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Artificial optical bleaching of the Aluminium center in quartz implications to ESR dating of sediments

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Abstract

Electron spin resonance (ESR) dating of quartz extracted from sediments may contribute to elaborate a Neogene and Quaternary chronostratigraphy, especially in the case of aeolian deposits, when methods such as thermoluminescence or K/Ar cannot be applied. The ESR method is applicable for aeolian, littoral and fluvial sediments when quartz is zeroed or bleached by an optical phenomenon (photoelectric effect due mainly to UV solar rays in this case).

ESR dating on bleached quartz is based on the presence of paramagnetic substituted atoms in the crystal lattice. The Al-center can be optically bleached, and its signal intensity decreases in fossil samples versus exposure to the solar light. After a long time, the ESR intensity reaches a plateau value corresponding to the electrons which cannot be "extracted" by the light energy. These electrons represent a "residual" dose which must be subtracted from the total equivalent dose in order to obtain the archaeological dose.

Our kinetic study has the objectives of obtaining a new modelization and to establish a correct time of natural bleaching for using quartz sample as appropriate for dating. We have investigated samples from a fossil fluvial sand from the Creuse river terraces system (France).

Our experimental bleaching curve obtained is compared with that one previously proposed by Walther and Zilles (Quat. Sci. Rev. 13 (1994) 611).

Keywords: ESR method; Sedimentary quartz; Optical bleaching; Aluminium center

1. Introduction

The presence of paramagnetic centers in quartz allows the dating of geological events such as fault gouge thanks to zeroing of traps by pressure (Ikeya et al., 1982, 1995; Toyoda and Schwarcz, 1996), volcanic events using quartz baked by lava flow (Yokoyama et al., 1986; Toyoda and Ikeya, 1989, 1991, 1994; Miallier et al., 1994), and tephra (Imai et al., 1985) and fluvial, eolian and littoral sediments by optical bleaching (Yokoyama et al., 1985; Falguères et al., 1988; Laurent et al., 1998).

This latter example has focused our attention because many prehistoric sites have been discovered in fluvial terrace deposits and cannot be dated by radiometric methods other than Electron spin resonance (ESR) applied on quartz.

A main part of these terraces are too old (more than 800 ka) to be dated by thermoluminescence or optically stimulated luminescence until now. No volcanic layers are associated with these formations, which forbid the use of K–Ar method. Finally, the archaeological sediments are often deposited in acid context which does not allow the preservation of bones and teeth. The optical bleaching presents the particularity to be not complete, especially the in aluminium center in quartz, which has a sufficient life time to be used on the Neogene and quaternary period (Laurent et al., 1998). ESR dating on bleached quartz implies knowing the residual amount of non-zeroed paramagnetic traps in order to determine the archeological dose.

We present the results obtained on the aluminium center exposed to artificial light, in order to model and understand the bleaching process.

2. Previous works

In quartz, different impurity centers have been identified (see Weil, 1984). Aluminium is the most frequent element substituted to silicon atoms and hence, is the most used in ESR dating (see references in Rink, 1997).

A preliminary artificial bleaching experiment demonstrated that the Al center is not completely bleached (Yokoyama et al., 1985; Falguères, 1986). To take into account this observation, the authors used an actual sediment considered as bleached (with a maximum value) and subtracted the equivalent “residual” dose from the total dose of the dated sample to obtain the archaeological dose. The main difficulty is finding an actual quartz which has the same chemical characteristics of the traps as the fossil one. To avoid this problem, the dated sample was artificially bleached in order to assess its own residual dose (Laurent et al., 1994). The decrease of ESR Al signal intensity versus light exposure has been described by Walther and Zilles (1994). Quartz originating from different environments (granitic, volcanic and sedimentary) were studied using this procedure (Toyoda et al., 2000).

