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Older than expected: fluvial aggradation of the Rhine's main terrace at Kärlich dated around 1.5 Ma by electron spin resonance

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S1. The archaeo-palaeontological record at Kärlich

S1.1. Main Sequence

The various stratigraphic units (from A to J) identified in the sedimentary sequence at Kärlich have delivered fossil remains of large and small mammals (see overview in van Kolfschoten and Turner, 1996). The possible presence of a very few (and somewhat questionable) lithic artefacts within layers A, B and H has also been reported (see Haidle and Pawlik, 2010 and references therein).

S1.2. Kärlich-Seeufer archaeological site

The nearby Kärlich-Seeufer archaeological site is associated to unit J of the local sequence (Gaudzinski et al., 1996) but is stratigraphically younger. It is well known for its abundant archaeological artefacts (attributed to the Mode 2, or Acheulean, technocomplex) and fossil remains, which are unlikely to be in primary position (Gaudzinski et al., 1996). Despite this, and the absence of a robust chronostratigraphic framework, the site has often been regarded as key Lower Palaeolithic locality in the German archaeological record and beyond (e.g., Haidle and Pawlik, 2010, Bosinski, 2006). The age of Kärlich-Seeufer has been tentatively assigned to the 0.2-0.4 Ma timespan despite the absence of any direct dating results based on petrographical, palaeontological and archaeological correlations (Boenigk and Frechen, 1998). From a biochronological point of view, the presence of the rodent taxa *Mimomys savini* and *Arvicola terrestris* in the lower units F and G, respectively, suggests that the site post-dates the Mimomys-Arvicola transition that is roughly constrained to the early Middle Pleistocene (van Kolfschoten and Turner, 1996; Wagner et al., 2011). ESR dating of an elephant tooth collected from the site yielded a tentative age ranging from 0.30 to 0.58 Ma (Debuyst et al., 2000). This result should, however, be considered with extreme caution given the significant uncertainty associated to (i) the absence of *in situ* dosimetry, (ii) the rough evaluation of the gamma attenuation produced by the tooth itself, (iii) and the absence of combined U-series and ESR data to model uranium uptake in dental tissues.

S2. Methodology

Sample preparation and ESR dose evaluation were performed at the University of Cologne (Germany) and CENIEH (Burgos, Spain), respectively, using the same analytical procedure and experimental conditions as in Bartz et al. (2020) and Parés et al. (2023).

S2.1. Multiple centre (MC) ESR dating: basic principles

The multiple centre (MC) approach applied to the two ESR samples was first suggested by Toyoda et al. (2000). This approach is based on the systematic measurement of at least two paramagnetic centres in quartz grains to account for different signal bleaching kinetics during sediment transport prior to deposition. In the present work, the ESR signals of both the Aluminium (Al) and Titanium (Ti) centres were measured in the two ESR samples. The Al signal is characterized by much slower

bleaching rates compared to those of the Ti centre, and there is even an unbleachable signal component that needs to be evaluated for each sample to avoid dose overestimation. For example, laboratory experiments have shown that the Al signal needs several tens of days of sunlight bleaching to reach its residual, unbleachable, signal intensity (e.g., Toyoda et al., 2000, Duval et al. 2017). In comparison, the Ti centre (option D *sensu* Duval and Guilarte, 2015), which corresponds to a mixture of Ti-Li and Ti-H signals, is characterized by much faster bleaching kinetics: a complete reset may be achieved in the laboratory after a few hours to a few days of sunlight exposure, depending on the signal selected (Toyoda et al., 2000, Duval et al. 2017). Given that all ESR signals of a given quartz sample should have been reset at the same time, and should therefore theoretically give a similar D_E estimate. If not, any difference in the D_E value derived from the Al and Ti centres (with $D_E(Al) > D_E(Ti)$) would most likely reflect an incomplete reset of the Al signal during sediment transport before burial. In this case, the Al signal would provide a maximum age constraint for the sample, while the Ti signal would yield the closest estimate to the true burial age.

