Assessing the influence of the cavity temperature on the ESR signal of the Aluminum center in quartz grains extracted from sediment

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Abstract

In the present work, we briefly assess the potential of the Bruker Digital Temperature control system for ESR dosimetry/dating purpose and try to quantify the influence of the cavity temperature on the ESR signal of Aluminum center.

Our results also show that it is possible to reach a consistent level of repeatability in the ESR measurements with the Bruker Variable Temperature Unit (VTU) system, not only in terms of ESR intensities, but also for the equivalent dose (D_E) values. As expected, our results show a strong influence of the temperature on the ESR signal of Aluminum center. Given that dependence, it is recommended to apply some corrections factors, especially when working around 90 K, in order to remove the systematic bias that may be induced by slight cavity temperature variations occurring during the measurement of a sample. However, despite the previous observations, there is no apparent impact of the temperature on the calculated D_E, whatever the cavity temperature between 90 and 110 K.

Introduction

One of the major specificities of ESR dating of Aluminium (Al) center in quartz is that ESR measurements have to be performed at low temperature, contrary to other materials like enamel or carbonates (e.g. Ikeya, 1993). Indeed, because of a very short spin-lattice relaxation time, the ESR signal of the Al center cannot be measured at room temperature. However, when the temperature lowers, the spin-lattice relaxation time becomes longer and the absorption lines are better resolved (Weeks, 1970).

A rapid overview of the bibliography indicates that the selected temperatures for the ESR measurements are quite variable (mainly from 77 K to 115 K), depending on the laboratories. Two systems are mainly used by the scientists dealing with ESR dating of Al center in quartz grains: the ESR measurements are usually carried out using either a finger dewar filled with liquid nitrogen or a variable temperature control unit based on a nitrogen gas flow input (e.g., Lin et al., 2006; Liu and Grün, 2011; Tissoux et al., 2007; Voinchet et al., 2003). Both systems show strengths and weaknesses. On the one hand, the finger dewar allows ESR measurements at liquid nitrogen temperature (77 K), but its volume capacity is limited (usually <200 ml) and thus it has to be regularly filled by liquid nitrogen. This prevents continuous measurements over several hours. In addition, the bubbling of liquid nitrogen inside the dewar that may sometimes happen must be carefully controlled, because it can strongly affect the measured ESR signal. On the other hand, there are other systems that can automatically control and adjust the desired cavity temperature using a nitrogen gas flow input. They usually provide stable experimental conditions over a long time (several hours) and the target temperature may be chosen according to the needs of the users, but the temperature cannot go as low as that of the liquid nitrogen systems.

In the present paper, we briefly assess the potential of the Bruker Digital Temperature control system for dosimetric/dating purpose and we try to quantify the influence of the cavity temperature on the ESR signal of Aluminum center.

Experimental

ESR spectrometer

The ESR dating laboratory at the CENIEH (Burgos, Spain) is equipped with an EMXmicro 6/1 Bruker ESR spectrometer (Fig. 1) coupled to a standard rectangular ER 4102ST cavity. To ensure constant experimental conditions over time, the temperature of the water circulating in the magnet is controlled and stabilized at 18ºC by a water-cooled Thermo Scientific NESLAB ThermoFlex 3500 chiller, and the temperature of the room is kept constant at 20ºC by an air conditioning unit.

Figure 1: *CENIEH's ESR spectrometry area: EMXmicro 6/1 Bruker ESR spectrometer connected to an ER4141VT Digital Temperature control system (with the flexible metal transfer line option).*

Variable Temperature Unit (VTU)

The temperature of the ESR cavity (or ESR resonator) is regulated with a ER4141VT Digital Temperature control system, which is based on the following principles: the liquid nitrogen stored in a large dewar (25-50 L) is converted into gas by the evaporator and then goes through a metal transfer line to a quartz dewar insert that is placed in the cavity (Fig. 1). The temperature of the flowing gas is monitored with a thermocouple introduced in the dewar insert, close to the sample's position. The target temperature programmed by the user is reached and stabilized by the temperature controller, by combining the power of the liquid nitrogen evaporator and a heater (see further details in Barr, 1999). All the acquisition parameters, including the temperature of the cavity, are automatically saved with the ESR spectrum.

Initial tests of the Variable Temperature Unit (VTU) showed that our system could reach a minimum temperature of 85 K.

