

# **Electron spin resonance (ESR) dating in Quaternary studies: evolution, recent advances and applications**

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## **Introduction**

Over the last few decades the importance of geochronology in Quaternary studies has significantly increased and the development of accurate numerical dating tools has become an essential foundation for reliable interpretations of palaeoenvironmental proxies, landscape evolution, geomorphic processes, palaeoclimate records, palaeoecological changes, archaeological histories and human evolution. There is now a wide array of numerical Quaternary dating methods available, though their applicability and accuracy may vary significantly at individual sites depending on a series of factors, including the age range of interest, the types and purity of preserved material, and its association (e.g. taphonomic history, stratigraphic correlation) with the event that is being dated (e.g. Ludwig and Renne, 2000; Grün et al., 2010; Rink and Thompson, 2015; Rixhon et al., 2017). Radiometric methods such as radiocarbon, argon-argon (Ar-Ar) and U-series dating typically offer the greatest analytical precision and are based on relatively standardized analytical procedures. Other techniques such as electron spin resonance (ESR), luminescence, and cosmogenic radionuclide (CRN) dating have not yet reached the same level of standardization, but they nevertheless offer invaluable age constraint across a wide range of sites, depositional contexts

and timeframes, particular when the more routinely used and standardized radiometric methods are not applicable.

## **1. 45 years of ESR dating**

The present Special Issue (SI) is being published 45 years after the first ESR dating application performed by Ibeya (1975) on stalactites from Japanese caves. Research interests within the ESR dating community have naturally evolved over the last five decades (see also Bahain, 2007; Falguères et al., 2020; Grün et al., 2020, this volume). A wide range of applications has been developed, and some have become increasingly popular within the ESR dating community, whereas others have been progressively abandoned. Figure 1 presents a (partial) overview of this evolution. In the 1980s, there was seemingly a more balanced interest within the community to develop a wide variety of applications, mostly on cave carbonates, but also on biohydroxyapatite (including fossil bones and tooth enamel), silicates (e.g., siliceous, heated and optically bleached quartz) and marine carbonates, including (among others) mollusc shells, foraminifera and corals. Grün (1989) and Ikeya (1993) have both provided excellent overviews of the state-of-the-art of the field during this period. In the 1990s, and the period since, the vast majority of ESR dating studies have been centered on fossil teeth and quartz. This contrasts with the clear progressive disinterest for the study of cave carbonates (Fig. 1), in spite of this material being the original focus of the seminal work by Ikeya (1975). This trend is most likely the direct consequence of the rapid development of mass spectrometry techniques (e.g., thermal ionization mass spectrometry [TIMS], inductively coupled plasma mass spectrometry [ICP-MS]) during that period, which have enabled the acquisition of much faster and more precise U-series ages compared with ESR. Similarly, ESR dating of fossil bones, initially tested in the 1980s (e.g. Ikeya and Miki, 1980), was completely abandoned a few years later, and substituted by fossil tooth enamel, a material that was rapidly found to be more suitable for dating purposes (Grün and Schwarcz, 1987). There has been an almost constant increase in the number of ESR dating applications to fossil tooth enamel over the last three decades. However, the most striking trend is probably related with the number of publications dedicated to quartz in the last ten years, which have multiplied by a factor of two in comparison with the previous decade (Fig. 1). The increased interest within the community for this specific application is illustrated by the recent establishment of a new generation of laboratories hosting both ESR and luminescence dating facilities and expertise (e.g., Leibniz Institute for Applied Geophysics, Germany;

Centro Nacional de Investigación sobre la Evolución Humana, Spain; University of Lausanne, Switzerland; Babeş-Bolyai University, Romania), and favouring thus the development of combined dating studies focused on quartz and feldspars. As of 2020, ESR dating of fossil tooth enamel and quartz have become the two most popular applications, by far (Fig. 1). In comparison, other materials such as corals and mollusc shells have received relatively constant, but significantly smaller, attention within the community over the last few decades.

### **Fig. 1 approx. here**

In summary, ESR has the advantage of being used with a wide range of materials such as carbonates, phosphates, silicates and sulfates, and it can also potentially cover the last 2.6 million years (Ma). These properties ensure that ESR dating is applicable across almost any Quaternary depositional environment and time range. The reader may refer to the successive review works by Grün (1989), Ikeya (1993), Rink (1997), Skinner (2014) and Blackwell et al. (2016) to obtain a complete overview of the variety of ESR dating applications developed in the last 45 years. Despite these strengths, the potential usefulness of the ESR method remains relatively unknown among the broader scientific community. This is partly due to the limited number of specialists in the field of ESR dating, and to the complex and time-consuming analytical procedures that are involved; both of which significantly limit the number of ages that can be produced. Additionally, the large number of parameters to be taken into account in the age calculation (potentially >20; Grün, 1992; Duval et al., 2017a) can make the whole dating process sometimes seen like a black box to end-users and non-specialists. Limited understanding of the dating process may also result in unrealistic expectations of the dating outcome, in particular when ESR is expected to achieve a similar level of accuracy and precision as well-established and -standardized methods. As a consequence, the reliability of ESR dating is also frequently questioned within the scientific community (sometimes with reason). The present SI of Quaternary International aims to fill this gap of knowledge by providing an updated overview of the potential and current limitations of the ESR dating method for Quaternary dating studies.

## **2. Overview of the Special Issue**

22 manuscripts were submitted to the SI: 16 of them (~70%) were accepted, while five were rejected and one was withdrawn by the authors. These data fall within the standards of

Quaternary International in terms of number of contributions (between 12 and 20 maximum) and rejection rate (~40%) per SI (see Chen et al., 2019 for comparison). The 16 original contributions of this SI cover a wide range of dating applications over the whole Quaternary period, and beyond (Table 1). In order to properly evaluate the accuracy and reliability of the ESR method, a special emphasis has been placed on including studies that involve cross-comparisons with other independent dating methods, such as radiocarbon (e.g. Richard et al., 2020, this volume; Azevedo et al., 2020, this volume; Schellmann et al., 2020, this volume), U-series (Richard et al., 2020, this volume; Schielein et al., 2020, this volume), Ar-Ar (Voinchet et al., 2020, this volume), luminescence (Beerten et al., 2020, this volume; Ben Arous et al., 2020, this volume; Duval et al., 2020, this volume; Demuro et al., 2020a and b, this volume; Bartz et al., 2020, this volume; Molodkov et al., 2020, this volume; Schellmann et al., 2020, this volume), CRN (Beerten et al., 2020, this volume; Duval et al., 2020, this volume), palaeomagnetism (Duval et al., 2020, this volume) and loess morphostratigraphic correlations (Richter et al., 2020, this volume). Additionally, a couple of the SI contributions include new multi-laboratory comparison studies (Bahain et al., 2020, this volume; Duval et al., 2020, this volume), which, unfortunately, continue to remain limited within the ESR dating community.

### **Table 1 approx. here**

This SI provides a representative overview of the research currently being undertaken within the ESR dating community. It is roughly consistent with the pattern shown in Fig. 1 for the last decade (Table 1), although there is an underrepresentation of fossil tooth dating applications. Half of the contributions (n=8) focuses on quartz dating, and there are four contributions on fossil teeth, two on mollusc shells and one on corals (note that one of the studies includes applications to both fossil tooth enamel and quartz grains). The various papers are led or co-authored by research groups from various continents (Europe, Asia, Oceania, North America, South America; Table 1). Together, they provide an overview of the current extent of the ESR dating community, although this should be considered as an incomplete view because some of the major actors in the field are missing. Some of these contributing groups are well-established, with a long tradition in ESR dating over the last decades (e.g., Museum national d'Histoire naturelle, France; Williams College, USA; Universidade de São Paulo, Brazil; University of Cologne, Germany; Tallinn University of Technology, Estonia; University of Bamberg, Germany), while others have appeared more recently,  $\leq 10$  year ago or so (e.g., Centro Nacional de Investigación sobre la Evolución

Humana, Spain; Leibniz Institute for Applied Geophysics, Germany; Nanjing Normal University, China; Griffith University, Australia).

