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OPTICAL BLEACHING AND DOSE-RESPONSE BEHAVIOUR OF AL AND TI CENTERS IN QUARTZ

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ABSTRACT: Zuccarello A. R. *et al.*, *Optical bleaching and dose-response behaviour of Al and Ti centers in quartz.* (IT ISSN 0394-3356, 2011).
Electron spin resonance (ESR) is one of the most suitable methods for the dating of sedimentary events during the Quaternary. However, in some cases, related to the specific samples under examination, ESR signals need to be previously analysed for the correct application of the methodology.
In this paper, a methodological study for ESR dating of geological sediments, by means of Aluminium (Al) and Titanium (Ti) centers in quartz, was carried out. In this case, it is necessary to verify the optical bleaching process of ESR centers and to study the behaviour of the corresponding signal intensity *vs* absorbed dose. The maximal bleaching percentage of these centers was evaluated exposing samples to the light from a solar simulator for different times. The results showed, on the one hand, that Ti center is totally bleachable, while the Al center is characterized by a hard to bleach component, whose evaluation is necessary to correct the ESR equivalent dose. On the other hand, in the case of Ti-center, the growth curve of ESR signal intensity *vs* dose showed a trend that, for high values, presented strong deviations from that of SSE (Single Saturation Exponential), normally used for equivalent dose determination.

RIASSUNTO: Zuccarello A. R. et al., Optical bleaching and dose-response behaviour of Al and Ti centers in quartz. *(IT ISSN 0394-3356, 2011).*
La risonanza di spin elettronico (ESR) è uno dei metodi più adatti per la datazione di eventi sedimentari del Quaternario. Tuttavia, a seconda della tipologia di campione in esame, è necessaria un'attenta analisi dei segnali ESR per la corretta applicazione della metodologia.
Il lavoro presentato in questa occasione riguarda uno studio metodologico per la datazione di sedimenti geologici da segnali ESR dei centri alluminio (Al) e titanio (Ti) dei cristalli di quarzo. In questo ambito, è necessario verificare l'avvenuto processo di bleaching ottico dei suddetti centri e analizzare l'andamento dell'intensità dei relativi segnali in funzione della dose assorbita. La percentuale massima di bleaching ottico è stata valutata esponendo i campioni alla luce proveniente da un simulatore solare per tempi differenti. I risultati ottenuti hanno mostrato, da un parte, che il centro Ti si svuota totalmente e in tempi relativamente veloci, a differenza del centro Al caratterizzato da una componente hard to bleach*, la cui valutazione si rende indispensabile per la correzione della dose equivalente ESR. D'altra parte, nel caso del centro Ti, la curva di crescita del segnale ESR in funzione della dose ha evidenziato un andamento che, ad alte dosi, si discosta da quello descritto matematicamente dalla funzione SSE (Single Saturation Exponential), normalmente utilizzata per la determinazione della dose equivalente.*

Keywords: Sediments, dating, ESR

Parole Chiave: sedimenti, datazione, ESR

1 - INTRODUCTION

Since the first successful experiment performed by Zavoisky (1945), electron spin resonance (ESR) has been applied to many fields of chemistry, physics, biology and geology. The interest in archaeological and geological ESR dating began after the pioneering work of Ikeya (1975) on a stalactite from Akiyoshi Cave in Japan. Since then, it has been applied to many materials and further studies have been made to improve the method. The most important dating applications concern minerals which are precipitated or biogenically secreted, such as carbonates in speleothems, mollusc shells, corals, …, or hydroxyapatite in tooth enamel, as well as materials which were heated in the past, such as volcanic minerals, and optically bleached (signal resetting by light exposure) (Ikeya, 1993). In this last field, ESR dating has been widely used to date sediments using signals from quartz inclusions as it contains several paramagnetic centers (Yokoyama *et al*., 1985; Tanaka *et al*., 1997; Voinchet *et al*., 2003; 2004; Tissoux *et al*., 2007; 2008; Rink *et al*., 2007). In this case, quartz is used as a dosimeter accumulating dose as a result of ionising radiation in the environment or inside the crystal. The assumption is that radiation-induced signals in quartz crystals are reduced or zeroed by daylight exposure during transportation and sedimentation, and then regrow during the burial of quartz in sediments due to exposure to natural radiation. The total absorbed dose (the equivalent dose D_E) is obtained by the additive dose method and converted to an ESR age by assessing the annual dose rate (Ikeya, 1993). ESR shares with OSL (Optically Stimulated Luminescence), the most common dating method for sediments, both the object of the measurements, quartz crystals, and the mechanism for zeroing of the centers connected to sunlight exposure. Nevertheless, ESR dating has a larger time range with respect to OSL (not more than some hundreds of thousands of years). Rink *et al*. (2007) showed, in fact, that ESR yields agreement with independent age control up to about 2.5 Ma, extending the range dating of optically exposed quartz in sediments by a factor of about 5: this places it among the most suitable methods for the Quaternary period.

