

## ESR DATING OF SEDIMENTARY QUARTZ FROM TWO PLEISTOCENE DEPOSITS USING Al AND Ti-CENTERS

HÉLÈNE TISSOUX<sup>1,2</sup>, SHIN TOYODA<sup>1</sup>, CHRISTOPHE FALGUÈRES<sup>2</sup>, PIERRE VOINCHET<sup>2</sup>, MASASHI TAKADA<sup>3</sup>, JEAN-JACQUES BAHAIN<sup>2</sup> and JACKIE DESPRIÉE<sup>2</sup>

<sup>1</sup>*Department of Applied Physics, Okayama University of Science,  
1-1 Ridai, Okayama, 700-0005, Japan*

<sup>2</sup>*Département de Préhistoire, Muséum National d'Histoire Naturelle,  
UMR 5198 du CNRS, 1 Rue René Panhard, 75013, Paris, France*

<sup>3</sup>*Regional Environment studies, Nara Women's university,  
Kita-Uoya-Nishimachi, Nara 630-8506, Japan*

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**Abstract:** One sample from a fluvial terrace of Loir river (France) deposited during isotopic stages 7-8 and two samples from isotopic stage 5 marine sediments of Echizen Coast (Japan) were dated by ESR of quartz grains. Both additive and regenerative techniques were used on Ti-Li and Ti-H centers of quartz. No change of sensitivity of the centers was observed during regeneration which significantly reduced the errors on the equivalent doses. Bleaching experiments indicated that the Ti-Li center is less sensitive to UV (ultra-violet)-A (365-412 nm) than to the full sun spectrum whereas UVA alone is sufficient to reset the bleachable component of the Al-center. This effect could be the origin of the strong overestimation of the ages determined using the Ti-Li center in this study. The comparison of the equivalent doses determined by the two Ti-centers indicated that bleaching before deposition of the fluvial sediment was apparently better than for the marine sample.

**Keywords:** ESR dating, Ti-H center, Ti-Li center, bleaching, regeneration.

### 1. INTRODUCTION

Quartz is a suitable mineral for ESR dating as it contains paramagnetic centers, and dating of sedimentary quartz is of great interest for geology and archaeology as well. However, this technique requires an event that resets the traps before the time of deposition, such as sunlight exposure. Two main ESR-centers are used for dating quartz grains, aluminium (Al) and titanium (Ti) related impurity defects, in which two sub-centers, Ti-Li and Ti-H, are commonly observed. First optically bleaching experiments using UV-lamps or solar simulators demonstrated that the Al center of quartz has two components, one bleachable and the other unbleachable (Falgüères *et al.*, 1988; Tanaka *et al.*, 1997; Toyoda *et al.*, 2000; Tissoux *et al.*, 2007). The estimation of the last exposure to sunlight can then be determined using the bleachable component of Al-center and this technique

allowed the estimation of ages estimates for Lower and Middle Pleistocene fluvial deposits (Laurent *et al.*, 1998; Bahain *et al.*, 2002; Voinchet *et al.*, 2004). The main advantage of the Ti-centers is total bleaching during exposure to sunlight (Toyoda *et al.*, 2000; Tissoux *et al.*, 2007) and these centers are promising for extending the age range of quartz grains dating beyond the limit of the methods based on luminescence (OSL). In that aim, recent investigations on ESR dating of sedimentary quartz using the Ti-centers on aeolian quartz grains (Berteen and Stesmans, 2006) and fluvial quartz grains (Tissoux *et al.*, 2007) were conducted. Unfortunately, in both cases individual Ti-H and Ti-Li ESR centers yielded inconsistent equivalent doses ( $D_E$ ). The comprehension of the phenomena that led to inconsistencies in results based on the use of different ESR centers, and the determination of a "right" way to date quartz grains using ESR needs investigations of the intrinsic characteristics of quartz and an accumulation of data on quartz from various origins, expected ages and deposition modes. In this study, we compare some characteristics of quartz from two different

Corresponding author: H. Tissoux  
e-mail: tissoux@mnhn.fr

deposits: Middle Pleistocene fluvial deposit from France and Early Upper Pleistocene marine sediments from Japan. Thermal stability of the Al, Ti-Li and Ti-H centers were investigated for the two sediments and bleaching experiments permitted to compare the influence of the stimulation by UVA and by solar simulator on the Al and Ti-related centers of quartz. Sensitivity change of the Ti-centers before and after heating the quartz grains was monitored before using the regeneration technique, together with the additive technique, for  $D_E$  determination. The advantages of the regeneration method over the additive method and the equivalent doses obtained using the three ESR centers of quartz are discussed.

## 2. SAMPLES

Two sedimentary quartz samples from different areas and with different modes of deposition were chosen to be compared. Fluvial quartz from the Loir valley system (France) and marine sediments from Fukui prefecture (Japan) were sampled.

Loir valley sample (Morée Villeprovert, MV) was taken in the alluvial sheet "B" (+2/+7m), in the "Haut-Vendômois" area. The chronological framework of the Loir valley system was determined by ESR using the Al-center on several samples taken in each terrace. Ages were reproducible within the same alluvial sheet and the age of each terrace was consistent with the stratigraphic sequence (Despriée *et al.*, 2003). The alluvial sheet "B" was deposited during isotopic stages 7/8 and the sample MV was dated by ESR using the Al-center where a  $D_E$  of  $326 \pm 22$  Gy was obtained (Voinchet, com. pers.). The age determined from this  $D_E$  was in agreement with the ESR-ages calculated from other samples of the same alluvial terrace and also with the global chronological framework of the fluvial system. We can then consider the  $D_E$  determined as a good estimation of the dose received by the sample since its burial.

