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Abstract

This is the story of the ESR team at Muséum national d'histoire naturelle of Paris, which has been involved in Quaternary dating for 40 years. It is a dedication to Yuji Yokoyama who created this laboratory and contributed to its development. The history of the ESR dating laboratory is presented since its beginnings in the CFR lab at Gif-sur-Yvette to its current location at the Muséum.

Key-words

ESR; Yuji Yokoyama; calcite; quartz; enamel

Introduction

Electron Spin Resonance as a dating method (ESR) was introduced by Motoji Ikeya who published the first paper on ESR dating of a calcite sample from Akiyoshi cave in Japan (Ikeya, 1975). This novel application was picked up by another Japanese researcher, Yuji Yokoyama, who was in France for working on lunar samples. He decided to implement the ESR method at the "Centre des Faibles Radioactivités" (CFR) at Gif-sur-Yvette. Jacques Labeyrie, at the head of the CFR, favoured the development of radiometric methods to date events related to past climates. At the time, CFR researchers developed thermoluminescence dating (Georges Valladas), U-series dating (Claude Lalou), and radiocarbon (Georgette Delibrias). The CFR dating laboratories drew the attention of many prehistorians including Henry de Lumley, Professor at the Museum of Paris, who understood the importance of the dating methods for prehistory. Yuji Yokoyama was an eminent specialist in nuclear physics with a particular interest in cosmic rays. He simultaneously developed ESR and gamma-ray spectrometry and set up a pioneering laboratory for U-series dating of human remains based on the non - destructive gamma-ray spectrometry (Yokoyama et Nguyen, 1980; 1981a). He formed an ESR team that began to work on fundamental studies on calcite and notably on the nature and stability of trapped electrons in this mineral. Then he moved to the Muséum national d'histoire naturelle where he founded a new dating laboratory with his students. For the first time in France, a dating laboratory was settled in a research environment dedicated to prehistory.

In the beginning was…. Arago cave!

The first prehistoric site involved in this story is Arago cave in southern France, excavated by Prof H. de Lumley and where more than 150 human remains have thus far been unearthed in association with hundreds of thousands of faunal and lithic artefacts along a ten meters thick sequence. Among them, the famous Arago XXI skull is the first human fossil to be dated by non-destructive gamma-ray spectrometry (Yokoyama and NGuyen, 1981a; 1981b). An age of 455 +∞ /-210 ka was obtained. In spite of heavy criticism at the time of the publication (see de Lumley and Labeyrie, 1981), this pioneering result has been reconfirmed by new dates obtained by U-series on calcite, ESR on quartz, and ESR/U-series on teeth (Falguères et al., 2004, 2015). In 1981, an international colloquium on *Absolute dating and isotope analysis in prehistory* was organized to discuss the chronology of the site. More than 250 samples were collected and distributed to about 20 international laboratories using a variety of methods including U-series, thermoluminescence, fission tracks, amino acid racemization, and electron spin resonance (see papers in Lumley de and Labeyrie, 1981). The large spread of the results was perplexing and obscured the true age of the site triggering hotly debated discussions (Figure 1). This first Colloquium, however, made both physicists and prehistorians aware of the difficulties in accurately dating a prehistoric site.

The ESR results presented at the colloquium were carried out on bones, calcite and quartz. The ESR section in the proceedings is opened by a review of M. Ikeya (1981) based on the previously published articles (Ikeya, 1975; 1978). The ESR dating paper by Yokoyama et al. (1981a) addressed some of the main problems such as uranium concentration variations, U-series disequilibrium (escape of radium and radon), water content and alpha/beta effectiveness, k-value, for which an analytical device was built according the description of Zimmerman (1971). Several values ranging between 0 and 1 were measured for k for three bones. Yokoyama et al. (1981a) experimentally determined a k-value of 0.084 for the bones from Arago. Grün and Katzenberger (1994) measured later a k value of 0.13±0.02 for enamel sample. At this time, the dose values, D_E, were calculated using a linear extrapolation with 5-6 data points and the obtained values varied from sample to sample by a factor of 10 implying a wide spread in the ages of the human bearing layers. Moreover, Unit G, the layer richest in human remains, is in places severely weathered by phosphates and bat guano. The bones from Unit G yielded ESR ages of between 145 and 285 ka, generally too young! These studies demonstrated the difficulties in ESR dating of bones. This subsequently led geochronologists to direct their research towards fossil tooth enamel, which seems intrinsically better suited for ESR dating than bones (see Grün and Schwarcz 1987) and for which the U-uptake history can be experimentally determined (Grün et al., 1988).

Preliminary results were presented on ESR dating on calcite samples coming from the base of the sequence (Ensemble I) and from Ensemble IV of Arago cave (Yokoyama et al., 1981b; 1982). The ESR spectra of calcite show several lines (see Ikeya, 1993). Most authors recommend the use of the signal at g = 2.0007, h_3, either for corals, mollusk shells, speleothems or travertines (see Grün, 1989; Rink, 1997). The lifetime of the line at g=2.0007, determined by the Arrhenius law, is short in speleothems and varies according to authors from 2 10^5 years (Yokoyama et al., 1983) to 6 10^7 years (Smith et al., 1985). Grün (1989) considered it to be a few million years range. The association of the CO_2^- radical, responsible for h_3, with water molecules within the crystal could skew the experimental determination of the thermal stability, which uses thermal annealing (Debuyst et al., 1993). Other processes such as recrystallization of carbonates may also have influence on the thermal stability (Barabas et al., 1992). Isochron annealing experiments suggested that the signal at g=2.0057 is the most stable observed in Quaternary natural carbonates (Bahain et al., 1994) despite the controversy caused by the fact that this signal was not sensitive to gamma radiation. Figure 2 shows that h_1 signal intensity increases when the sample is irradiated with a gamma dose of 47 krad (470 Gy) after pre-annealing for 16h at 190°C (Figure 2A). Figure 2B shows an increase of h_1 line while h_3 signal decreases as a function of annealing time at elevated temperatures. This phenomenon may correspond to a spontaneous transfer of electrons from h_3 to h_1 which would also occur at ambient storage temperatures during the geological history of the sample (Yokoyama et al., 1981b; 1983).The decrease of h_3 is therefore not only due to the release of the trapped electrons, as a result of temperature (thermal release), but also to the destruction of the trap itself (trapdecay), which does not occur during geological time (Barabas et al., 1992b ; Walther et al., 1992). A comparative study was performed on a thick stalagmitic floor and dated using several ESR signals (Bahain et al., 1994). The first results implied that the h_3 results were too young, suggesting a short life-time of h_3 line. However, several authors consider that the use of h_1 signal after thermal annealing experiments leads to age overestimations (Hennig and Grün, 1983; Skinner, 1983; Grün, 1989). Presently, the discussion is not over but the development of mass spectrometric U-series dating is used on carbonates and allows the determination of ages of up to 600 ka with an excellent precision (Edwards et al., 1987; Potter et al., 2005). A recent article on Basura stalagmitic floor yielded U-series age confirming the antiquity of the calcite of more than 530 ka (Pozzi et al., 2019).

