Report to SAHRA on ESR and U-series dating at Olieboomspoort (Limpopo Province, South Africa) using two fossil equid teeth

By Mathieu Duval[1,2] in collaboration with J.X. Zhao[3]

1- Australian Research Centre for Human Evolution (ARCHE), Environmental Futures Research Institute, Griffith University, 170 Kessels Rd, Nathan, QLD 4111, Australia
2- Centro Nacional de Investigación sobre la Evolución Humana (CENIEH), Paseo Sierra de Atapuerca, 3, 09002 Burgos, Spain
3- Radiogenic Isotope Facility, School of Earth and Environmental Sciences, The University of Queensland, Brisbane, QLD 4072, Australia

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Material

The recovery of ungulate teeth during the 2018 excavation at Olieboomspoort offers the possibility to date directly the faunal assemblage and to provide an age constraint for the associated MSA lithics. We collected two *Equus* sp. molars (lab IDs: #536 and #537) from the GS/Unit 1 deposits in sub-square B2c, together with the associated sediment for combined U-series and ESR dating. The first tooth was found in *décapage* 11 of the unit GS and the second tooth was found 4 cm deeper, in *décapage* 13 of the same unit. Horizontally speaking, both teeth were found ~20 cm from one another within square B2c.

Methods: combined U-series-ESR dating

Sample preparation

We prepared the fossil teeth following a standard ESR dating procedure, as in Duval et al. (2019). The enamel layer was mechanically separated from the other dental tissues and both inner and outer surfaces were removed with a dentist drill to eliminate the volume that received an external alpha dose. Initial and removed enamel thicknesses were measured using a digital calliper. The clean enamel and dentine samples were ground and sieved <200 µm to obtain homogenous powders for ESR and U-series analyses.

ESR dose evaluation

We performed the ESR dose evaluation at the *Centro Nacional de Investigación sobre la Evolución Humana* (CENIEH), Spain. Dose evaluation utilised the multiple aliquot additive dose (MAAD) method. The enamel powder was split into eleven aliquots and irradiated with a Gammacell 1000 Cs-137 gamma source (dose rate = 6.27 ± 0.14 Gy/min) to the following doses: 0, 49.0, 98.0, 147.0, 245.0, 342.9, 489.9, 685.9, 881.9, 1469.8 and 3429.5 Gy.

We carried out ESR measurements at room temperature with an EMXmicro 6/1 Bruker ESR spectrometer coupled to a standard rectangular ER 4102ST cavity. We used the following procedure to

minimise the analytical uncertainties on the measurements: (i) all aliquots of a given sample were carefully weighed into their corresponding tubes and a variation of <1 mg was tolerated between aliquots; (ii) ESR measurements were performed using a Teflon sample tube holder inserted from the bottom of the cavity to ensure that the vertical position of the tubes remained exactly the same for all aliquots. We used the following acquisition parameters: 1-15 scans depending on the aliquots and samples considered, 1 mW microwave power, 1024 points resolution, 15 mT sweep width, 100 kHz modulation frequency, 0.1 mT modulation amplitude, 20 ms conversion time and 5 ms time constant. All aliquots were measured within a short time interval (<1 h). We repeated this procedure twice over successive days without removing the enamel from the ESR tubes between measurements in order to evaluate intensity and equivalent dose (D_E) precisions.

We extracted the ESR intensities from T1-B2 peak-to-peak amplitudes of the ESR signal (Grün 2000a) after a cubic baseline correction, and then normalised to the corresponding number of scans and aliquot mass. D_E values were obtained by fitting a single saturating exponential (SSE) through the mean ESR intensities derived from the repeated measurements. Fitting was performed with Microcal OriginPro 9.1 software, which is based on a Levenberg-Marquardt algorithm by chi-square minimisation. Data were weighted by the inverse of the squared ESR intensity ($1/I^2$) (Grün and Brumby 1994). The ESR dose response curves (DRC) are displayed in Fig. 1, while the detailed fitting results are provided in Table 1.