Stability of the system at low temperature

In ESR dosimetry/dating, it is really crucial to ensure constant experimental conditions, in order to eliminate, or at least minimize, the variations of the ESR signal that are induced by the system and to make sure that only the variations derived from the sample itself are recorded. In addition, the sample should be perfectly placed in the center of the cavity to ensure that all the aliquots of a sample are measured under identical conditions. Following our standard protocol for the Aluminium center, each aliquot of a given sample is measured 3 times after ~120º of rotation in the cavity, in order to take into account the angular dependence of the ESR signal. Usually, at least 1 hour is needed to complete the measurement of one sample formed by 10-12 aliquots. It is therefore crucial to make sure that the system (i.e., EMX spectrometer + VTU) is sufficiently stable to allow highly repeatable measurements over several hours at low temperature (<100 K).

Consequently, the stability of the system was assessed by leaving one aliquot in the cavity and by running continuous measurements at low temperature over a given time. Three examples of measurements at 85, 90 and 95 K are given in Fig. 2. The ESR intensities show a coefficient of variation (i.e., the ratio of the standard deviation to the mean) of < 2%, i.e. of 0.8% at 95 K over 1 hour, 1.1% at 90 K over 3 hours and 1.5% at 85 K over 2 hours. Even though it seems that the lower the temperature is the least reproducible, this apparent pattern is not confirmed by supplementary measurements. Overall, repeated measurements do not show any systematic trend or significant drift in the ESR signal intensity with time. Consequently, it seems that the system is sufficiently stable to get repeatable measurements with less than 2% of variation. Perhaps our main recommendation when using the VTU, is to wait for a minimum period of 10 minutes once the system reaches the required temperature before starting the ESR measurements, in order to avoid the temperature and gas flow variations linked with the stabilization of the system.

Samples

We selected two samples from the palaeontological site of Villaroya (Rioja, Spain) (see Agustí and Oms, 2001 and references therein). Quartz grains were extracted following a standard procedure similar to that described in Voinchet et al. (2007). Gamma irradiations were performed with a Co-60 source at the following doses (dose rate=12.81 Gy/min): 250, 400, 630, 1000, 1600, 2500, 4000, 6300, 10000, 16000 and 25000 Gy.
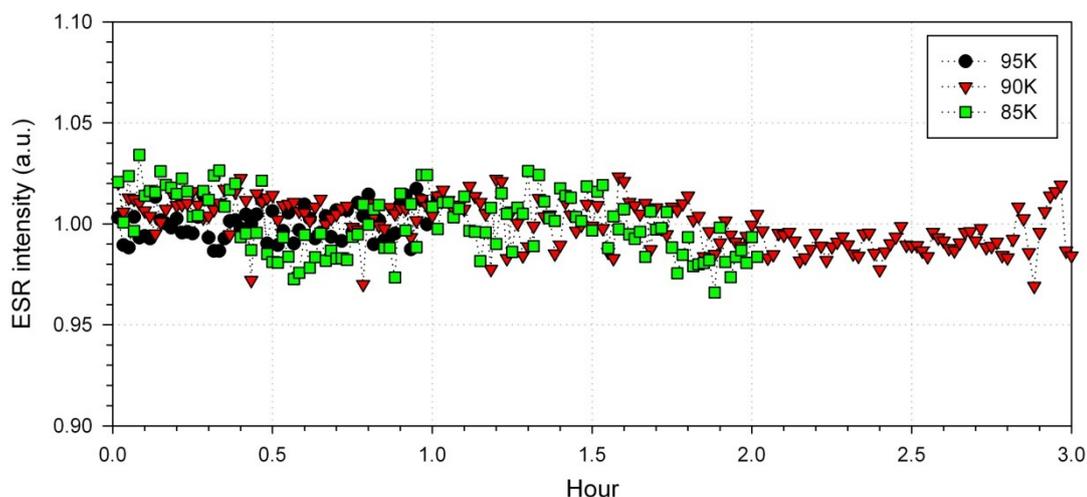
Figure 2: *Evolution of the ESR intensity of three different samples with time. ESR intensities were normalized to the mean ESR intensity obtained for each sample.*

Influence of the temperature on the ESR signal of the Al center in quartz

To evaluate the influence of the temperature on the ESR signal of the Al center in quartz, we ran a couple of wide range temperature sweeps from 90 to 300 K, with the two aliquots irradiated at 25 kGy from samples BUR1107 and BUR1108. Some examples of ESR spectra are shown in Figure 3. As expected, there is a clear correlation between the temperature of the cavity and the intensity of the ESR signal. Basically, the definition of the peaks and the intensity of the ESR signal of Al center are at a maximum when temperatures are at their lowest. Around 120 K, peaks almost disappear and only an envelope signal remains. Contrary to the ESR signals of Al- or Ti- center, the other ESR signals that are usually observed at room temperature (e.g., E', Germanium etc.) are becoming stronger and better defined as soon as the temperature increases (Fig. 3A). Further details about those paramagnetic centers may be found in Ikeya (1993).