Some studies were performed on quartz grains at room temperature (Quaegebeur and Yokoyama, 1981). ESR spectra showed sharp lines and broad absorption band which could correspond to E’ and peroxy centers. No dating procedure was made.

Sea, quartz and sun!

ESR dating of quartz began in the late sixties with three papers of McMorris (1969; 1970; 1971) introducing the possibilities of using this ubiquitous mineral. Physicists had already published several important studies on ESR applications on quartz and silicas (Mackey et al., 1970; Griscom, 1978; Poole et al., 1978; Marfunin, 1979; Weil, 1984). One of the first papers on ESR dating of bleached quartz was published by our team (Yokoyama et al., 1985), and we have not stopped working on this mineral since. Beach and wind-blow sands from the Terra Amata and Arago sites were tentatively dated by ESR using the aluminium center in quartz grains measured at low temperatures (93°K). A comparison of the dose response curves of each hyperfine lines of Al center is made and leads to the D_E by measuring the signal intensity peak to peak height between the top of line #1 (g= 2.0185) to the bottom of line #16 (g= 1.9928). This method was confirmed by Toyoda and Falguères (2003). It avoids a potential interference by the peroxy signal (Odom and Rink, 1989). A second important point is the observation of saturation effects in the aluminium dose response curves, which are well fitted by an exponential equation as already suggested for other types of samples (Apers et al., 1981; Ikeya, 1981). The residual signal, corresponding to an incomplete bleaching of the aluminium center, is extracted from modern-analogue samples such as present beach sands and surface alluvial soils, and is subtracted from the natural ESR intensity allowing the determination of the D_E value. The first UV bleaching experiments were conducted on Arago samples but the 4W black UV lamp used was apparently too weak for emptying the traps and the experimentally determined residual level was 80% of the natural intensity. In spite of large errors accompanying these preliminary ages, the results were consistent with other data obtained on both sites (Lumley H. de, 1967; Lumley H. de and Lumley M. A. de, 1971).

When working on quartz, the first idea was to look at burnt sediments in order to minimize the problem of the residual signal. A preliminary study was performed on sediments baked by lava-flows and comparing for the first time the D_E obtained by Al and Ti centers (Yokoyama et al., 1986). For the Ti center, three components are identified in accordance with the literature (McMorris, 1971) but the measurement of the signal intensity was made without dissociating Ti-Li, Ti-H and Ti-Na, leading to conclusions on thermal annealing of this complex center that have been reconsidered since (Toyoda, 1992; Voinchet et al. 2007; Duval and Guilarte, 2014). The burnt sediments were provided by the “Laboratoire de Physique corpusculaire” of Clermont-Ferrand, which had measured the TL on quartz, marking the beginning of a fruitful collaboration with D. Miallier and his team.

Preliminary analyses were performed on the same type of burnt quartz but it was not possible to correlate the ESR signals (Al and Ti centers) and TL peaks (RTL around 600-620 nm at 380°C) probably because of the sensitivity difference between the methods (Falguères et al., 1991; Miallier et al., 1994). Later, measurements were performed on detrital marine, aeolian sands, and on volcanic and baked sediments. In some samples, the presence of the E' center (Feigl et al., 1974) was observed at room temperature (Falguères et al., 1994). Based on laboratory annealing experiments, it seems possible to use E' center for evaluating the effective temperature at which the samples heated to by the contact with volcanic materials (Figure 3).

An optical bleaching device was built to understand the bleaching characteristics of the aluminium center in natural sedimentary quartz. A bleaching curve of quartz from fossil sediment shows that the maximum bleaching for Al center is about 52% after around 820 h of laboratory light exposure (halogen and UV lamps) equivalent to 6 months of sun light (Figure 4) (Voinchet et al., 2003; 2007). This process to evaluate the maximum bleaching level has been criticized by some OSL users (Stokes, public comment, 2002). However, today thermally transferred optically stimulated Luminescence (TT-OSL) utilizes deep traps for dating the Early Pleistocene period (Arnold et al., 2015). These TT-OSL signals in single grains show also relatively slow optical characteristics (Arnold et al., 2019).

The sun light bleaching responses of the Al and Ti centers were studied in collaboration with Prof S. Toyoda with whom we share an interest in ESR dating on quartz and particularly in sun light bleaching characteristics and the sensitivity of Ti centers (Ti-Na, Ti-H, Ti-Li, Toyoda et al., 2000). This paper established the basis of the Multiple Centre Approach which represents a major breakthrough in ESR Dating of quartz. A JSPS grant was obtained by our colleague H. Tissoux who spent 2 years in Toyoda's lab working on the potential of Al and Ti centers for dating sediments (Tissoux et al., 2007; Tissoux et al., 2008).