Finally, the scientific quality of this SI has undoubtedly benefitted from the thorough peer-review process carried out by a large panel of referees (see detailed list in Table 2). We would like to sincerely thank all of the reviewers for their time-consuming and dedicated work.

## Table 2 approx. here

### 3. Contributions of this SI: contextualising the main outcomes

#### *3.1. ESR dating from an historical perspective*

This SI begins with two somewhat unconventional contributions providing very interesting historical perspectives on the development and application of the ESR dating method since the early 1980s. Hopefully, these works will prove especially useful for the younger generations of the dating community. First, Falguères et al. (2020, this volume) presents the history of the French ESR dating team at the Museum national d'Histoire naturelle (MNHN) of Paris, whose existence stemmed from Yuji Yokoyama, the pioneer of ESR dating in France. Yokoyama rapidly saw the potential of the method as a dating application tool after the first publication by Ikeya (1975). His work initiated a long tradition of ESR dating in France, propelled by the foundation of the ESR dating laboratory at the MNHN with the active support of Professor Henry de Lumley. For the last 40 years or so, this laboratory has significantly contributed to the field of ESR dating, and Quaternary studies in general, via methodological investigations and dating applications, mostly related to archaeological contexts. This is well illustrated in the present SI by numerous first-authored contributions from the “first” generation (Falguères et al., 2020, this volume; Bahain et al., 2020, this volume) and “second” generation of researchers trained at the MNHN (Ben Arous et al., 2020, this volume; Duval et al., 2020, this volume; Richard et al., 2020, this volume; Voinchet et al., 2020, this volume). Falguères et al. (2020, this volume) provides an interesting overview of the long-term research performed on calcite, quartz and fossil teeth by the team (see also Bahain, 2007). Among their many methodological achievements was the publication of one the very first ESR dating studies of optically bleached quartz extracted from Quaternary sediment. The group has undoubtedly played a leading role within the community for the promotion of this application, in particular with the

development of an extensive dating program focused on the fluvial deposits of the Centre Region, France. In this regard, the work by Duval et al. (2020, this volume) is the latest example of a long research tradition initiated >20 years ago.

This first historical perspective is followed by Grün (2020, this volume), who provides a first-person description of his own personal journey in the field of ESR dating. The author, who coincidentally retired shortly before the publication of the present SI, walks us through the development of the method, progressive improvement in the understanding of the fundamentals, and the evolution of analytical processes in ESR dating of fossil teeth over the last 35 years. One should be aware that this is only a small part of the global contribution by the author to the field of ESR dating, who also worked on a large variety of materials and applications (e.g. quartz, carbonates) and expanded his research expertise beyond ESR. Related research fields of luminescence, U-series, and radiocarbon dating, among others, have all benefitted from Rainer Grün's sharp mind and even sharper diplomacy skills. The paper nicely describes the intellectual pathway that has led to some of the major methodological breakthroughs over the last decades, such as the definition of the US uptake model for a combined U-series and ESR dating approach, single aliquot dose evaluation of enamel fragments, and high-resolution U-series analyses by laser ablation ICP-MS. In particular, the combination of the latter two approaches has led to the development of the famous 'semi non-destructive approach' (a glass-half-full take on the fossil conservation impacts of ESR dating), which has enabled provision of direct age constraints on a significant number of human fossils that lie beyond the limits of radiocarbon dating (see the overview Table 2 in Grün, 2020, this volume). Finally, from his ~40 years of experience in the field of ESR, the author also warns about the need and importance to continue undertaking methodological investigations. Dating applications on fossil tooth enamel are flourishing (Figure 1), but many questions around the basics of the method (e.g. in relation to the nature and composition of the radiation-induced ESR signal or the migration of uranium into dental tissues) remain to be fully understood.

### *3.2. Fossil tooth enamel*

The following four SI contributions deal with fossil tooth enamel. The first three are centred on the dating of Late Pleistocene archaeo-palaeontological localities from three different continents. Azevedo et al. (2020, this volume) perform an ESR dating study of

several 10-20 thousand year (ka) old megafauna teeth from Lagoa Uri de Cima (Brazil), while both Richard et al. (2020, this volume) and Ben Arous et al. (2020, this volume) focus on somewhat older localities (30-50 ka). Richard et al. (2020, this volume) present dating results linked to Neanderthal occupations at Hohlenstein-Stadel cave (Germany). Ben Arous et al. (2020, this volume) provide new numerical age constraints for El Harhoura 2 cave (Morocco) and, thereby, for the Middle Stone Age in Northern Africa. These three studies illustrate the specificities of dating relatively young samples. Dental tissues usually display low uranium concentrations, and thus carry very limited weight in the dose rate evaluation. In other words, the uranium uptake modelling has an almost negligible impact on the calculated age. This is a very particular (most likely unique) situation in which a combined U-series and ESR dating approach may not be required. For example, Azevedo et al. (2020, this volume) derive age estimates based on the so-called parametric U-uptake models (early uptake [EU], linear uptake [LU], combined uptake [CU] models) that are all within error. The age difference does not exceed 3 ka, whatever the uranium uptake model selected. In contrast, Richard et al. (2020, this volume) and Ben Arous et al. (2020, this volume) employ the combined U-series/ESR dating approach but reach a similar conclusion: the weight of dental tissues on the total dose rate is so low (<2% and 1-15 %, respectively) that the impact of uranium uptake modelling is, again, very limited. As a consequence, the sedimentary environment instead becomes of crucial importance to the total dose rate evaluation. It is therefore essential to properly assess the gamma dose rate, which may be extremely challenging in very heterogeneous sedimentary contexts like cave infills. Richard et al. (2020, this volume) and Ben Arous et al. (2020, this volume) more or less successfully tackle this issue by performing several *in situ* measurements throughout the stratigraphic layers containing the teeth in order to evaluate the lateral variability of this parameter. While the results obtained for El Harhoura 2 cave are generally consistent, those from Hohlenstein-Stadel cave are extremely scattered (up to ~60 % of variability in some layers), suggesting significant uncertainty remains around the true gamma dose rate. This unfortunately underlines the intrinsic limitations of dose rate reconstructions for fossil teeth originating from very heterogeneous sedimentary environments. Interestingly, for both studies, the ESR ages can be directly compared with either radiocarbon (Richard et al., 2020, this volume) or optically stimulated luminescence (OSL) results (Ben Arous et al. 2020, this volume). In the first case, the various ages are generally consistent (despite some well-identified outliers), although the ESR estimates display much larger associated uncertainties, as might be expected. For El Harhoura 2 cave, the new combined US-ESR dating results are

systematically and significantly younger than the previously obtained OSL ages, by about 15 ka. While the authors discuss the possible origin of such discrepancies, which apparently do not come from evaluation of the gamma dose rate, it should also be kept in mind that the two methods do not date the same material (quartz grains vs. fossil teeth), nor the same event (OSL: the last exposure to sunlight; ESR: the burial of the fossil teeth). Consequently, although the origin of the discrepancy remains open at El Harhoura 2 cave, the age difference observed between the two independent approaches may not necessarily be the result of a methodological bias. It may also arise from other causes, perhaps reflecting more complex site formation or taphonomic processes than initially expected.