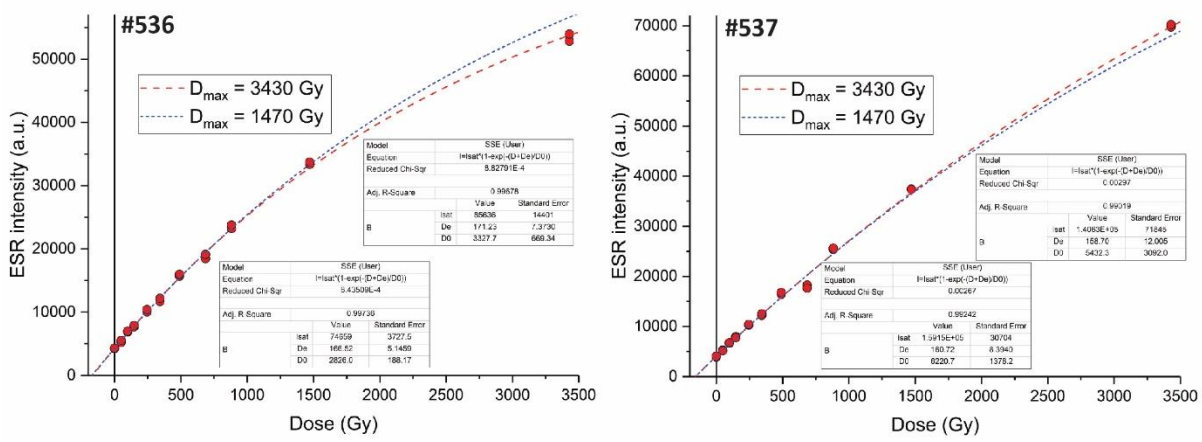

Fig. 1 ESR dose response curves obtained for the two samples. Fittings were performed over the full dose range (D_{max} = 3430 Gy) and for a selected D_{max} of 1470 Gy in order to meet the recommendations by Duval and Grün (2016).

TABLE 1. ESR fitting results obtained for the various enamel samples. Intensity precision is expressed as the mean coefficient of variation of the ESR intensities obtained for all the aliquots of a given sample over the three repeated measurements. D_E precision is the variation of the D_E values derived from each repeated measurement of a given sample. All errors are given at 1-σ confidence level.

Sample	**#536**	**#537**
Average weight per aliquot (mg)	19.7 ± 0.4	19.5 ± 0.5
Number of repeated measurements	2	2
Measurement precision (%)	1.7	0.3

Fitting #1 (data weighting by $1/I^2$)		
D_E precision (%)	0.1	3.1
Adj. r-Square	0.997	0.992
D_{E1} (Gy)	167 ± 5.15 (3.1%)	160.7 ± 8.39 (5.2%)
D_{max} (Gy)	3430	3430
D_{max}/D_{E1}	20.6	21.3
Fitting #2 (data weighting by $1/I^2$)		
Adj. r-Square	0.997	0.990
D_{E2} (Gy)	171 ± 7.37 (4.3%)	159 ± 12.0 (7.6%)
D_{max} (Gy)	1470	1470
D_{max}/D_{E1}	8.6	9.3
D_{E2}/D_{E1} ratio	1.03	0.99

Solution U-series analyses by MC-ICPMS

Solution U-series analyses of powdered enamel and dentine were carried out using a Nu Plasma HR MC-ICP-MS in the Radiogenic Isotope Facility (RIF) at the School of Earth and Environmental Sciences, University of Queensland (Australia), following chemical treatment procedures and MC-ICP-MS analytical protocols described elsewhere (e.g. Zhao et al. 2001; Clark et al. 2014). Powdered sub-samples weighing 1-5 mg were spiked with a mixed ^{229}Th-^{233}U tracer and then completely dissolved in concentrated HNO_3. After digestion, each sample was treated with H_2O_2 to decompose trace amounts of organic matters and to facilitate complete sample-tracer homogenisation. U and Th were separated using conventional anion-exchange column chemistry using Bio-Rad AG 1-X8 resin. After stripping off the matrix from the column using double-distilled 7N HNO_3 as eluent, 3 ml of a 2% HNO_3 solution mixed with trace amount of HF was used to elute both U and Th into a 3.5-ml pre-cleaned test tube. After column chemistry, the U-Th mixed solution was injected into the MC-ICP-MS through a DSN-100 desolvation nebuliser system with an uptake rate of around 0.07 ml per minute. U-Th isotopic ratio measurement was performed on the MC-ICP-MS using a detector configuration to allow simultaneous measurements of both U and Th. Closed-system U-series ages were calculated using the Isoplot/Ex 3.75 Program (Ludwig 2012) and decay constants from Cheng et al. (2000). Analytical results are given in Table 2.

TABLE 2. U-series dating results obtained from solution MC-ICPMS analyses performed at University of Queensland. All errors are 2-σ. Ratios in parentheses are activity ratios. Bulk-Earth ^{230}Th/^{232}Th value of 4.4 x 10^{-6} with arbitrarily assigned 50% uncertainty was used for detrital ^{230}Th correction to calculate the corrected ^{230}Th ages. uncorr. and corr. denote uncorrected and corrected, respectively.