S2.2. Field measurements

In situ measurements of the gamma dose rate were performed at each sampling spot with a Canberra Inspector 1000 instrument, made of a NaI probe connected to a multichannel analyser. Additional sediment samples were collected for laboratory analyses (i.e. radioelement content and water content evaluation).

S2.3. ESR dosimetry

Quartz samples were divided into 13 aliquots: one was kept untouched (natural aliquot), one was UV-bleached using a solar simulator (Hönle SOL2), and twelve were gamma irradiated using a Gammacell-1000 Cs-137 source up to 50.1 kGy. ESR measurements were carried out at 90 K, with an EMXmicro 6/1Bruker X-band ESR spectrometer coupled to a standard rectangular ER 4102ST cavity (so-called setup #1 in Guilarte et al., 2022). The Al and Ti centres were measured following the measurement protocol by Bartz et al. (2020).

The ESR intensity (Fig. 3a) 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 last peak (g=1.9928) (Toyoda and Falguères, 2003). The ESR intensity of the Ti centre (Fig. 3a) was measured from the peak-to-baseline amplitude of the peak at g=1.913 (i.e., option D *sensu* Duval and Guilarte, 2015). Final Dose Response Curves (DRCs) were obtained by plotting the mean ESR intensities and associated one standard deviation derived from the repeated measurements. An exponential+linear function (EXP+LIN) was fitted through the Al ESR intensities (Duval, 2012) over the full dose range, with data weighting by the inverse of the squared intensities ($1/I^2$) and the inverse of the squared experimental errors ($1/s^2$). Fitting of the Ti ESR intensities was carried out using the so-called Ti-2 function as in Duval and Guilarte (2015) with data weighting by $1/s^2$, and a single saturating exponential (SSE) function (Duval et al., 2009) with data weighting by $1/I^2$ up to the maximum ESR intensities at 9.1 kGy. Fitting was performed with Microcal OriginPro 9.1 software, which is based on a Levenberg-Marquardt algorithm by chi-square minimisation. For further details about the ESR dose evaluation procedure and the relevant associated bibliography, the reader may refer to Parés et al. (2023).

S2.4. Dose rate and ESR age calculation

The total dose rate value was derived from a combination of *in situ* and laboratory measurements. *In situ* gamma dose rates were calculated from the "threshold technique" (Duval and Arnold, 2013). For each sample, the corresponding radioelement (U, Th, K) concentrations were determined by High Resolution Gamma Spectrometry (HRGS) analysis at the University of Cologne. Dry, raw sediment (ca. 400 g) was powdered and stored for about four weeks to allow secular equilibrium to be attained between ^{222}Rn and its parent ^{226}Ra in the uranium decay chain. The waiting time is essential to allow the ^{226}Rn-^{222}Rn mother-daughter products to reestablish as the ^{222}Rn content of the sample can be decreased due to manipulations of the sample in the laboratory when preparing the sediment for HRGS measurements (De Corte et al., 2006).

Concentration values were used to derive external alpha and beta dose rate components using the dose rate conversion factors from Guérin et al. (2011), while the gamma dose rate was taken from the *in situ* measurements. Dose rates and ESR ages were calculated with DRAC (Durcan et al., 2015). Dose rate values were calculated assuming a mean grain size of 150 µm, and an assumed thickness removed by HF etching of 20 µm following Duval et al. (2018). Internal dose rate was assumed to be 30 ± 10 µGy/a, based on the work from Vandenberghe et al. (2008) and using an alpha efficiency of 0.07 ± 0.01 (Bartz et al., 2019). Values were corrected with beta and alpha attenuation values for spherical grains (Brennan et al., 1991; Brennan, 2003). Current water contents were evaluated in the laboratory by drying the sediment at 50 ºC in an oven during three weeks. We obtained relatively low values of 10.4 % (RHE1502) and 3.9 % (RHE1502), which very likely represent a minimum estimate of the long-term water content, as outcropping sedimentary section resulting from the quarrying activities has probably partially dried out over the last decade prior to sampling. Consequently, we assumed a slightly higher value of 15 ± 5 % (% wet weight) as a more suitable estimate of the long-term water content. A 1σ relative uncertainty of 33 % has been assigned to the water content estimate in order to cover any potential variations in moisture conditions during burial. *In situ* gamma dose rate values were corrected accordingly. The cosmic dose rate was calculated using formulae from Prescott and Hutton (1994), with depth, altitude and latitude corrections, and assuming two scenarios. Scenario A is based on the assumption that the depth below the top of the fluvial deposits (about 8 m) has prevailed throughout the burial history, while scenario B is based on the maximum depth (ca. 30 m) below the top of the sequence. ESR ages are given at 1σ (Table 1).

