ESR dosimetry of optically bleached quartz grains from the Loire basin (France) using MAA, MAR and MARA approaches

Exchange visit report - Walter Minnella

Introduction

The alluvial deposits in the Loire Basin (Centre region, France) have delivered among the oldest evidence of hominid presence in France with the discovery of Mode 1 and Mode 2 lithic tools in various fluvial terraces of the river system (e.g. Despriée et al. 20004, 2011; Moncel et al. 2013; Voinchet et al. 2010). The absence of faunal remains associated with artefacts, as well as volcanic minerals, precludes any biochronological interpretation and Ar-Ar dating, respectively. Actually, Electron Spin Resonance (ESR) is one of the very few numerical dating methods that can be potentially applied to these Pleistocene sedimentary sequences. Previous ESR dating studies of optically bleached quartz grains highlighted the suitability of these deposits for the application of the ESR method provided chronologies from Early to Late Pleistocene, showing an almost continuous hominid occupation in that area during 1 Ma (e.g. Voinchet et al 2010). This is why additional sediment samples were collected in the area in order to further explore the potential of new methodological developments in ESR dating.

ESR dating of quartz grains: basic principles

Electron spin resonance (ESR) dating applied to optically bleached quartz grains extracted from sediment is based on the detection of paramagnetic centres, e.g. Aluminium (Al) or Titanium (Ti), that are created by the interaction of the natural radioactivity with the quartz sample (Ikeya, 1993).

Similarly to the Optically Stimulated Luminescence (OSL) dating, ESR is an optical dating method that relies on the zeroing of any previously present ESR signal by sunlight exposure at the time of deposition (see details in Yokoyama et al., 1985). However, while OSL is usually limited to late Middle Pleistocene time range, ESR may potentially go further back in time and cover the whole Quaternary time range (e.g. Voinchet et al., 2010).

Purpose of the visit

With the idea to refine the chronology of some of the sites of the Loire Basin, several sediment samples for ESR dating have been collected by Dr Mathieu Duval (MD) in April 2010. The ESR study of these samples has been carried out at Centro Nacional de Investigación sobre la Evolución Humana (CENIEH, Burgos, Spain) within the framework of my Master thesis under the supervision of MD, research scientist in charge of the ESR dating laboratory, and following the standard procedure based on the multiple aliquots additive (MAA) dose method developed at CENIEH (e.g. Duval, 2012; Duval and Guilarte, 2012).

In order to push further the limits of the ESR method, financial support has been requested to the ESF for a two month research stay, in order to develop a new analytical protocol based on the multiple aliquots regenerative (MAR) dose approach, which is a common procedure in Luminescence (OSL) dating, but so far has been barely studied in ESR. Such an approach requires specific facilities (in particular, access to a gamma irradiation source) that are available at CENIEH and may potentially provide more accurate dating results than the classic additive dose method (Lian, 2007).

Material and method

Basically, the work has been focused on two archaeological sites from France: Lunery, which has delivered a Mode 1 (Oldowan like) lithic industry (Despriée et al, 2011), and la Noira, considered among the oldest evidence of Acheulean (Mode 2) occupation in Europe (Moncel et a, 2013). Two samples per site (4 in total) have been analyzed during the two month stay. First, each sample has been divided into 4-5 aliquots, UV bleached to reset the ESR signal to 0, and then gamma irradiated at increasing doses, as requested for a MAR procedure. Both Al and Ti paramagnetic centers have been measured by ESR in order to compare the equivalent dose values (D_E) via the multiple centers method (Toyoda et al, 2000). Further details about the methodology may be found in Minnella (2014). Results have been then compared with those derived from the standard procedure, i.e. the MAA approach, obtained during my Master thesis. Both MAR and MAA data set have been finally combined for a new MARA procedure, based on the SARA developed by Mejdahl and BØtter-Jensen (1994).

Gamma irradiation and ESR measurements have been carried out during the first half of the stay, while data reduction and interpretation have been performed in the second half of the stay.

Results

In the first part of our study, we explored the potential of the Multiple Aliquots Regenerative dose method (MAR) ESR dosimetry. In order to make a quantitative analysis, we compared this data with the ones obtained with previous measurements on the same samples, performed by myself at the CENIEH, using the multiple Aliquots Additive dose method (MAA). In Fig. 1 are shown the methods employed to extract the ESR intensity from the Al and Ti centers.

