Brazilian Journal of Physics (2022) 52: 25
https://doi.org/10.1007/s13538-021-01030-2

GENERAL AND APPLIED PHYSICS

Using Dentine as well as Enamel in ESR Dating

Anne R. Skinner[1] · Bonnie A. B. Blackwell[1] · Joel I. B. Blickstein[1] · J. Lundberg[2]

Received: 1 November 2021 / Accepted: 29 November 2021 / Published online: 19 December 2021

Abstract
Both tooth enamel and dentine contain hydroxyapatite, the mineral which provides the strong electron spin resonance (ESR) signal used in enamel dating. The radiation-induced signals in dentine are considerably weaker than those in enamel and also appear less stable. Clearly, enamel is preferred for ESR dating. Some teeth, however, do not possess enough enamel to date. Even if some enamel is present, dating the dentine yields additional age estimates for the tooth. While the dentine ESR signal is weak, its properties (e.g., dose response and response to power saturation) are the same as for enamel. Measurement can be improved by signal averaging. For the samples in this study, no significant signals from organic contamination were found, although the presence of organic material seriously complicated isothermal measurements of the signal lifetime. Evaluating the internal dose rate has been problematic, because U mobility affects dentine to a much greater extent than enamel. Moreover, multiple uptake events are more common in dentine. The best results were obtained with teeth aged between 40 and 400 ka. Dentine will not replace enamel as a dosimeter. Every new material that can be used, however, even in limited cases, widens the range of sites and samples that can be dated by ESR.

Keywords Electron spin resonance · ESR dating · Dentine · Properties of dental components

1 Introduction

Electron spin resonance (ESR) dating using tooth enamel has been applied to samples as young as a few thousand years and as old as a few million years [1, 2]. This broad time range, as well as the relative abundance of datable material, makes ESR a method of choice in archaeological and paleontological sites. The method has its limitations. First, while several groups are working on semi-non-destructive techniques [3, 4], in most cases it remains a destructive method and, therefore, only rarely useable directly on hominid teeth [5, 6]. Second, teeth are not closed systems with respect to uranium uptake from ground water. Accuracy requires determining the pattern for such uptake. In 1988, Grün defined a parameter p [7]. The simplest cases are: early uptake (EU), where the tooth absorbed essentially all the uranium shortly after deposition ($p = -1$); linear uptake (LU), where the tooth has absorbed uranium continuously during burial ($p = 0$); and recent uptake (RU), where the tooth absorbs the bulk of the uranium shortly before excavation ($p > 0$). Clearly intermediate scenarios are also possible, including cases in which the model changes during deposition with alteration in the environmental geochemistry. A critique of this simple case is that the selection of model tends to be chosen not on an absolute basis, but rather on the basis of agreement with other site information, including other dating methods. Fortunately combining ESR and U-series dating is one proven way to determine the appropriate model [7–10]. While U-series dates on open U-uptake systems are also inaccurate, iterating results from the two techniques will yield a reliable age. However, there remain samples for which no U-series age can be calculated, including the samples in this study. Thus innovations are valuable that improve the information available.

To determine diagenesis within a tooth, as well as to provide measures of statistical variation, one should obtain more than one age from a given sample. For example, one can take several enamel subsamples from a tooth and date them independently. Additional information could be obtained by dating the dentine, which would prove especially useful for small or damaged teeth that would not yield

✉ Anne R. Skinner
askinner@williams.edu

[1] Chemistry Department, Williams College, Williamstown, MA 01267, USA

[2] Department of Geography, Carleton College, Ottawa, ON K1S 5B6, Canada

more than one enamel subsample and also are often inappropriate for the combined U-series/ESR method. Dating both dentine and enamel also satisfies the criterion of independent methods. Furthermore, most teeth contain considerably more dentine than enamel. Finally, if the archaeologist or paleontologist wishes to preserve the tooth crown or occlusal surface, dating just the root dentine would provide an age.

2 Dentine

Dentine differs from enamel in several important ways, as summarized in Table 1. A number of studies [11–15] have looked at dentine for dosimetry and were primarily concerned with signal intensity and stability. Both dentine and enamel contain hydroxyapatite (HAP), the mineral showing the radiation-sensitive dating signal. The precise percentage of HAP in either dental tissue varies with species [16] and for dentine with the age of the sample and degree of fossilization. However, for all materials, there is less HAP in dentine than in enamel (Table 1). The smaller HAP percentage in dentine implies a smaller signal for a given sample mass. The authors further hypothesize that smaller crystal size means that more radicals formed by natural or artificial radiation will be on the crystal surface, where they can easily be annealed by reaction with water, oxygen, or organic matter. The small crystal size may also result in a shorter signal lifetime in dentine than in enamel.