Sample ID	**Tissue**	**U (ppm)**	**^{232}Th (ppb)**	**(^{230}Th/ ^{232}Th)**	**(^{230}Th/^{238} U)**	**(^{234}U/ ^{238}U)**	**uncorr. ^{230}Th Age (ka)**	**corr. ^{230}Th Age (ka)**
#536	Enamel	0.0979 ± 0.0003	22.95 ± 0.037	10.88 ± 0.11	0.840 ± 0.009	1.539 ± 0.003	81.4 ± 1.2	77.1 ± 2.0

	Dentine	8.420 ± 0.051	270.4 ± 1	6.75 ± 0.033	0.0715 ± 0.0005	1.448 ± 0.007	5.506 ± 0.047	4.85 ± 0.33
#537	Enamel	0.1655 ± 0.0004	6.560 ± 0.013	62.22 ± 0.49	0.813 ± 0.006	1.521 ± 0.003	79.06 ± 0.90	78.34 ± 0.94
	Dentine	3.498 ± 0.001	95.67 ± 0.15	65.26 ± 0.19	0.588 ± 0.002	1.493 ± 0.003	53.00 ± 0.24	52.48 ± 0.31
	Cement	5.370 ± 0.003	181.60 ± 0.17	61.53± 0.11	0.686 ± 0.001	1.523 ± 0.002	62.75 ± 0.16	62.13 ± 0.28

U-series/ESR age calculations

U, Th and K contents were obtained from the ICP-OES/MS analysis of the dry raw sediment (previously powdered and homogenized) following a four-acid digest preparation procedure. We used the following parameters for the dose rate calculations: an alpha efficiency of 0.13±0.02 (Grün and Katzenberger-Apel 1994), Monte-Carlo beta attenuation factors from Marsh (1999), dose-rate conversion factors from Guérin et al. (2011), an estimated water content of 0 and 5 ± 3 wt.% in enamel and dentine, respectively. A sample geometry sediment/enamel/dentine and cement/enamel/dentine was used for the beta dose rate attenuations of samples #536 and #537, respectively.

We performed age calculations with USESR, a Matlab-based program (Shao et al. 2014) using the US and AU models defined by Grün et al. (1988) and Shao et al. (2012), respectively. We also carried out additional CSUS-ESR age calculations using DATA, a DOS-based program (Grün 2009). The CSUS-ESR model defined by Grün (2000b) is based on the assumption that all of the uranium migrated into the sample at a time given by the closed system U-series age. The CSUS-ESR age is the maximum age that can be derived from a given U-series and ESR data set. Age calculations using the US or AU and CSUS models encompass all possible uptake scenarios. Table 3 presents data inputs and outputs.

TABLE 3. Data inputs and outputs corresponding to the combined US-ESR age calculations. All errors are given at a 1-σ confidence level, including the U-series data (1) taken from Table 6. Final D_E errors are made of a combination of errors from the fitting (Table 5) and the dose rate from the gamma source (2.3%). Post-Rn equilibrium was considered in dental tissues and sediment. n.a. = not applicable.

SAMPLE	**#536**	**#537**
Enamel		
Dose (Gy)	171.2 ± 8.4	158.7 ± 12.5
U (ppm) (1)	0.098 ± 0.000	0.166 ± 0.000
$^{234}U/^{238}U$ (1)	1.539 ± 0.002	1.521 ± 0.001
$^{230}Th/^{234}U$ (1)	0.546 ± 0.003	0.534 ± 0.002
Alpha Efficiency	0.13 ± 0.02	0.13 ± 0.02
Water content (%)	0	0
Initial enamel thickness (µm)	1143 ± 114	1436 ± 144