Even if the bleaching mechanism is not yet completely understood, it has opened the door for ESR dating of a number of open air prehistoric sites associated with fluvial deposits located in the northern part of Europe (Despriée et al., 2018; Voinchet et al., 2010; 2015; Moncel et al., 2013), Spain (Duval et al., 2015; Moreno et al., 2012; Toro-Moyano et al., 2013), Southeast Asia (Ingicco et al., 2018) and China (Voinchet et al., 2019). Presently, when old sites are not located in volcanic areas, ESR applied on optically bleached quartz and, thanks to the great stability of Al center (Toyoda and Ikeya, 1991), is the only method able to provide ages as far as 2.4 Ma (Sahnouni et al., 2018).

Modeling the uranium uptake in fossil enamel

After the first tentative attempts of ESR dating of hydroxyapatite (Ikeya, 1978), ESR dating was applied to bones but the results were not satisfying, as mentioned previously, due to the frequent heterogenous distribution of uranium and "the great complexity of the diagenetic processes" in bones (Grün and Schwarcz, 1986). At the end of the eighties, an important paper provided an equation allowing the determination of the uranium uptake parameter in fossil enamel with the restriction that the sample should not undergo any uranium leaching (Grün et al., 1988). To solve for the uranium uptake parameter, p, it is necessary to measure U-series ages on the dental tissues that contribute to the dose in the enamel, i.e. the enamel itself, as well as adhering dentine and, if present, cement. The p-value is derived from the combination of the ESR and U-series age equations (US-ESR model). Mammalian teeth and particularly thick herbivorous enamel are suitable for obtaining reliable results. Y. Yokoyama wrote a program allowing the age calculation of several prehistoric sites using the p-value system well before the publication of the program written by Grün (2009).

A comparative approach was performed on teeth from Isernia dated by ESR and minerals by K-Ar method (Bahain et al., 1992). The US-ESR model using a hypothesis of inverse correlation between ESR signal height and uranium concentration resulted in an age of about 450 ka, far from the first 736 K-Ar age (Coltorti et al., 1982) which was later adjusted by $^{40}Ar/^{39}Ar$ measurements to 610 ka (Coltorti et al., 2005), and recently to 583-561 ka on sanidine crystals (Peretto et al., 2015). The heterogeneous uranium distribution observed in the elephant tooth enamel was a reason explaining the age difference between the ESR and K-Ar methods. Due to their lamellar structure they may favour uranium migration which is strongly correlated with the fossilization processes (Grün and Invernati, 1985). The authors conclude that "it is necessary to develop a model of U-uptake for each bone and tooth". Large proboscidian teeth were subsequently not used for ESR dating, at least by the French team. We suspected that the ESR age underestimation was due to the variations in the external gamma-dose rate. The archaeological layer contains a very large number of bones and these may have accumulated uranium in recent times. Such a process results in a much higher gamma dose rate today than it was in the past (Shao et al., 2011). In Figure 5, time-integrated gamma doses are calculated using the Ar-Ar age as a reference, and assuming that a massive uranium uptake occurred during an interglacial period. The results suggest that this event occurred during MIS7 and not during MIS5 as proposed previously (Falguères et al., 2007). While ESR dating has provided reliable results for Middle Pleistocene sites (Bahain et al., 2015; Falguères et al., 2010; Pereira et al., 2017), it is more difficult to obtain reproducible results for sites older than 800 ka. Except for the Gran Dolina sequence, for which a multi-methods approach yielded ages ranging between 800 and 900 ka for TD6 layer containing *Homo antecessor* (Perez-Gonzalez and Pares, 1995; Falguères et al., 1999; Moreno et al., 2015; Arnold et al., 2016; Berger et al., 2008), combined ESR/U-series applied to various Lower Pleistocene prehistoric sites highlighted the difficulties for establishing chronologies for this period. A study of 20 teeth from different Spanish sites showed a general trend of age underestimation probably in relation with their geological context and their state of conservation (Duval et al., 2012). A 3-D LA ICPMS MC investigation on a horse tooth (Figure 6) demonstrated that this type of analysis allows the evaluation of the most appropriate areas of dental tissues to be dated avoiding the altered zones presenting heterogeneous uranium distributions (Duval et al., 2011). Several studies have recently been published on dating the final Middle Palaeolithic cultures by ESR/U-series (Richard et al., 2015; Ben Arous et al., 2019). Paradoxically, for such an important period in human evolution, marked by the disappearance of Neanderthals, it is difficult to obtain a well resolved chronologies, because radiocarbon is limited to samples younger than 40-45 ka, whereas luminescence and ESR ages are associated with relatively large errors on this period range. Several constraints such as a clear identification of the transitional layers in sites, heterogeneity of sedimentary deposits increased by the difficulties for getting accurate isotopic ratios and U concentration in tissues, render problematic the production of accurate results allowing a firm attribution of the archaeological layers to *Homo sapiens* or Neanderthals (Higham et al., 2014).

Conclusion

This contribution, which presents some of the results obtained during the 40 years of the life of the Parisian ESR team is a tribute to Yuji Yokoyama (1926-2015) who had introduced ESR as a dating method in France opening the gate for a generation of researchers. He contributed greatly to include dating methods as an essential tool in any multidisciplinary approach in prehistorical studies. Table 1 refers the great major part of the work performed by his team using ESR and U-series methods, with a list of publications and PhD defences in Supplement Information. He had a vision for the place of the geochronology in prehistory but he was also fully aware of the problems that are involved in obtaining reliable ages. He was one of the first to make *in situ* measurements of the external dose rate and to perform analyses on the alpha/beta effectiveness. I would like to thank him on behalf of all his students for having given us the taste of scientific curiosity and analytical precision, not such an easy task! His name is inseparable from the development of ESR dating in France.