The Fukui quartz F1 and F3 were sampled in two localities of the M2 terrace, along the Echizen Coast (Yamamoto *et al.*, 1996). The age of this terrace has been estimated to be 110-115 ka, from the presence of the Sambe-Kisuki Tephra (Machida and Arai, 2003). F1 was taken in the first locality and F3 in the second locality. The F6 sample was taken in a higher terrace of Marine Isotope Stage 5e at the second locality and the supposed age is ca. 125 ka (Takada, pers. com.).

## 3. EXPERIMENTAL PROCEDURE

### Sample preparation and irradiation

Grain size used in the study for the MV sample was 100-200  $\mu\text{m}$ . A 250-500  $\mu\text{m}$  fraction was used for the Fukui samples, as the marine sediment didn't contain many 100-200  $\mu\text{m}$  grains. For each sample, the fraction was selected by wet sieving. Samples were soaked in  $\text{H}_2\text{O}_2$  for several hours, then in HCl for one night. After rinsing and drying, minerals heavier than a density of 2.67 were removed using heavy liquid. Finally, the samples were etched by 40 % HF for 1 hour, rinsed with HCl and dried. Magnetic minerals were removed using a

Franz magnetic separator. Fukui samples were then crushed and sieved in order to obtain a 100-200  $\mu\text{m}$  powder.

In order to establish additive dose curves, parts of samples MV, F1 and F6 were divided into 11 aliquots. 9 of these were irradiated using a  $^{60}\text{Co}$  gamma ray source at doses ranging from 30 to 1200 Gy for Fukui samples and from 30 to 2800 Gy for MV at a dose rate of 60 Gy/h at the Japan Atomic Energy Research Institute in Takasaki. One aliquot of each sample was optically bleached using UVA lamps (wavelength of 365 nm with a power of  $18 \mu\text{W}/\text{cm}^2$  located 4 cm above the sample) for 1368 hours in order to determine the residual dose of Al-center (Voinchet *et al.*, 2003).

At the same time, regenerated curves were also constructed; a fraction of natural MV, F1 and F6 was heated for 2 h at 300°C and slowly cooled, then separated into 10 aliquots and 9 of them were irradiated with doses ranging from 30 to 2800 Gy at a dose rate of 60 Gy/h.

### Bleaching and annealing experiments

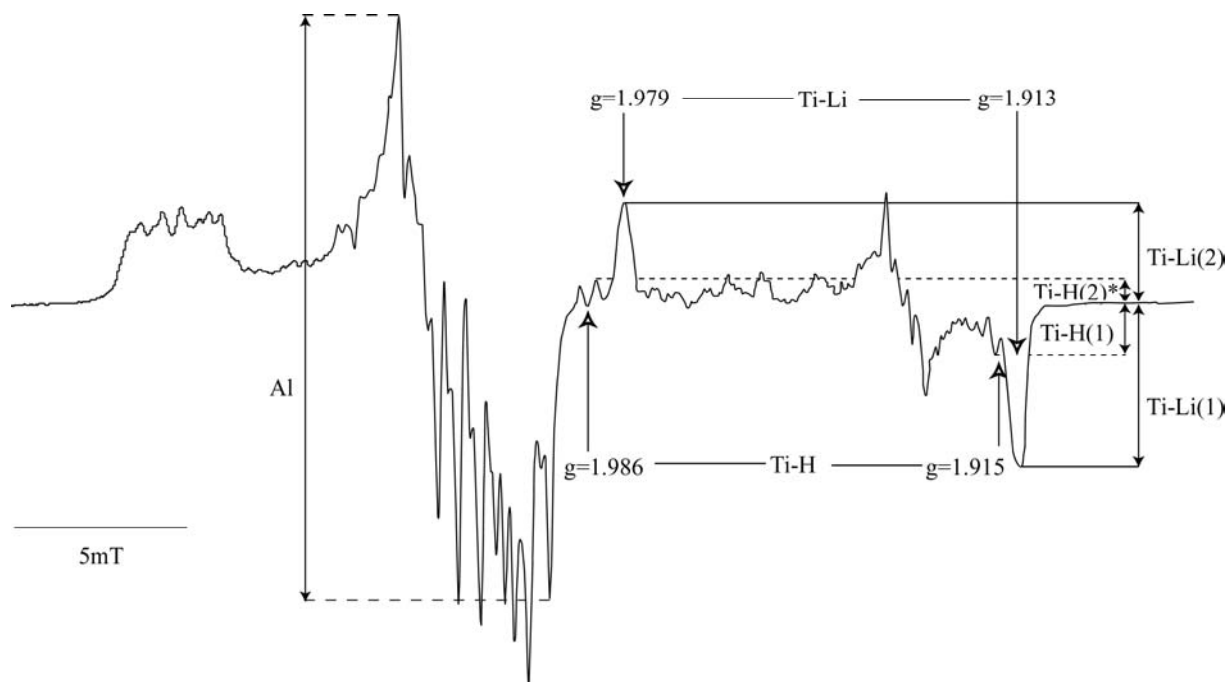
Bleaching experiments were performed on the MV sample. A part of this sample was bleached for 1368 h using the UVA lamps described above, another was bleached for 1128 h using a 150 watt uniform illumination (Thermo-Oriel solar simulator, type 960005) and another for 28 days by exposure to sunlight in Okayama (Japan) corresponding to a maximum of 220 hours of illumination in august 2006.

One aliquot of each natural F3 and MV quartz were isochronally heated. The samples were heated for 15 minutes at several temperatures varying from 150 to 390°C and the signal intensities of the Al, Ti-Li and Ti-H centers were measured for each temperature step.