Dentine		
U (ppm) [(1)]	8.420 ± 0.026	3.498 ± 0.002
$^{234}U/^{238}U$ [(1)]	1.448 ± 0.003	1.493 ± 0.002
$^{230}Th/^{234}U$ [(1)]	0.049 ± 0.000	0.394 ± 0.001
Water (%)	5 ± 3	5 ± 3
Removed enamel thickness (µm)	152 ± 15	49 ± 5
Cement		
U (ppm) [(1)]	n.a.	5.370 ± 0.001
Th (ppm) [(1)]	n.a.	1.523 ± 0.001
K (%) [(1)]	n.a.	0.450 ± 0.000
Water (%)	n.a.	5 ± 3
Removed thickness (µm)	n.a.	133 ± 13
Sediment		
U (ppm)	3.47 ± 0.14	2.83 ± 0.12
Th (ppm)	11.34 ± 0.48	12.04 ± 0.51
K (%)	0.34 ± 0.01	0.36 ± 0.01
Water (%)	15 ± 5	15 ± 5
Removed thickness (µm)	158 ± 16	n.a.
Combined U-series/ESR age calculations		
internal dose rate (µGy a^{-1})	19 ± 4	32 ± 6
beta dose rate, dentine (µGy a^{-1})	9 ± 2	12 ± 2
beta dose rate, sediment or cement (µGy a^{-1})	88 ± 7	18 ±
Gamma + cosmic dose rate (µGy a^{-1})	1032 ± 44	1004 ± 44
Total dose rate (µGy a^{-1})	1141 ± 107	1065 ± 136
p or *n* enamel	-0.4	-0.3
p or *n* dentine	24.7	0.5
P cement	n.a.	0.1
US-ESR age (ka)	**150 ± 12**	**149 ± 15**

Results and discussion

ESR data

The two enamel samples were measured using a similar amount of material (about 20 mg per aliquot) (Table 1). Intensity precision was good (<2 %), resulting in highly repeatable D_E estimates (D_E variation between 0.1 and 3.1 %). Fitting was performed using a maximum irradiation dose (D_{max}) of 1470 Gy in order to meet the recommendations of Duval and Grün (2016), who had previously shown that the D_{max}/D_E ratio should be somewhere between 5 and 10 for D_E values >100 Gy. This results in D_E estimates that slightly differ by only 1-3% with the values initially derived from the DRC fitting with D_{max} = 3430 Gy (Table 5), demonstrating that the two sets of fitting results remain within 1-σ error. Final D_E values are 171 ± 7 Gy and 159 ± 12 Gy for teeth #536 and #537, respectively (Fig. 1).

U-series results

Solution U-series analyses returned very low uranium concentrations in the enamel samples (<0.2 ppm; Table 6), while they vary between ~3.5 and ~8.4 ppm in the dentine and cement. Additionally, there was no evidence of apparent uranium leaching, as all samples returned finite U-series ages. These observations suggest that the samples are suitable for ESR dating.

Apparent U-series ages measured in the dental tissues vary between ~52 and ~78 ka, except for the dentine of #536, which returns a significantly younger age of ~4.8 ka. In this case, the measured $^{234}U/^{238}U$ activity ratio of 1.448 is the lowest of the data set (Table 2). It corresponds to an initial $^{234}U/^{238}U$ of 1.458, whereas it ranges from 1.576 to 1.716 for the other samples: these differences suggest that the younger age result obtained for the dentine of #536 may result from a more recent overprint associated with a different uranium uptake event compared to the other samples. This may have partially impacted the dentine and cement of #537, which also return slightly younger ages. In comparison, the two enamel samples return highly consistent apparent ages of 77-78 ka, which may be interpreted as the most reliable chronological constraints: these ages should be regarded as minimum age estimates for the fossils, as uranium uptake may sometimes be significantly delayed after the death and burial of the teeth.

Dose rate considerations

Radioelement concentrations in the sediment vary within relatively narrow range (Table 3): 2.8-3.47 ppm of U, 11.34-12.04 ppm of Th and 0.34-0.36 % of K. They result in very close gamma dose rate values of 818-846 µGy/a for the two teeth, showing the relative homogeneity of the sediment in the vicinity of the samples.

Combined U-series and ESR dating

Because combined U-series and ESR age calculations did not show any evidence of uranium leaching, we could employ the US model for all dental tissues without any restrictions, while the use of the AU model was not required. These calculations return highly consistent US-ESR estimates of 150 ± 12 ka and 149 ± 15 ka for samples #536 and #537, respectively (Table 3). A mean age of 150 ± 14 ka (1σ), corresponding to the arithmetic averages of the individual ages and errors, may be calculated from these two teeth. These results show that the dental tissues carry little weight in the total dose rate (<6%), unlike the sedimentary environment, which accounts for between 77 and 82 % depending on the tooth considered.