However, for the optimal application of the technique, it is important to know the optical bleaching behaviour of the ESR dating signals. The Aluminium (Al) and Titanium (Ti) related impurity defects are usually used to date quartz grains by ESR method. They are measured at cryogenic temperatures (77 K), differing from other paramagnetic centers typical of materials cited above. Bleaching experiments showed that Al-center has two components, one bleachable and the other non-bleachable (Yokoyama *et al.*, 1985; Laurent *et al.*, 1998; Voinchet *et al.*, 2003; 2004; 2007). Thus, the presence of this last component must be taken into account in order to determine the real total dose absorbed by samples since their burial after the bleaching process. Similar experiments on Ti-center have shown that it can be fully zeroed (Tanaka *et al.*, 1997; Toyoda *et al.*, 2000; Rink *et al.*, 2007; Tissoux *et al.*, 2007; Gao *et al.*, 2009). In the present work we used the Ti-Li center because the two other types of Ti signals (Ti-H and Ti-Na) were not detected above the background in samples under examination.

In this report we tested the effect of the Al non-bleachable component and, following the additive dose protocol, artificial gamma irradiations were made in order to verify the degree of the eventual correction and to analyse the trend of Al and Ti-Li signals *vs* dose.

2 - EXPERIMENTAL

2.1 Sample preparation and irradiation

Sedimentary quartz samples from marine terraces of the South of Italy were used for the study. The samples preparation was carried out under controlled lighting with our laboratory standard protocol (adapted from Wintle, 1997 and cited references; Aitken, 1998) to provide a 100-200 μm quartz fraction. Each sample was treated with 10% HCl for 1h to remove carbonates, 35% H_2O_2 for at least one day to remove organic material, followed by washing with distilled water and drying. Sodium polytungstate was used to separate the quartz from the feldspars and other silicate minerals. Then, samples were etched by 40% HF for 45 min to remove the outer part of the quartz grains that was affected by alpha irradiation and fluorides were eliminated using 10% HCl for 10 min. Finally, quartz grains were rinsed with distilled water and dried.

Artificial irradiation was performed using a ^{60}Co calibrated source at the *Ente per le Nuove tecnologie, l'Energia e l'Ambiente (Casaccia, Rome)*. Additional doses up to 25000 Gy were given.

2.2 Bleaching experiments

Optical bleaching experiments were performed to evaluate the behaviour of the ESR intensity under sunlight exposure. The quartz samples were divided into seven aliquots of about 100 mg. Each aliquot was then put in a stainless steel dish, where grains were spread out as a thin layer on a surface of 2.5 cm in diameter. The dishes were placed on a copper plate with a water cooling system. Quartz grains were bleached using a 150 W ozone free xenon lamp (66002 Oriel solar simulator) for different exposure times. The air mass filters A.M.0+A.M.1 were used to simulate solar spectrum at ground level when the sun is directly overhead. The illuminance was about 10^5 lux and the samples were continuously exposed from 0 to 400 h.