### ESR measurements and $D_E$ calculation

All the samples were measured with a JEOL PX-2300 ESR spectrometer at Okayama University of Science, at 80 K, using a nitrogen gas flow system. The following parameters were used : microwave power 5 mW, width of the magnetic field 10 mT scanned in 1 min. with accumulation of 5 to 10 scans, modulation amplitude 0.1 mT, time constant 0.03 s., frequency of 100 kHz. Measurements were repeated five times, in order to obtain five different spectra for each aliquot, while rotating the sample tube within the cavity.

The ESR signals of the Al, Ti-Li and Ti-H centers were observed in all samples. The Al center intensity was measured from the top of the first peak to the bottom of the 16<sup>th</sup> peak of part of the main hyperfine structure (Yokoyama *et al.* 1985; Toyoda and Falguères, 2003). The Ti-Li center intensity was taken from the bottom of the peak at  $g = 1.913$  to the baseline and the Ti-H center signal intensity from the bottom of the doublet at  $g = 1.915$  to the baseline, according to Toyoda *et al.* (2000). Ti-Li center intensities for samples MV and F1 were also measured from the top of the peak at  $g = 1.979$  to the baseline and Ti-H center intensities from the top of the doublet at  $g = 1.986$  to the baseline, after a baseline correction (Fig. 1). For each center, the average and the standard deviation of the five measurements were calcu-



**Fig. 1.** ESR spectrum of Al and Ti-centers observed at 80 K for sample Fukui 1 irradiated with a dose of 1200 Gy. The intensities were taken as shown. \*Ti-H(2) intensity is measured after correction of the baseline at  $g = 1.986$  as this is influenced by the Al signal.

lated and the average ESR intensity was divided by the mass of the sample in the tube and by the amplitude of the measurement for normalization.

$D_E$  values were determined using the additive method for Al, Ti-Li and Ti-H centers and, for the Ti-Li and Ti-H centers, by interpolation of the natural intensity on a regenerative dose curve. In both cases, an exponential function was used.

#### Dose rate

In order to estimate the expected  $D_E$  for the samples from Fukui, the environmental dose rate was determined. For each sample, the gamma dose emitted by the surrounding sediment was measured *in-situ* using a portable gamma-ray spectrometer. These sediments were also measured by gamma-ray spectrometry in the laboratory with a pure germanium semiconductor detector system. Water content was estimated by weighting the sediment before and after drying for 3 days at 120°C and was 11.4% for F1 and 6.5% in F6. The saturation water content was also measured at the Nara Women's University and was 54% for F1 and 46% for F6.

## 4. RESULTS

### Choice of the Ti-signal

The Ti-Li peak at  $g = 1.913$  is not pure Ti-Li signal as it may be influenced by the presence of one of the two hyperfine lines of the Ti-H center. However, it is the easiest way to measure the Ti-Li intensity because the baseline for the line at  $g = 1.979$  (associated with the Ti-Li center only) is distorted by the Al center signal (**Fig. 1**) and must be corrected. In this study, the intensities of the Ti-Li peaks at  $g = 1.913$  and  $g = 1.979$  (after baseline

correction) have been measured for MV and F3, additive dose curves were constructed (**Fig. 2a**) and compared and  $D_E$  values were calculated and compared.

For each sample, the shapes of the two curves constructed from the two peaks related to the Ti-Li center are similar, and the difference between the calculated  $D_E$  values is less than 10% (lower than the individual error range of the  $D_E$ ). These results seem to indicate that the use of one or the other of the Ti-Li peaks gives the same  $D_E$ , *i.e.* the influence of one of the two hyperfine lines from the Ti-H center on the  $g = 1.913$  peak is negligible when measuring the Ti-Li center as indicated on **Fig. 1** (Ti-Li(1)).

Ti-H intensities determined from the bottom of the two lines at  $g = 1.915$  to the baseline and from the top of the doublet at  $g = 1.986$  (after a baseline correction) to the baseline are similar, as expected (**Fig. 2b**).

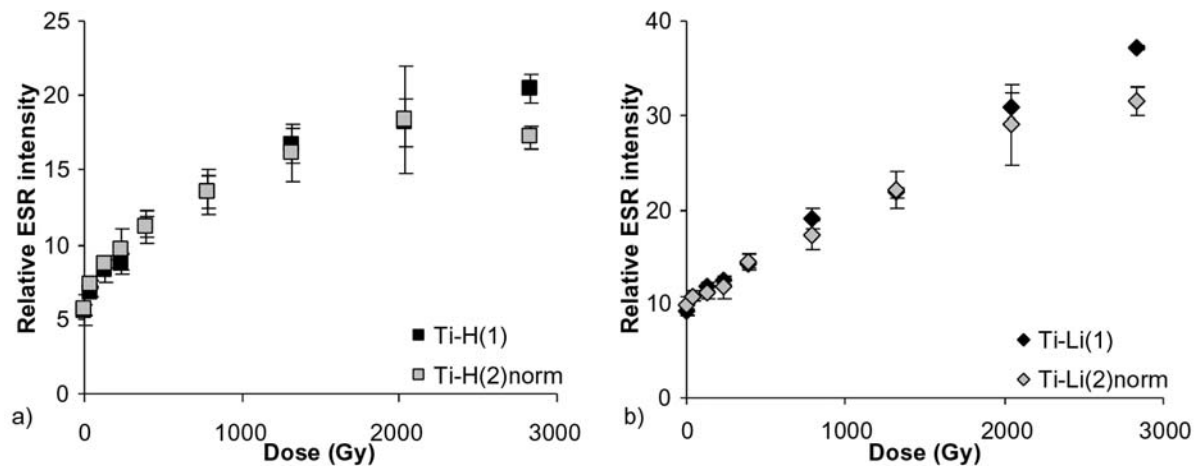
Consequently, the Ti-Li center intensity measured from the bottom of the peak at  $g = 1.913$  to the baseline and the Ti-H center signal intensity measured from the lower magnetic field of the two lines at  $g = 1.915$  to the baseline will be used in the study.