The fourth study by Bahain et al. (2020, this volume) presents the results of a multi-laboratory ESR dating study based on both fossil teeth and optically bleached quartz grains from the Neanderthal site of Tourville-la-Rivière (France). Several fossil teeth from the archaeo-palaeoanthropological level were independently collected at two different locations and ESR dated by two research groups. The results consistently point towards a marine isotope stage (MIS) 7 chronology for the fossils, despite the two sets of samples showing clearly different equivalent dose ( $D_E$ ) values ( $153 \pm 22$  vs.  $195 \pm 14$  Gy) and U-series data (homogeneous apparent U-series ages between 140 and 217 ka vs heterogeneous apparent U-series ages between 75 and 656 ka and several occurrences of uranium leaching). This outcome indirectly outlines the robustness and reproducibility of the dating method for this time range, as the different radioactive environments and diagenetic processes experienced by the fossil teeth at the two distinct locations within the same layer do not unduly influence the final dating results. Even more interestingly, this work also provides a detailed comparison of the analytical procedures employed by each laboratory and evaluates some potential methodological biases, which is, to our knowledge, very rare (see also Dirks et al. 2017). Contrary to the Late Pleistocene dating studies included in this SI (Azevedo et al. 2020, this volume; Richard et al., 2020, this volume; Ben Arous et al., 2020, this volume), the dental tissues at Tourville-la-Rivière carry a significant weight in the total dose rate, and the uranium uptake modelling has a clear impact on the final age result. As an example, Bahain et al (2020, this volume) observed a 15-20 ka difference between the US-ESR and CSUS-ESR age estimates.

In summary, the four SI contributions centred on fossil tooth enamel serve to illustrate both the application potential of this approach and its specificities, depending on the time range considered. ESR dating can be used as an alternative (although significantly less



precise) approach to radiocarbon over the 0-50 ka time range, providing direct ages on fossils. While the limited impact of uranium uptake modelling simplifies the analytical procedure for relatively young samples, the evaluation of the environmental dose rate from the sediment instead becomes crucial, and may be extremely challenging in very heterogeneous environments. Beyond 50 ka, ESR becomes the only numerical dating method that can provide direct, finite age constraint on fossils, and has thus become especially popular for dating hominin fossils (see Grün, 2020, this volume). The 50-500 ka time window is usually considered as the optimum range for this dating application, because: (i) the dose rate evaluation is not dominated by a single component, and dental tissues and sedimentary environment carry a more balanced weight; (ii) fossil teeth tend to be suitable for dating from a methodological perspective, i.e. the uranium concentration of the enamel generally remains low (<1.5 ppm) and uranium leaching from the dental tissues does not frequently occur. However, contrary to younger samples, the combination of ESR and U-series data is essential to properly model the uranium uptake in dental tissues of >50 ka fossil teeth.

### *3.3. Optically bleached quartz grains*

Half of the contributions to this SI deal with ESR dating of optically bleached quartz extracted from Plio-Pleistocene sediment. The work by Bahain et al. (2020, this volume) includes a multi-laboratory ESR dating study based on quartz, but the direct comparison of the results appears to be less straightforward than for fossil teeth because most of the samples were collected from different layers. ESR dating was performed by two different teams as part of independent dating studies, although their analytical protocol is fairly similar and the ESR measurements were performed in the same facility. The results clearly highlight the benefits of using the Multiple Centre (MC) approach: while the Al and Ti-Li (option D *sensu* Duval and Guilarte, 2015) signals yield overestimated ages, the Ti-H signal (option C *sensu* Duval and Guilarte, 2015) provides an estimate that is consistent with the results from the fossil teeth. This work demonstrates the potential of the Ti-H centre to date late Middle Pleistocene deposits with  $D_E$  values that do not exceed 200 Gy.

Duval et al. (2020, this volume) present a multi-technique and multi-laboratory dating study of two key Lower Palaeolithic sites in the Centre Region (France) that have early Middle Pleistocene chronologies. The archaeology-bearing fluvial deposits at these sites were

previously extensively dated by ESR, but using the Al centre only. Interestingly, the independent ESR dating performed in the latest study by Duval et al. (2020, this volume) yields generally consistent ages for the Al centre, despite many differences in the analytical procedure. This work thus represents a unique opportunity to directly and thoroughly evaluate potential laboratory biases in  $D_E$  and dose rate evaluation. The MC approach provides further age constraints on the sites, which demonstrates the importance of systematically measuring both the Al and Ti centres in a given quartz sample. In particular, the comparison of these two signals is currently the only way to ‘internally’ evaluate possible incomplete resetting of the ESR signal associated with the Al centre. In Duval et al. (2020, this volume), the combined use of these two signals provides consistent results when compared with independent age control obtained from a combination single-grain thermally transferred OSL (TT-OSL), palaeomagnetism and CRN. In contrast, the Ti-H signal (Option C) systematically underestimates the expected dose estimates, showing that this signal may not be suitable for early Middle Pleistocene deposits. This agrees well with the observations made by Voinchet et al. (2020, this volume).

The study by Demuro et al. (2020a, this volume) also investigates fluvial deposits, but focuses on a late Middle Pleistocene to Late Pleistocene archaeological context. The authors undertake new TT-OSL analyses of several sediment samples from the Acheulean site of Porto Maior (Spain), complementing the previously published MC ESR and post-infrared infrared stimulated luminescence (pIR-IRSL) ages of Méndez-Quintas et al. (2018). The combination of all available ESR and luminescence data enables the establishment of a robust Bayesian-modelled chronology for the sequence. In particular, the Ti-Li centre (option D) provides ages that are consistent with the TT-OSL and pIR-IRSL results over the 200-300 ka time range, while the Al signal yields significant age overestimation. This comparative study shows the suitability of the Ti-Li (Option D) signal for providing accurate dose estimates over the 750-1100 Gy range. Although the weak intensity of the Ti-H signal (option C) precluded reliable ESR measurement in the initial dating study of Porto Maior (Méndez-Quintas et al., 2018), this signal was evaluated in greater detail for one sample in the latest study by Demuro et al. (2020b, this volume). The Ti-H signal is shown to produce an age underestimate of about 80 ka when compared with option D for this particular sample. Interestingly, the studies by Bahain et al. (2020, this volume) and Demuro et al. (2020a, this volume) deal with samples of a similar age (~200-250 ka) but the outcomes regarding the suitability assessments are somewhat different for the Ti-Li and Ti-H signals. Specifically, at

Tourville-la-Rivière, the Ti-Li (option D) signal produces overestimated ages, while the Ti-H ages are in agreement with independent age control (Bahain et al. 2020, this volume). Consequently, we cannot exclude the possibility that the magnitude of the environmental dose rate plays a non-negligible role in the different suitability of the Ti ages observed at the two sites. It is probably not a coincidence that the Ti-H centre yields accurate dose estimate in a low dose rate environment like Tourville-la-Rivière ( $<1000 \mu\text{Gy/a}$  for the layer D1), contrasting with the high dose rate environment of Porto Maior ( $>3000 \mu\text{Gy/a}$ ), where the Ti-H centre provides dose underestimation. Interestingly, the stratigraphically highest sample studied by Demuro et al. (2020a, this volume) comes from the very top of the Porto Maior sequence and is much younger than the other samples considered in this study. This sample yields a luminescence age of  $\sim 20$  ka, but all of the ESR signals (Al, Ti-Li and Ti-H) display much older age estimates. The Ti-H age is in closest agreement with the luminescence age, but still overestimates the latter by a factor of about 2. Although this outcome might reflect incomplete bleaching of the ESR signals, it could also illustrate the inability of all Al and Ti signals to accurately determine  $D_E$  values  $<100$  Gy in such a high dose rate environment. The latter could be caused by the limited radiation sensitivity of the ESR signals or by the use of a somewhat inappropriate analytical procedure (see full discussion in Bartz et al., 2020, this volume). Finally, Demuro et al. (2020a, this volume) provide a very interesting comparative table summarizing published quartz dating studies that have combined ESR and single-grain TT-OSL methods. Unlike the Al centre, which frequently yields overestimated ages in these published comparisons, there is general agreement between the Ti-Li (option D) ages and the TT-OSL ages spanning the 200 ka and 1.1 Ma range.