3. Artificial bleaching experiment

3.1. Sample preparation

Our work is based on a kinetic study which describes the observed results using a modeling of the real phenomenon. We bleached a quartz extracted from a modern sediment and a quartz coming from a fossil fluvial terrace. Both actual and fossil samples have been taken in fluvial terraces of the Creuse valley (France). The modern one has been extracted from sands brought by the river Creuse today and represents the most recent fluvial formation of the terrace system. The fossil sample comes from a middle Pleistocene fossil terrace, which provided Acheulean artefacts assemblage.

A fraction of 100-200 μm was selected by water sieving. Quartz was then separated using a chemical and physical protocol already detailed in the literature (Yokoyama et al., 1985; Laurent et al., 1994).

3.2. Artificial bleaching device

The samples were separated into 35 aliquots of 50 mg each. Each aliquot was then put into a small plastic dish, where grains were spread as a monolayer.

The dishes were put in an air and water cooling system in order to minimize thermal bleaching. Three 200W halogen lamps and one 240W UV lamp located 40 cm above (Fig. 1) the samples were used to illuminate the quartz grains. The combination of these lamps allows to imitate the solar spectrum.

The light intensity received by each sample ranges between 3.2 and 3.4 $\times 10^5$ Lux. The luminosity of the sun around noon in Paris in July is 1.08 $\times 10^5$ Lux. Therefore, 1 h of artificial bleaching with our device is approximately equivalent to 3 h of natural illumination.

The distribution of the luminosity in the box was determined with a LX-10⁵ Lutron light meter. The sample was continuously exposed to the light from 0 to 1200 h.