ESR intensities of the Al signal were plotted versus the temperature for both aliquots (Fig. 3B). They show a similar evolution. There is first a strong temperature dependence between 89 and 93 K, with a decrease of 24% in intensity over the 4 K temperature range, i.e. -6%/K. Then, at higher temperature this influence is lower, with a value of -2%/K observed from 93 to 117 K. This correlation does not seem to be sample dependent, since similar trends were also observed using other quartz samples.

In order to get an overall description of the evolution of the ESR intensity of the Al signal with temperature, all the data were fitted with a polynomial function (5th order). Consequently, this equation can be used to correct the ESR intensity according to the temperature in the cavity for a given

ESR spectrum. Temperature correction factor values (normalized to T=90 K) are given in supplementary material. Consequently, given the strong correlation between ESR intensity and temperature (r^2=0.99), it is recommended to systematically correct the ESR intensity by a given factor, in order to remove the bias induced by the cavity temperature variations during the ESR measurement of a sample. This is especially crucial for temperatures less than 93 K. As an example, when working at 90 K, a variation of 0.1 K may induce a variation of about 1% in the ESR intensity. At 100 or 110 K, the same 1% of variation in the ESR intensity is caused by a variation of 0.7 and 0.9 K, respectively. For a given ESR spectrum, the temperature of the cavity is automatically saved with all the other acquisition parameters and can be simply obtained through the parameter list via the Bruker WinEPR Processing software. Therefore, each ESR measurement may be systematically associated to a given temperature value, and the ESR intensity may be corrected accordingly.

Influence of the temperature on the D_E values

We performed ESR measurements of the two samples BUR1107 and BUR1108 at 3 different temperatures (90, 100 and 110 K). Following the standard protocol described in Duval (2012), for a given temperature and a given sample: (i) each aliquot was measured 3 times after a ~120º rotation in the cavity in order to consider the angular dependence of the ESR signal, and (ii) 3 replicate measurements of the whole series of aliquots were carried out to check data repeatability. Consequently, a total of 9 ESR intensities were obtained for each aliquot. Each ESR intensity was corrected by the weight of the aliquot, the receiver gain and the cavity temperature and then normalized by the mean
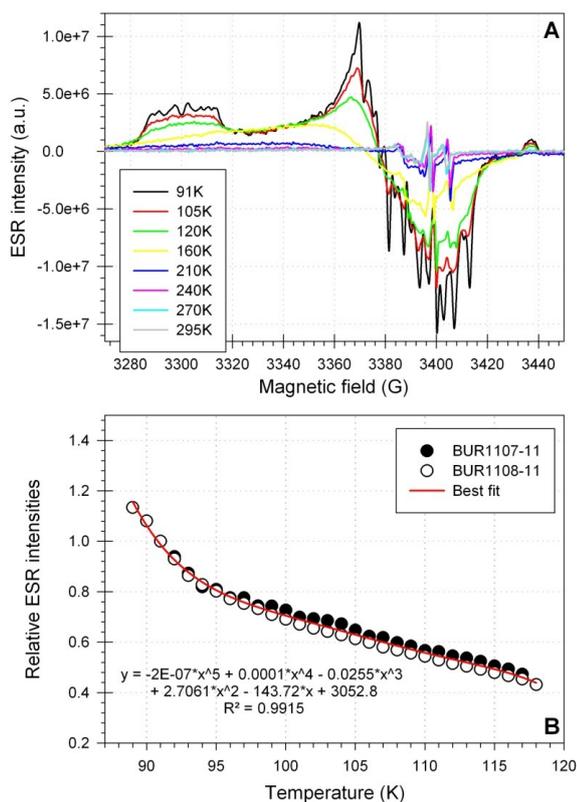
Figure 3: *Influence of the temperature on the ESR signal of Al center in quartz. (A): Evolution of the ESR signal of the sample BUR1108 (D=25 kGy) from T=91 K to T=295 K (room temperature). Acquisition parameters: 10 mW microwave power, 2048 points resolution, 100 mT sweep width, 100 kHz modulation frequency, 0.05 mT modulation amplitude, 30 ms conversion time, 10 ms time constant and 3 scans. (B): Evolution of the ESR intensities (normalized for T=91 K) according to the temperature. The ESR intensity of the Al signal was extracted from peak-to-peak amplitude measurements between the top of the first peak (g=2.0185) and the bottom of the 16th peak (g=1.9928) (Toyoda and Falguères, 2003).*

intensity of the natural aliquot for a given sample, in order to get comparable data from one series of measurements to another (ESR data are available in Supplementary Information). For each sample, the D_E values were calculated by pooling the 9 normalized ESR intensities and fitting an exponential+linear function through the experimental data points (see Duval, 2012), using Microcal OriginPro 8.5 software. Data were weighted by $1/I^2$.