Voinchet et al. (2020, this volume) took advantage of the intense volcanic activity in Central and Southern Italy during the Quaternary to perform a comparative Middle Pleistocene dating study of several Lower to Middle Palaeolithic sites using both ESR and Ar-Ar methods. However, this age comparison is not as straightforward as it may seem at first glance. Again, it must be borne in mind that these two methods utilise different materials and do not date the same event, i.e., the last exposure to sunlight for ESR vs the formation of volcanic minerals for the Ar-Ar method. Therefore, it becomes essential to check whether the volcanic minerals dated from the fluvial deposits are in primary position or have been reworked from other deposits, as openly discussed in Voinchet et al. (2020, this volume). Similar to Duval et al (2020, this volume), Bahain et al (2020, this volume) and Bartz et al. (2020, this volume), the authors used the MC approach and measured the signals from the Al,

Ti-Li (option D) and Ti-H (option C) centres. Most of the samples provide ESR ages that are consistent with the Ar-Ar method, though with much larger errors. Consequently, this work demonstrates that the ESR method may provide reliable ages over the 300-700 ka time range. Additionally, the authors identify possible saturation of the Ti-H centre above 300-400 Gy, which may thus represent the upper threshold (i.e., highest dose value) that can be accurately detected with this centre. Further investigations should, however, be carried out to evaluate whether this saturation level is sample dependent. Voinchet et al. (2020, this volume)'s results show a clear correlation between high environmental dose rate (between 2000 and 4000  $\mu\text{Gy/a}$ ) and underestimated Ti-H age estimates. In contrast, two of the three samples collected from relatively low dose rate environments ( $< 1000 \mu\text{Gy/a}$ ) yield accurate Ti-H estimates; the inaccurate result of the third sample being most likely due to some issues with the dose rate evaluation (i.e., unrelated to the Ti-H centre).

In contrast, the study by Bartz et al. (2020, this volume) focuses on a much younger time period. This comparison study evaluates the potential of pIR-IRSL and MC ESR methods to date Late Pleistocene deposits from coastal alluvial fan complexes of the Atacama Desert (Chile). As these deposits contain quartz with unsuitable OSL properties (see e.g. May et al., 2015), the application of other numerical methods is needed to obtain reliable chronological constraints. Both the pIR-IRSL and MC ESR methods were therefore tested on different types of deposits (marine, aeolian, matrix-rich debris-flow and clast-rich debris-flow), resulting in generally consistent ages for all but the clast-rich debris-flow deposits. Additionally, this study highlights the difficulties of achieving complete optical bleaching of these sediments, which severely limits the use of the Al and Ti (option D) centres and instead seems to favour the Ti-H centre in this context. As an aside, the authors also examined optimisation of the acquisition parameters, given the relatively weak Ti ESR intensities. In particular, they compared two measurement procedures consisting of either Al and Ti signal acquisition using a single spectrum (e.g. similar to Voinchet et al., 2020, this volume; Beerten et al., 2020, this volume) or separate spectra (like Duval et al., 2020, this volume; Demuro et al., 2020a & b, this volume). The second approach has the advantage of enabling specific optimisation of the acquisition parameters for each centre, but the measurements are significantly more time consuming than with the first approach. Regardless, Bartz et al. (2020, this volume) show that both procedures yield similar results for most samples. This study also includes an interesting discussion of the potential of the ESR method for reliably dating Late Pleistocene deposits. The authors summarize previously published results for this

time range and reach the conclusion that the Ti-H signal is probably the most appropriate in this specific context. Owing to higher radiation sensitivity and faster bleaching kinetics, the Ti-H signal is best suited for detecting  $D_E$  estimates of a few hundred Gy. This signal, however, seems to provide less accurate ages for higher  $D_E$  values, which is consistent with the observations by Voinchet et al. (2020, this volume) and Duval et al. (2020, this volume). Whichever ESR signal is selected, the detection of small  $D_E$  values may also require adjustment of the analytical procedures, by selecting smaller dose steps, accumulating more scans, and/or by employing a regenerative dosing approach rather than an additive dosing approach.

These latter observations may also apply to the ESR dating results presented by Beerten et al. (2020), who test the MC approach on the Plio-Pleistocene white sands of the so-called Mol formation (Belgium). Despite the fact that the dating study is focused on a much older time range than Bartz et al. (2020), the extremely low environmental dose rate ( $<200 \mu\text{Gy/a}$ ) implies  $D_E$  values of relatively limited sizes. Two sediment samples were collected and dated by three different methods: ESR, OSL and CRN. Although both the Al and Ti (options B and E *sensu* Duval and Guilarte, 2015) centres yield consistent results of around 5 Ma, they seem to significantly overestimate the expected age, which is stratigraphically constrained to between 2.6 Ma and 3.6 Ma. This age bias is attributed to non-optimal bleaching conditions, which led to incomplete resetting of the ESR signals prior to sediment deposition. This interpretation is consistent with the results presented by Bahain et al. (2020, this volume) and suggests that fluvial-estuarine environments are most likely unsuitable for complete resetting of Al and Ti (-Li) signals. In contrast to Bahain et al. (2020, this volume), the Ti-H signal (option C) was unfortunately not dated by Beerten et al. (2020, this volume) due to its weak, and sometimes immeasurable, ESR intensity. This signal would have been, in theory, the most appropriate to use for this sample, given its faster bleaching kinetics and the expected magnitude of the  $D_E$  estimates (a few hundred Gy), as shown by Bartz et al., (2020, this volume). However, it should be noted here that the exact thermal lifetime of the Ti-H signal is unknown; it therefore remains unclear whether it can provide accurate ages beyond a few hundred thousand years. In comparison, both OSL and CRN methods yield broadly compatible, albeit younger than expected, ages for this study: an OSL age estimate of about 1.5 Ma is obtained, while the burial CRN method gives a minimum depositional age of around 1 Ma on average (though with extremely large errors, notably due to very low cosmogenic  $^{26}\text{Al}$  concentrations). Based on these relatively imprecise results, the “true” age

of the deposits is suggested to be between ~1.5 (OSL age estimate) and ~5 Ma (ESR age estimate). However, since the OSL signal is seemingly not in saturation and the method apparently provides a finite age, an Early Pleistocene burial age of the Mol formation, which had not been numerically dated previously, cannot be reasonably discounted. Importantly, CRN concentrations measured in the Mol formation highlight an increase in erosion rates in the last 0.5-1 Ma in the Belgian lowlands.