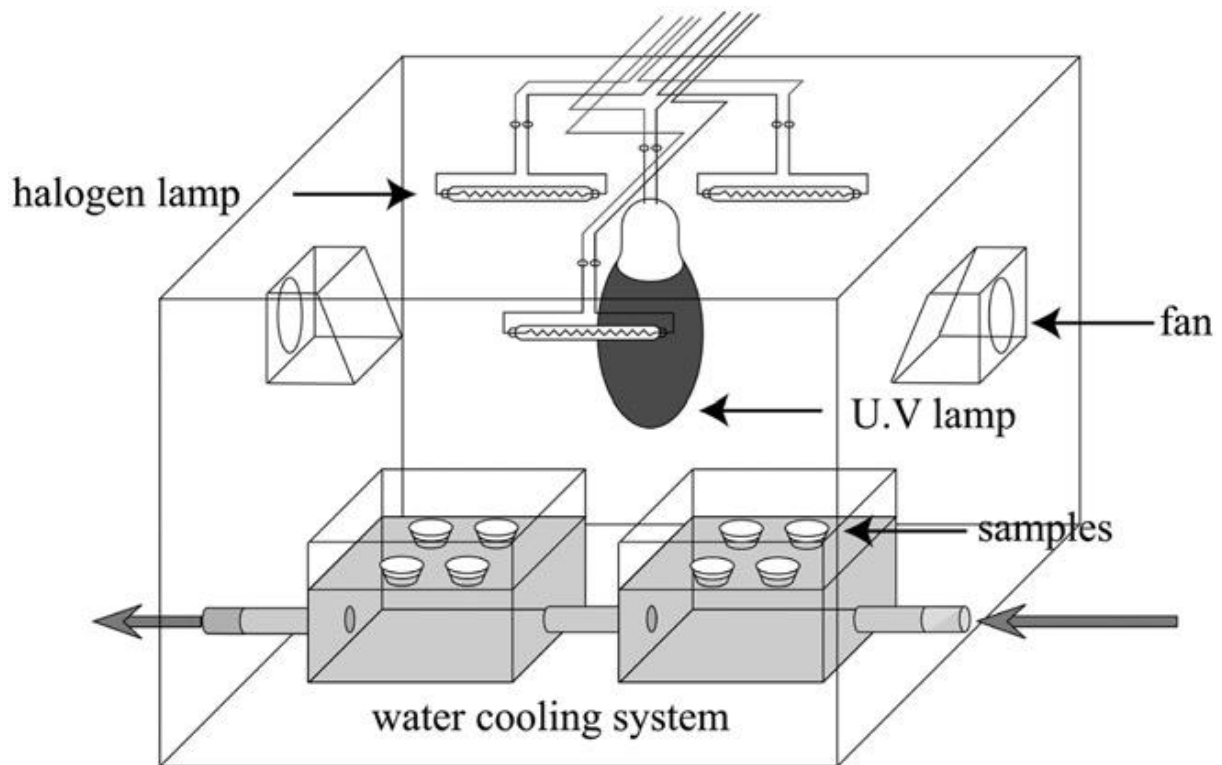


Fig. 1. Artificial bleaching device used in IPH laboratory.

3.3. ESR measurements

The ESR signal of the Al center was observed with a Varian E109 ESR spectrometer at the university of Paris VI. It was observed at 90 K using a nitrogen gas flow system. The microwave power was 5 mW and the width of the magnetic field was 20 mT. The time constant was 0.131 s, the modulation amplitude was 0.1 mT and the frequency modulation was 100 KHz.

In agreement with Yokoyama et al. (1985), the Al signal intensity was measured between the top of the first peak ($g = 2:018$) and the bottom of the 16th peak ($g = 2:002$) of the part of the main hyperfine structure.

4. Results and discussion

The first experiment has been performed on quartz extracted from a sand bank deposited by the present river. Fig. 2 shows that the Al center is optically bleached without observed significant decrease, for the first 50 light exposition hours the signal decreased about 2%. Each measurement is given with a 5% error range. These data correspond to a maximum value which is equivalent to the residual dose.

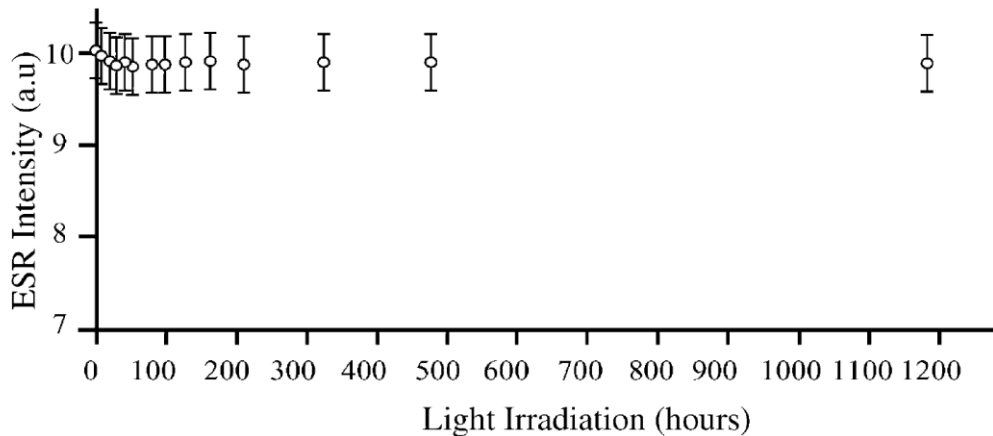


Fig. 2. Bleaching curve of quartz extracted from a recent sediment. For each point, uncertainty of ESR measurement was estimated to 72.5 % (one sigma).

The second experiment concerns a fossil sediment taken in the terrace previously described. Thirty five samples were bleached from 5 min to 1200 h. Fig. 3 shows ESR AI intensities versus light exposure. A rapid decrease of the signal intensity is observed during the first hour (about 20 %) Then between 1 and 400 h, the signal intensity decreased by about 25 %. The curve reaches a plateau value after 820 h of artificial light exposure. This value is considered as a maximum bleaching value which corresponds to electrons located in traps for which activation energy is high important than photon energy brought by light. For this sample, the maximum bleaching value is about 50 %.

