zero age' samples of Arago, these proportions are 60+5% and 32% respectively. These 'zero age' signal levels are relatively high but comparable to those observed by TL for high temperature TL peaks of quartz large grains (Prescott, 1983). Predepositional doses ED0 are then estimated by equation (I) from these 'zero age' signal strengths: 1020Gy (+/- 10%) and 1045 Gy (+/- 10%) for Arago cave and Terra Amata respectively.

3.6. *Paleodose, annual dose and age*

Paleodose, PD, is obtained by the subtraction of these predepositional doses from the total dose ED: PD=ED-ED0. Paleodoses of 1010 +/-149 and 750 +/- 147 Gy are deduced for Arago cave and Terra Amata respectively.

Table 1. Annual doses for quartz from Arago cave and Terra Amata

	Arago cave No. 43 Unit III, sol E-F	Terra Amata No. 3155 Unit C1a
^{233}U (dpm g^{-1})	1.30 ± 0.06	0.77 ± 0.09
^{226}Ra (dpm g^{-1})	1.02 ± 0.08	1.10 ± 0.20
^{222}Rn (dpm g^{-1})	1.04 ± 0.02	0.82 ± 0.03
^{232}Th (dpm g^{-1})	1.37 ± 0.02	0.74 ± 0.03
K (%)	1.05 ± 0.01	1.22 ± 0.03
Dose (mGy yr^{-1})		
α	0.38 ± 0.30	0.15 ± 0.12
β	1.22 ± 0.06	1.20 ± 0.06
γ	0.70 ± 0.04	0.56 ± 0.04
cosmic	0.04 ± 0.01	0.06 ± 0.01
total	2.34 ± 0.31	1.97 ± 0.14

U, Ra, Rn, Th and K contents are those of the sediments. Disequilibria in the uranium series in the continental sediments are essentially due to the dissolution of ^{226}Ra and the emanation of ^{222}Rn (Murray and Aitken, 1982; Yokoyama *et al.*, 1982a). These disequilibria are measured by the γ-ray spectrometry and taken into account for the calculation of annual dose. (Large ^{230}Th excess such that found in deep oceanic sediments doesn't exist in continental sediments).

On the other hand, radioelement contents in quartz are negligible. Attenuations of α-rays and β-rays in quartz are estimated from the calculations of Bell (1980) and Mejdahl (1979): the mean absorbed dose fractions are 0.38 (α) and 0.96 (β) for Arago cave sample and 0.23 (α) and 0.95 (β) for Terra Amata one.

A k-value of 0.2 + 0.1 is supposed. The removal of the α -ray exposed layer by HF etching was discussed by several authors (Bell and Zimmerman, 1978; Bell, 1979; Valladas and Valladas, 1982). We assumed a removal efficiency of 0.5 + 0.3. The uncertainties for the evaluation of α dose are quadratically summed up and a global uncertainty of + 80% is estimated. The contribution of dose in the total dose is small for the large grain technique, but the uncertainty of the total dose is mainly due to that of α-dose.

Gamma doses and cosmic doses are the results obtained by our *in situ* γ-ray spectrometry. Gamma-doses measured by TL capsules are 0.74mGy/yr for Unit III sol E-F of Arago cave (Aitken, personal communication) and 0.38 mGy/yr for Unit Cla of Terra Amata (Wintle and Aitken, 1977).

Errors for the radioelement contents are l σ counting statistic ones. Errors for the dose rates include uncertainties involved in their estimation, and errors less than 5% are set to 5%. The addition of errors is quadratically done.

These ages are in good agreement with the ages estimated by faunal studies of these sites: 450 and 380 kyr respectively. The Unit III of Arago cave has no stalagmitic floor. The absolute datings of this unit were carried out on bone samples and the results were scattered (Bernat, 1981; Bishoff and Rosenbauer, 1981; Ikeya and Miki, 1981; Lalou and Hoang., 1981;

Yokoyama and Nguyen, 1981a, 1981 b; Yokoyama *et al.,* 1981a). The stalagmitic floor of upperlying Unit IV were dated by different methods but the results were also scattered (Amosse *et al.,* 1981; Apers *et al.,* 1981; Bishoff *et al.,* 1981: Debenham *et al.,* 1981a; 1981b; Hennig *et al.,* 1981; Ikeya and Miki, 1981; Lalou and Hoang, 1981; Ohta, 1981; Schwarcz, 1981; Turekian and Cochran, 1981; Valladas *et al.,* 1981; Yokoyama and Nguyen, 1981b; Yokoyama *et al.,* 198lb, 1982, 1983; Yokoyama and Shen, 1985). The results obtained by our group showed more than 350 kyr by the U-Th method and 490+/- 50kyr by the ESR method. The value of 425 +/- 80 kyr for Unit III sediments obtained by the present work is consistent with these ages of upperlying Unit IV.

For Terra Amata, Wintle and Aitken (1977) reported an age of 230 +/- 40 kyr by TL of two burnt flints taken also from the same beach layer C I a as our beach sands. The difference of the ages" between their burnt flints and our solar bleached sand is not yet explained but both these ages are tentative ones, and their conclusion that "it would be presumptuous to place too much weight on a date" is also ours.

4. CONCLUSION

Our preliminary study promises the feasibility of ESR dating of sunlight bleached quartz. Main difficulty is the estimation of the residual strength after the sunlight bleaching. The major interests of the use of ESR in regard to that of TL lie on its possibility of distinction between the signals from different (known) centers and on the fact that the measurements are carried out without drain of trapped electrons.

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