A very personal, 35 years long journey in ESR dating

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Abstract

This paper describes a personal journey in ESR dating and gives some insights of the progress made over 35 years in ESR dating of tooth enamel. When I started, samples were irradiated with four additive dose steps of 5, 10, 15 and 20 krad and the linear extrapolation yielded the dose value. An assumed dose rate of 100 mrad/a yielded the age of the sample. Since then I learned that one actually has to measure the dose rate. I also learned that the dose response can be described by a single saturating function, or perhaps two, and that errors can be appropriately calculated. Rather than having a single anisotropic CO_2^- radical, tooth enamel consists of two anisotropic CO_2^- radicals and two isotropic CO_2^- radicals, one stable, one unstable. Also, the dose response shows spatial differences in the production of these different radicals in response to beta and gamma rays. Then there is the problem of uranium uptake over time. We solved this by combining ESR and U-series analyses. We can even measure appropriate beta attenuation factors from sequential laser ablation U-series analyses. Even better, all analyses can be carried out on small enamel fragments, which can be glued back into their original position with little to no visible damage. Still, when using the most sophisticated dose rate calculations, they're often close to $1000 \mu\text{Gy a}^{-1}$.

In the late 1970s, I was a geology student under the supervision of Prof Karl Brunnacker who was the Professor of Quaternary geology at the Universität zu Köln. He farmed me out to the Institut für Kernchemie (nuclear chemistry) to learn, under the supervision of Gerd J. Hennig, U-series dating, a new, revolutionary dating method for Quaternary geology. My Diploma thesis (Grün 1982) was on the U-series dating of spring deposited travertines, a study that was published in the same year (Grün et al. 1982). The samples consisted of about 500 g of travertine, a dirty calcitic material, which was dissolved, went through iron co-precipitation etc. For connoisseurs of chemical pre-treatments, we used ion exchange columns that were about 30 cm long with a diameter of about 1 cm (today, pipette tips will do nicely). The tops often clogged up with some phosphate precipitations, which contained nearly all Th isotopes. U and Th eluates were electroplated onto 2 cm diameter steel disks, which were subsequently measured by an alpha counter. Data processing was carried out on a mainframe computer and we used cardboard punch strips for data storage. While I was mightily impressed by the computational facilities (we had none in geology), I did not particularly like the chemistry aspect.

Gerd Hennig had started to work on ESR dating a couple of years earlier and had published his work on the Petralona skull in Nature (Hennig et al. 1981). ESR dating was easy (Hennig and Grün 1983): take a sample, produce five aliquots by grinding and sieving (my kind of pre-treatment), irradiate with 0, 5, 10, 15 and 20 krad (rad is the old unit for radiation dose; $100 \text{ rad} = 1 \text{ Gy}$), measure with ESR. The intensity of any ESR line that showed a response to the dose was plotted against the five dose steps and linear extrapolation yielded the dose value (Figure 1). While we were aware about some aspects of the intricacies of dose rate calculations, we usually assumed a dose rate of 100 mrad/a to get an estimate of the age of the sample. A sample with 10 krad is a hundred thousand years old, voilà.

In the years to follow, I embarked on a research career, which focussed mainly on ESR dating, a method for which there is absolutely no reason whatsoever that it could possibly work. Nevertheless, there were cases where it yielded surprisingly sensible results. In the following, I will mainly refer to my work on ESR dating of tooth enamel. Just before I started my doctoral thesis, Gerd Hennig arranged for me to attend the Third

Specialist Seminar on TL and ESR dating organised by Vagn Mejdahl at Helsingør in July 1982. Of course, being completely unaware at the time, this meeting was a defining moment for me to join the luminescence/ESR fraternity. Gerd arranged a lift with Ulrich Radtke in a battered, dark brown Datsun station wagon. We both clicked instantly and have been life-long friends since. Firstly, we were mightily impressed by the arrival of David Sanderson in an open top MGB. We were both daunted by the prospect of attending a conference where the language was English. Trying to avoid our non-German speaking colleagues, Ulrich and I walked on the grounds of the venue when we met a short guy with silver hair and a small suitcase who said "Hi, I'm Henry Schwarcz, who are you?". We replied that we were students working with Gerd Hennig and Henry responded, "I came all the way from Canada to meet with Gerd!". Wow! The meeting was attended by all godmothers and godfathers of TL and ESR dating, including Ann Wintle (the only international scholar I had met before), Martin Aitken, John Prescott, Paul Levy, Motoji Ikeya, Désiré Apers, George Valladas, Ashock Singhvi, K.S.V. Nambi, Yuji Yokoyama, Galina Hütt, Helen Rendell, Peter Townsend, Glenn Berger, Andrew Murray, Steve McKeever, Ian Bailiff, Sheridan Bowman, Augusto Mangini, Günther Wagner, Lars Bøtter-Jensen, Hélène Valladas. Many of these scholars had significant influence on my career. I will always be grateful to Gerd Hennig who made all this happen. His early passing robbed the luminescence/ESR community of one of its great pioneers (Grün 1992).

At the start of my doctoral thesis, Gerd asked me to join him in writing a review on ESR dating. Since we were offered a fee of £8 per page, we embarked on writing a paper as long as possible. We managed 82 pages. At the time, I could contribute only a few results, but did most of the figures (with Rotring ink pens on transparent drawing paper, using razor blades for corrections). The paper was published at the end of 1983 (Hennig and Grün 1983).

During my doctoral thesis, I carried out many of my measurements at the Laboratoire de Chimie Inorganique et Nucléaire at the Université Catholique de Louvain in Louvain-la Neuve. The chair was Prof. Désiré Apers who, with his associates Rene Debuyst and Fernand Dejehet, were supervising a single PhD student, Pierre DeCannière. They were actually not interested in dating, they were working on the underlying physical and chemical principles of ESR dosimetry. They were asking questions about the correct dose response, errors, and dose rate calculations (obviously guessing 100 mrad/a wasn't quite good enough here). Irradiation of my valuable samples with more than just 4 dose steps and higher doses clearly demonstrated that the dose response was not linear at all, but instead followed an exponential function, as shown by Apers et al. (1981). It did not quite convince Henry Schwarcz, who brought that topic up at a discussion at the 4th International Specialist Seminar on Thermoluminescence and Electron-Spin-Resonance Dating in Worms. On Henry's statement "We really have to explore whether the dose response is linear or exponential" Paul Levy replied, "we knew since the early 50s that there is nothing like a linear dose response". Martin Aitken commented: "I think that answers your question, Henry". One would have thought that settled the question indeed, well far from it, see the discussion in Grün (1996).