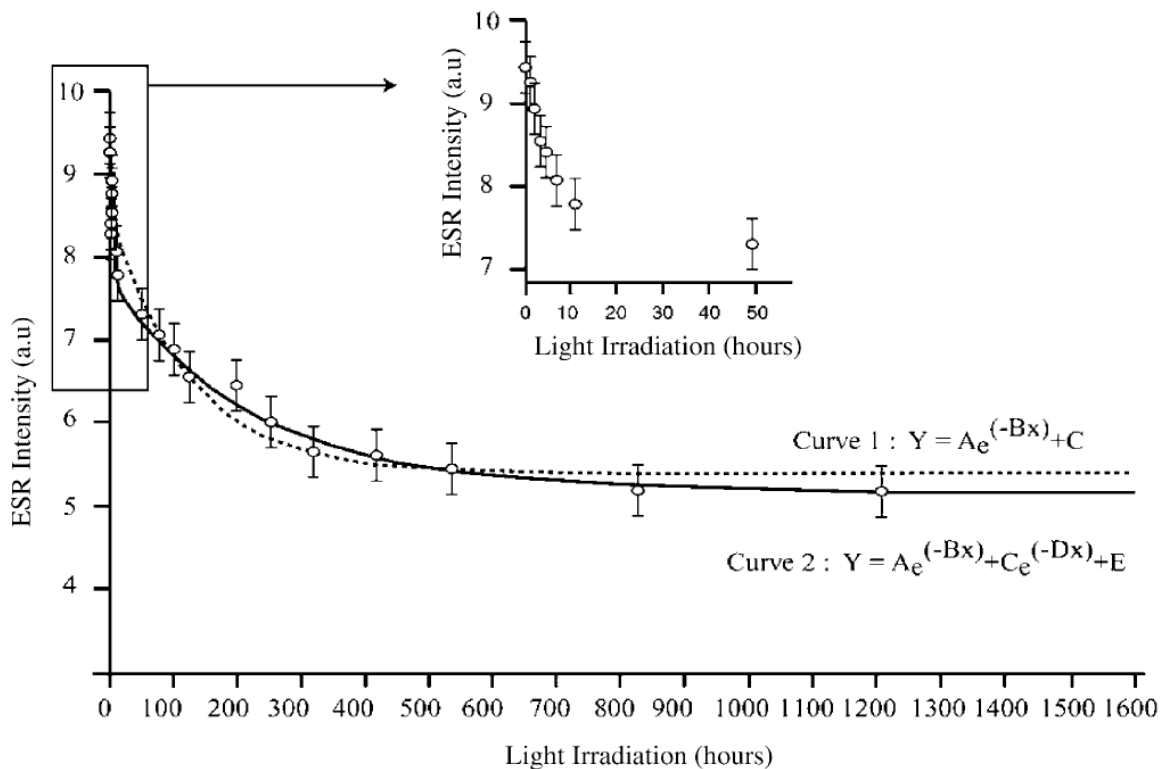


Fig. 3. Bleaching curve of quartz extracted from a fossil sediment. For each point, uncertainty of ESR measurement was estimated to 72.5% (one sigma):

1. fitting by Walther and Zilles formula: $y = A e^{(-Bx)} + C$
2. fitting by the equation: $y = A e^{(-Bx)} + A' e^{(-B'x)} + C$

In Fig. 3, curve 1 shows a mathematical fitting used by Walther and Zilles (1994): $y = A e^{(-Bx)} + C$. This function does not fit well the measured point curve and does not allow to describe the bleaching mechanism and overestimates the residual dose value. This leads to an underestimation of the archaeological age.

The curve 2 has been fitted using a double exponential function: $y' = A e^{(-Bx)} + A' e^{(-B'x)} + C$.

This function fits better the decreasing of the measured points, especially in the 0-50 h part of the curve where many experimental points have been analyzed. This function is able to represent more accurately the rapid bleaching of Al-center. Table 1 shows the different values for A ; A' ; B ; B' parameters and for C constant determined according to the two equations used to fit the curve.

| | A | B | A' | B' | C |
|------|-------|-------|-------|-------|-------|
| y | 2.995 | 0.008 | | | 4.406 |
| y' | 2.441 | 0.005 | 1.081 | 0.372 | 4.206 |

Table 1: Parameters and constants determined for the bleaching curves 1 and 2

In agreement with the new equation, a six-month long initial solar light exposure of the quartz sample, during the transport phase, before the burial deposit, is necessary to zero the sample.