### Thermal stability of the defects

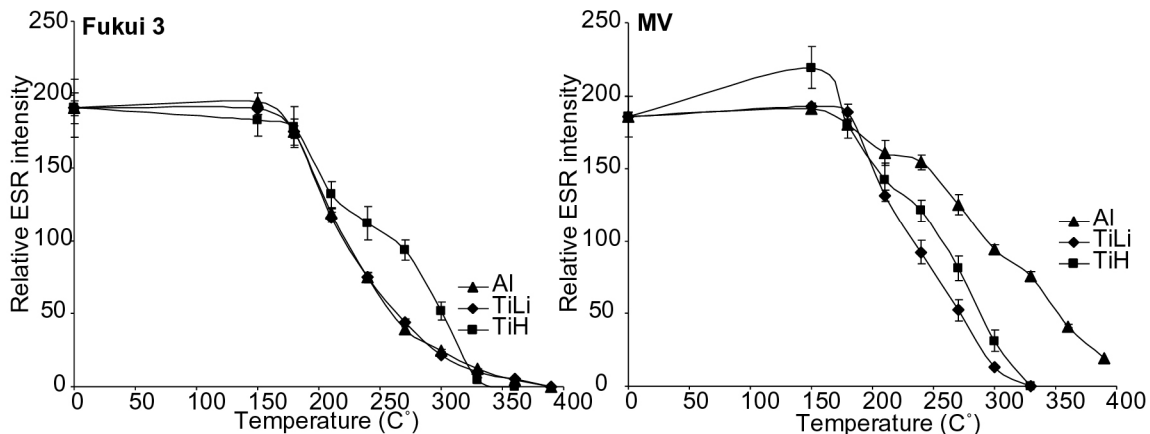
The results of the isochronal annealing experiments are shown in **Fig. 3**.

The ESR intensities of Al and Ti-center initially decrease at 180°C in both samples. The ESR signal of the Fukui samples is totally annealed at 390°C for Al and Ti-Li center and at 360°C for Ti-H. MV ESR signal is totally annealed at 330°C for Ti-Li and Ti-H centers but more than 400°C are necessary to remove the Al-center.

The shapes of the Al curve and Ti-Li curve after normalization are closely comparable for Fukui 3 indicating a similar behaviour of Ti-Li center and Al center with



**Fig. 2.** Additive dose curves obtained from the 2 different peaks of (a) Ti-Li center (Ti-Li(1) at  $g = 1.913$  and Ti-Li(2) at  $g = 1.979$ ) and (b) Ti-H center (Ti-H(1) at  $g = 1.915$  and Ti-H(2) at  $g = 1.986$ ) for the MV sample.



**Fig. 3.** Plot of ESR intensities versus temperature of heating for the Al, Ti-Li and Ti-H centers of natural and irradiated aliquot of F3 and MV. Intensities are normalized to the Al natural point for Ti-Li and Ti-H. Each step of heating was for a duration of 15 minutes.

heating. In the MV sample, Ti-Li center thermal stability is lower than the ones of Ti-H and Al centers.

A similar experiment was done by Toyoda and Ikeya (1991). The Ti and Al signals of quartz from Mannari granite (Japan) initially decreased at 170°C and 220°C and were completely annealed at 260°C and 380°C respectively. Beerten and Stesman (2005) observed a total annealing of both Ti-Li and Ti-H center in a quartz grain at 300°C. These results indicate that the thermal stabilities of Ti-H, Ti-Li and Al centers are sample dependent.

### Bleaching experiments

Bleaching rates calculated for the samples are presented in **Table 1**. The bleaching rate calculated after UVA illumination of the Al center is higher in the Fukui samples ( $42 \pm 2\%$  and  $43 \pm 2\%$  for F1 and F6 respectively) than in MV ( $38 \pm 5\%$ ) but always less than 50%. Ti-H center in MV is totally bleached, whatever the bleaching device employed. It is interesting also to remark that the Ti-Li center of MV is totally bleached using solar simulator but only 54% of the signal is erased after exposure to UVA lamp whereas the bleaching rate calculated on Al

center is the same using sun simulation or UVA illumination ( $38 \pm 5\%$  and  $36 \pm 6\%$  respectively).

### Equivalent doses

#### Additive and regenerative dose curves

Additive dose curves were constructed from Al, Ti-Li and Ti-H center intensities and regenerative dose curves

**Table 1.** Bleaching rate calculated for sample MV after 1368 h of illumination by a UVA lamp, 1128 h using a Thermo-orient solar simulator and by exposure to natural sunlight for 28 days in Okayama (Japan) corresponding to a maximum of 220 h of illumination in summer 2006 and for F1 and F6 after more than 1000 h of exposure to a UVA lamp.

Sample	Center	Bleaching (%)		
		UVA	Solar simulator	Sunlight
MV	Al	$38 \pm 5$	$36 \pm 6$	-
	Ti-Li	$54 \pm 5$	100	-
	Ti-H	100	100	100
F1	Al	$42 \pm 2$	-	-
F6	Al	$43 \pm 2$	-	-

were constructed from Ti-Li and Ti-H center intensities only. In the additive and regenerative doses curves, data were fitted with an exponential function. The  $D_E$  obtained by the additive dose method and the regenerative dose method are presented in **Table 2** and in **Fig. 4**. The  $D_E$  obtained by the two methods are in agreement for Ti-H center in F1 and F6 samples and for Ti-Li center in MV and F1 samples.