The structure of dentine includes thousands of tubules from the pulp cavity to the dentine/enamel junction. Water can enter these tubules from outside the tooth, and exchange of water can occur. In addition, as U is taken up by dentine tissues, more U can diffuse into the tubules. While this uptake may not be continuous, it would suggest that for teeth in sites that are not arid, dentine uptake is unlikely to be simply EU. The higher dentine porosity clearly suggests that uranium uptake will be both greater and more complex than for enamel, with a greater probability of multiple uptake and/or leaching events. Since, however, dentine normally contains considerably more uranium than enamel, small fluctuations in uranium concentration caused by minor uptake events may not lead to statistically significant changes in calculated ages.

To use dentine for dating requires knowing additional parameters that differ between enamel and dentine such as tissue density, tissue water content, and tissue radiation sensitivity. The difference in density is, of course, known [17]; note that density of fossil tissues is greater than modern. Effects of water content and radiation sensitivity are explored in this study.

The type and amount of organic material in modern teeth do affect their dosimetric signal [12]. In a number of Quaternary fossil teeth, some of the collagen may have degraded but many Quaternary teeth retain most of their collagen [18, 19]. Dentine from teeth found in caves is more likely to retain pristine dentine than those from waterlogged sites or other open-air sites [20] (Table 2).

We report here some first steps in investigating dentine as a potential dating material. In this study, we used only dentine from teeth that have been well dated by ESR enamel dating and other comparative methods where available. The sites fall into two general age ranges: <400 ka and >400 ka. Our aim was to see if the dentine and enamel ages agreed, on the assumption that, if so, the method was sufficiently promising to justify more detailed work with a larger range of teeth.

3 Samples

Samples selected represented teeth for which a reliable enamel age had been calculated. The primary criterion was a growth curve with low uncertainty. The external dose rate would be the same for dentine and enamel, except for root dentines where the sedimentary β dose is greater (Table 4). Despite this case, variations in external dose rate due to, say, changing sedimentary water content, were not considered. The teeth were chosen to provide a range of ages, not a range of site types. Most of the sites (Mesmaiskaya, Matuska, Praydarol, and Treugol'naya) are caves or rock shelters; the stability of these sites tends to improve the quality of tooth preservation. Senèze is an open-air site. We did not use as a criterion whether the tooth had been crucial to dating the site itself since that would not affect the quality of the age comparisons of interest herein.

Dates for most of these sites have been published. A summary is in Table 3 with references [21–24]. Note that the mollusc ages at Treugol'naya are mostly taken from a different level [24]. Table 3 notes the ones from the same level. ESR dates have not been published for Makapansgat, but there is a description of the site [25]. Matuska Cave has also been described [26]. There is an overview of the Senèze site [27]. The published ESR ages for Senèze were derived using an RU model. For the other sites, the LU enamel ages cited here do generally agree with the published dates of the sites as shown in Table 3. However, not all the samples in this study were included in the publications as some were analyzed after publication.

4 Experimental Procedure

While small samples can be analyzed, using repeated irradiations, 300–500 mg of clean, crushed dentine is generally considered the minimum necessary. Root dentines are particularly desirable because they contain enough dentine to both allow ESR analysis and an additional 100–200 mg