Then there was the question of alpha efficiency. We did not have alpha sources in Köln, so I visited the Research Laboratory for Archaeology and the History of Art where the formidable Joan Huxley taught me to prepare fine grain samples for alpha irradiation. The source was made from smoke detector Am-241 foils with a collimator of about 1 cm diameter, designed for the irradiation of TL fine grain disks. As there were a lot of discs required for one ESR sample, I thought we could do better and asked the workshop at the Institut für Kernchemie to build one with a 10 cm diameter alpha source (Grün and Katzenberger-Apel 1994), very useful for ESR experiments and a headache for people with occupational health and safety concerns. Pierre De Canniere did one better and used Po doping for alpha irradiation (De Canniere et al. 1986). Now we had a value for the alpha efficiency of tooth enamel (0.13 ± 0.02 , Grün and Katzenberger-Apel 1994), which has since been used in most ESR dating publications, but never been re-measured. I was interested in the uranium distribution in teeth and used fission track mapping (Grün and Invernati 1985). A mica waver was mounted onto the sample and irradiated in a reactor. ²³⁵U fissions when exposed to neutron beams (how to build an atomic bomb 101) and the material coming from the reactor was highly radioactive. It was unpacked on a table with a lead brick wall in front of me. Of course, I had a finger dosimeter and a Geiger counter. I checked behind the lead brick wall and it went tick..tick..tick. Surely, I was safe. After a while I was contemplating about the wooden nature of the table and the possible radiation exposure of my reproductive organs. Thus, I moved the Geiger detector under the table. The instrument's loud screeching made me jump

backwards for quite a distance. Furthermore, the mica wavers had to be etched with conc. HF in a process that underpinned my aversion to chemical pre-treatments.

During my PhD we carried out fieldwork in Greece and Spain to collect speleothem records for the reconstruction of palaeoclimate (see Hennig et al. 1983). One of the places we visited in 1983 with Adolfo Eraso and Emiliano Aguirre was Atapuerca. We went down the Sima and discussed how to date the site. As there were no visible speleothem floors intercalated with the sediment I replied that it was not possible. We took a sample from the railway trench that was published some years later (Grün and Aguirre 1987). Shortly afterwards, excavations began at the Sima, and a team member asked me whether I wanted to do the dating of the site. I replied that I was about to start my postdoc fellowship in Canada and did not want to take on more projects and categorically stated "...and, by the way, there is absolutely nothing there.....".

Shortly after obtaining my doctoral degree in early 1985 (Grün 1985a), I joined Henry Schwarcz at McMaster University as a postdoc. Henry had probably the greatest influence on my academic career, through inspiration, mentoring and friendship. Those fortunate to know him will attest to his genial butterfly mind, exploring new research opportunities and continuously producing ideas, some absolutely brilliant, many very entertaining and only a few not so brilliant, and nobody actually having the time to pursue most of them. Fortunately for me, Hamilton, Ontario, was in 1985, not the most inspiring place distracting freshly baked postdocs with idle attractions. This ambiance helped me to focus on research. One of the main problems for ESR dating of teeth was the unknown U-uptake. Ikeya (1982) had recognised this problem early on and had proposed two possible U-uptake models: early U-uptake (EU), where all uranium that is measured in a sample was taken up within a very short period after burial (in effect instantaneously) and linear U-uptake. Since one had no idea, which model was correct, one conveniently chose the one that matched the expected result. I found that slightly unsatisfactory (see also Grün 2009a) and thought of combining ESR and U-series dating, as both face the same problem, but to a different extent. Henry recommended contacting John Chadam to sort out the math. Until then I had never met a mathematician and I was unaware that they spoke a different language. Whenever I described "the problem" John produced a series of formulae on a white board and asked: "do you mean this?" to which I replied, "I have no idea". John was very keen to know the spatial distributions of uranium in the dental tissues so that he could calculate the dose rate distributions and integrate them properly. It took three months of continual misunderstandings until I succeeded of dumbing John down to my level (we only have U-concentration, $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{U}/^{234}\text{U}$ activity ratios for each tissue, but have no idea how it gets into the sample and where it actually sits, hey, let's not worry about this, in most cases we cannot measure the data anyway), and to agree on a one-parameter diffusion equation ($U(t) = U_m (t/T)^{P+1}$ where U_m is the measured U concentration, T the age of the sample and p the diffusion parameter) and write a computer program to solve for p and T for a given data set. The reason for using this equation, rather than an exponential, was that it can compute sub-linear U-uptake histories. For the above mentioned parametric models, $P=-1$ represents the EU model and $P=0$ the LU (Grün et al. 1988). We also wrote a paper with all equations and submitted to a prominent geochemistry journal, but it was rejected on the grounds of being "too mathematical". It took only another 27 years to get the equations out to the scientific community (Shao et al. 2015). The paper originally had little impact as it was difficult to measure U-isotopes in dental tissues with conventional alpha spectrometric methods.

Then there was the continuing problem of calculating errors for the exponential dose response. These had hitherto either been neglected or assumed. Henry recommended contacting Peter Macdonald, a statistician at McMaster University. Communication was reasonably straight forward, and Peter suggested using jack-knifing for error assessment. It involves continuously dropping out one data point of the set and re-calculating the dose value. The error is derived from the distribution of these dose values. Unfortunately, for data sets with a few values, the errors become very large (Grün and Macdonald, 1989). While in Canada, I was asked to write a review for a book on dating methods for the Quaternary to be delivered at the INQUA congress 1987 in Ottawa. It turned out that I was the only one who had actually written the review by the deadline. The deadline was extended several times, and, in the end, the book was never published. In the meantime, I got in contact with Springer for a book on ESR dating in German. So, I translated my English manuscript into German and that book was published earlier (Grün 1989a) than the original English manuscript, which came out as a stand-alone paper (Grün 1989b). It is still among the 10 highest cited papers published in Quaternary International.

Another problem arose from the beta attenuation. While data were available for grains in TL dating (Mejdahl 1979), nothing had been published for layers. I calculated beta attenuation factors for the various decay chains. It turned out that an initial calculation, using the average beta energy (in formula (1) of Grün 1986) yielded beta attenuation curves that implied a much stronger attenuation compared to the experimental results of Aitken et al. (1985). However, a reasonable match was obtained when using the maximum energy. Later, one group theory (Brennan et al. 1997), as well as Monte Carlo calculations using the emission spectra of various beta emitters (Yang et al. 1998, Marsh 1999) showed that the beta attenuation was indeed much stronger than calculated by Grün (1986).