Richter et al (2020, this volume) test the accuracy of the ESR dating method on chronologically well-constrained Chinese loess deposits, over a time ranging from about 30 ka to 620 ka. The authors employ an innovative approach based on the single-aliquot regenerative dose (SAR) protocol. This is quite rare for ESR dating, and especially for optically bleached quartz (see also Beerten et al., 2006; Tissoux et al., 2008), given that dose evaluations are routinely performed via the Multiple Aliquot Additive Dose (MAAD) procedure. The resultant ESR ages are in agreement with independent age control for the 250-350 ka time range (corresponding to  $D_E$  estimates of between 800 and 1000 Gy), whereas they are overestimated and underestimated for the <200 ka and >350 ka samples, respectively. Interestingly, this pattern is consistent with previous observations from Beerten et al. (2006). While Richter et al (2020, this volume) interpret the age overestimation for the younger samples as evidence of incomplete bleaching of the Ti signal, it remains unclear why this would only affect the younger samples. These results are broadly consistent with previous observations showing the difficulty of reliably determining dose values of a few hundred Gy using ESR signal (e.g., Bartz et al, 2020, this volume; Demuro et al., 2020a, this volume), despite using a more appropriate dose evaluation method (SAR). The studies by Bartz et al. (2020, this volume) and Demuro et al. (2020a, this volume) show that the Ti-H signal (option C) could have been the most appropriate signal to evaluate the age of the <200 ka samples, given the magnitude of their expected  $D_E$  (<300 Gy). Unfortunately, the Ti-H signal could not be isolated with the experimental conditions employed by Richter et al (2020, this volume). In contrast, the Ti ESR age for the >600 ka sample is underestimated but agrees with the independent loess chronology after fading corrections. This seems, in the first instance, somewhat inconsistent with the studies by Duval et al. (2020, this volume) and Voinchet et al. (2020, this volume), for which no Ti age underestimation was observed for samples of similar ages. Finally, major differences are observed between the natural dose response curves (DRCs) of the Al and Ti centres presented by Richter et al (2020, this volume) (and references therein), compared to the laboratory DRCs typically presented in the

other studies. For the latter, the Al signal does not typically show saturation at high doses, whereas the Ti signals options D and C tend to reach apparent saturation (i.e., a local maximum) around 10 and 6 kGy, respectively (e.g. Bartz et al., 2020, this volume). In summary, the study of Richter et al. (2020, this volume) raises a series of key questions regarding the Ti signal and its ability to provide accurate burial dose estimates. Although some of the observations seem to contradict other conclusions presented in this SI, these differences may simply reflect dissimilar analytical procedures and experimental conditions. It is presently not known how the latter may impact ESR dating results (e.g., MAAD vs SAR; grain size: 100-200  $\mu\text{m}$  vs 63–100  $\mu\text{m}$ ), particularly as there are also uncertainties regarding the sample-dependent nature of certain ESR properties (e.g. radiation sensitivity, saturation level, etc.) (see also Demuro et al., 2020b, this volume). That said, there are signs that the main source of the disparity likely lies in the way the Ti signal intensities have been evaluated by Richter et al. (2020, this volume). The relatively high measurement temperature (123 K), for instance, precluded acquisition of the ESR spectrum with sufficient resolution to differentiate the Ti-Li from the Ti-H lines. Consequently, a mixture of option C and D (*sensu* Duval and Guilarte, 2015) intensities have been measured, unlike the majority of the other studies in this SI. This factor severely limits extrapolation or direct comparison with other ESR studies that have employed different Ti centre intensity evaluations. The corresponding overall bias that has potentially been induced by these specific experimental setup and analytical procedure would benefit from further investigation.

Finally, the last ESR quartz application of this SI (Demuro et al., 2020b, this volume) presents a novel characterisation study to investigate the possible relationships between ESR and luminescence signals. This study focuses on two sets of samples from Middle Pleistocene archaeological sites in Spain (dated to 200-300 ka), which were known from previous studies to display very different ESR and luminescence properties (Arnold et al., 2016; Duval et al 2017b; Méndez-Quintas et al., 2018). The authors present a very detailed dating comparison using the MC ESR approach (with Ti signal measured following options A, C, D and E *sensu* Duval and Guilarte, 2015) and single grain TT-OSL techniques. While the Ti centre (option D) ages are in agreement with the luminescence results at one site (Porto Maior), a distinctly different pattern is observed at Cuesta de la Bajada, with the Ti-H (option C) results agreeing with the independent age control and the Ti (option D) results yielding age overestimates. It is possible that the magnitudes of the environmental dose rates again play a significant role in these differences. The underestimation of the Ti-H ages at Porto Maior may be attributed to

signal saturation due to the high dose rate environment at the site ( $>3000\ \mu\text{Gy/a}$ ; see Demuro et al., 2020a, this volume). In comparison, the results at Cuesta de la Bajada demonstrate that the Ti-H signal can provide accurate dose estimates up to about 600 Gy, despite the dose rate being not especially low (about  $2000\ \mu\text{Gy/a}$ ) compared to other environments studied in this SI (e.g. Bahain et al., 2020, this volume; Beerten et al., 2020, this volume; Voinchet et al. 2020, this volume). Importantly, Demuro et al. (2020b, this volume) take the comparative study further by using a wide array of novel techniques to characterise the ESR and luminescence properties of their samples. Among other results, it is shown that the quartz samples from Cuesta de la Bajada contain a much higher proportion of grains producing TT-OSL signals, as well as much brighter TT-OSL signals, compared to those from Porto Maior. Analyses of 3D thermoluminescence (TL) spectra reveal that the Cuesta de la Bajada samples are dominated by two major TL peaks in the red emission band, which are up to seven times more intense than the corresponding signals observed for Porto Maior. Additionally, the Cuesta de la Bajada samples exhibit exceptionally strong Ti-H intensities, which seem to correlate with higher Ti contents for these particular quartz extracts. The strong Ti-H intensities have a direct impact on the composition of the Ti signal that is being measured: while option D measured on the Cuesta de la Bajada samples is typically a mixture of contribution from Ti-Li and Ti-H signals, the latter has a negligible influence on the Option D signal from the Porto Maior sample. At Porto Maior, Option D is largely dominated by the Ti-Li contribution, and therefore does not suffer from the same signal mixing complications. Further investigations are still required on a wider range of quartz from different origins and age ranges, but the study by Demuro et al. (2020b, this volume) is an important first step towards better identification and definition of the inherent properties that make quartz samples suitable for luminescence and ESR dating.

Collectively, these eight quartz application studies cover a wide range of sedimentary environments (e.g., estuarine, fluvial, loess, coastal, alluvial fan) and chronologies (from the Pliocene to the Late Pleistocene). They provide an unprecedented amount of comparative data that undoubtedly contributes towards better defining the potential and limitations of the ESR quartz dating method. The results of these studies underscore how the development of the MC approach a couple of decades ago by Toyoda et al. (2000) was a major breakthrough for the ESR quartz dating method. The works also show that the various Al and Ti signals display different radiation sensitivities, saturation levels, bleaching kinetics and ESR intensities, ensuring they have different suitabilities depending on the time range being



considered and the magnitude of the burial dose. Together, the various studies of this SI provide several new insights into the potential of the different ESR signals. The Ti-H seems more suitable for samples <200 ka or to evaluate  $D_E$  estimates <300-600 Gy (Bartz et al., 2020, this volume; Bahain et al., 2020, this volume; Demuro et al., 2020b, this volume). Between 200 ka and 750 ka, several of the studies show that Ti-Li (option D) ages are mostly in agreement with independent age control, while the Al results are either consistent with, or overestimate, available age control (e.g. Demuro et al., 2020a and b, this volume; Duval et al., 2020, this volume; Richter et al., 2020, this volume; Voinchet et al., 2020, this volume). However, in case of low dose rate environments, the possibility remains for using the Ti-H centre to date early Middle Pleistocene samples, although the exact thermal lifetime of this signal is currently unknown. Other recent works have also demonstrated that the combination of Al and Ti signals could provide accurate ages beyond the Middle Pleistocene, over the 1-2 Ma time range (e.g., Bartz et al., 2018; Sahnouni et al., 2018). Additionally, it should also be kept in mind that apparent agreement between Ti and Al ESR age estimates should not necessarily be considered as evidence for accurate results. Both signals could well be overestimating the true age, as well illustrated by Beerten et al. (2020, this volume). Nevertheless, all these studies directly or indirectly advocate the systematic use of the MC approach, which should, in our opinion, be considered as a minimum requirement for any quartz ESR dating study, as proposed by Duval et al. (2017a).