The invariability of the illuminated samples ESR intensity value after 820 h of artificial light equivalent to six months of natural light exposure, shows the applicability of the method to date fluvial sediments. This exposure time is the main problem reason for age estimation having large error, ranging between 15 % and 20 %.

The archaeological dose (AD) is then determined by subtraction of the residual dose (RD) evaluated from the maximum bleaching value (more than 820 h) to the total dose (TD) (Fig. 4) which is obtained by a saturated exponential function (Yokoyama et al., 1985).

We observed also in Fig. 4, that between 2000 and 4000 Gy, a possible inflexion point which suggest that the growth curve cannot be fitted using a single saturation exponential function. This fact has been observed by Woda et al. (2002). Currently, we cannot conclude at this state of our experiment.

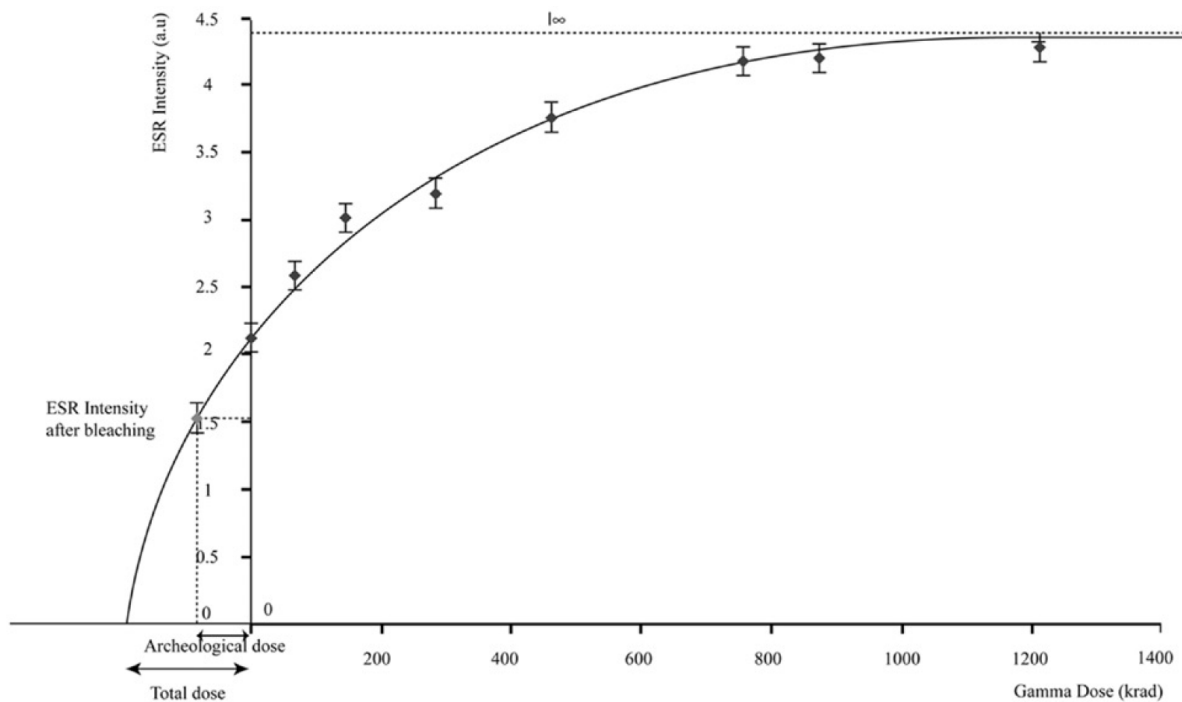


Fig. 4. Archeological dose (AD) determined by subtraction of the residual dose (RD) to the total dose (TD).

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