One of the highlights of my time in Canada was the attendance of the 1st International Symposium on ESR Dating, 1985 in Ube. The meeting was organised by Motoji Ikeya and was the forerunner of the present EPR Biodosimetry conference series (see Ikeya and Miki, 1985). Amongst many EPR luminaries, the conference was attended by Shenhua Li and Christophe Falgueres (when Christophe and I had significantly more hair than today, see Figure 2), Toshikatsu Miki, Katsujiro Tanaka, Huang Pei-Hua, Anne Skinner, Dieter Regulla, Ruth Lyons, Pete Smart and KSV Nambi. The other was the Colloque International L'Homme de Neanderthal, 1986 in Liege, organised by Marcel Otte (see Otte 1988). Here, I first met with Chris Stringer and Jean-Jacques Hublin, as well as Eduoard Bard, who subsequently decided to pursue a career in U-series rather than ESR dating (see what happened to him!). I won't mention a very fine recital of the runner-up performance originally entered at the Oxford Student Burping competition.

In 1987, Henry ran out of money for my position and I was very lucky that Ann Wintle was looking for someone to take over her position as head of the luminescence laboratory at the Subdepartment of Quaternary Research, University of Cambridge. Ann took me under her wings and I was one of many upcoming researchers who Ann mentored and promoted during her long and extremely successful career. I was supported by the fastidious Susan Packman and had the pleasure to watch LiPing Zhou and Geoff Duller taking their first steps in luminescence dating under Ann's tutelage. Hence, my temporary meddling in the affairs of luminescence dating, including one of the first single grain luminescence analyses (Grün et al. 1989), and developing an interest in TL kinetics (Grün 1994, Grün and Packman 1994). The time at Cambridge cemented my collaboration and friendship with Chris Stringer, resulting in my first Nature paper on the age of the modern human site at Skhul (Stringer et al. 1989) and a review of ESR dating and modern human evolution (Grün and Stringer 1991). It was shortly followed by my first first-authored Nature paper on the ESR dating of Border Cave (Grün et al. 1990a). I even managed to have my boss, Nick Shackleton, to co-author a paper with me (Grün et al. 1990b). At Cambridge, I was joined by Ed Rhodes and Jack Rink. Ed and I thought that it was much more convenient to model rather than to actually measure data points. Ed developed a true random number generator and we simulated dose response curves (Grün and Rhodes 1991, 1992, Rhodes and Grün 1991) to assess the best dose step distributions (exponential), number of dose steps (around 10) and maximum additive doses (around ten times the expected D_e value). I am pleased to report that more than 25 years later; the exact same conclusions were reported by Joannes-Boyau et al. (2018). I spent much of my time writing software, DATA for calculating ESR ages and AGE for TL age calculations and data evaluation programs for the Risø reader. It dawned on me in 2009 that I should write a couple of short papers explaining the two programs (Grün 2009b,c). These have been cited around 80 and 40 times, respectively. I wonder what their citation numbers would have been had I published the papers twenty years earlier when people were actually using the programs (they were written in Quick basic and one needs a DOS computer to run them). And for those who complain of small offices (like me), at Cambridge, at one stage, I shared the office with John Chappell, Margaret Deith, Susan Packman, Ed Rhodes, Jack Rink and Henry Schwarcz. The office had one window and on stepping on a box and cranking one's head, one could find out whether it was raining. One also learned to work while wearing headphones.

Again, a lack of research funds signalled that it was time for a move. In 1991, John Chappell from the ANU spent his sabbatical with Nick Shackleton to continue work on the reconstruction of late Pleistocene sea-levels (Chappell and Shackleton 1986). John had previously lured me into attending a fieldwork campaign at Huon Peninsula in PNG. It turned out to be one of the wettest, mosquito infested dry seasons ever. Other victims of this infamous venture, amongst others, were Yoko Ota, Akio Omura, Art Bloom, Larry Edwards, Brad Pillans, Helmut Brückner, Morti Stein, and Jerry Wasserburg. Brad and I spent many days soggy wet in

the elevated reefs collecting samples and devouring the four essential food groups for the tropics: peanut butter, cream cheese, tinned mackerels and biscuits, while dreaming of warm beer. Still, a paper on ESR dating of corals was the outcome (Grün et al. 1992). Back in Cambridge, John, being aware of my impending unemployment, asked: "are you aware of the position in the radiocarbon lab at ANU?" to which I replied "No". "Do you want to apply for it?" - "No". "Hey Rainer, let's have a beer". A few months later, my family and I were on a plane to Australia.

I started in February 1992 as Head of the ANU Radiocarbon Dating Laboratory, originally at the Research School of Pacific Studies. The ANU C-14 laboratory was run semi-commercially, and looking back at the time, I don't think I was very good at either running a commercial lab or radiocarbon dating. We expanded the radiocarbon laboratory with ESR and luminescence dating and called ourselves the Quaternary Dating Research Centre. Nigel Spooner took over the luminescence aspect. On a field trip to the Simpson Desert, John, Giff Miller and I came up with the idea to start a journal on Quaternary Geochronology, which started in 1994 as a part of Quaternary Science Reviews and became independent in 2006. At ANU, I met with Stephen Brumby to finally calculate proper errors for the dose values (Grün and Brumby 1994). These were fortunately much smaller than those of the jack-knifing approach. In 1998, I joined the Research School of Earth Sciences, which became my academic home for the next 17 years.

The most important event in the early years at ANU was an invitation by James Brink from the National Museum in Bloemfontein to visit the Florisbad site and to work out whether we could date the famous Florisbad hominid. We collected samples from all layers at the site and found that the results highly scattered. Initially, I had no appreciation for the site formation. The site is an artesian spring, which forms a lake which traps windblown sand forming a sequence of horizontal layers. The water from the springs in the bedrock bubbles through these layers and while a particular spring is active, it forms a vent. Any bone deposited within the sand layers that the vent transverses as well as bones deposited at the surface of the vent, will accumulate at its base. This was also the case for the human bones. The results for samples from the vent collection ranged from 40 to 400 ka. When John Vogel, the head of the dating laboratory at Pretoria, asked me how my dating was coming along, and I told him the results, he replied "I could have told you that". Indeed. Since I know little to nothing about human fossils, I asked James whether the fossil had teeth. He replied yes in a way. A human tooth was found at the same time and since all human bones come from one individual, it could be assumed that the tooth originated from that individual as well. It was clear, even to me, that I could not take the tooth home to remove the enamel and grind it up. So, I suggested to remove a small piece of enamel so that I could analyse this fragment as a single aliquot. Later one could glue it back. Very much to my surprise, James agreed to that and proceeded to remove a small piece of tooth enamel (well, he actually got two). The procedure of removing a tooth enamel fragment is highly sophisticated: one needs three pieces of equipment: (1) plasticine (or Blue Tack if you live in Australia), which is wrapped around the tooth so that nothing gets lost; (2) a small screw driver, pointing to the enamel section to be removed and (3) a small mallet/pestle/hammer giving a little tick onto the screw driver. Most fossil teeth have cracks in their enamel, the fragments are easily removed. The reason for breaking rather than cutting the sample is that no material is lost, when cutting one loses the material in the cut. Figure 3 shows the Tabun C1 mandible before (Figure 3 top row) and after removing a fragment (Figure 3 middle row), and backfit of the enamel piece (Figure 3 bottom row). With a little paint the removal becomes invisible (i.e. the ESR analysis is virtually non-destructive). The main message, however, is: never ever remove the piece yourself, always let the palaeoanthropologist in charge of the fossil to do the deed. Contrary to various reports, I have actually never done this. This started the protocol for semi non-destructive ESR dating of human fossils. The results on Florisbad were duly published in *Nature* (Grün et al. 1996). James's invitation initiated a long-standing research agenda in South Africa and led to a close friendship.