These eight contributions also highlight the main challenges currently facing the ESR field. In particular, the method would undoubtedly benefit from the development and increased use of new analytical procedures for dose evaluation. The study by Richter et al. (2020, this volume) is very important in that regard. The SAR and MAR procedures offer a series of advantages over the routinely-employed MAAD approach, as they require a much smaller amount of material and should lead to more precise  $D_E$  estimates (because the  $D_E$  estimates are determined via interpolation rather than extrapolation of the DRCs). The absence of standardization in analytical protocols is another significant issue that currently complicates attempts to directly compare ESR results across different studies. Each laboratory has its own best practice and there is no general agreement on measurement conditions, signal evaluation or procedures of data reduction. In particular, there is a disparity in the way the Ti signal has been measured between the different studies included in this SI, which may prove to be a major barrier against further development of the MC approach going forward. Beerten et al. (2020, this volume) measure the Ti (ESR absorption line 2) and

556 Ti-Li (ESR absorption line 1) signals following options B and E *sensu* Duval and Guilarte  
557 (2015), respectively. In comparison, the other studies employ options C (Ti-H) and D (which  
558 is, most of the time, a mixture of Ti-Li and Ti-H; see Demuro et al., 2020b, this volume)  
559 *sensu* Duval and Guilarte (2015), with the exception of Richter et al. (2020, this volume).  
560 Due to limited spectrum resolution, the latter authors could not differentiate Option C and D  
561 Ti signals, which appeared as a single peak and were thus measured as a combination. It is  
562 presently unknown what impact this issue may have on Ti centre dating results, thereby  
563 impeding direct comparisons between studies. The thermal conditions of signal measurement  
564 also vary significantly between laboratories: measurement temperatures of about 90 K (Duval  
565 et al., 2020, this volume; Bartz et al., 2020, this volume; Demuro et al., 2020a & b, this  
566 volume), 100 K (Voinchet et al., 2020, this volume; Beerten et al., 2020, this volume), 107 K  
567 (Bahain et al., 2020, this volume) and 123 K (Richter et al., 2020, this volume) have been  
568 employed, which has direct consequences on spectrum resolution, as mentioned earlier.  
569 Some research groups routinely perform several rotations of the sample tube before  
570 successive measurements in order to take into account the angular dependence of the ESR  
571 signal (e.g. Bartz et al., 2020, this volume; Richter et al., 2020, this volume; Voinchet et al.,  
572 2020, this volume). The magnitude of this dependence varies among samples (and most  
573 likely among laboratories as well) and may sometimes be significant (see Duval and Guilarte,  
574 2015). More importantly, repeated measurement over successive days is unfortunately not a  
575 common practice among ESR laboratories, despite the fact that temporal repeatability may be  
576 a major source of uncertainty. Indeed, the significance of proper evaluations of  $D_E$   
577 measurement uncertainties remains underestimated in the literature. These uncertainties most  
578 likely result from a variable combination of factors, including the short- and long-term drifts  
579 of the spectrometer, the heterogeneity of the quartz samples, imperfections in the glass  
580 tubing, and some variability in the vertical position of the sample within the cavity (e.g.  
581 Guilarte and Duval, 2020). Although  $D_E$  repeatability does not surpass 5-10% under ideal  
582 circumstances, it can sometimes exceed 20% with some samples showing especially low ESR  
583 intensity and/or significant heterogeneity, resulting in highly variable measurements (see  
584 examples in Bartz et al., 2020, this volume; Duval et al., 2020, this volume). This can  
585 therefore explain inconsistent or inaccurate ages if not adequately captured in empirical  
586 evaluations. Similar to other numerical dating methods, there is a need to develop objective  
587 criteria for evaluating the quality of ESR datasets. In the first instance, the repeatability of  
588 ESR intensity measurements and of  $D_E$  estimates, as well as goodness-of-fit, could be  
589 considered good proxies to evaluate the methodological reliability and robustness of ESR

datasets. The quartz dating studies from this SI serve to illustrate the diversity of analytical procedures employed within the ESR community, and highlight the need for standardization of laboratory practices.

### *3.4. Other materials*

This SI includes two further contributions involving ESR dating of mollusc shells. First, Molodkov (2020, this volume) presents a selected overview of his long-term research into the Late Pleistocene sedimentary record of the Eurasian Arctic region. In particular, the author provides the detail of about 60 ESR ages obtained on different species of (mostly marine) mollusc shells with associated independent age control derived from luminescence, radiocarbon and U-series methods. In comparison, Schellmann et al. (2020, this volume) examines terrestrial molluscs (mostly shells of small land snails) from late Middle to Late Pleistocene loess and fluvial deposits in the Bavarian Alpine Foreland (Germany), with independent age control being provided by luminescence and radiocarbon methods. Beyond the useful age constraints provided by these dating applications, both studies are of special interest for the present SI, illustrating the great potential of less routine ESR dating applications. Despite a few local discrepancies, most of the ESR dating results appear to be consistent with the available independent age control. These results demonstrate the accuracy of ESR mollusc shell dating applications over an age range spanning from MIS7 to the Holocene. Interestingly, both studies reach a similar conclusion that the use of different species of mollusc shells does not induce any significant bias, with the calculated ages being within error of each other regardless of the chosen species. This important outcome implies that different species could be mixed together if there is insufficient material available for analyses at a given site.

One of the major questions regarding the suitability of mollusc shell dating is whether this material may be considered as an open system for U-series evaluation, as with tooth enamel. Since the ESR age calculations by Schellmann et al. (2020, this volume) and Molodkov (2020, this volume) have been mostly performed using the Early Uptake (EU) model (= assuming a closed system), the overall consistency with independent age control for both studies may be considered as indirect evidence that the majority of mollusc shells behave as closed-systems. Molodkov (2020, this volume) also observe that the U content of mollusc shell is on average  $0.8 \pm 0.7$  ppm for 95% of the samples, and  $0.5 \pm 0.4$  ppm for 82% of the samples (n~460 shells). According to the author, unexpectedly high uranium concentrations

beyond this range may generally be considered as evidence supporting recent uranium uptake processes, and thus non-closed system behaviour. Schelmann et al. (2020, this volume) also observe relatively limited U concentrations in shells, which do not exceed 0.5 ppm for most cases (70%), and are >1 ppm for only 10% of the samples (n=20). The resultant internal dose rates contribute relatively little to the total dose rate (<6%) for most samples (95%), consistent with the observations of Molodkov (2020, this volume) (9% of the total dose rate on average from all the samples analysed). As a consequence, for all samples analysed by Schelmann et al. (2020, this volume), the EU-ESR and LU-ESR ages are within error of each other, and the final ages do not differ by more than 1 ka for 90% of the samples. It therefore seems that the closed-system assumption may be reasonable for most of the mollusc shells considered in these studies.

The final contribution to this SI is by Schielein et al. (2020, this volume), who present the results of an original ESR dating application on coral samples from Cuba. This type of application was quite popular in the 1990s but has progressively disappeared with the development of mass spectrometry techniques that have allowed rapid and high-precision U-series dating of coral, with the need for minimum amount of sample material. Nevertheless, ESR can be particularly useful when the corals behave as open systems, which may be an increasingly significant issue when studying older corals. In this latest study, the ESR ages are calculated using the EU model, and the validity of the closed-system assumption is supported by apparent consistency with U-series ages for most of the samples. There are, however, discrepancies between the two methods for some of the samples. This may be related to recrystallization issues or dose rate evaluation, but it could also be due to uranium leaching in cases where the apparent U-series age is older than the EU-ESR results. Although the analytical procedure for ESR coral dating is time consuming and results in less-precise ages compared to the U-series method, it can nevertheless help to cross-check and evaluate the reliability of the apparent U-series dating results, as this study by Schielein et al. (2020, this volume) nicely illustrates.