Similar equivalent doses were expected when using the two measurement methods, however some differences were observed between the equivalent doses calculated by regeneration and by additive method on Ti-Li for F6 and on Ti-H for MV. One possible hypothesis is a change of sensitivity of the center to irradiation after heating. To test this, the regenerative dose curves and the additive dose curves were compared by adding the value of the  $D_E$  determined by regeneration to the doses received by the aliquots used for building the additive curve (**Fig. 5**). As a result, the shapes of the regenerated curve and the additive curves look similar, both for Ti-Li and for Ti-H, in all the samples and seem to indicate that no change of sensitivity occurred. Then, the differences in the equivalent doses calculated by the two methods could be due to differences in the regression curves parameters, related to the large errors on the intensities of the Ti-H center (inherent to the strong angular variation during measurement), or to the large extrapolation necessary in the equivalent dose calculation for Ti-Li center, especially for sample F6 (**Fig. 6c**) in the case of the additive method. It is also important to point out that the errors on the  $D_E$  calculated using regeneration are systematically smaller than those obtained using the additive dose method.

**$D_E$  and expected  $D_E$**

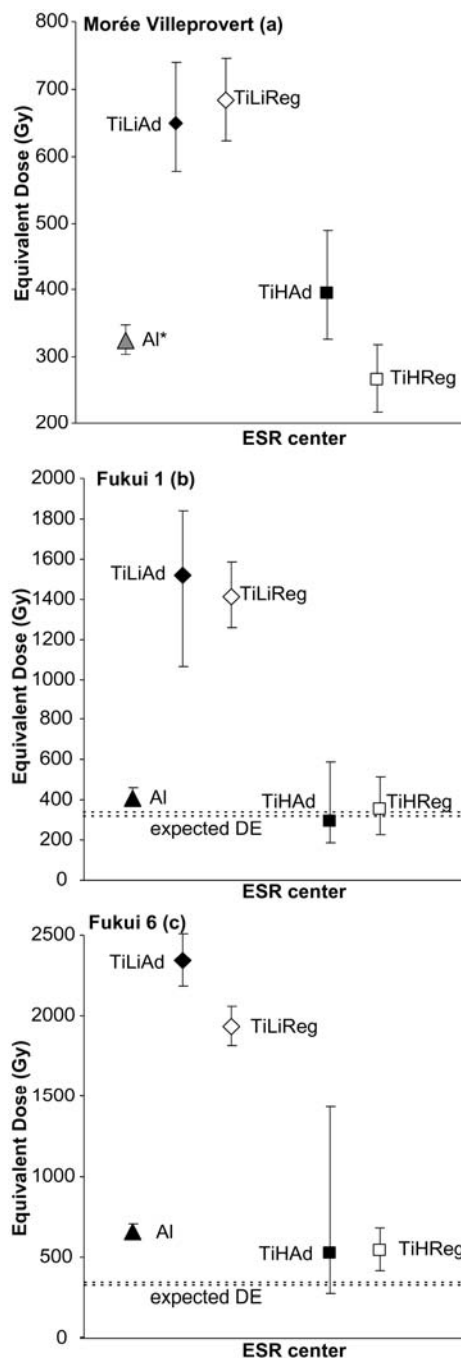
The expected  $D_E$  for the Fukui samples was determined using the current water content. The expected dose range is 314-332 Gy for Fukui 1 and 321-328 Gy for Fukui 6 (**Fig. 4** and **Table 2**). If we consider the saturation water content, the minimum equivalent doses can be determined as 153 Gy for F1 and 191 Gy for F6.

In the MV sample, we can observe an agreement between the  $D_E$  previously determined for the Al center and the  $D_E$  determined from the Ti-H center, even though this is different when using the regenerative dose method or the additive dose method. In the F1 and F6 quartz, the Al center provided overestimated  $D_E$  values however this is less important for F1 than for F6.

**Table 2.**  $D_E$  calculated using the additive dose curve method and the regenerated dose curve method for samples MV, F1 and F6. \* Equivalent dose previously determined by Voinchet 2002.

	MV		Fukui 1			Fukui 6		
	$D_E$ (Gy)	+ -	$D_E$ (Gy)	+ -	-	$D_E$ (Gy)	+ -	-
Expected			314-332			321-328		
Al ad.	326*	22 22	411	47 39		662	45 41	
Ti-Li ad.	650	90 73	1520	322 455		2338	170 151	
Ti-Li reg.	683	63 60	1411	173 152		1932	124 117	
Ti-H ad	394	94 67	297	288 108		528	907 252	
Ti-H reg	266	53 48	352	162 126		541	145 121	

F1 quartz provided a  $D_E$  value calculated using the Ti-H center in agreement with the expected  $D_E$  whereas the Ti-H center  $D_E$  of F6 is higher than expected. Finally, the equivalent doses calculated from the Ti-Li center are strongly overestimated in the 3 samples and whatever the method of determination we used. Nevertheless, it is interesting to note that the difference of  $D_E$  using Ti-H and Ti-Li centers is higher in the marine quartz than in the fluvial quartz.



**Fig. 4.** Representation of  $D_E$  calculated using the additive dose method (Ad) and the regenerative dose method (Reg) for Ti-Li and Ti-H center of MV (a), Fukui 1 (b) and Fukui 6 (c) compared with the  $D_E$  obtained on Al center for MV and with the expected  $D_E$  for F1 and F6. \* Equivalent dose previously determined by Voinchet 2002.