S3. ESR results

Fitting results are given in Table S1. Repeated ESR measurements show a variability of the ESR intensities (Al: 0.6-1.4 %; Ti 0.8-2.0%) and resulting D_e values (Al: 8.3-12.4 %; Ti 7.9-12.3 %) that are within usual standards for both the Al and Ti signals (Duval et al., 2024). DRC fitting of the Al intensities with the EXP+LIN function and data weighting by $1/I^2$ returns D_E values of 2391 ± 180 Gy and 1960 ± 230 Gy for RHE1501 and RHE1502, respectively. Additional fitting carried out with the same function but with data weighting by $1/s^2$ return D_E values higher by 7-8 %, but nevertheless within 1σ error. Similarly, DRC fitting of the Ti intensities carried out with the Ti-2 ($1/s^2$) and SSE ($1/I^2$) yield D_E results that agree for a given sample. However, it is worth observing that the SSE results are likely to be less reliable, as they systematically show a lower goodness-of-fit, resulting in relatively large errors (>15 %). To sum up, the relatively good consistency between the dose estimates derived from various fitting functions and data weighting options indicate that there is no significant fitting bias. For the ESR age calculations, we use the dose estimated derived from the fitting with the highest goodness-of-fit (highest adjusted r^2), i.e., considered more reliable.

Table S1: Summary of the ESR data collected from the repeated measurement of the Al and Ti centres in samples RHE1501 and RHE1502. Bleaching coefficient is expressed as the relative difference (%) between the ESR intensities of the natural and bleached aliquots. Repeatability of the ESR intensities is assessed through the variability (1 relative standard deviation) of the mean ESR intensities obtained after each day of measurements. Similarly, the repeatability of the D_E values corresponds to the variability (1 relative standard deviation) of the D_E values calculated for each day of measurement. Key: (W-1/I^2) and (W-1/s^2) refer to the data weighting by the inverse of the squared intensities (1/I^2) and by the inverse of the squared experimental errors (1/s^2), respectively.

Al signal				**EXP+LIN (W-1/I^2)**			**EXP+LIN (W-1/s^2)**	
Sample	**Repeated meas.**	**Bleaching Coefficient (%)**	**Repeatability of the ESR intensities (%)**	**Repeatability of the D_E estimates (%)**	**Adj. r^2**	**D_E (Gy)**	**Adj. r^2**	**D_E (Gy)**
RHE1501	3	55.6 ± 1.4	0.6	8.3	0.994	2391 ± 180	0.980	2602 ± 143
RHE1502	3	51.6 ± 2.3	1.4	12.4	0.994	1960 ± 230	0.997	2109 ± 211
Ti signal				**Ti-2 (W-1/s^2)**			**SSE (W-1/I^2) D_{max} = 9.1 kGy**	
Sample	**Repeated meas.**		**Repeatability of the ESR intensities (%)**	**Repeatability of the D_E estimates (%)**	**Adj. r^2**	**D_E (Gy)**	**Adj.r^2**	**D_E (Gy)**
RHE1501	3		0.8	10.3	0.993	2431 ± 243	0.980	2683 ± 455
RHE1502	3		2.0	7.9	0.992	2232 ± 240	0.964	2652 ± 592

References

Bartz, M., Duval, M., Brill, D., Zander, A., King, G. E., Rhein, A., Walk, J., Stauch, G., Lehmkuhl, F., and Brückner, H.: Testing the potential of K-feldspar pIR-IRSL and quartz ESR for dating coastal alluvial fan complexes in arid environments, Quaternary International, 556, 124–143, https://doi.org/10.1016/j.quaint.2020.03.037, 2020.