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Figure caption

Figure 1: ESR and U-series dating on bones (red and grey squares) and on calcite (red and grey circles) showing a very large spread of the ages for the human bearing occupation layers. These analyses were performed by several labs and presented at the colloquium of Tautavel in 1981 (modified from Falguères et al., 2004).

Figure 2: A) ESR spectra of Arago stalagmitic calcite YC62. (a) natural spectrum, (b) natural + artificial gamma-ray of 47 krad, (c) natural spectrum after pre-annealing at 190°C for 16h, (d) natural + artificial gamma-ray of 47 krad after pre-annealing at 190°C for 16h. B) Decrease of the h_3 and increase of the h_1 line as a function of annealing time at an annealing temperature of 200.5°C (after Yokoyama et al., 1983).

Figure 3: ESR spectra of non irradiated samples: a) sand dune showing OHC and E' centers; b) pumice in which no center is observed. P= 2mW; modulation = 1.25 G, cavity temperature = 300°K (modified from Falguères et al., 1994).

Figure 4: Bleaching curve of quartz extracted from a fossil sediment. For each point, uncertainty of ESR measurement was estimated to one sigma (from Voinchet et al., 2003). 1) fitting by Walther and Zilles formula: $y = Ae^{(-Bx)} + C$ (Walther and Zilles, 1993) 2) fitting by the equation: $y = Ae^{(-Bx)} + A'e^{(-B'x)} + C$ (Voinchet et al., 2003)

Figure 5: Comparison of combined ESR/U-series dates with that obtained by $^{40}Ar/^{39}Ar$ age of the Pleistocene site of Isernia la Pineta (with isotopic data from Lisiecki and Raymo, 2005). The "In-situ, MIS 11, MIS 9, MIS 7 and MIS 5" ages are the weighted means (W ¼ 1/s2) ESR/U-series dates calculated using the present-day dosimetry value and the simulated gamma-dose rates for the different MIS respectively. The ESR/U-series ages are given with 1 sigma error bars while $^{40}Ar/^{39}Ar$ age is given with 2 sigma bars (Coltorti et al., 2005) (after Shao et al., 2011).

Figure 6: U-series analyses of a tooth from Venta Micena site (VM0502), performed by LAICP-MS at the University of Melbourne (after Duval et al., 2011).
(A) Position of the three laser ablation tracks (labelled 1 to 3) carried out on the longitudinal section of VM0502.
(B) $^{234}U/^{238}U$ and $^{230}Th/^{234}U$ ratios along the three transversal profiles. Red solid lines represent the values obtained by alpha spectrometry on the same tissues. Keys: d=dentine, e=enamel, c=cement. Domains close to the cement–enamel junction and dentine–enamel junction (in grey) show clearly more constant U-series data values and these were used for age calculation. Numerical mean values are also shown. Standard errors correspond to 1s. Average ratios of the grey areas of the three laser tracks are: $^{234}U/^{238}U = 1.47 \pm 0.01$ and $^{230}Th/^{234}U=1.02 \pm 0.03$ for dentine; $^{234}U/^{238}U = 1.44 \pm 0.03$ and $^{230}Th/^{234}U = 1.05 \pm 0.05$ for cement.

Table 1: List of publications versus sample types, countries. Detailed references may be found in Supplementary information.