Table 1 Fresh dentine and enamel composition

	Gross composition			Mineral crystals[a]				Organic composition[b]		Porosity		Permeability
Tissue	Mineral	Organic	Water	Shape	L	W	Th	Collagen fibers (%)	Non-collagen lagenous (%)	Elements	Volume	
Dentition stage	Matrix (wt%) [vol%]	Matrix (wt%) [vol%]	{fossil} (wt%) [vol%]		(nm)	(nm)	(nm)			{fossil}	{fossil} [vol%]	
a. Enamel												
Permanent (mature)	95–97 [86–89]	0.4–0.8 [0.8–1.6]	3–4[h] [9–12] {<2–3}	Ribbon	≥1000 −40	25	20	0	100	None [cracks[c]]	[0] {[<2[g]]}	0 {near 0[g]}
Deciduous mature	95–97 [86–89]	0.5–1.0 [2.0–2.5]	3–4[h] [9–12] {<2–3}	Ribbon	≥1000 −40	25	20	0	100	None [cracks[c]]	[0] {[<2[g]]}	0 {near 0[g]}
Deciduous immature	70–75 [50–60]	15–20 [20–40]	5–10[i] [15–30] {<10[d,g]}	Ribbon	160 −1000	1.5	1.5	<5	>95	Capillaries[c] {capillaries[d], Cracks[c]}	[<2–5[d]] {[1–5[g]]}	Low[c] {low[c,g]}
b. Dentine												
Intertubule mature	75 [50–60]	19–21 [40]	4–6[i] [12–18] {<10[d,g]}	Ribbon	20 −100	20	2–3	~95 Type 1 0.1–0.2 µm long von Korff's fibers	~5 4.5% citric acid	30,000–70,000 tubules/mm^2 Diam.: 1.5 µm + capillaries {capillaries[d,e],cracks}	[12–18[e]] {[5 − 10[f,g]]}	Very High[f] {very high[f,g]}
Peritubular mature	90–92 [80–83]	3–5 [12–15]	5–7[i] [15–21] {<5[d,g]}	Globular masses	0.25–0.30 nm in diameter			0	100 mucopolysaccharides	Capillaries {capillaries[d,e], cracks}	[5–7[f]] {[5 − 10[f,g]]}	Low {low[d,e,g]}

[a]Abbreviations: *L* length, *W* width, *Th.* thickness, *Diam.* diameter, {fossil} = typical values seen in fossil tissue

[b]Relative to the overall organic material concentration

[c]Not found in fresh teeth, cracks develop when tooth dries or is crushed

[d]Depends on calcification

[e]Empty or nearly so when tooth dries, capillaries fill with water if the tooth sits in groundwater

[f]High due to tubules and canals in all teeth, although cracks can also add to the effect

[g]Depends on secondary calcification, (re)mineralization, and infaunal boring

[h]Interstitial water within HAP crystals and organic matrix

[i]Also includes water in porosity elements. Data are summarized from [16, 52–62]

Table 2 Dentine and enamel chemistry

Tissue	Density	Major elemental composition							Fossil [U][a]		Propensity for diagenesis
		[H]	[C]	[N]	[O]	[P]	[Ca]	[S]	Caves[b]	Max.[c]	
	(g/cm)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(ppm)	(ppm)	
Enamel	2.95	0.2222	0.5454	~0.0	44.3324	17.4	35.8	~0.0	0.1–5	200	Rare
Dentine	2.85	4.7234	14.433	4.199	44.6096	10.497	20.993	0.315	1–50	1666.[d]	High[e]

[a]Abbreviations: [x] = elemental concentration

[b]Teeth from caves typically have the lowest U concentrations given other conditions

[c]The maximum concentrations are in open-air sites with a ready source of dissolved U

[d]The natural highest concentration known, but possible to be concentrated more under lab conditions. Some data are summarized from [16, 53]

to provide NAA radioisotope analysis for dosimetry. Some dentine samples were specifically prepared for dating; these include both root and inner (underneath the enamel of the tooth) dentines. Samples were powdered, sieved to 75–154 µm, and divided into 10–15 aliquots of approximately 30 mg each. For comparison, enamel dating aliquots use 20 mg of the fraction between 34 and 90 µm. Irradiations were performed at the McMaster University Reactor using a ^{60}Co source at a dose rate of 0.010–0.015 Gy/s. Maximum doses were 7–10 × the accumulated dose (AD). The aliquots were then annealed for 3 days at 90 °C, as for enamel.

Spectra of both dentine and enamel were analyzed on a JEOL RE1X spectrometer at the same conditions: 2 mW power, 0.1 mT modulation amplitude, and 1.25 mT/min scan speed over a field of 360.0 ± 5 mT. For natural and low-dose samples, 6–10 accumulated scans were averaged. The peak at 2.0018 was used for determining peak intensity [28]. This is generally referred to as T-B1. Currently, measurements of the entire peak, T-B2, are preferred; checking a few samples showed no difference in extrapolated dose within experimental uncertainty, although future experiments should consider changing the measurement in order to be consistent with best practices.

Accumulated doses (AD) and associated errors were derived from the peak heights using Vfit [29], assuming a single saturating exponential function. Even with signal averaging, the S/N ratio for many dentine spectra is poor relative to that for enamel, and the precision on the AD's reflects this. While 2–5% precision is routine for enamel, 5–8% was common for dentine.