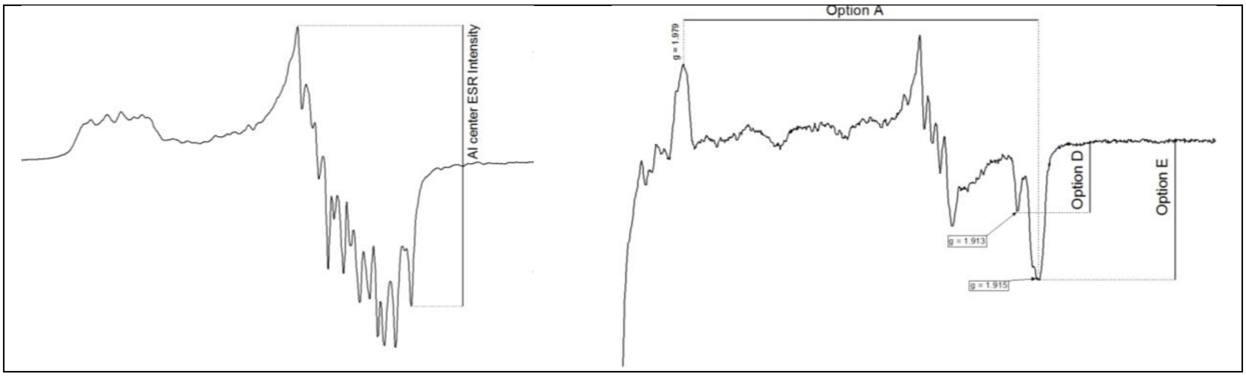

Fig. 1: ESR signal of Al center (left) and Ti centers (right).

Table 1 shows a synthesis of the D_E results obtained. As expected, the uncertainty on the D_E using MAR is lower than the one usually obtained with MAA (~3-5 % against ~10-12 %) because of the different analytical process employed (data interpolation versus back extrapolation). Also, the reproducibility of the D_E values over repeated measurements of the same sample is better with MAR than with MAA, especially for option D where it has decreased from ~50 % to ~11 % in the case of NOI1104 for example. As for MAA, option D yields always lead to the lowest equivalent dose values. The exact reason of such a discrepancy is not clear yet. Anyway, analyzing the dose response curves of the various centers it is evident that Ti-H (= option D) behaves differently from Ti-Li, in particular it saturates at lower doses (Fig. 2 and 3).

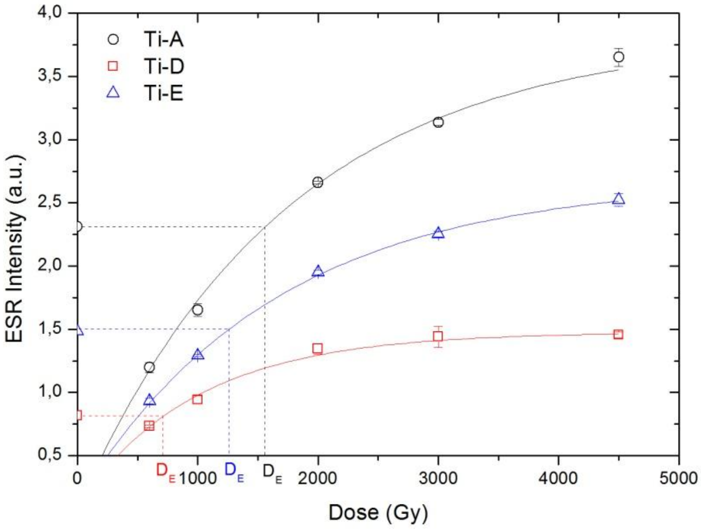

Fig. 2: MAR growth curves of Ti-Li (Option A and E) and Ti-H centers and relative D_E for sample LUN1101.