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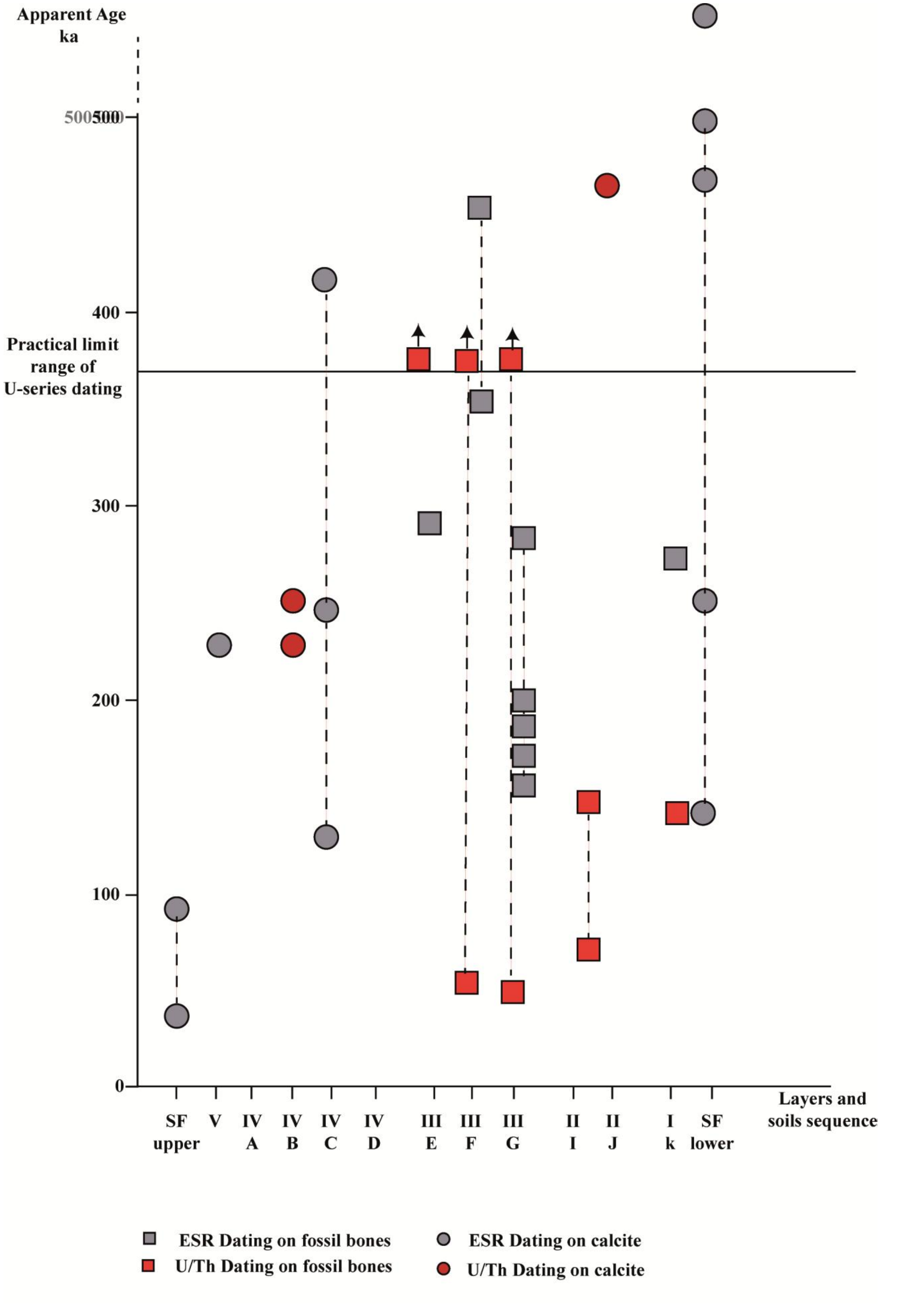
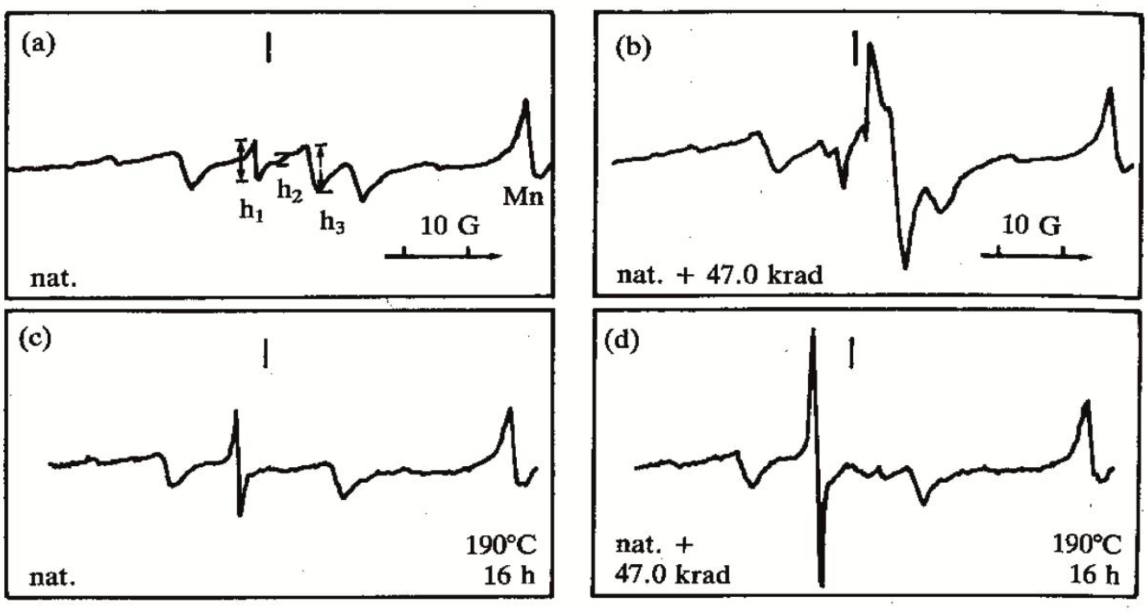


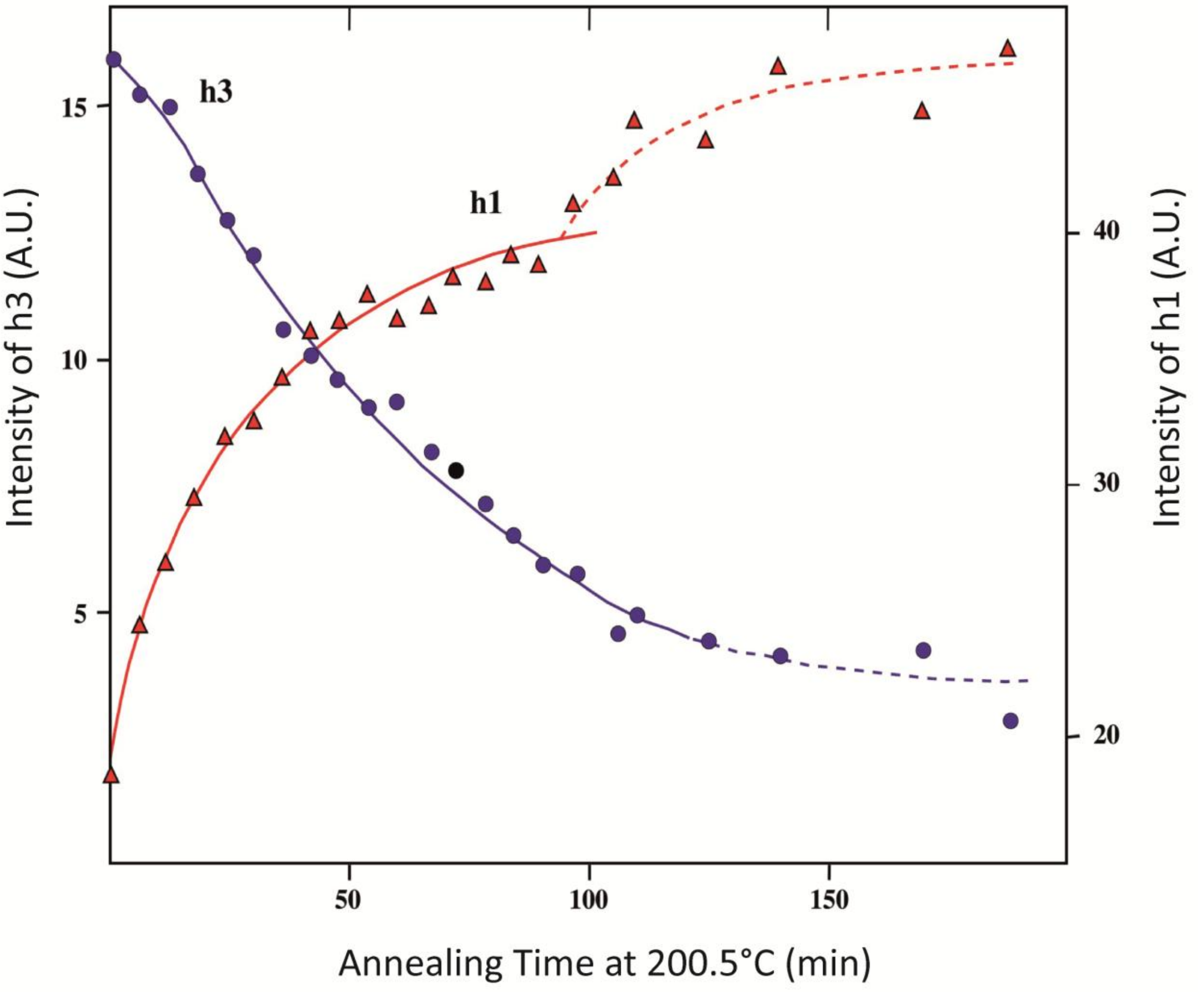
Apparent Age
ka
500
400
300
200
100
0
Practical limit
range of
U-series dating
Layers and
soils sequence
SF
upper
V
IV
A
IV
B
IV
C
IV
D
III
E
III
F
III
G
II
I
II
J
I
k
SF
lower
ESR Dating on fossil bones
U/Th Dating on fossil bones
ESR Dating on calcite
U/Th Dating on calcite