Consequently, the uncertainty around the uranium uptake modelling has a very limited (and almost negligible) impact on the calculated ages: the CSUS-ESR estimates are only 2-3% older than the US-ESR results. Instead, we identified a few sources of uncertainty around the evaluation of the sedimentary dose that may have a more significant impact on the age results. For example, we performed age sensitivity tests by varying the long-term water content from 5% to 25%: these resulted in an increase of about 32-33 ka, from 134-135 ka (5% water content) to 166-168 ka (25%) (Fig. 2). In any case, regardless of the water content value considered, the US-ESR age estimates systematically indicate an MIS 6 chronology (191-130 ka; Lisiecki and Raymo 2005) for the two teeth. While current water content in the sediment has been measured to <2% as part of the parallel ongoing luminescence dating study performed on a couple of samples collected from the test-trench, i.e. ~3.5 m away from the B2 square, we consider in first

instance that this value is unlikely to be an accurate estimate of the long-term water content. The proximity of the dripline and wall of the rock shelter as well as of the river (~ 5m away) may have contributed to the circulation of percolating water through the sediment as well as more overall humid conditions in the past. Consequently, we consider the assumed value of 15 ± 5 % as a more reasonable estimate of past humidity conditions. Moreover, the large absolute error of 5% at 1-σ confidence level accounts for any fluctuation of humidity over time within the range of 5 to 25% at a 2-σ confidence level. The calculated US-ESR age estimates and associate error already encompass some variability in the long-term water content.

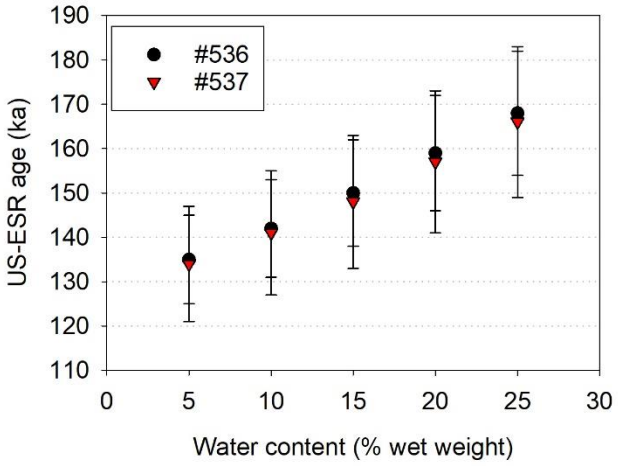

Fig. 2 Sensitivity tests evaluating the impact of the water content on the calculated US-ESR age results.

We performed cosmic dose rate evaluation using depth as the main source of uncertainty. However, one cannot reasonably exclude that the proximity of the wall and the presence of a partial sandstone cover several meters above the excavation area may have played a role in attenuating some of the cosmic dose rate. Assuming a rough attenuation of the cosmic dose rate by 50% following Richard et al. (2017) would produce an age increase of about 9%, up to around 163 ka. This extreme scenario illustrates the relatively limited impact of this parameter on the calculated age, which would still be consistent with an MIS 6 chronology.

Finally, we acknowledge that one of the major sources of uncertainty in the dose rate evaluation results from the heterogeneity of the sedimentary environment around the teeth, with the presence of blocks and clasts in a silty to sandy sedimentary matrix. The majority of the clasts result from *in situ* breakdown and decaying of the walls and roof of the rock shelter (sandstones). Although the raw sediment samples analysed by ICP were previously powdered and homogenised, it is unlikely that the gamma dose rate derived from these analyses fully captured the true gamma dose rate with the exact proportion of clasts and sediment. Instead, we suspect the clasts were probably underrepresented in the laboratory analyses. A quick age simulation assuming a decrease or increase of the gamma dose rate by 15% would make the US-ESR estimates older by ~13% and younger by ~10% respectively. They would reach 169 ka and 135 ka, but would still remain consistent with an MIS 6 chronology. Although this gives

a rough idea of how this uncertainty may impact the age results, at this stage any further interpretation of the current data would be speculation in the absence of the measurement of *in situ* radioactivity.

In summary, the two samples yield highly consistent combined US-ESR age estimates of about 150 ka. However, we do acknowledge the existence of a series of sources of uncertainty that may have a non-negligible impact on the age results, as illustrated by the various sensitivity tests performed. In any case, all scenarios consistently point towards an MIS6 age (130-191 ka) for the samples, which is at present the most reasonable and cautious conclusion. These results provide an indirect chronological constraint for the MSA lithic and ochre assemblages found in association with the fossil bones. New analyses in the future, and in particular *in situ* evaluations of the gamma dose rate, should help to refine the chronology of the site. Additionally, the samples collected a few meters away from the southern wall for luminescence dating purpose will not only give some key insights about the contemporaneity of the deposits with the fossil assemblage, but also help to chrono-stratigraphically correlate the units identified from the test-trench with the deposits excavated in the B2-B3 squares.

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