2.3 ESR measurements and DE calculation

ESR measurements were carried out on a JEOL FA-100 X-band spectrometer in a finger dewar cooled to 77 K by liquid nitrogen, using microwave power of 5 mW and modulation amplitude 0.16 mT. The Al-center intensity (see 1 in Fig. 1) was measured from the top of the first peak to the bottom of the last peak of the part of the main hyperfine structure (Yokoyama *et al.*, 1985), while the Ti-Li intensity (see 2 in Fig. 1) was evaluated from the bottom of the peak at g = 1.913 to the baseline (Toyoda *et al.*, 2000). ESR intensities were normalized by the aliquots weights. A single saturating exponential (SSE) function was fitted to the experimental data points in order to get D_E value (Apers *et al.*, 1981):

$$I(D) = I_S\left(1 - e^{-(D+D_E)/D_S}\right)$$

where $I(D)$ is the measured ESR signal intensity, D the laboratory added dose, I_S the ESR saturation level and D_S the characteristic saturating dose. D_E value was calculated by extrapolating the SSE function to the zero ordinate, considering only the first steps of irradiation. For the Al-center, this value is comprehensive of the residual dose D_R due to a non-bleachable component, evaluable from the bleaching response to the solar simulator light. Therefore, the corrected equivalent dose D_E is determined by subtracting D_R from the total dose. For the Ti-center the D_E value was obtained directly by additive dose method, assuming that complete optical bleaching of the associated ESR signal has occurred in the sedimentation phase.

3 - RESULTS AND DISCUSSION

All the samples analysed exhibit ESR signals of Al and Ti-Li centers, as shown in Figure 1 where a typical spectrum of a natural sample is reported.

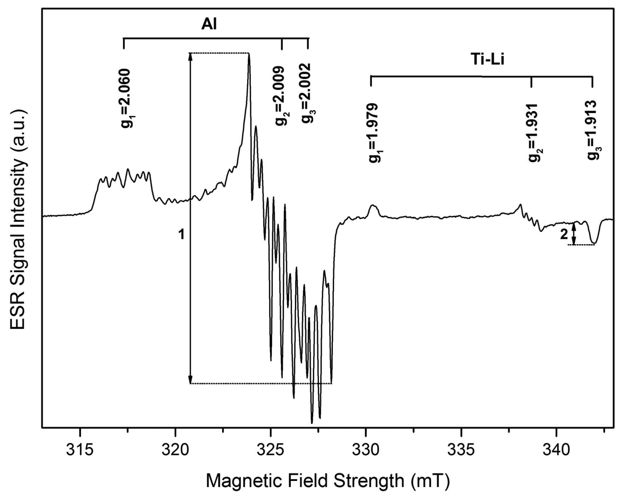

Figure 1 - ESR signals of Al and Ti-Li centers observed at 77 K for natural quartz grains extracted from marine terrace sediments.

Segnali ESR dei centri Al e Ti-Li di quarzo estratto da terrazzi marini osservati a 77 K.

Bleaching experiments showed that ESR intensity decreased with illumination time, even if with a different decay-rate for the two Al and Ti-Li centers. An example of experimental Ti-Li intensity decay of natural samples is plotted in Figure 2a. It can be observed that, in a time less than 200h, it is totally erased. For this reason, the equivalent dose D_E was calculated directly by the additive dose method applied to Ti-Li signal, without any subtraction of residual dose (Fig. 2b).

For the Al-center, the intensity reduced and then reached a plateau representing the residual intensity linked to the non-bleachable component by sunlight exposure. In this case, the data were fitted (Fig. 3 on the left) using the exponential function, proposed by WALTHER and ZILLES (1994): $y = ae^{(-bx)} I_0$, in which x is the exposure time to the sunlight, y is the measured ESR intensity, a and b are the parameters of the fit and I_0 the residual intensity. From this last value and from natural ESR signal intensity I_{nat}, it is possible to calculate the maximal bleaching percentage that, using the formula $Bl(\%) = \frac{I_{nat} - I_0}{I_{nat}}$ x 100, was between 20% and 30% for samples analysed. For this reason, the equivalent dose evaluated from Al center was corrected for the presence of the residual level equal to that obtained in the laboratory bleaching, following the procedure described in VOINCHET *et al*. (2004). In this way, only the bleachable component of the Al-center was taken into account (Fig. 3).