For a given temperature and a given sample, ESR intensities show good repeatability, with an average coefficient of variation ranging from 1.2 to 1.8% (supplementary information). For a given sample, no

apparent correlation is observed between the ESR intensity variability and the temperature.

Table 1 shows the D_E calculated for each target temperature. Dose response curves are given in Fig. 4. All the D_E values show a deviation of less than 5% for a given sample. For BUR1107, the D_E value obtained at 90 K (2531±122 Gy) is slightly higher, by ~5%, than those obtained at 100 K and 110 K (2415±108 Gy and 2415±131 Gy, respectively). For BUR1108, the deviation is even smaller (< 3%) and D_E values range from 1996±78 (100 K) to 2057±69 Gy (110 K). Nevertheless, it is worth noting that all the values are consistent at ±1σ, thus indicating that there is no apparent impact of the temperature on the D_E.

Temperatures registered for each ESR spectrum are very stable during the measurement of all the aliquots of a given sample, but also over the series of 3 full measurements. In addition, we also observed that temperature variations may be minimized if a pause before each measurement is included in the protocol, to ensure that the temperature is stabilized and remains constant at, at least, ±0.3 K from one measurement to another. Depending on the series, the amplitude of temperature variations over a given series usually ranges from 0.1 to 0.2 K, though a higher value (0.4 K) may be sometimes be observed (see supplementary information). The influence of these slight temperature variations on the ESR intensities may be then simply removed by using the corresponding correction factors. However, as mentioned above, this temperature variability is less crucial for higher temperature (110 K) measurements, since the ESR intensity remains more or less stable over ~0.9 K.

In addition, it is also worth taking into account some practical considerations when working at low temperatures. We observed that between each aliquot the system needs much more time to stabilize the temperature around 110 K (~1 min) than at 90 K (a few seconds), requiring then a longer measurement time for a given sample comprising 10-12 aliquots (around 15 minutes more). This may seem a priori somewhat counterintuitive, since it is easier for the system to initially drop in temperature and stabilize at 110 K than at 90 K. However, this may be simply explained as following: at 110 K, when replacing one tube with another, the environmental conditions in the cavity quickly change once the tube is out, and the temperature drops by a few K, because the power of the evaporator and the heater remain constant for a few seconds. Then, the system tries to stabilize the temperature at the desired value, by adjusting the heater power, and induces some temperature oscillations around the target temperature value before stabilization. However, at 90 K, the evaporator
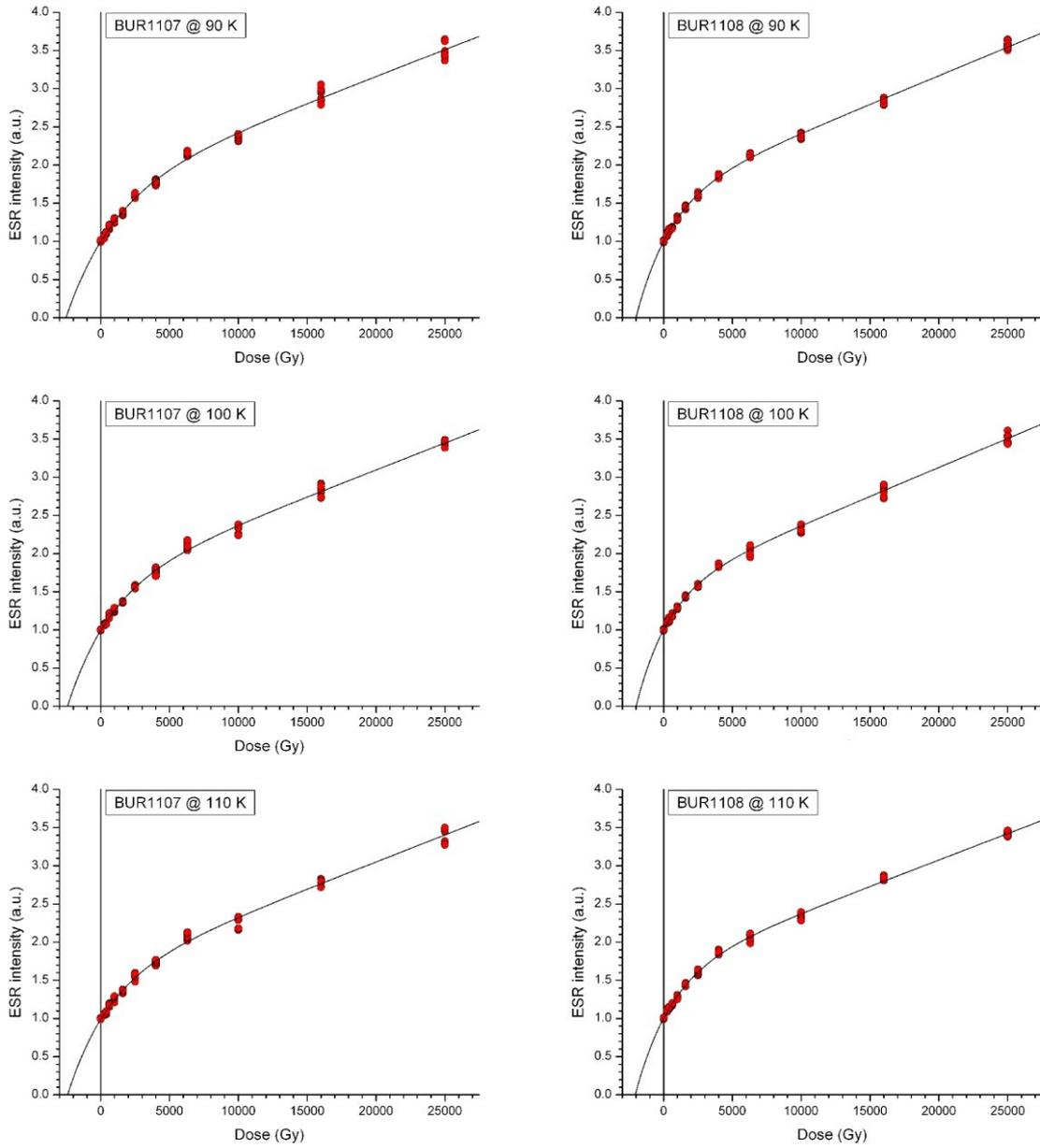
Figure 4: *Dose response curves obtained for samples BUR1107 and BUR1108 at 90, 100 and 110 K.*