#### **4. Conclusion**

It is perhaps fitting, albeit purely coincidental, that this SI is being published on the 45<sup>th</sup> anniversary of the first ESR dating application by Ikeya (1975), and also in the year of retirement of Prof. Rainer Grün, undoubtedly one of the major contributors to the field. These noteworthy events provide added historical backdrops to the significance of this SI. Beyond

the scientific interest of each contribution, the SI provides a unique opportunity to look back and appreciate the evolution of the ESR method over the last four decades, and it represents one of the few historical testimonies available for the ESR dating community (and beyond).

This SI provides a representative overview of the current state-of-the-art of the ESR method and its usefulness as a numerical dating tool for Quaternary studies. Though ESR cannot yet compete with other well-established radiometric methods such as radiocarbon, Ar-Ar, or U-series in terms of reliability and precision, it can nevertheless be considered as a credible dating tool for many settings and age ranges. This is nicely demonstrated in the present SI by the numerous dating studies that compare ESR results with independent age control. The versatility of ESR dating makes it a useful “alternative” method in many contexts considered problematic for other dating techniques. It can, for instance, offer advantages (although with less precision) over: (i) radiocarbon, when a fossil preserves insufficient organic material or is older than 50 ka; (ii) Ar-Ar, when dating Pleistocene sediment that does not contain volcanic material; (iii) luminescence, when dating Early to Middle Pleistocene deposits that lie beyond the practical limits of conventional OSL or extended-range luminescence approaches; (v) U-series, for any Pleistocene materials showing open-system behaviors (e.g., carbonates, teeth, corals, shells), and; (vi) CRN burial dating, for dating Pleistocene deposits that have insufficient overburden thicknesses or complex sedimentary recycling histories. Collectively, the works of this SI contribute towards resolving some of the questions surrounding the reliability, reproducibility, and accuracy of the ESR dating method, which are commonly raised within the community of Quaternary scientists.

For ESR to become a widespread reference technique for Quaternary research, it now appears imperative that progress is made towards attaining a minimum level of standardization for the two most popular ESR dating applications (fossil tooth enamel and quartz), which are routinely employed by several laboratories around the world. Some attempts have been made in this regard for ESR data reporting (e.g., Grun, 1992; Duval et al., 2020) but this cannot be achieved without the full support of the ESR dating community and the peer-review journals. This ESR community is relatively small (see a non-exhaustive list in Table 3) but has been experiencing a substantial renewal in numbers over the last decade. In particular, two historically significant institutions in the field, McMaster University (Canada) and The Australian National University (Australia) have progressively disappeared from the map, with the successive retirements of Profs. Henry P. Schwarcz, Jack W. Rink and Rainer Grün. These losses in expertise have been compensated by the recent appearance of

new research groups, such as those based at Southern Cross University and Griffith University (Australia), Babeş-Bolyai University (Romania) and the University of Lausanne (Switzerland), among others. The changing composition and geographic focus of the ESR community provides a timely opportunity to develop new laboratory inter-comparison programs with the aim of (i) enabling full disclosure of analytical procedures and (ii) permitting proper and systematic evaluations of potential laboratory biases. Such an initiative would also act to strengthen collaborative links between research groups. Unfortunately, only a few attempts at inter-comparison studies have been made so far – primarily those related to ESR dating of carbonates (e.g. Barabas et al., 1993 and references therein) a few decades ago, and similar initiatives organised on a more regular basis by the community of specialists working on retrospective dosimetry of modern tooth enamel (Wieser et al., 2005 and references therein). However, we are not aware of any inter-comparison programs related to fossil tooth enamel and quartz grains. In this regard, the studies by Bahain et al. (2020, this volume) and Duval et al. (2020, this volume), together with the study by Dirks et al. (2017), are probably the closest examples of relevant laboratory inter-comparison initiatives, although they cannot be strictly considered as such *per se*. Owing to its long history, demonstrated usefulness and strong (partly unrealised) potential, we conclude that a concerted, community-wide effort is needed towards standardization of the ESR dating method in the near future. Such an initiative would undoubtedly contribute to raise ESR dating to the level of other well-established radiometric methods in Quaternary geochronology.

### Table 3 approx. here

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	<b>Study</b>	<b>Leading Institution</b>	<b>Material</b>	<b>Age range</b>	<b>Independent age control (material)</b>
#1	Falguères et al. (2020, this volume)	Museum national d'Histoire naturelle, France	n/a	n/a	n/a
#2	Grün (2020, this volume)	Griffith University, Australia	n/a	n/a	n/a
#3	Azevedo et al. (2020, this volume)	Universidade Federal de Pernambuco, Brasil	Fossil teeth	second half of the Late Pleistocene	OSL (quartz) and radiocarbon (carbonate concretions)
#4	Richard et al. (2020, this volume)	Université Bordeaux-Montaigne, France & Museum national d'Histoire naturelle, France	Fossil teeth	second half of the Late Pleistocene	U-series (flowstone) & radiocarbon (bones)
#5	Ben Arous (2020, this volume)	Museum national d'Histoire naturelle, France	Fossil teeth	second half of the Late Pleistocene	OSL (quartz)
#6	Bahain et al. (2020, this volume)	Museum national d'Histoire naturelle, France	Fossil teeth and Quartz grains	late Middle Pleistocene	ESR (fossil teeth and quartz) <sup>1</sup>
#7	Duval et al. (2020, this volume)	Griffith University, Australia & Centro Nacional de Investigación sobre la Evolución Humana, Spain	Quartz grains	early Middle Pleistocene	ESR (quartz) <sup>1</sup> , single-grain TT-OSL (quartz), TCN (quartz), palaeomagnetism
#8	Demuro et al. (2020a, this volume)	University of Adelaide, Australia	Quartz grains	late Middle-to-Late Pleistocene	Single-grain TT-OSL (quartz)
#9	Voinchet et al. (2020, this volume)	Museum national d'Histoire naturelle, France	Quartz grains	Middle Pleistocene	Ar-Ar (sanidines or feldspathoids leucites)
#10	Bartz et al. (2020, this volume)	University of Cologne, Germany	Quartz grains	Late Pleistocene	pIR-IR (K-feldspars)
#11	Beerten et al. (2020, this volume)	Belgian Nuclear Research Centre, Belgium	Quartz grains	Plio-Pleistocene	OSL (quartz) and TCN
#12	Richter et al. (2020)	Leibniz Institute for Applied Geophysics, Germany	Quartz grains	Middle-to-Late Pleistocene	loess chronology
#13	Demuro et al. (2020b, this volume)	University of Adelaide, Australia	Quartz grains	late Middle Pleistocene	Single-grain TT-OSL (quartz),
#14	Molodkov (2020, this volume)	Tallinn University of Technology, Estonia	Marine mollusc shells	Late Pleistocene	IRSL (K-feldspars), time-resolved OSL (quartz), U-series (mollusc shells)
#15	Schellmann et al. (2020, this volume)	University of Bamberg, Germany	Land snail shells (Gastropods)	late Middle Pleistocene to Holocene	OSL(quartz), IRSL (K-feldspars), radiocarbon (land snail shells)
#16	Schielein et al. (2020, this volume)	University of Bamberg, Germany	Corals	late Middle-to-early Late Pleistocene	U-series (corals)