Radioisotope concentrations in dental tissues and sediment, needed to determine external and internal dose rates, were measured through neutron activation analysis (NAA) [30, 31]. Direct gamma spectroscopy was not possible. The ages were calculated using ROSY v.2 [17]. For dentine, the parameters for "enamel" were rewritten to correspond to those for dentine (composition, density, and water content, for example). For composition, see Table 2, where the

Table 3 Teeth in this study

Site		Type of site	Published		LU ESR ages (ka)[a]		References
Country			Ages	Method	Dentine	Enamel	
Mezmaiskaya, Caucasus Mt., Russia		Cave	56.5–70.6	ESR (enamel)	80	55	[21]
	±		7.0		16	5	
Matuzka, Caucasus Mt., Russia		Cave	Middle–Late Pleistocene	Pollen Mammals			[26]
	±						
Pradayrol, Lot, France		Cave	330	ESR (enamel)	286	304	[22, 63]
	±		5		35	24	
Layers 3–4, Treugol'naya, Caucasus Mt., Russia		Cave	352.8–374.6	ESR (enamel)	273–376	256–369	[23]
	±		8		34	30	
Layer 5B, Treugol'naya, Caucasus Mt., Russia		Cave	393	ESR (molluscs)	299	342	[24]
	±		34		32	22	
Senèze, Massif Centrale, France		Open-air	Olduvai	^{39}Ar/^{40}Ar	[b]	[b]	[27, 64, 65]
	±	Maar Lake	Chron				

[a]Abbreviations: *LU* assuming linear (continuous) U uptake, $p = 0$

[b]RU model age

Table 4 Internal and external dose rates for samples

Sample		LU internal dose rate[a,b]		External dose rate[c,d]	
		Dentine (μGy/yr)	Enamel (μGy/yr)	Dentine (μGy/yr)	Enamel (μGy/yr)
CT58den4		82	37	1045	589
	±	19	2	40	41
RT88den1		645	30	794	794
	±	62	11	80	80
RT97den1		266	34	717	545
	±	38	4	30	42
FT9denR		111	25	708	545
	±	20	1	35	20
RT89den1		457	56	204	204
	±	52	23	20	20
FT19den3		1422	415	785	785
	±	141	14	74	74
FT66den1		1445	324	820	820
	±	224	10	150	150
RT38den4		252	49	209	209
	±	22	3	15	15
FT2denR		2296	674	765	456
	±	401	26	60	90
RT91den1R		1174	341	295	295
	±	198	33	55	55
CT60den5		2070	331	540	540
	±	189	10	53	53
CT60den4		1536	448	540	540
	±	133	12	53	53
RT87den1		2638	825	301	301
	±	175	23	46	46
RT90den1		1425	346	291	291
	±	25	10	50	50
FT1denR		1490	158	488	456
	±	228	10	90	80
RT85den1		9201	6165	1212	1212
	±	825	215	81	81
RT67den1		7663	2607	1262	1262
	±	1086	90	61	61
RT67den2		7611	2607	1262	1262
	±	1236	90	61	61
RT67den4		8456	2752	1262	1262
	±	1314	100	61	61

[a]Abbreviation *LU* assuming linear (continuous) U uptake, $p=0$

[b]Calculated with

enamel density, $\rho_{en}=2.95\pm0.02$ g/cm^3

dentine density, $\rho_{den}=2.85\pm0.02$ g/cm^3

initial U activity ratio, $[^{234}U/^{238}U]_0=1.20\pm0.20$

enamel water concentration, $W_{en}=2\pm2$ wt%

dentine water concentration, $W_{den}=5\pm2$ wt%

radon loss from the tooth, $Rn_{tooth}=0\pm0$ vol%

[c]Calculated with external dose rate parameters specific to the site

[d]For root dentine, the external dose rate includes sedimentary β dose rate

elemental composition includes water content. For root dentines, the "dentine" parameters in the program were left blank; for inner dentines, the "dentine" parameters were replaced by parameters for the enamel around the dentine.

Calculations tested the effects of changing several experimental parameters. Because root dentines are asymmetric and some dimensions exceed 2 mm, sample thickness was varied by factors from 0.5 × to 3 ×. Dentine water content may depend on the environment, especially for root dentines, so this parameter was also varied from 5 to 10%. Finally, several values of κ_α, the α/γ-efficiency, from 0.15 to 0.04, were tested. This parameter has not been accurately measured against γ irradiation, although it was measured for photon and neutron irradiation [15].