As a proof of concept, I was keen to get hold of Border Cave 5 (BC5). It is a human mandible that was found by Peter Beaumont *in situ* in a layer called 3rd white ash (3WA), about a meter below the surface (see Figure 4). This was an important find, as it was from an anatomically modern human individual, found in a layer previously dated to around 64 to 74 ka. Sillen and Morris (1996) had carried out some infrared analysis as well as nitrogen concentration measurements on bone material from Border Cave and concluded that BC5 was most likely of Iron Age. It was somehow transferred from the Iron Age layers close to the surface to the 3WA. Peter Beaumont was very distraught about the implication that he simply did not see a ditch dug about

1 m down from the surface. One has to keep in mind that the stratigraphy at Border Cave is very simple (see Figure 4). As we had a complete ESR sequence of the site (Grün et al. 1990, Grün and Beaumont 2001), we should be able to determine whether the tooth came from the layer where Peter had found it, or from the surface. Again, I needed a fragment. The Border Cave material is housed at the University of the Witwatersrand and the famous Phillip Tobias was in charge of it. The first problem was that a compatriot of mine with the same first name had collected human samples for amino acid racemisation dating that had caused significant damage of a number of very famous human fossils (the round hole on the top of BC1 resulted from coring, half of a baby skeleton, BC3, vanished, a large chunk of the Florisbad cranium was cut out, etc.). After leaving a comprehensive track of destruction, results were never published. Not surprisingly, the incident had made Phillip very hesitant to consider any further removal of material from the Border Cave human specimens. Assuring that only a small piece of tooth enamel was required and that it would be returned, Phillip took BC5 out of the safe and started to study it under the microscope. When he mumbled "uh, I really don't know how to remove a piece of tooth enamel" I made the mistake and offered a G-pick. That set the sampling back by two years. The enamel fragment was again analysed by a single aliquot ESR protocol and for the first time we used laser ablation ICP mass spectrometry to assess the U-concentrations in the enamel and dentine. In the end we could prove that BC5 had received a dose in the same range as the surrounding faunal teeth and that its age was most likely around 74 ± 5 ka (Grün et al. 2003), see Figure 5.

The Research School of Earth Sciences has a long tradition of developing cutting edge mass spectrometers, particularly SHRIMPs: sensitive high-resolution ion micro probe - it is clearly always useful to start with an acronym and then end up with the name of the equipment. The ANU laser ablation cell was developed by Stephen Eggins who introduced me to the equipment and I him to the fascinating world of archaeological and palaeoanthropological applications. We embarked on a close and lasting research collaboration and friendship. Here I really must mention Les Kinsley, who has been in charge of the Earth Environment mass spectrometer facility. Without his encyclopaedic knowledge of all aspects of the Neptune mass spectrometer (and any other spectrometer in his charge) and his ingenious ability to find and rectify faults, plus his patience with this impatient researcher, I'd never have been able to run nearly as many samples as I did. Under his tutelage, the RSES Neptune has been running on average 11 months a year. While visiting many other labs, I noted more non-operating than running Neptunes.

As outlined above, understanding the process of U-uptake in bones is crucial for ESR dating. In the late 1990s, Robert Hedges and Andrew Millard (Millard 1993, Millard and Hedges 1996) proposed the diffusion-adsorption (DA) model, which is based on experimental results. This model was refined by Alistair Pike during his PhD work at Oxford (Pike 2000, Pike et al. 2002). In short, a bone is regarded as a homogeneous slab. Any water contains U isotopes but not any Th. When a bone is exposed in such a solution (i.e. groundwater) the surface will equilibrate more or less instantly. With time, U will diffuse into the bones and is adsorbed at crystal surfaces or organic molecules. While the uranium is still mobile within the bone, any radiogenic ^{230}Th , derived from the decay of ^{234}U , is immobile and will stay in the place where it was generated. In an ideal case, the bone will have u-shaped U-concentration as well as age profiles. The age in the domain close to the surface of the bone would be the time when the bone was first exposed to the solution (i.e. the burial of the bone). After some unspecified time, the system becomes closed. The model has the great advantage that bones can be checked whether they adhere to the model or not. Leaching can be recognised by a U-loss close to the outside and secondary overprints by inverted age profiles. At the time of Alistair's thesis, bones were first checked for the U-concentration profiles. That entailed drilling samples out and preparing them for ICP-MS. This involves column chemistry! After a week or so one can decide whether the bone is suitable for U-series analysis. Again, chemistry is required prior to the 5 to 8 TIMS (thermal ionisation mass spectrometry) measurements that are required for the DA modelling of a cross section. That would take a few weeks per bone sample. With laser ablation, sample preparation takes about 5 to 10 minutes per bone and the measurements of 30 sample points across a bone profile can be done in a few hours (Figure 6). Alistair visited the ANU several times to run samples on our laser system (see e.g. Pike et al 2004, 2005, Grün et al 2010, Aubert et al. 2012). After Alistair accepted a position in Bristol, he vanished from any email contact. Our problem was that we could produce a large number of data sets on bones, but we could not apply any DA calculations. The program was only available on the mainframe of Oxford University and the only one who could run it was Alistair. So, Stephen and I contacted Malcolm Sambridge from the Geophysics section of our school to write a DA program for us that could be used on a personal