	T=90 K	T=100 K	T= 110 K	Ratios		
	1	2	3	2/1	3/1	3/2
BUR1107	2531±122 Gy	2415±108 Gy	2415±131 Gy	0.95	0.95	1.00
BUR1108	2007±68 Gy	1996±78 Gy	2057±69 Gy	0.99	1.02	1.03

Table 1: *D_E values derived from ESR measurements performed at 90, 100 and 110 K.*

power is at 100% and the system is very close to the minimum possible temperature, so that any changes of tube only produce a small variation of the cavity temperature (1-2 K max.). It is thus easier and faster for the system to get stabilized at 90 K after every change of tube in the cavity.

Conclusions

Our results show that it is possible to reach a consistent level of measurement repeatability with the Bruker VTU. This system offers the possibility of working at any temperature from room temperature to ~85 K, and shows several points of interest: (i) it provides stable experimental conditions over several hours (<1.5% of variation) for temperatures <95 K, (ii) the temperature is registered for each measurement, allowing some further corrections for each single spectrum, (iii) the temperature remains stable during the measurements of all aliquots of a given sample (<0.4 K of amplitude), (iv) the ESR intensities of a given aliquot are very reproducible (<2% of variation) from one measurement to another.

As expected, our results show the strong influence of the temperature on the ESR signal of the Al center. The signal and the peaks are well resolved around 90 K, while at 110 K the peaks cannot be identified and only an envelope signal of the Al center can be observed. Given the dependence of the ESR intensity on the temperature, it is recommended to apply corrections factors, especially when working around 90 K, in order to remove the systematic bias that may be induced by slight temperature variations during the measurement of a sample. At this temperature, a variation of 0.1 K may induce 1% of variation on the ESR signal intensity.

However, despite the previous observations, there is no apparent impact of the temperature on the calculated D_E, since all the values are consistent at $\pm 1\sigma$, whatever the temperature between 90 and 110 K. Nevertheless, it is worth considering that working at 110 K may create some additional problems. Indeed, since the ESR signal is not well resolved at that temperature, the peak-to-peak measurement may be sometimes quite complicated and inaccurate. In addition, between each aliquot the system needs much more time to stabilize the temperature around 110 K than at 90 K, requiring then a longer measurement time for a given sample.

Supplementary Information for this article is available at www.aber.ac.uk/ancient-tl

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Reviewer
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