Internal and external dose rates are shown in Table 4. Note that for root dentines, where the dentine is directly in contact with sediment, the external dose includes the beta dose from the sediment and is, therefore, different from the external dose for the enamel.

5 Results

Figure 1 compares the natural spectra for enamel and dentine from the same tooth, normalized to the same gain. From Table 5, the AD's are 623 ± 30 Gy for the dentine and 394.5 ± 6.9 for the enamel. Although the dentine has apparently received roughly 50% more radiation, the signal is still very small, and the S/N ratio is poor.

Table 5 summarizes the results. LU ages of dentine and enamel have been compared, and the final column notes whether they agree within the quoted errors. The

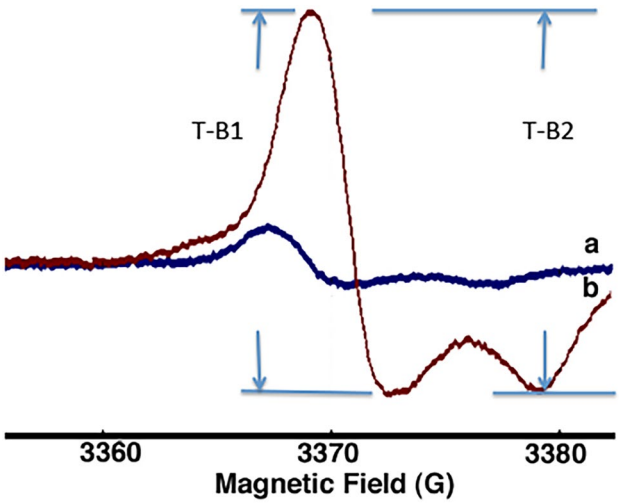

Fig. 1 ESR spectra from FT19 for (**a**) dentine (den3) and (**b**) enamel (en3) at the same gain. Although the dentine sample received 1.5 times the dose received by the enamel, the dentine HAP peak has only about 15% of the enamel intensity

Table 5 Comparing dentine and enamel ages

Sample	Site		Dentine			Enamel			Model age agreement?[e]	
			Accumulated dose, AD	ESR age[a]		Accumulated dose, AD	ESR age[b]		EU[a]	LU[b]
				EU[b,d]	LU[b,d]		EU[b,c]	LU[b,c]		
			(Gy)	(ka)	(ka)	(Gy)	(ka)	(ka)		
CT58dn4z	Mezmaiskaya		58.9	46.4	50.5	39.5	61.1	64.2	Yes	Yes
		±	15.1	12.2	13.2	1.2	4.4	4.7		
RT88den1	Mezmaiskaya		46.9	22.3	32.5	31.8	37.1	38.5	No	Yes
		±	3.5	2.3	3.3	2.2	4.4	4.6		
RT97den1	Mezmaiskaya		114	158	159	35.5	57.1	61.2	No	No
		±	25	35	36	0.8	4.1	4.6		
FT9denR	Matuska		90	85	98	78.3	130	138	Yes	Yes
		±	38	37	42	2.6	10	11		
RT89den1	Matuska		80.1	68.5	110	41.2	93	126	No	Yes
		±	11.3	7.6	13	2.1	5	7		
FT19den3	Pradayrol		623	172	283	394.5	243.4	334.2	No	No[f]
		±	30	24	35	6.9	7.3	11.5		
FT66den1	Pradayrol		657	177	290	312	208	273	Yes	Yes
		±	25	22	36	14	73	38		
RT38den4	Makapanskat		83.5	177.8	247	64.3	205	250	Yes	Yes
		±	3.0	8.3	13	11.6	13	16		
FT2denR	Treugol'naya		856.6	160	273	290.9	159.9	256.2	Yes	Yes
		±	6.5	24	45	6.5	10.7	22.6		
RT91den1R	Treugol'naya		640	229	376	268.2	249	369	Yes	Yes
		±	46	34	50	6.3	19	38		
CT60den5	Treugol'naya		495	165	278	308.8	252	355	No	No[f]
		±	26	22	35	7.0	14	24		
CT60den4	Treugol'naya		624	182	311	351.6	246	362	No	Yes
		±	60	28	46	9.7	14	24		
RT87den1	Treugol'naya		848	158	288	350	181	310	No[f]	Yes
		±	52	8	16	10	11	20		
RT90den1	Treugol'naya		613.2	199	357	228.9	231	359	Yes	Yes
		±	2.7	6	13	3.7	15	30		
FT1denR	Treugol'naya		563	165	284	204.6	259	333	No	Yes
		±	22	21	35	6.6	32	49		
RT85den1	Senèze		2813	146	263	3753	516	901	No	No
		±	748	29	54	371	58	99		
RT67den1	Senèze		2216	138	248	2353	361	608	No	No
		±	214	22	39	119	25	39		
RT67den2	Senèze		2974	186	335	3020	448	817	No	No
		±	170	29	51	139	32	51		
RT67den4	Senèze		3604	204	371	3022	444	753	No	No
		±	438	38	67	160	32	52		