computer. Malcolm thought that it was boring just to re-write an existing program, he was more interested in the actual process. So, we came up with the diffusion-adsorption-decay model. The argument was that while a bone is in contact with a solution, uranium ions will continuously diffuse into the bone and the system is actually never closed. The outcome of this is that the $^{234}\text{U}/^{238}\text{U}$ ratio at the surface of the bone remains constant. If the $^{234}\text{U}/^{238}\text{U}$ ratio in the water is > 1 (it usually is), then depending on the rate of diffusion the $^{234}\text{U}/^{238}\text{U}$ ratio becomes smaller further inside the bone (Sambridge et al, 2012). That would have the general advantage that the $^{234}\text{U}/^{238}\text{U}$ ratio could be used as a stand-alone chronometer, particularly for old bones where the $^{230}\text{Th}/^{234}\text{U}$ is in equilibrium. If the $^{234}\text{U}/^{238}\text{U}$ ratio is > 1 , the DA and DAD ages will be similar for younger bones (< 100 ka), but the DAD results will be significantly older for older bones (for $^{234}\text{U}/^{238}\text{U} = 1$, DA and DAD results are the same). Regardless of which model is applied, one has to keep in mind that U-series results on skeletal material need to be regarded as minimum age estimates. We cannot pick up a longer phase where no or little U-diffusion takes place followed by a more massive U-uptake. In several instances, the U-series ages reflect phases of groundwater activation, where horizontal sediment layers are dissected by rivers, due to a lowering of the sea levels during glacial times.

Figure 6 shows a laser ablation data points across a bone. The U-concentration profile is u-shaped and so is the age profile. Indeed, this is a bone that adheres to the criteria outlines in the DA and DAD models. On the right side of Figure 6 is a comparison of laser ablation and solution ICP-MS results on the same samples. While there is some discrepancy for the U-concentrations, only one sample is outside the 2- σ range for the $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ ratios. One has to say that u-shaped concentration and age profiles apply only to very small number of bones. Most do not behave like a homogeneous layer; many bones have pores or are denser close to the outer surface. One often observes smaller U-concentrations near the outside along with younger ages etc. which may be the result of a secondary U-uptake phase along with a smaller actual surface area per volume available for adsorption. There is also U-micro-migration (Duval et al. 2011). Some bones show several U-uptake pulses, most of which seem to happen in short time ranges (hundreds rather than thousands of years (Grün et al. 2014)). Nevertheless, for understanding any of these processes it is necessary to analyse cross sections. The best, of course would be a complete map (e.g. Aubert et al. 2012). The problem with analysing human teeth is the cutting of cross sections. Although a cut with a say 100 μm diamond blade is semi non-destructive in my book as the cut is difficult to spot once the parts are put back together. Instead, I suggested to simply drill into a sample with the laser and analyse whatever comes out of the hole it creates. "Don't do it" said Steve, as he was aware of the different ablation behaviour of U and Th (which makes it also difficult to use continuous laser ablation tracks for U-series analysis). I thought I should do it anyway. Firstly, we needed to find out what the laser does to faunal material. We used an enamel layer with a thickness of around 2 mm and ablated with laser beams of variable diameters for about 1500 s (see Figure 7). All holes are conical and only the two widest laser beams drilled through the sample, the rest got "stuck". The reason for the conical shape is that the area in the centre of the beam is hotter than the area close to the cooler sidewalls, causing slightly more ablation in the centre. The conical shape then causes the laser to bounce off the side walls. The net result is that some material is ablated from the side walls as well as the base. Additionally, some of the ablated material will plate out at the side walls. Altogether, mixing occurs. Here I'd like to point out the ingenious way Harry Kokkonen cut this sample. The smallest hole has a diameter of 13 μm at the top, in order to see the cross section of the conical hole, the horizontal and vertical alignment has to be perfect, probably better than 1-2 μm . How did he do this?

We used a tooth from Garba that had a very distinct U-series isotope distribution. First, we analysed cross sections with continuous tracks and distinct sampling spots. Then we analysed the sample by drilling into it from the side. As can be seen in Figure 8, the results from the drilling reflects the cross-section data for the first 1000 μm after which complete mixing occurs. Laser drilling now allows the analyses of valuable human bones and teeth with minimum damage while still being able to obtain insights into the U-diffusion processes. This was, for example, vital for the interpretation of the analyses on the Saudi finger bone from Al Wusta (Groucutt et al 2018). Table 1 summarises laser ablation U-series analyses on fossil human bones. Although the U-series results need to be considered as minimum age estimates (see above), they contributed greatly to the understanding of human evolution: the *Homo floresiensis* fossils from Liang Bua turned out to be considerably older than the 18 ka derived from radiocarbon dated seemingly associated material. The modern human bones from Wajak were much older and showed that modern humans were already in southeast Asia when they just began to migrate into Europe (Storm et al. 2013). There were humans in the

Philippines well before 50 ka (Mijares et al. 2010). In this context I have to remind the reader of the ingenious approach of Yokoyama using gamma spectrometry for completely non-destructive U-series dating of fossil material (Yokoyama and Nguyen 1981a,b, see also Simpson and Grün 1998), which lead to the dating of many important human fossils, including Tautavel (Yokoyama and Nguyen 1981b), Qafzeh (Yokoyama et al. 1997), Mungo 3 (Thorne et al. 1999), Ngandong and Sambungmacan (Yokoyama et al. 2008). While this approach is indeed completely non-destructive, it is often associated with large errors because of the difficulty of precisely measuring ^{234}U (see discussion in Grün 2006a).

In the early 1990, Chris Stringer and I embarked on the dating of Broken Hill (Kabwe). Before one gets too excited, the study is still not finished. This time, three small enamel pieces were removed so that they could be measured along the three major axes. I thought, I had conclusively shown that the ESR signal used for dating tooth enamel was from a single CO_2^- radical and that the natural and laboratory irradiated signals were identical (Grün 2002, 2006b, see Figure 9). Depending on how the tooth enamel piece is mounted in the cavity, its ESR spectrum changes. That is simply the result of the internal, non-isotropic magnetic field interfering with the external magnetic field (Figure 10). The enamel fragments were mounted onto a specific holder that allows removal, irradiation and reinsertion into the ESR spectrometer of the fragment into exactly the same physical position. Each fragment is rotated by 360° and measured every 10° . The spectra were then stacked yielding 3D ESR spectra as shown in Figure 10. Now, if the ESR spectrum consisted only of one component, the 3D spectra would look similar to the ones shown in Figure 10, but more importantly, any dose estimation would give the same result. Unfortunately, the opposite turned out. The gamma induced ESR spectra (Figure 11, second row) are very different to the natural ESR spectra (Figure 11, first row). In the second configuration (BHL), the residual spectra, which show the qualitative differences between the natural and irradiation induced spectra, are massive. The dose values were highly dependent on the physical position of the fragment in the ESR spectrometer, and which part of the spectrum was used for dose assessment (Figure 11, bottom row)). On the other hand, when all spectra were merged, the resulting average spectrum was that of a powder CO_2^- radical (Figure 12) and the natural and irradiation spectra are closely similar. This implied that tooth enamel contained at least two different components, one similar to a powder spectrum originating from a non-orientated CO_2^- radical (NOCOR) and an orientated, anisotropic CO_2^- radical (AICOR). In 2006, I was joined by Renaud Joannes-Boyau whose job it was to quantify the different CO_2^- radicals. Figure 13 shows the process: the natural spectra (Figure 13, top row) were analysed for various isotropic lines. Then each spectrum was decomposed by three or four Gaussian lines (R1 to R4). It turns out that the natural spectra are better approximated by four lines. R_1 is associated with an orthorhombic CO_2^- radical, R_2 with an axial CO_2^- radical, R_3 contains the sum of all misalignments and R_4 is the sum of g_y and g_z of the aforementioned anisotropic radicals plus the g_z of the non-orientated CO_2^- radicals (for more details, see Joannes-Boyau and Grün 2011). After subtracting the natural spectrum from the natural+gamma, the irradiation spectrum was decomposed in the same way (Figure 13 bottom row). The irradiation spectra of some samples did not contain the axial component (R_2), others did. This decomposition was then carried out for all angles of an irradiation step and then for all irradiation steps. After that the various components are integrated to obtain the relative percentages on AICORS and NOCORS in the sample.