A)

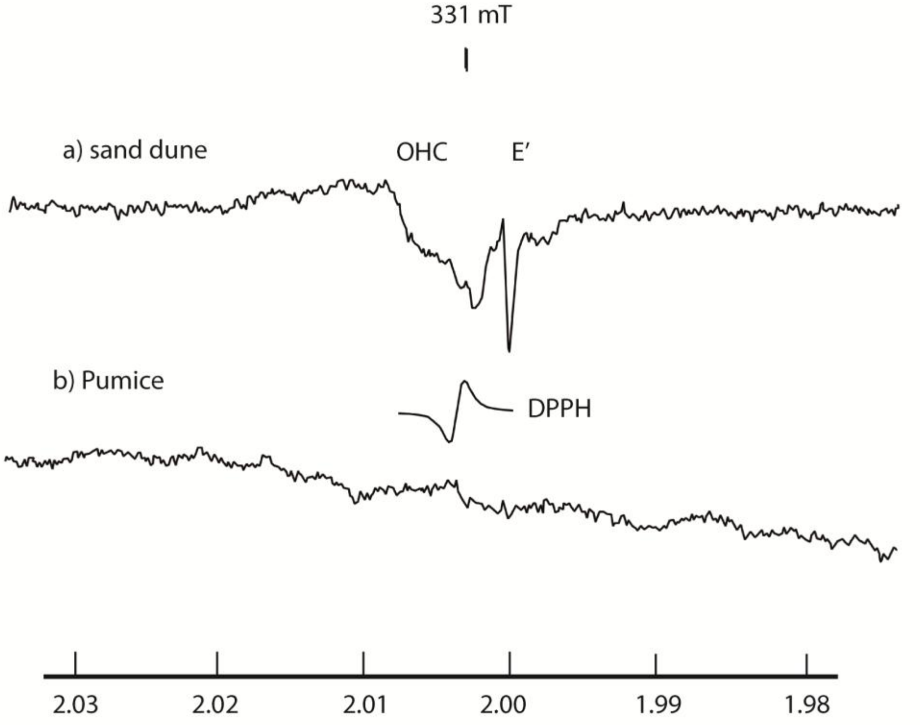


(a)
h1
h2
h3
Mn
10 G
nat.
(b)
10 G
nat. + 47.0 krad
(c)
190°C
16 h
nat.
(d)
nat. +
47.0 krad
190°C
16 h