[a]Abbreviations: *EU* assuming early U uptake, $p=-1$; *LU* assuming linear (continuous) U uptake, $p=0$

[b]Calculated using the parameters listing in Table 3

[c]Calculated using enamel α efficiency factor, $\kappa_{\alpha,\mathrm{en}}=0.15\pm0.02$

[d]Calculated using dentinal α efficiency factor, $\kappa_{\alpha\ \mathrm{mol}}=0.08\pm0.02$

[e]Given the uncertainties for both, the dentine and enamel ages agree at the 95% confidence level

[f]These ages do agree at the 99% confidence

experimental uncertainities are similar for dentine and enamel. The majority of samples show agreement for LU ages < 400 ka.

The results vary somewhat with uptake models. Table 5 shows several examples for which LU ages agree, but EU ages do not agree. For RU models, the agreement would be better, but that is a mathematical artifact. In calculating ages for RU models, the programs assume a lower time-averaged uranium concentration, which decreases the effective difference between [U] in dentine and enamel.

Of all the parameters tested, only variation in κ_α affected the calculated dentine age outside experimental uncertainty. Water content, dentine thickness, and tooth geometry (i.e., presence or absence of enamel) had no effect. Assuming $\kappa_\alpha = 0.08$, however, yielded the dentine LU ages that agree overwhelmingly with LU enamel ages (Table 5). Normally $\kappa_\alpha \sim 0.11$–0.13 is used for enamel [32]. It is unlikely that κ_α in the HAP of dentine is in fact different from that in enamel. It would be more accurate to call this value of κ_α an "effective value". Theory supports this analysis for κ_α in dentine. Unlike enamel, significant amounts of uranium in dentine may reside in an organic fraction external to the HAP crystals, reduced by reaction with carbon [33, 34]. Therefore some α energy will be absorbed by the collagen. Also, some of the α energy will form radicals on the HAP crystal surface where the radicals have very limited lifetimes. The surface-to-volume ratio increases sharply as the crystal size decreases. Although an "effective" κ_α value of 0.08 resulted in the greatest number of LU age agreements, that does not, of course, prove that this value is correct. Quite possibly the actual value is even less than 0.08, since some of those ages that do not agree show younger dentine ages than enamel ages. Lowering the κ_α value will lower the internal dose and, therefore, increase the sample age. For the youngest samples, where the external dose rate constitutes the majority of the total dose rate, the LU ages were insensitive even to κ_α, but the EU ages did show better agreement when κ_α was reduced below 0.08.

Figure 2 shows nearly linear correlation between LU dentine and enamel ages. Given the dentine porosity, which allows for continuous interaction between tooth and environment, we suggest that linear uptake is the most probable model for dentine; note that some researchers assume $p = -1$ (EU) for young teeth [35]. Experimental studies of fossil and modern dentine and enamel have demonstrated that both tissues can absorb U continuously over time, if U is readily available in the environment [36]. This is merely a suggestion; determination of p values is needed to confirm or dispute this. In any case, the youngest samples (from Mezmaiskaya) are model-independent. Recent uptake should only be found in sites with significant recent alterations in geochemistry or in degraded teeth. Intermediate models are also possible, of course.

All the dentine ages for the old samples from Senèze are approximately 50% of the enamel values. There are two possible explanations for this. First, a relatively short lifetime for the dentine signal may have led to fading. We have attempted to determine the signal lifetime by isothermal annealing experiments. Given the small initial peak size, the precision on these measurements is very poor and to date no Arrhenius plot has yielded a quantitative estimate. Alternatively, perhaps these teeth have experienced recent uptake. A calculation for these dentines using $p = 5$ results in ages that agree precisely with those for enamel. For fossil teeth, there is some evidence that older enamel