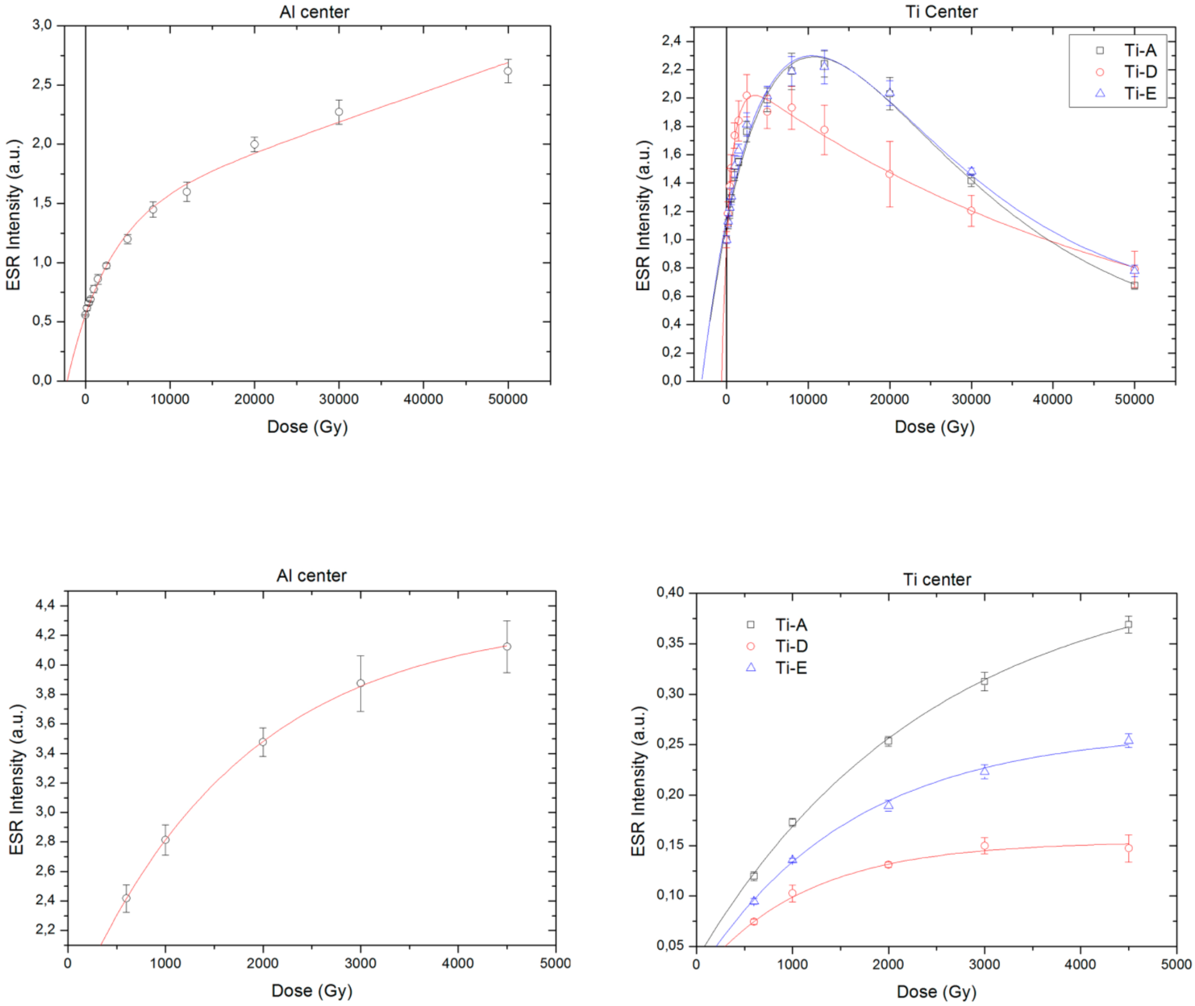

Fig. 3: MAA growth curves (above) and MAR growth curves (below) for both Al and Ti centers, sample LUN1103.

From our study did not emerge which should be the most reliable way to evaluate the ESR signal of the Ti center. Indeed, comparing the results of Al center and Ti center, when subsist a match (LUN1101, LUN1103 and NOI1101) we note that it is not always with the same option: it is option A for LUN1101 and option E for LUN1103 and NOI1104.