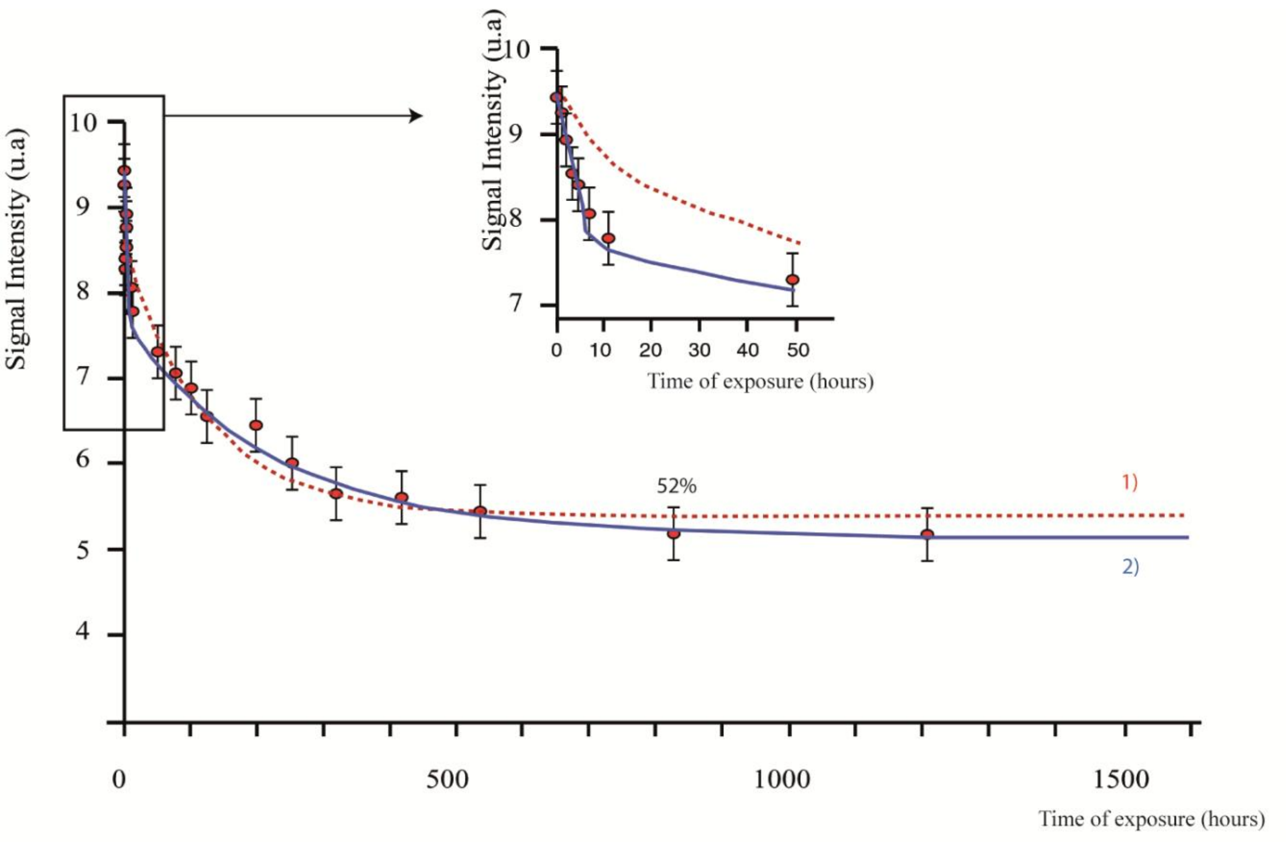
B)

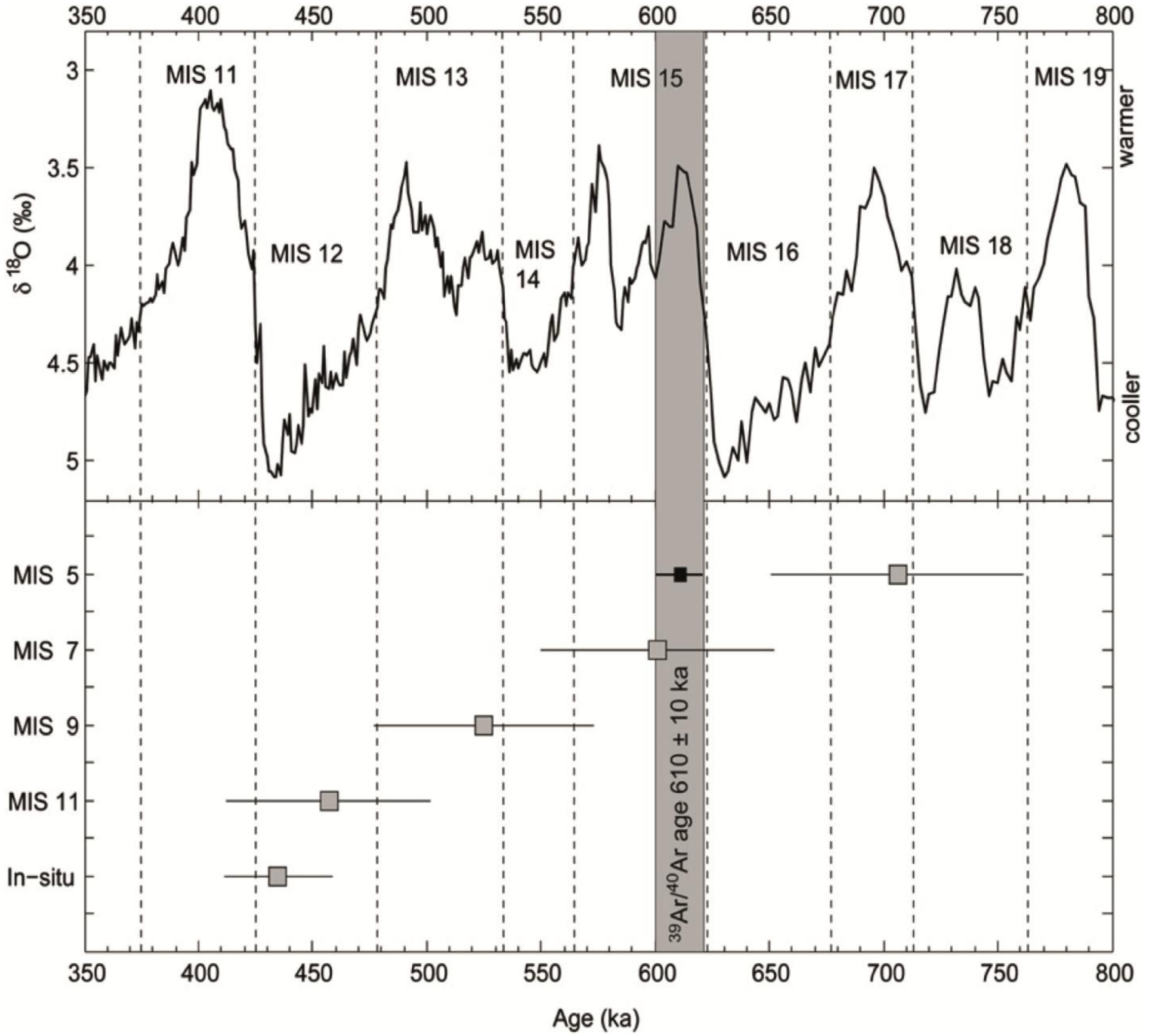


h3
h1
Intensity of h3 (A.U.)
Intensity of h1 (A.U.)
Annealing Time at 200.5°C (min)
15
10
5
40
30
20
50
100
150