869 *Table 1: Overview of the contributions to this Special Issue. Key: n/a = not applicable; <sup>1</sup> Independent*  
870 *age control was obtained from ESR ages originating from another, independent, laboratory.*  
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872 **Table 2.**

Lee J. Arnold	Christophe Falguères	Anatoly Molodkov	Anne Skinner
Oswaldo Baffa	Rainer Grün	Davinia Moreno	Xuefeng Sun
Jean-Jacques Bahain	Fei Han	Ulrich Radtke	Alida Timar-Gabor
Melanie Bartz	Renaud Joannes-Boyau	Tony Reimann	Hélène Tissoux
Koen Beerten	Angela Kinoshita	Mailys Richard	Shin Toyoda
Bonnie B. Blackwell	Chun-Ru Liu	Gilles Rixhon	Sumiko Tsukamoto
Stéphane Cordier	Marco Martini	Gerhard Schellmann	Pierre Voinchet
Matthieu Duttine	Norbert Mercier	Henry P. Schwarcz	
Mathieu Duval	Veronique Michel	Qingfeng Shao	

873 *Table 2: Reviewers involved in the present Special Issue.*

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<b>Continent</b>	<b>Institution</b>	<b>Main members</b>	<b>Main speciality</b>
America	McMaster University, Canada	H.P. Schwarcz (retired), J.W. Rink (retired)	Fossil tooth enamel, quartz
	Williams College, USA	A. Skinner, B. A. B. Blackwell	Fossil tooth enamel, mollusc shells
South America	Universidade de São Paulo, Brasil	O. Baffa, A. Kinoshita	Fossil tooth enamel
Europe	University of Cologne, Germany	<i>M. Bartz. C. Burow</i>	Quartz
	University of Bamberg <sup>(1)</sup> , Germany	G. Schellmann, P. Schielein	Mollusc shells, corals
	Leibniz Institute for Applied Geophysics, Germany	S. Tsukamoto, M. Richter	Quartz
	Museum national d'Histoire naturelle, France	C. Falguères, J.-J. Bahain, P. Voinchet, <i>M. Richard, E. Ben Arous</i>	Fossil tooth enamel, quartz, calcite
	Bureau de Recherches Géologiques et Minières (BRGM) <sup>(2)</sup> , France	H. Tissoux, I. Serin-Tuikalepa	Quartz
	Centro Nacional de Investigación sobre la Evolución Humana (CENIEH), Spain	M. Duval, D. Moreno, V. <i>Guilarte</i>	Fossil tooth enamel, quartz
	Tallinn University of Technology, Estonia	A. Molodkov	Mollusc shells
	University of Lausanne, Switzerland	G. King, M. Bartz	Quartz
	Babeş-Bolyai University, Romania	A.Timar-Gabor, K. Benzid	Quartz
Asia	Nanjing Normal University, China	Q. Shao	Fossil tooth enamel
	China Earthquake Administration, China	Y. Gongming, C. Liu, F. Han	Fossil tooth enamel, quartz
	Cold and Arid Regions Environmental and Engineering Research Institute, China	J. Zhao	Quartz
	Institute of Tibetan Plateau Research <sup>(3)</sup> , China	C. Yi	Quartz
	Okayama university, Japan	S. Toyoda	Quartz, barite, tooth enamel (dosimetry)
Oceania	The Australian National University, Australia	Rainer Grün (retired)	Fossil tooth enamel
	Southern Cross University, Australia	Renaud Joannes-Boyau	Fossil tooth enamel
	Griffith University,	Mathieu Duval & Rainer	Fossil tooth enamel, quartz

	Australia	Grün (retired)	
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877 *Table 3: Non-exhaustive overview of the main ESR dating Research Groups. The information indicated*  
878 *in the table is based on the authors' personal knowledge, in combination with the information collected from*  
879 *recent peer-reviewed publications. Consequently, we acknowledge that the information displayed in this table*  
880 *may not be fully accurate, or complete. Key: In italics, early-career researchers who may have recently moved*  
881 *to other institutions; <sup>(1)</sup> The ESR measurements are usually performed at the University of Cologne; <sup>(2)</sup> The ESR*  
882 *measurements are usually performed at the Museum national d'Histoire naturelle; <sup>(3)</sup> The ESR measurements*  
883 *are usually performed at the China Earthquake Administration.*

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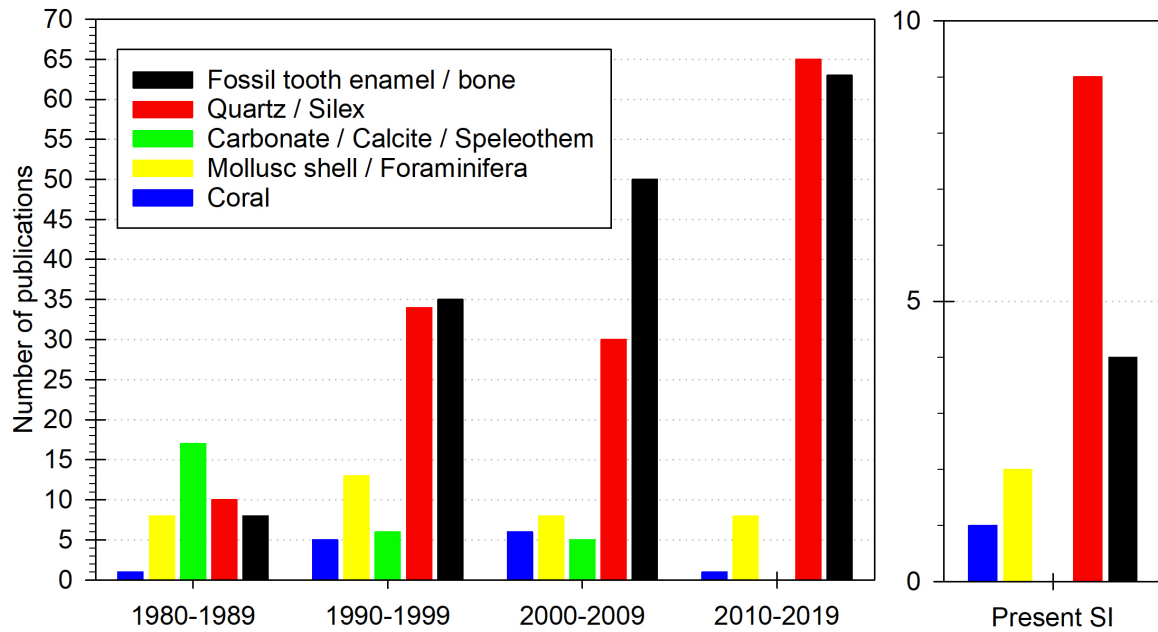


Figure 1. Evolution with time (by decade) of the most popular ESR dating applications since 1980, expressed by number of publications (left), and comparison with the present SI (right). Source: Scopus search (24/06/2020) based on the selection of journals that have traditionally included ESR dating studies: *Quaternary Geochronology* (data available since 2006), *Quaternary Science Reviews* (since 1982), *Quaternary International* (since 1989), *Journal of Human Evolution* (since 1972), *Radiation Measurements* [including the former *Nuclear Tracks and Radiation Measurements*; *International Journal of Radiation Applications and Instrumentation. Part D. Nuclear Tracks and Radiation Measurements*; *Nuclear Tracks and Radiation Measurements* (1982)] (since 1982). Note: (i) the papers from the present SI that have been available online before 2020 have not been included in the left graph, but only in the right graph; (ii) The ESR dating study by Bahain et al. (2020, this volume) includes applications to both fossil tooth enamel and quartz grains, and has thus been counted twice in the right graph; (iii) In contrast, the historical review papers by Grün (2020, this volume) and Falguères et al. (2020, this volume) have not been included in the right graph.