The main problem when using the regenerative method is that the artificial bleaching imposed to the sample could induce sensitivity changes in itself. A technique that may monitor these contingent changes is the Multiple Aliquot Regeneration Added dose (MARA), where data from MAA and MAR are combined in order to assess this problem. In particular, these data should have a linear dependency, with a slope close to unity if no sensitivity changes occur. While this technique yielded to reliable (low dispersion between measurements) and consistent (with MAR) D_Es, it is evident that a slope far from the unity, as it has been observed in the majority of the cases, did not imply a big difference between MAR and MARA equivalent dose, especially for Al center, which gave the highest values for the slope. Furthermore, we found option A to be the one always leading to the highest D_Es. This is in contrast to what has been found by Toyoda *et al*. (2009), who observed in the majority of the cases slopes close to 1 and the Al center as the one systematically overestimating the equivalent dose. This should be further explore in the future in order to understand this apparent discrepancy with the results by Toyoda *et al*. (2009).

Finally, when comparing all the techniques that have been employed in this work (MAA, MAR and MARA) it emerges a clear discrepancy between D_E results derived from MAA and MAR-MARA, being much lower the latter (Table 1 and Fig. 4). The only exception in this perspective is option D for the Ti center. The reason of this difference is hypothesized to lie in the choice of the fitting function. MAA-DRCs were then fitted again with SSE to check this hypothesis. Result show that Al center is now matching only in one case (LUN1101), while Ti-Li it is in all 4 samples, but not always using the same option. Finally option D, once again, systematically provides always D_Es in agreement between MAA (with SSE) and both MAR and MARA.

This final observation is maybe the most interesting result of this work. In fact, the least reproducible option to extract the ESR signal of the Ti center, i.e. option D = Ti-H, is the only one that systematically provides consistent equivalent dose with every techniques that has been employed in this work.