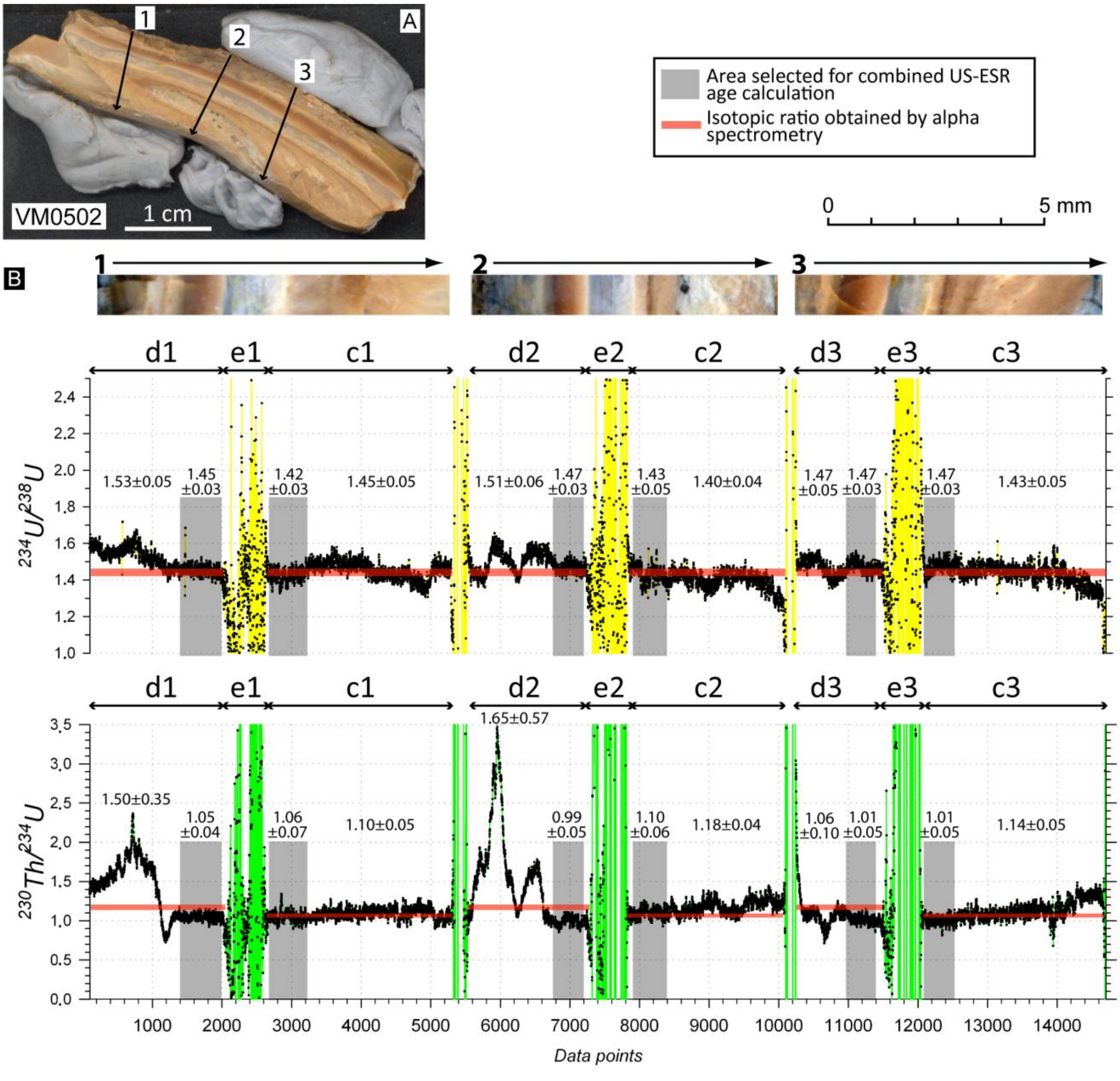


E′ center natural	E′ center irradiated	Initial heating	Dating method
-	-	> 550°C	ESR and TL
-	+	400°C<T<550°C	ESR and TL
+	+	Non sufficient	incomplete zeroing process
		Adequate	Contamination


Signal Intensity (u.a)
10
9
8
7
6
5
4
0
500
1000
1500
Time of exposure (hours)
52%
1)
2)
Signal Intensity (u.a)
10
9
8
7
0
10
20
30
40
50
Time of exposure (hours)



350
400
450
500
550
600
650
700
750
800
MIS 11
MIS 12
MIS 13
MIS 14
MIS 15
MIS 16
MIS 17
MIS 18
MIS 19
δ 18O (‰)
3
3.5
4
4.5
5
warmer
cooller
MIS 5
MIS 7
MIS 9
MIS 11
In−situ
39Ar/40Ar age 610 ± 10 ka
Age (ka)



A
VM0502
1 cm
1
2
3
Area selected for combined US-ESR age calculation
Isotopic ratio obtained by alpha spectrometry
0
5 mm
B
d1
e1
c1
d2
e2
c2
d3
e3
c3
$^{234}U/^{238}U$
1.53±0.05
1.45 ±0.03
1.42 ±0.03
1.45±0.05
1.51±0.06
1.47 ±0.03
1.43 ±0.05
1.40±0.04
1.47 ±0.05
1.47 ±0.03
1.47 ±0.03
1.43±0.05
$^{230}Th/^{234}U$
1.50±0.35
1.05 ±0.04
1.06 ±0.07
1.10±0.05
1.65±0.57
0.99 ±0.05
1.10 ±0.06
1.18±0.04
1.06 ±0.10
1.01 ±0.05
1.01 ±0.05
1.14±0.05
Data points