It turned out that there are at least two AICORS (one axial, one orthorhombic) and two NOCORS (one stable, one unstable). Also, the AICORS and NOCORS behave differently to beta and gamma irradiation, and the orthorhombic AICORS may transfer to axial AICORS and a significant amount of NOCORS transfer to AICORS (Figure 14). Confused? It's all explained in Joannes-Boyau and Grün (2011). The main outcome was that the distribution of NOCORS in a piece of tooth enamel is uneven. There are significantly more NOCORS close to the dentine enamel junction than close to the outside, furthermore, uranium migrates from the dentine into the enamel (Grün et al., 2008), which makes the domain close to the dentine much less suitable for dating than the enamel domain close to the outside. Renaud found a fast way to quantify the amount of NOCORS created in the gamma irradiation process (Joannes-Boyau 2013) with the outcome that some samples have a considerable amount of gamma induced unstable components, others don't.

During one of my stays at the Département de Préhistoire du Muséum National d'Histoire Naturelle, Paris, thanks to the generosity of Christophe Falguères, Jean-Jacques Bahain and François Sémah, I met with a PhD student, Mathieu Duval, who tried to understand the ESR dose response of tooth enamel. After some discussions, we agreed to have significantly more data points in the high dose region (up to 50 kGy). He found that the dose response was best described by two saturating functions, instead of one (Duval et al. 2009). The data sets require several high dose steps, in the range of 10 kGy to 50 kGy, to define the second saturating function. Now this had serious implications for ESR dating. If it was really required to produce high dose data and fit the points with two saturating functions to derive accurate results, then all previously published dose values were perhaps slightly iffy. Some years later, Mathieu and I revived Ed Rhodes's random number generator and found that the concern was unfounded. If the maximum irradiation dose is roughly kept to eight times the De value, results from fitting a single exponential function to this data set are indistinguishable from results fitting a double exponential function to a data set that was irradiated to much higher doses (Duval and Grün 2016). This has two advantages, firstly there were no problems with previously published De values and secondly, high additional dose steps are not required, which, depending on the strength of the gamma source, may take considerable time (days to weeks).

Since working on Border Cave 5, I have been using laser ablation ICP mass spectrometry to obtain U-series data on the teeth used for ESR dating. Laser ablation analysis requires my kind of chemical pretreatment (my aversion to chemistry hasn't changed). Cut the sample, press it into a holder filled with Blue Tack (plasticine), press it down with a glass plate until the cross section is flush with the rim of the holder, insert into laser ablation cell and run. Even cleaning is done with the laser (for the detailed systematics, see Grün et al. 2014). As laser ablation U-series analysis has become more widely available, the combination of ESR and U-series has more often been applied, making Grün et al. (1988) a modern classic in ESR dating (cited more in the last ten years than the first twenty). Mathieu visited the ANU to work with Maxime Aubert on laser ablation U-series analysis of archaeological teeth, which resulted in a 3D reconstruction of the diffusion processes U-series isotopes in an archaeological horse tooth (Duval et al. 2011).

Coming back to the beta attenuation. The luminescence group at Bordeaux has developed sophisticated programs for the calculation of beta attenuation factors, *Dosivox*, based on the actual distribution of beta emitters and the minerals used for luminescence dating based on the *geant 4* simulation software (Martin 2015). As I am marginally involved in ESR thermochronometry (see Grün et al. 1999), we required an approach to calculate realistic beta dose rates in metamorphic and igneous rocks. Loïc Martin and my student Fang Fang worked on the development of 2D mineral scanning and beta dose calculations on polished rock sections (Martin et al., in press, Fang et al., in press). Mathieu and I invited Loïc to Brisbane to work on the beta attenuation in tooth enamel. The input data are the actual laser ablation U-series measurements, along with the p-value open system. Now, after more than 30 years after I began my collaboration with John Chadam, we are finally able to determine the spatial distributions of uranium isotopes and the dose rates within a tooth (the paper is forthcoming).

So, how is ESR dating of tooth enamel **properly** done? Firstly, a tooth should be collected *in situ*. The sediment around the tooth is collected for the assessment of water, Th, K and U. Next, *in situ* gamma spectrometry measurements are carried out. If there is a discrepancy between the elemental analyses and the *in-situ* measurements, U-series disequilibrium measurements (with a high-resolution Ge detector, e.g. Simpson and Grün 1998) on a larger sediment sample needs to be carried out. This was, for example, crucial for the dating of the megafauna site on Kangaroo Island (Grün et al. 2006), which initially indicated a much younger age than the previously established "extinction event" for the Australian megafauna (Roberts et al. 2001). The tooth is then cross sectioned, and laser ablation U-series analyses are carried out. These will give already an idea about the age of the sample and show the uranium distribution in the dentine and enamel. The enamel volume close to the dentine enamel junction should be avoided for two reasons: (1) there are significantly more unstable NOCORS in this volume and (2) uranium generally migrates from the dentine into the enamel rather than from the outside (Eggins et al. 2005, Grün et al. 2008). The variable amount of unstable NOCORS is probably the reason why isochron approaches (Blackwell et al. 1993, 2001) usually do not work. The laser ablation data can then guide how much thickness is best removed from the outer enamel volumes. Ideally, the extracted enamel fragment is measured as a whole as a single aliquot so that the amount of unstable, radiation induced NOCORS can be estimated (Joannes-Boyau 2013). As we do not have

any 2D or depth information for the U-isotope distribution, the fragment is then powdered and analysed for U-series isotopes, using TIMS (e.g. Shao et al. 2011). The internal dose rates are calculated from the TIMS results and self-dosing factors, the external dose rates can be calculated from the laser ablation isotope distribution, elemental and water analyses of the adhering sediment, beta attenuation factors and the *in-situ* gamma dose rate (using *Dosivox*). If the tooth was part of a mandible, or skull, the adhering bone material will, on the one hand, attenuate the sediment gamma dose rate and, on the other hand, provide a partial gamma dose rate derived from its U-series isotopes (Nathan and Grün 2003), which may need to be measured.