From the point of view of optical bleaching experiments, it can be observed that the use of Ti-Li center could be more practical, above all when it and Ti-H and Ti-Na signals (when observed) give concordant D_E values, as reported in TOYODA *et al.* (2000). However, it is important to consider also the expected equivalent dose of samples under examination and assuring that the ESR center used for its determination is not saturated. With this aim, we irradiated the samples up to 25000 Gy and the results from ESR measurements are reported in Figure 4. In the case of the Al center (Fig. 4a), we observed a rising in the dose-response curve, suggesting the possibility to determine higher D_E than those here reported, as also suggested by RINK *et al.* (2007). The different approach for Ti-Li center (Fig. 4b) that already saturated for doses of some thousands of

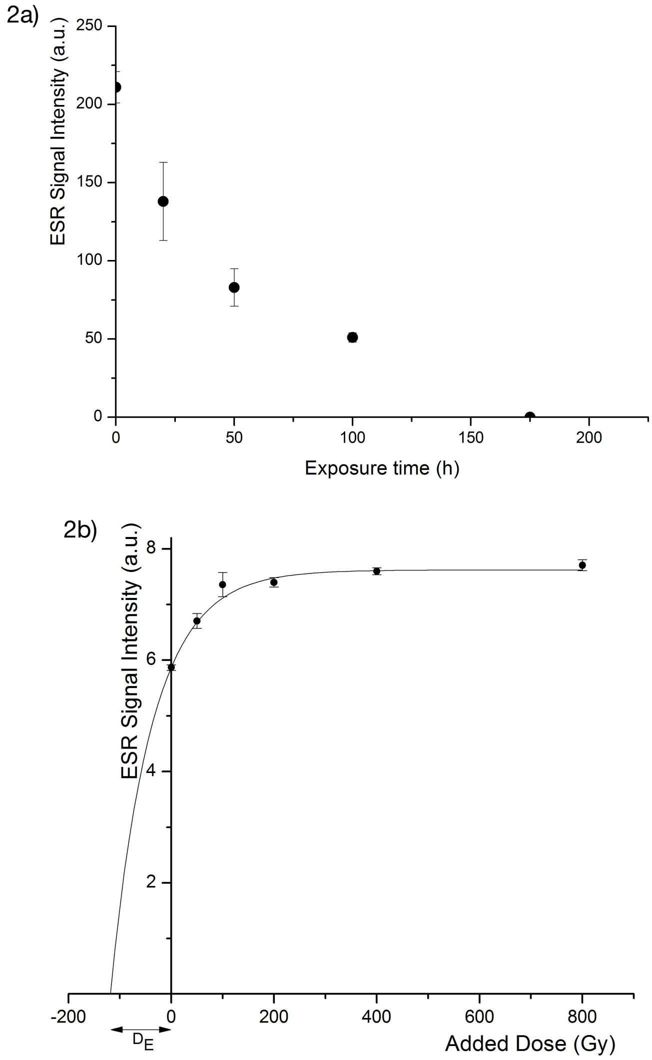

Figure 2 – Example of optical response of the Ti-Li center to the solar simulator light exposure (a) and growth curve of the same signal *vs* dose (b).

Esempio di curva di decadimento del centro Ti-Li in funzione del tempo di esposizione alla luce proveniente dal simulatore solare (a) e curva di crescita dello stesso segnale in funzione della dose (b).

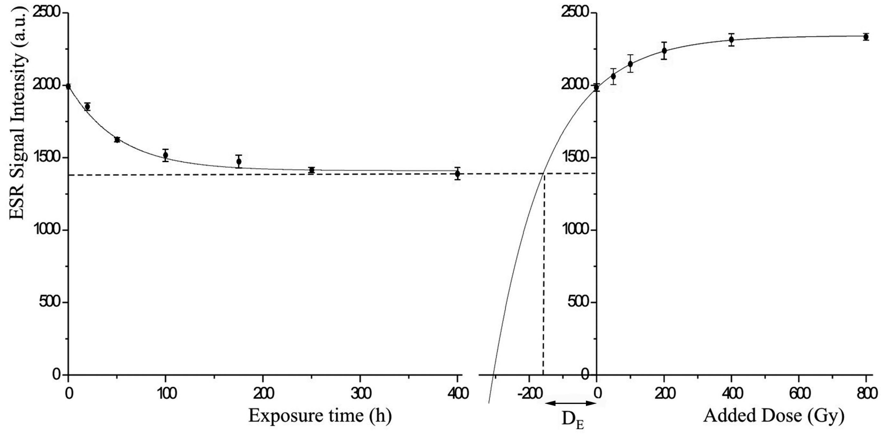

Figure 3 – Example of optical response of the Al-center to the solar simulator light exposure (on the left) and of growth curve of Al intensity *vs* dose (on the right), together with the procedure described in VOINCHET *et al*. (2004) for the determination of the corrected D_E, calculated only from the bleachable component.