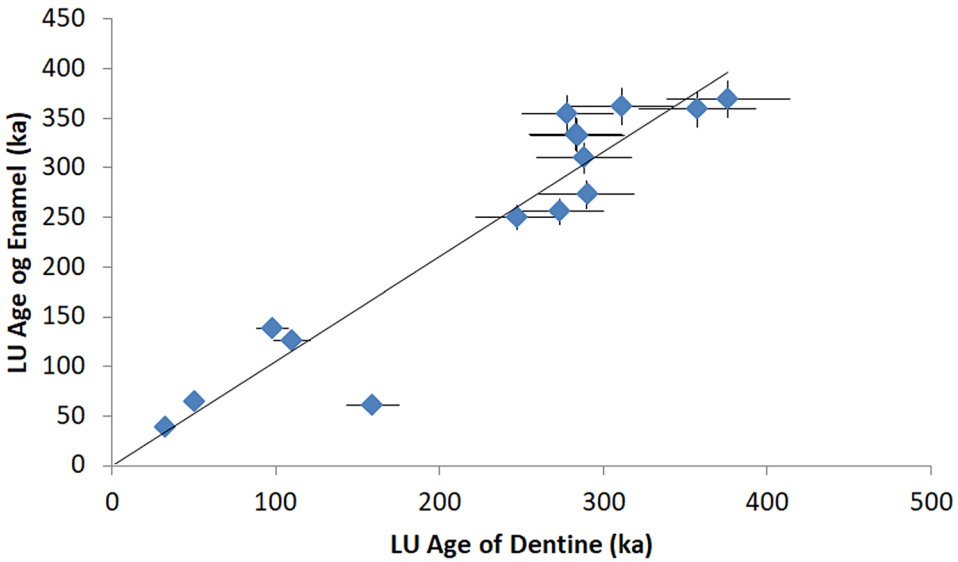

Fig. 2 Relationship between LU (dentine) ages and LU (enamel) ages for samples with LU ages < 400 ka. The line slope = 1. Except for 3 points, no points differ significantly from the line

experiences recent uptake as the HAP crystalline structure begins to break down [37, 38]. Dentine would not be expected to show the same effect. The higher crystal surface-to-volume ratio in dentine implies that small changes in the crystal surface, on a percentage basis, would not be as detectable. Furthermore, RT67 yielded an infinite $^{230}Th/^{234}U$ age, which suggests that it did not experience significant recent uptake. Perhaps the most likely explanation remains that fossilization has altered the nature of dentine. Clearly, older samples have less collagen and what is left may be degraded. Thus, parameters such as κ have changed. Possibly also there has been a diagenesis of the HAP; with smaller crystals, this is more likely than for enamel. More investigations using older teeth, plus better annealing experiments should allow us to clarify these possibilities and test whether dentine has any potential for dating teeth samples older than 400 ka.

Including dentine results can significantly improve isochrons [39]. Isochrons, in which a plot of AD against internal dose for tooth subsamples for a single tooth yields the age as the slope, can provide insight into uptake events [40, 41]. Isochrons can suggest whether the uranium accumulation in a tooth has been interrupted by leaching events or accelerated by periods of rapid uptake. Even with coupled U-series/ESR dating, the resulting p value is a time-averaged one and does not reveal the uptake pattern. For some samples, the enamel subsample

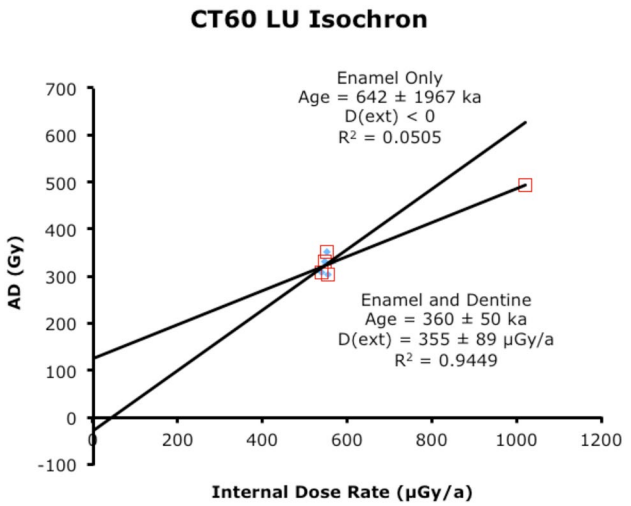

Fig. 3 LU isochron for CT60, Treugol'naya Cave, Russia, showing increased precision using dentine data. With enamel data only (line), the negative intercept suggests U remobilization, and the age from the slope of the line (642 ka) is nearly twice the value in Table 5 (362 ka). With the addition of dentine values (red square), the age (360 ± 50 ka) equals the value in Table 5. The positive intercept gives an external dose rate of 355 ± 88 µGy/a, compared to the calculated modern sediment dose rate of 540 ± 53 µGy/a [23]. The sample may have experienced some remobilization