Of course, the alternative is to irradiate the sample with 0, 50, 100, 150 and 200 Gy and apply a linear extrapolation (Figure 1). The D_e overestimation from linear fitting will compensate to some extent for unstable NOCORS. Then, an assumed dose rate of say $1000 \pm 200 \mu\text{Gy a}^{-1}$ is applied. After compiling the results from all human fossils hitherto dated by US-ESR (Table 2), this approach will give reasonable ages for many of the samples. Keep in mind that many assumptions used for the calculation of the dose rate values in Table 2 may or may not be correct. The real dose rate could be much closer to $1000 \mu\text{Gy a}^{-1}$, well, or not.

I firmly believe in evolution, and that also applies to universities and their departments. If old farts like me refuse to retire, young aspiring scientists don't have a future. So, I decided that I should retire at the age of 60 and signed a pre-retirement contract (Australian universities do not have a compulsory retirement age). I, of course, had in mind to live out my academic career somewhere in France (it is well known that I do like Paris and Bordeaux). Whilst preparing for my life after the ANU, I discovered the French tax man. To cut a long story short, it shut the door on my academic life in France. Instead, Michael Westaway and my old postdoc Maxime Aubert lured me to Griffith University where my brief was to set up the Australian Research Centre for Human Evolution (ARCHE). Here I was joined with my earlier collaborators Mathieu Duval and Tanya Smith (see Smith et al. 2007). I will now effectively retire at the end of 2019. ESR research will continue at ARCHE by Mathieu while I may focus on the theme that has been haunting me for all of my career: how does uranium migrate into bones????

Looking back at the last 35 years, what do I regard as my main scientific contributions? I remember my first original idea when measuring mollusc shells at the Laboratoire de Chimie Inorganique et Nucléaire at Louvain-la Neuve, sometime in 1984. Molluscs have two signals one of which is unstable, the other one is "stable". It occurred to me that if I knew the mean life of the unstable signal, I should be able to estimate the dose rate the mollusc had been exposed to and then use the stable signal for dating (Debuyst et al. 1984, Grün 1985b). That made me truly excited. I couldn't ring anybody since it was around 12 am (night owl syndrome). Anyway, a month or so later, I visited Oxford and told Martin Aitken about my great idea and he replied "oh, there was a French group, which suggested that for TL" (Langouet et al. 1976, 1979). I was a bit devastated to find that others had the same idea. Well, at least it was original for me. The second one was to combine ESR and U-series to solve for U-uptake. The third one was to use ESR for palaeothermometry. Although some ESR work had been carried out before (Agel et al. 1991, Scherer et al. 1993, 1994), the study on the Eldzhurtinsky granite was the first to investigate the ESR systematics for palaeothermometry and came up with denudation rates that actually made sense (Grün et al. 1999). There was also a very interesting fieldtrip associated with this study where a Russian truck drove us through the Caucasus, partly without functioning brakes. There was also a great poker evening near Mt Elbrus with Steve Robertson, Atsushi Tani, Anatoly Gurbanov and Dmitry Koshug. I didn't pursue ESR palaeothermometry any further until recently. Nevertheless, I thought it was a groovy application. It seems that playing squash with Frederic Herman caused some leakage of the method into luminescence. I am pretty pleased that I could develop the protocol for nearly non-destructive dating of human fossils, from both the ESR and U-series side and that the results had some impact on our understanding of the timing of human evolution. The other stuff is just slow systematic work on things I was working on. I have to say, the best ideas usually come while measuring samples. Thus, it is a good habit to continue measuring samples until one leaves the field.

One reviewer raised the question why ESR is not widely applied. There are some reasons for it. After an initial flurry of applications, it turned out that ESR could be applied to a number of materials, but each had their problems that could not easily be resolved. In addition, many materials, e.g., corals or speleothems,

could be much better dated with other dating methods, U-series in particular. When it comes to tooth enamel, it was actually quite difficult to apply ESR dating because U-series analyses on small samples could not easily be obtained. This has changed with the introduction of laser ablation analysis. While it is true that there are presently only a few ESR dating laboratories, they are slowly expanding. Unfortunately, research into the basics of ESR dating is widely neglected.

Acknowledgment

I apologise to my wife Fiona, who has not yet forgiven me yet that I dragged her to Australia. As this paper focuses (very badly) on ESR dating of tooth enamel, many colleagues and collaborators are not mentioned. Since I have absolutely no plans to write an extended version of this paper, I can only say: tough! (or relief I presume).

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Figure Captions

Figure 1: Dose response curve (from Hennig and Grün 1983)

Figure 2: Attendees of the 1st International Symposium on ESR Dating, 1985 in Ube (selected delegates): (1) Toshikatsu Miki, (2) Motoji Ikeya, (3) Huang Pei-Hua, (4) Ruth Lyons, (5) Peter Smart, (6) Shenhua Li, (7) Christophe Falgueres, (8) Henry Schwarcz, (9) Anne Skinner, (10) K.S.V. Nambi

Figure 3: Extraction of a piece of tooth enamel. Top row, the mandible of Tabun C1. Middle row: teeth after the extraction of an enamel fragment. Lower row: After re-insertion of the enamel fragment. The fragments easily break off along the natural cracks. Ideally, no material is lost due to cutting (Photos courtesy of C.B. Stringer)

Figure 4: Border Cave. Left: Photo taken shortly after the discovery of BC5 (arrow with B). The sub-circular feature (arrow with a) seemed of particular importance. As can be seen from the photo and the respective drawing (right), the sediments at Border Cave are easy to follow and any burial of BC5 from Iron Age layers close to the surface down to 3WA, more than one metre below, should be easily visible (from Grün et al. 1990b)

Figure 5: ESR chronology of Border Cave compared to C-14 results and position and age of BC5 (from Grün et al. 1990b)

Figure 6: Left column: Laser ablation measurements on a bone from Ngandong. Top, the sample is bracketed by three measurements of an NBS standard glass, three measurements of a rhino standard, followed by the measurements of the sample. The measurements show a clear u-shaped profile across the bone. The middle diagram shows the initial seven measurements, and the lower diagram the $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ ratios for the first seven measurements. Both ratios decrease from the outside towards the interior on the bone.