## 5. DISCUSSION

### $D_E$ calculation

The main, and strong interest of the regenerative dose is that no extrapolation is involved, only interpolation and so, higher precision is attainable. Indeed, in this study, the additive method led to large errors on the  $D_E$  when large extrapolations had to be done whereas the errors on the regenerative  $D_E$  values are smaller (Table 2). Moreover, the errors on the measured intensities for the Ti-H center, large when using the additive method, are smaller after the sample has been heated (Figs 5b, d, f). Finally,

the dose response for the regenerated aliquots is systematically better than for the additive ones. Indeed, using the additive method, a larger scattering of the data around the best fitting function is observed (Fig. 6). The same fact was noticed by Grün *et al.* (1999) and led them to apply the regeneration technique.

Nevertheless, a wrong equivalent dose can be obtained by regeneration technique if a change of sensitivity of the center occurs after heating. Grün *et al.* (1999) observed no apparent change in sensitivity between the additive and the regenerative dose response curves after heating; Imai *et al.*, (1992) detected that the growth rate of the Ti-center with irradiation decreases gradually as

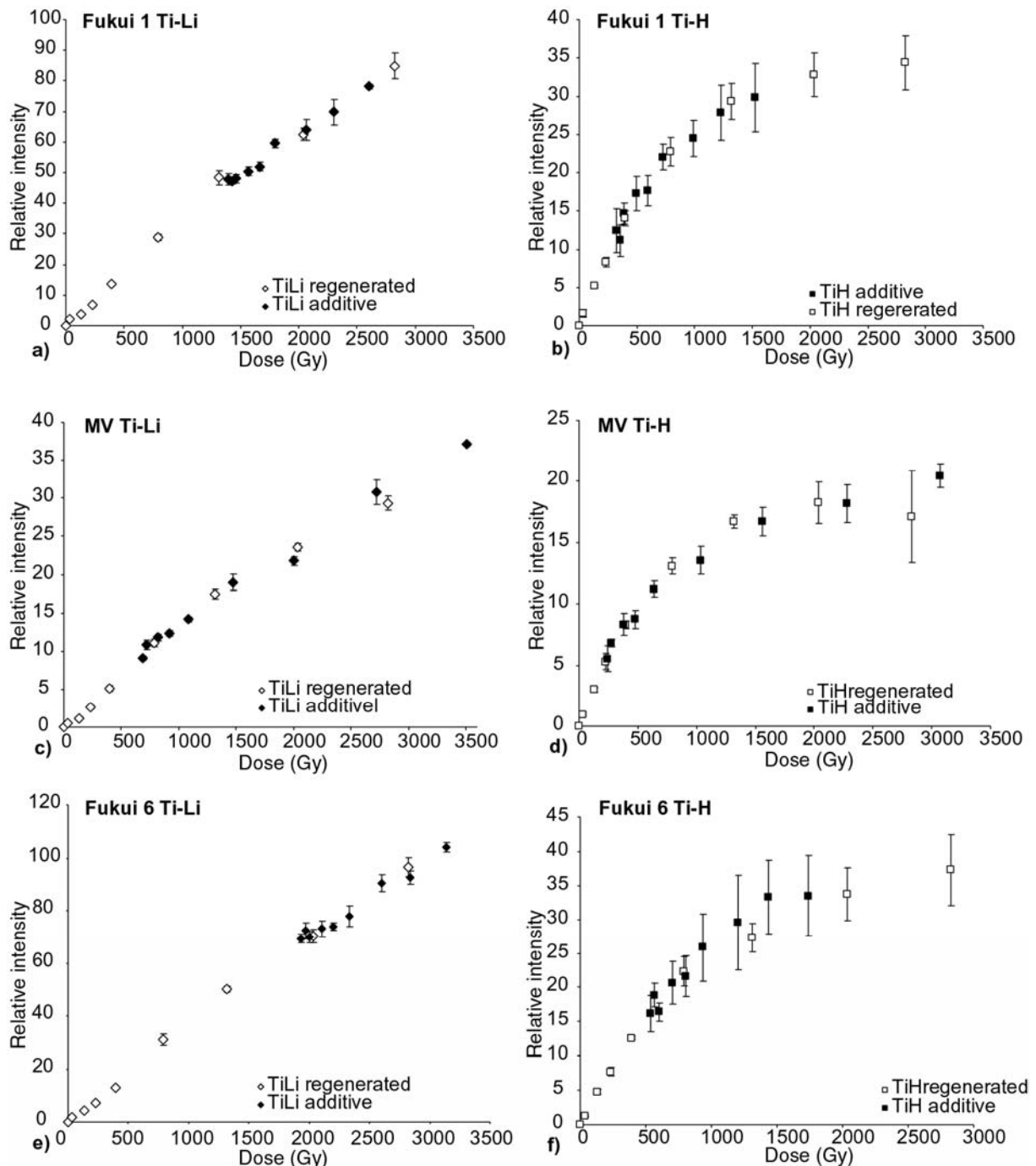
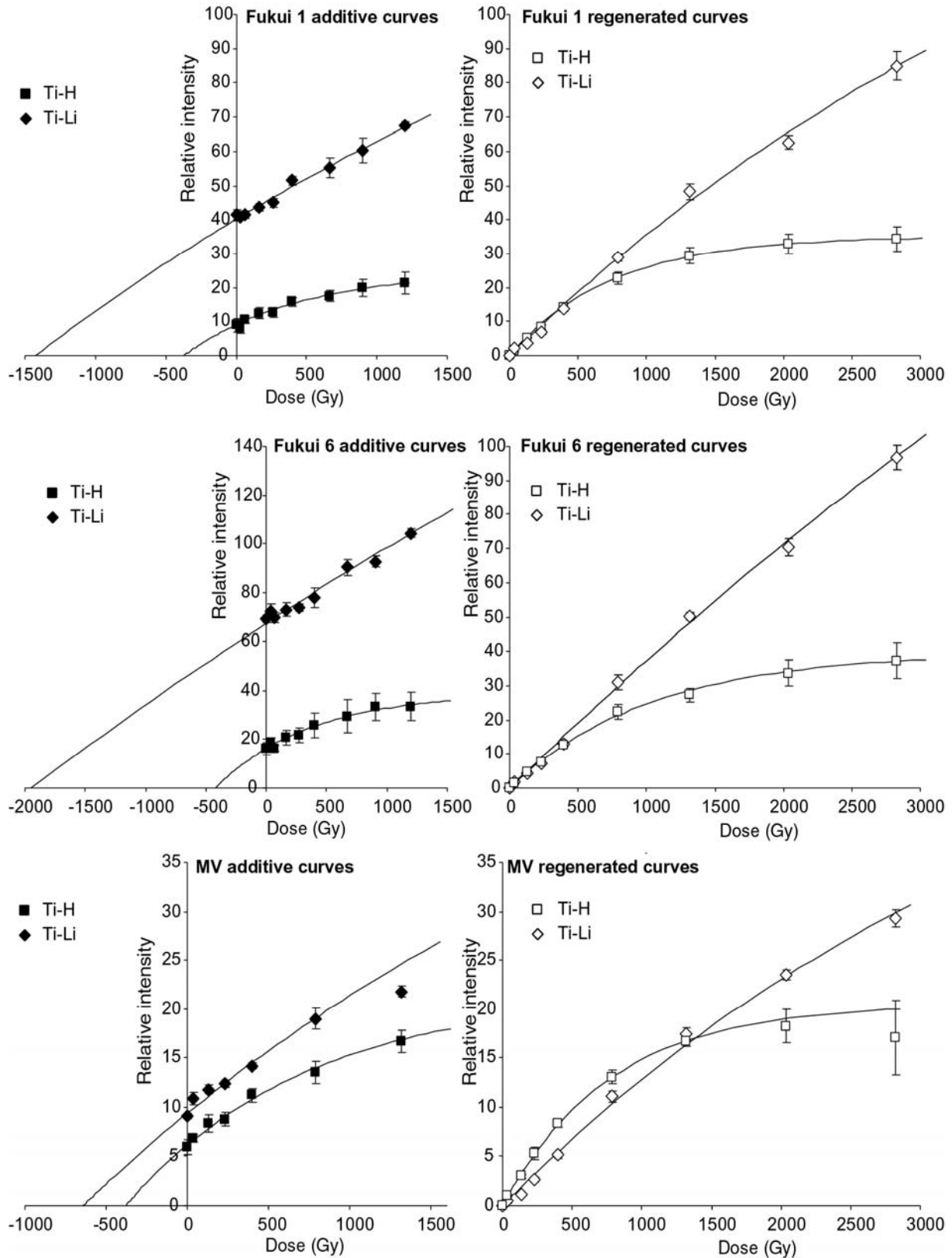