Esempio di andamento del segnale del centro Al in funzione del tempo di esposizione alla luce proveniente dal simulatore solare (a sinistra) e di curva di crescita dello stesso in funzione della dose (a destra), nonché della procedura descritta in VOINCHET et al. *(2004) per la determinazione della D_E corretta, calcolata solo dalla componente otticamente svuotabile.*

Gy, as also observed in Tissoux *et al*. (2007). At this state, the trend of the experimental data allows the use of the lower first steps of irradiation as SSE function does not fit them for the presence of a knee region not followed by saturation.

4 - CONCLUSIONS

For the dating of sediments, it is very important to evaluate the optical bleaching behaviour of the signal being used for dating. The Al and Ti-Li signals of samples from marine terrace sediments were observed and their response to sunlight exposure was investigated. This confirmed the need for using only the bleachable portion of Al-center while no correction was necessary in the case of Ti-Li signal. On the other hand, the methodological study at doses up to 25000 Gy led to some observations. In particular, Al signal dose response-curve presented a trend well described by SSE function, while for Ti-Li center further measurements and phenomenological models are necessary to better understand the behaviour of the experimental data. In fact, anomalous behaviours of the ESR signals may influence the age determinations.

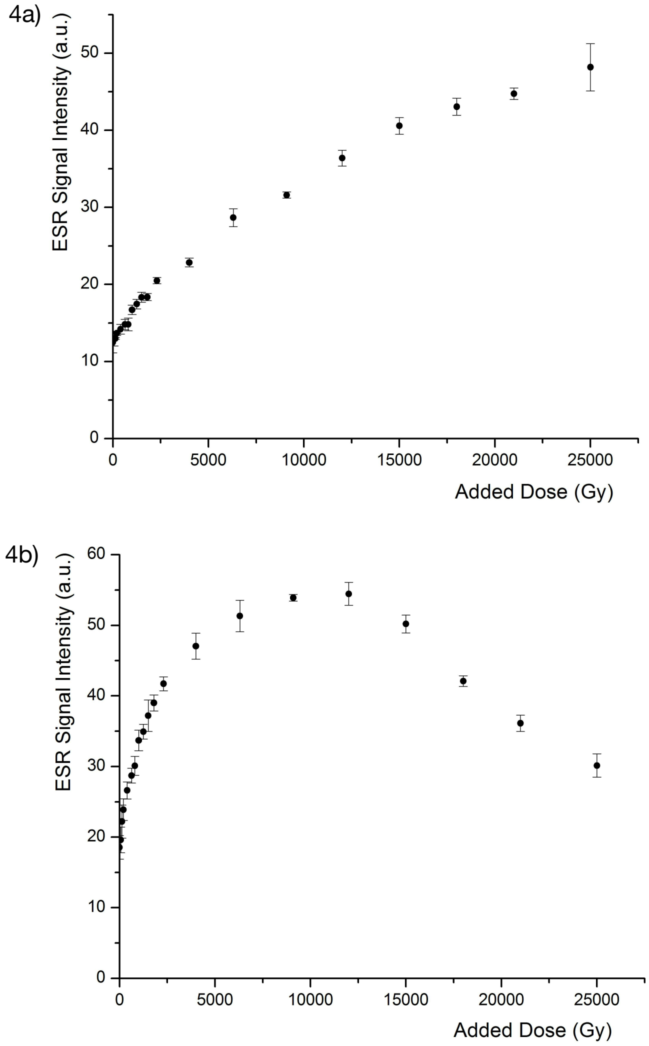

Figure 4 - Example of growth curve of ESR intensity of Al (a) and Ti-Li (b) signals for γ irradiated aliquots up to 25000 Gy.

Esempio di curva di crescita dell'intensità dei segnali Al (a) e Ti-Li (b) su aliquote irraggiate tramite sorgente gamma con valori di dose fino a 25000 Gy.

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