Bartz, M., Arnold, L. J., Spooner, N. A., Demuro, M., Campaño, I., Rixhon, G., Brückner, H., and Duval, M.: First experimental evaluation of the alpha efficiency in coarse-grained quartz for ESR dating purposes: implications for dose rate evaluation, Sci Rep, 9, 19769, https://doi.org/10.1038/s41598-019-54688-9, 2019.

Boenigk, W., Frechen, M.: Zur Geologie der Deckschichten von Kärlich/Mittelrhein. Eiszeitalter und Gegenwart 48, 38–49, 1998.

Bosinski, G.: Les premiers peuplements de l'Europe centrale et de l'Est, C R Palevol, 5, 311–317, https://doi.org/10.1016/j.crpv.2005.09.004, 2006.

Brennan, B. J.: Beta doses to spherical grains, Radiat Meas, 37, 299–303, https://doi.org/10.1016/S1350-4487(03)00011-8, 2003.

Brennan, B. J., Lyons, R. G., and Phillips, S. W.: Attenuation of alpha particle track dose for spherical grains, Int J Rad Appl Instrum D, 18, 249–253, https://doi.org/10.1016/1359-0189(91)90119-3, 1991.

Debuyst, R., Callens, F., Frechen, M., Dejehet, F.: ESR Study of elephant tooth enamel from the Kärlich-Seeufer site in Germany. Applied Radiation and Isotopes 52, 1327–1336. https://doi.org/10.1016/S0969-8043(00)00091-9, 2000.

De Corte, F., Vandenberghe, D., De Wispelaere, A., Buylaert, J.-P., and Van den Haute, P.: Radon loss from encapsulated sediments in Ge gamma-ray spectrometry for the annual radiation dose determination in luminescence dating, Czechoslovak Journal of Physics, 56, D183–D194, https://doi.org/10.1007/s10582-006-0504-9, 2006.

Durcan, J. A., King, G. E., and Duller, G. A. T.: DRAC: Dose Rate and Age Calculator for trapped charge dating, Quat Geochronol, 28, 54–61, https://doi.org/10.1016/j.quageo.2015.03.012, 2015.

Duval, M.: Dose response curve of the ESR signal of the Aluminium centre in quartz grains extracted from sediment, Ancient TL, 30, 41–49, 2012.

Duval, M., Guilarte, V., Bartz, M., Alonso Escarza, M. J., Ben Arous, E., del Val, M., and García Rodríguez, C.: ESR dating of optically-bleached quartz grains: Evaluating measurement repeatability and reproducibility, Radiation Physics and Chemistry, 215, 111313, https://doi.org/10.1016/j.radphyschem.2023.111313, 2024.

Duval, M., Guilarte, V., Campaña, I., Arnold, L., Miguens, L., Iglesias, J., and González-Sierra, S.: Quantifying hydrofluoric acid etching of quartz and feldspar coarse grains based on weight loss estimates: implication for ESR and luminescence dating studies, Ancient TL, 36, 1–14, 2018.

Duval, M., Arnold, L. J., Guilarte, V., Demuro, M., Santonja, M., and Pérez-González, A.: Electron spin resonance dating of optically bleached quartz grains from the Middle Palaeolithic site of Cuesta de la Bajada (Spain) using the multiple centres approach, Quat Geochronol, 37, 82–96, https://doi.org/10.1016/J.QUAGEO.2016.09.006, 2017.

Duval, M. and Guilarte, V.: ESR dosimetry of optically bleached quartz grains extracted from Plio-Quaternary sediment: Evaluating some key aspects of the ESR signals associated to the Ti-centers, Radiat Meas, 78, 28–41, https://doi.org/10.1016/j.radmeas.2014.10.002, 2015.