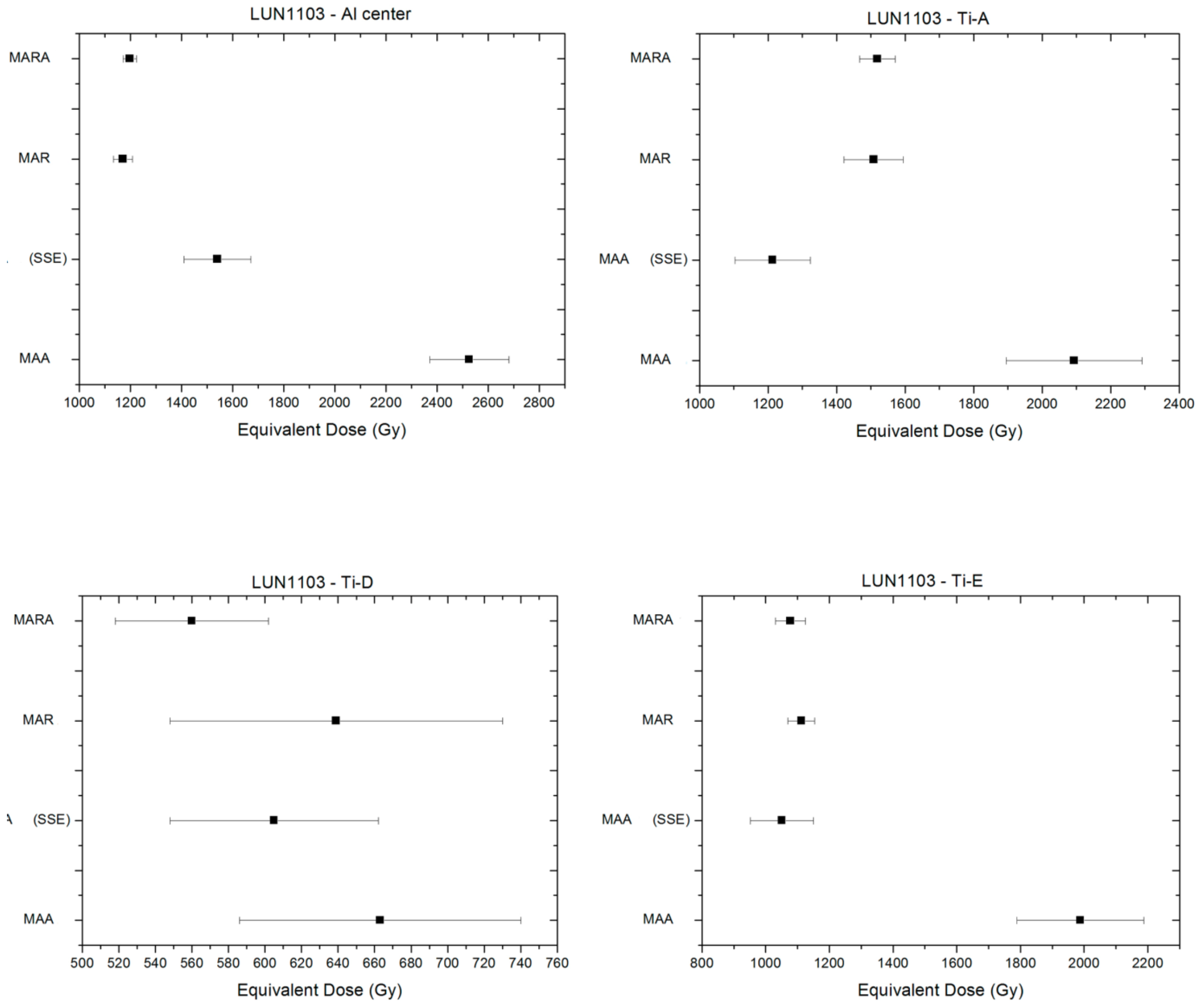

Fig. 4: Comparison between equivalent dose values obtained with MAA, MAA (SSE), MAR and MARA for each center for sample LUN1103.

Sample	LUN1101	LUN1103	NOI1101	NOI1104
	D_E [Gy]	D_E [Gy]	D_E [Gy]	D_E [Gy]
MAA Al	2741 ± 184	2526 ± 155	1886 ± 117	2786 ± 168
MAA Al (SSE)	1507 ± 170	1541 ±131	1324 ± 218	2528 ± 181
MAR Al	1528 ± 67	1171 ± 37	851 ± 44	1519 ±67
MARA Al	1405±105	1198±26	762±65	1195±276
MAA Ti-A	2605 ± 201	2093 ± 198	1828 ± 102	2487 ± 92
MAA Ti-A (SSE)	1744 ± 294	1213 ± 110	1150 ± 55	1935 ± 103
MAR Ti-A	1637 ± 53	1508 ± 87	1171 ± 28	1733 ± 26
MARA Ti-A	1693 ± 37	1519±52	1193±12	1689±51
MAA TI-E	2011 ± 197	1988 ± 199	1762 ± 141	2193 ± 162
MAA TI-E (SSE)	1241 ± 192	1051 ± 99	882 ± 90	1282 ± 90
MAR Ti-E	1232 ± 42	1112 ± 42	878 ± 23	1355 ± 19
MARA Ti-E	1278 ± 44	1078±47	897±34	1344±82
MAA Ti-D	886 ± 116	663 ± 77	556 ± 50	1268 ± 287
MAA Ti-D (SSE)	704 ± 71	605 ± 57	517 ± 42	701 ± 27
MAR Ti-D	731 ± 17	639 ± 91	471 ± 17	693 ± 40
MARA Ti-D	1559 ± 117	560 ± 42	501 ± 42	876 ± 122

Table 1: Summary table including all the results obtained during the 2 month stay: comparison between equivalent dose values obtained with MAA, MAA (SSE), MAR and MARA.

Conclusion and perspectives

Our results highlight the differences that may exist between each approach (MAA, MAR and MARA) as well as between the ESR signals studied. If further work is clearly needed to improve our understanding of the reasons for such discrepancies, these results raise new questions worth exploring in the future.

Based on the results obtained in this research stay we would really like to explore more deeply the potentiality of the Ti-H center. In particular we would like to perform new measurements using a ESR cavity with higher sensitivity in order to obtain measurements with a higher signal-to-noise ratio. This could face the main problem when using Ti-H in ESR dating, i.e. the low reproducibility of the measurements. For this reason, we are currently looking for financial support, in order to have the possibility to continue a path that looks very promising and that could greatly improve ESR dating's methodologies.

The results obtained in this work have been incorporated in my Master thesis (Minnella, 2014), entitled "*ESR dosimetry of optically bleached quartz grains extracted from sediment of the Loire Basin (France)*", which I successfully defended at the University of Catania on the 28th of March.

Finally, this two month research stay at CENIEH helped me to obtain new and original ESR data that will be combined with the already available dose rate data in order to provide new ESR ages on La Noira and Lunery sites. These results will be used to write a couple of scientific papers focused on methodological and archaeological issues where the support from the ESF will be acknowledged.

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