Fig. 5. Superposition of the regenerative and the additive intensities of the Ti-Li and Ti-H centers for MV, F1 and F6. The  $D_E$  obtained by regeneration was added to the dose received by each aliquot of the additive dose in order to overlay the 2 curves.

the temperature of heating increases, but the experiment was done with temperature of resetting higher than 400°C; the regenerated and exponential curves for a single grain analysed in Beerten and Stesmans (2005) appear

to follow a similar trend, even after two consecutive regenerations at 300°C for 2 h, however the same authors (Beerten and Stesmans, 2006) observed also a grain dependence of the sensitivity change after thermal anneal-



**Fig. 6.** Comparison of regenerative dose curves and additive dose curves of the Ti-Li and Ti-H centers fitted using an exponential function for MV, F1 and F6.

ing, under the same conditions. In this study, we observed some differences between the regenerated  $D_E$  and the additive  $D_E$  that could be linked to a change of sensitivity, but we also observed that the regenerated curve and the additive curve, after sliding, have a similar shape (**Fig. 5**). As no significant sensitivity change is detected, the regeneration method could then give reliable results. Furthermore, we noticed for the Ti-Li center that the higher the  $D_E$ , the greater the difference between the additive and the regenerative  $D_E$ . Under these conditions, the additive  $D_E$  could be incorrectly estimated due to the large extrapolations necessary for  $D_E$  calculation.

One other important fact is that in the studies mentioned above, the data were fitted with a linear function. In this study, we had to fit the data with an exponential function, especially for Ti-H. The saturation of the Ti-H center occurs here at lower doses than for Al and Ti-Li centers, and the linear section of the curve is limited to the first few hundred grays (up to about 250 Gy for MV). A regenerative technique incorporating a linear function reduces the error range on the  $D_E$  compared with an exponential function, but can be applied on the Ti-H center only for low  $D_E$  values. The Ti-Li center saturates at high doses and a fitting with linear function is possible for  $D_E$  up to several kGy but unfortunately, in this specific case, the natural intensities measured for Ti-Li, and then the  $D_E$ , are extremely high and do not match up anymore with the linear section of the regenerative dose curves.

#### Ti-H center

The strong advantage of the Ti-H center is to be quickly and totally optically bleached (Toyoda *et al.*, 2000; Tissoux *et al.* 2007). In this study, no Ti-H signal was remaining in sample MV after exposure to UVA as well as to the solar simulator, and even after only 28 days of exposure to the natural light. This last one corresponds to 220 h of illumination considering 7 to 8 hours of sunlight per day, all days, and should be considered as a maximum.