Right column: comparison of laser ablation with solution TIMS analysis. Only one sample falls outside the combined 2- σ error range for the $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ ratios (from Grün et al. 2014).

Figure 7: Laser ablation holes drilled for 1500 s into the enamel layer of sample 2104. The tooth surface after drilling (top), cross section with cavity profiles below. The maximum depths for holes 3 to 12 are shown on the right (from Benson et al. 2013).

Figure 8: Comparison of U-series isotopic ratios from cross section scanning and spot analysis (233 μm spot size for cleaning and 178 μm for analysis) with depth profile drilling (233 μm) on tooth enamel of a hippopotamus tooth from the archaeological site of Garba Melka Kunture (Chavaillon and Berthelet, 2004). Top: Cross scan and spot analyses, below: isotope data aligned with the track in the photo (from Benson et al., 2013).

Figure 9: ESR spectra of sample 2122A. Top: natural and natural+ irradiation spectra, middle: rescaled irradiation spectra, bottom: scaled natural and irradiation spectra. The residual shows that apart from a small interference in the middle (due to a methyl line) both spectra are qualitatively the same (from Grün 2006)

Figure 10: left: configuration of the enamel fragment in the external magnet of the ESR spectrometer. Right: Spectrum stack for ESR measurements with 10° incremental rotations (from Grün 2008)

Figure 11: Left column: configuration as in Figure 10. Right column: configuration along the third major axis (not shown in Figure 10). Top row: Stack of natural spectra, second row: irradiation spectra, third row: residual spectra showing the qualitative differences between the natural and irradiation spectra. Bottom row: dose estimations for using various features in the ESR spectra (from Grün et al. 2008).

Figure 12: Merged spectra (from stacks in Figures 10 and 11): Left: natural and natural + irradiation, Right rescaled natural and irradiation spectra. When merging all spectra over all three configurations, the resulting natural and irradiation spectra are qualitatively very close assimilate spectra of powders (Figure 9) (from Grün 2008).

Figure 13: Top row: Deconvolution of a natural spectrum. A: identification of the isotropic lines, Deconvolution of the remaining spectrum with four (B) and three (C) Gaussian lines (from Joannes-Boyau et al. 2010a). Second row: Deconvolution of an irradiation spectrum. (D): Isotropic lines, (E) deconvolution with four Gaussian lines. It turns out that the irradiation spectrum does not contain the R2 component (from Joannes-Boyau et al. 2010b). R_1 is associated with an orthorhombic CO_2^- radical, R_2 with an axial CO_2^- radical, R_3 contains the sum of all misalignments and R_4 is the sum of g_y and g_i of the aforementioned anisotropic radicals plus the g_i of the non-orientated CO_2^- radicals

Figure 14: Beta and gamma irradiation of different enamel domains. The composition of the natural samples is the same within error for all four radiation experiments. Beta irradiation is qualitatively similar to the natural sample and to each other, apart from a higher percentage of NOCORS produced in the domain close to the dentine. The gamma irradiation produced virtually no axial and a much larger percentage of NOCORS in the domain closer to the dentine. As the composition of the natural samples, as well as the beta induced AICORS are the same, the indications are: a significant number of gamma induced NOCORS are unstable, some are stable. In addition, some NOCORS need to convert into orthorhombic CO_2^- radicals. Whether axial CO_2^- radicals are directly produced from NOCORS or indirectly via orthorhombic CO_2^- radicals remains unclear (from Joannes-Boyau and Grün 2011).

Table 1: Direct laser ablation U-series analysis of human fossils

Hominid	Publication	Minimum Age (ka)
Skhul IX	Grün et al. (2005)	131±2
Payre	Grün et al. (2008)	140 ka
Callao bone	Mijares et al. (2010)	~ 67
WLH 50	Grün et al. (2011)	12.2±1.8
Iwo Eleru	Harvati et al. (2011)	6.3-11.7
Omo Kibish 1	Aubert et al. (2012)	171±16
Wajak	Storm et al. (2013)	>28.5-37.4
Callao tooth	Grün et al. (2014)	~ 50 ka
Tourville-la-Rivière	Faivre et al. (2014)	not directly datable
Taiwan	Chang et al. (2015)	not directly datable
Lezetxiki	de-la-Rua et al. (2016)	164±9
Nataruk	Mirazón Lahr et al. (2016a,b)	early Holocene
<i>Homo floresiensis</i> (Liang Bua)	Sutikna et al. (2016)	54.6±2.1-86.9±7.9
Moula Guercy	Willmes et al. (2016)	~ 90 - ~120
early <i>Homo floresiensis</i>	Brumm et al. (2016)	357±9.9/>640
Apidima	Bartsiokas et al. (2017)	172±11
Al Wusta	Groucutt et al. (2018)	87.6±2.5

Table 2: ESR analysis of enamel fragments of human fossils

Hominid	Publication	Dose (Gy)	Total Dose Rate ($\mu\text{Gy a}^{-1}$)
Florisbad	Grün et al. (1996)	127.5±4.1; 137.0±8.1	499±65
Mungo 3	Thorne et al. (1999)	26±2	419±40
Tabun C1	Grün and Stringer (2000)	166-180	~1544(EU), ~1217 (EU)
Swartkrans	Curnoe et al. (2001)	726±49, 746±70	777±102(EU), 532~52(LU)
Border Cave 5	Grün et al. (2003)	150±5	2026±121
Tabun BC7	Coppa et al. (2005)	87.6±2.1	1068±185(EU), 952±186(LU)
Skhul II	Grün et al. (2005)	93.8±7.8	808+299/-167 (US-ESR)
Banyoles	Grün et al. (2006b)	15.5±0.6	235±25(US-ESR)
Irhoud*	Smith et al. (2007) Richter et al. (2017)	326±16	1159±113(US-ESR)
El Sidron	DeTorres et al. (2010)	32.3±1.1	873±72(EU), 808±61 (LU)
Thomas Quarry 1	Raynal et al. (2010, 2011)	691±30	1379+247/-218 (US-ESR)
<i>Homo naledi</i>	Dirks et al. (2017)	1788: 159±10 1810: 232±30	754±87 to 978±129 (US-ESR) 870±190 to 1102±219 (US-ESR)
Mislya-1	Herschkovitz et al. (2018)	112.6±1.8	647±38 (US-ESR)
<i>Homo antecessor</i>	Duval et al. (2018)	804±31	1115±128

2104

Drilling Depth (in 100 μm)