Duval, M. and Arnold, L. J.: Field gamma dose-rate assessment in natural sedimentary contexts using LaBr3(Ce) and NaI(Tl) probes: A comparison between the "threshold" and "windows" techniques, Applied Radiation and Isotopes, 74, 36–45, https://doi.org/10.1016/j.apradiso.2012.12.006, 2013.

Duval, M., Grün, R., Falguères, C., Bahain, J. J., and Dolo, J. M.: ESR dating of Lower Pleistocene fossil teeth: Limits of the single saturating exponential (SSE) function for the equivalent dose determination, Radiat Meas, https://doi.org/10.1016/j.radmeas.2009.03.017, 2009.

Gaudzinski, S., Bittmann, F., Boenigk, W., Frechen, M., Van Kolfschoten, T.: Palaeoecology and Archaeology of the Kärlich–Seeufer Open-Air Site (Middle Pleistocene) in the Central Rhineland, Germany. Quat Res 46, 319–334, https://doi.org/10.1006/qres.1996.0070, 1996.

Guérin, G., Mericier, N., and Adamiec, G.: Dose-rate conversion factors: update, Ancient TL, 29, 5–8, 2011.

Guilarte, V., Fang, F., Grün, R., and Duval, M.: ESR dating of quartz grains: Evaluating the performance of various cryogenic systems for dosimetric purpose, Radiat Meas, 155, 106802, https://doi.org/10.1016/j.radmeas.2022.106802, 2022.

Haidle, M.N., Pawlik, A.F.: The earliest settlement of Germany: Is there anything out there? Quat Int 223-224, 143-153. https://doi.org/10.1016/j.quaint.2010.02.009, 2010.

Parés, J.M.; Haddoumi, H., Duval, M.; Álvarez-Posada, C.; Aouraghe, H; Pla-Pueyo, S.; Benito-Calvo, A.; Rodríguez-Hidalgo, A.; van der Made, J.; Piñero, P.; Agustí, J.; Oujaa, A.; Grün, R.; Chacón, M. G.; Sala-Ramos, R.: First magnetostratigraphic results in the Aïn Beni Mathar-Guefaït Basin, Northern High Plateaus (Morocco): the Dhar Iroumyane composite section. Geobios 76, 17-36, https://doi.org/10.1016/j.geobios.2023.01.004, 2023.

Prescott, J. R. and Hutton, J. T.: Cosmic ray contributions to dose rates for luminescence and ESR dating: Large depths and long-term time variations, Radiat Meas, 23, 497–500, https://doi.org/10.1016/1350-4487(94)90086-8, 1994.

Toyoda, S., Voinchet, P., Falguères, C., Dolo, J.M., Laurent, M., Bleaching of ESR signals by the sunlight: a laboratory experiment for establishing the ESR dating of sediments. Applied Radiation and Isotopes 52, 1357–1362, https://doi.org/10.1016/S0969-8043(00)00095-6, 2000.

Toyoda, S. and Falguères, C.: The method to represent the ESR signal intensity of the aluminium hole center in quartz for the purpose of dating, Advances in ESR Applications, 20, 7–10, 2003.

Vandenberghe, D., De Corte, F., Buylaert, J. P., Kučera, J., and Van den haute, P.: On the internal radioactivity in quartz, Radiat Meas, 43, 771–775, https://doi.org/10.1016/j.radmeas.2008.01.016, 2008.

van Kolfschoten, T., Turner, E.: Early Middle Pleistocene mammalian faunas from Kärlich and Miesenheim I and their biostratigraphical implications, 1st Edition. ed. CRC Press, 1996.

Wagner, G.A., Maul, L.C., Löscher, M., Schreiber, H.D.: Mauer – the type site of Homo heidelbergensis: palaeoenvironment and age. Quat Sci Rev 30, 1464–1473. https://doi.org/10.1016/j.quascirev.2010.01.013, 2011.