The main problem is to ensure that we can recover the dose received by the grains using this center. Indeed, some underestimations of the  $D_E$  determined using the Ti-H center were reported by Tissoux *et al.* (2007) for Middle Pleistocene samples ( $D_E$  expected >300Gy) and by Beerten *et al.* (2006) for samples with  $D_E$  higher than 180 Gy. In both cases, one hypothesis was the possible low stability of the Ti-H center. According to the thermal annealing experiment, the thermal stability of Ti-H center in our samples is not lower than the one of Ti-Li. Another hypothesis proposed by Beerten and Stesman (2006) to explain the underestimation of  $D_E$  determined by Ti-H and the overestimation calculated using Ti-Li was a link between the Ti-H center and Ti-Li center. Such a transfer may exist but cannot be observed on the isochronal curves (**Fig. 3**). In this study, only the regenerated dose method on MV provided an underestimated Ti-H equivalent dose. However we have to keep in mind that the Ti-H  $D_E$  of F1 and F6 could be overestimated, due to the presence of a residual dose at the time of deposition. To avoid this problem, experiments are planned on samples for which residual dose is not thought to exist.

The three samples F1, F6 and MV are from two different origins but the saturation of the Ti-H center is in the same range. It implies that measurement of  $D_E$  up to 1000 or 1500 Gy using this center is possible.

#### Ti-Li center

The equivalent doses determined using the Ti-Li center of quartz for samples MV, F1 and F6 are highly overestimated. The regenerated doses curves for Ti-Li and Ti-H (**Figs 6b, d, f**) show that when the samples receive a dose less than around 500 Gy, as we expect here, the ESR intensity of Ti-Li should be equal (**Figs 6b** and **d**) or smaller (**Fig. 6f**) than the ESR intensity of the Ti-H center (this assumption is valid if we consider no change of sensitivity of the center with heating when we construct the regenerated curve). However, the additive dose curves (**Figs 6a, c, e**) show a natural Ti-Li ESR intensity much higher than the Ti-H one. As Ti-H and Ti-Li centers are supposed to have received the same natural irradiation dose, two hypotheses can explain such an overestimation of the natural Ti-Li ESR intensity. The first was described above and is a possible transfer between the Ti-H center and the Ti-Li center. This would raise serious implications for future dating using these centers, so further investigations are needed to ensure the presence or absence of relation between the two centers. In this study, we don't have any indication of such a transfer. Then, the most probable and simplest assumption to explain such high Ti-Li  $D_E$  values is incomplete bleaching of the Ti-Li center when the sediment was deposited, *i.e.* the presence of an important residual dose in Ti-Li center at the time of deposition of the sediment.

The Ti-Li  $D_E$  is systematically more overestimated than the one determined from the bleachable component of Al center. Such a strong overestimation of the Ti-Li  $D_E$  has been reported previously (Tanaka *et al.*, 1997; Beerten *et al.*, 2006). However, the bleaching experiments made by Toyoda *et al.*, (2000) and Tissoux *et al.* (2007) demonstrated that the Ti-Li center is more rapidly bleached than the Al center by the sunlight. It is then surprising to notice that the Ti-Li center in this study was apparently less bleached than the bleachable component of the Al center at the time of deposition. Bleaching experiments made in this study on sample MV indicate that the Ti-Li can be totally bleached by the sunlight but showed a lower sensitivity to UVA, whereas the Al center bleaching is similar using UVA only or using a solar simulator (**Table 1**). Further studies are then necessary to determine the relationship between the deposition mode of the sediment and the quantity and quality of the illumination received by the quartz grain, but one hypothesis is that the Ti-Li was not bleached sufficiently due to the deposition mode (in water).

#### Dating

According to the multiple-center method (Toyoda *et al.*, 2000) when all centers are satisfactorily bleached at the time of deposition, the three  $D_E$ 's values should coincide. Here we assumed that Ti-Li was not totally bleached at the time of deposition, but we can compare the  $D_E$  obtained by Al center and Ti-H center.



In MV, the difference of  $D_E$  obtained for the Ti-H center using the additive and the regenerative dose method do not allow us to conclude firmly an agreement between the  $D_E$  calculated with the Al and Ti-H, but they are close enough to presume satisfactory bleaching of the Ti-H and Al centers at the time of deposition.

In F1 and F6, the Al  $D_E$  is higher than the Ti-H  $D_E$ , and also higher than the expected  $D_E$ , indicating that the Al center was probably not totally bleached when the sediment was deposited. The comparison of the Ti-H  $D_E$  with the expected  $D_E$  indicates that if the bleaching of Ti-H center in F6 was not sufficient, the one of F1 seems satisfactory (**Table 2**).

The difference in the  $D_E$  obtained using the Al, Ti-Li and Ti-H centers is interpreted as reflecting the quantity and quality of sunlight received by the sample: the smaller the difference, the better the bleaching. In our sample, it is obvious that the fluvial sample received more complete bleaching than the marine sample of the first locality (F1) itself better bleached than F6 in the second locality. Tanaka *et al.*, 1997 also related insufficient bleaching of marine sediment sampled about 50 km north of our sample locations. We can suppose that the grain-sizes we used (200-500  $\mu\text{m}$ ) were rapidly deposited in the water and were not sufficiently exposed to sunlight. The bleaching of the fluvial quartz centers is apparently much more complete, maybe due to an extended transportation, a smaller grain size, and thus a better bleaching of the sediment from the river in comparison to the coarse-grains from the sea.

## 6. CONCLUSION

The Al, Ti-Li and Ti-H centers of quartz grains of three samples from two deposits were observed. Some differences in behaviour were noticed, particularly, the thermal stability of the centers proved to be sample dependent. In contrast, for all the samples, no change of sensitivity could be observed between the additive dose curve and the regenerative curve. This one represents an encouraging observation, which may provide several advantages. In our samples, the bleachable component of the Al-center was systematically more fully bleached than the Ti-Li center, possibly due to a difference of sensitivity to UVA of these two centers. Finally, the resetting of the ESR centers was apparently more complete in the fluvial sample than in the marine sample.

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