internal dose rates and ADs are so close that the isochron lacks statistical significance. Adding the dentine data to an isochron provides a much greater range of Dint values, thereby greatly increasing the precision on the isochron statistics. Figure 3 shows an isochron whose results, once the dentine points have been considered, agree with the age in Table 5, with an external dose rate not completely inconsistent with the value in Table 4, implying that only a single uptake event occurred during deposition. Without the dentine points, the isochron suggests variable uptake.

6 Another Suggestion

There is another possible explanation that should be explored. As noted, combined U-Series/ESR dating allows the measurement of the parameter, p, for both dentine and enamel. In this study, the comparison between dentine and enamel ESR ages assumes that the ratio between the U uptake rate, p, for dentine with that for enamel, namely $p_{en}/p_{den} \sim 1$. Grün [42] showed that for teeth from cave sites, $p_{en}/p_{den} \cong 1.0 \pm 0.5$ was true for most teeth, while in open air sites, $p_{en} / p_{den} \cong 1.0 \pm 1.0$ for most teeth with $p < 2$. While combined dating was not performed on the teeth in Table 4, p values for enamel and dentine have been published in multiple studies [e.g., 43–49] and can serve as a proxy for the importance of this parameter. With the exception of Payre [49], all of the ones quoted come from caves. In about 80% of samples in the same 40–400 ka range, the differences $(p_{en} - p_{den})$ are within the 2σ error of measurement. However, where this is not true, the value for dentine is almost always more negative than for enamel. This is consistent with the assumptions of U-uptake. Uranium is believed primarily to be taken up into dentine, and then diffuse into enamel. Thus uptake into dentine is always "earlier" than into enamel. In fact for younger teeth (< 50 ka), authors generally simply assume $p_{den} = -1$ [35]. The effect on the calculated dentine age of a more negative p value would increase the calculated age, as does reducing the the effective κ_α value. Note also a published study that showed U is taken up into dentine and enamel proportionally [50] for teeth with enamel U ≥ 1–2 ppm, concentrations usual for teeth in the 40–400 ka range. This suggests similar, though not identical, uptake patterns.

When one looks at much older sites [51], with ages in the Ma range, the differences between enamel and dentine are both larger than errors and almost entirely more negative for dentine. In this age range, then, differences in U-uptake models may account for differences in calculated age for the Senèze samples in Table 5.

7 Conclusions

Despite the promising suggestion that dentine can be used for dating, given certain parameters, enamel will always be preferred. The signal is stronger, probably because the HAP content is higher, and the lifetime is extremely long.

In the absence of $^{230}Th/^{234}U$ analyses, assuming that the LU model gives the best age remains uncertain. Nonetheless, within Grun's data [42] using $p > 0.5$ provided a maximum limit for enamel samples, while using $p = 0$ provided a median for dentine samples from caves. In open air sites, $p = 0$ acted as a median value for both enamel and dentine samples. An implication of the LU assumption is that the dentine must be less sensitive to radiation than is enamel, namely κ_α (dentine) $< \kappa_\alpha$ (enamel). κ_α depends on the biochemistry for dentine, not its external dose rate or its U concentration, both of which depend on environmental conditions. However, this also suggests that a hypothesis that the only factor responsible for age agreement is κ_α (dentine) = 0.08 is oversimplified. If that were the case, the EU ages would also agree. It may still be true that the value of κ_α is critical but that it is not precisely 0.08. Once the value of is found experimentally, other model assumptions such as p_{en} / $p_{den} \sim 1$ must also be tested.

Thus, this study does not solve all the issues in ESR dating of dentine, merely provides a place to begin. While dentine is less satisfactory than enamel as a dating material, it can add substantial information about tooth ages. In general, the data presented here show that, if we assume κ_α (dentine) = 0.08, enamel, and dentine LU ages agree within their errors for samples with enamel ages ≤ 400 ka. Where the two ages disagreed, the dentine ages were usually younger than the enamel ages. In samples with enamel ages > 400 ka, systematically smaller dentine ages by either EU or LU calculations, suggest one or more of the following:

1. the dentine signal may have faded;
2. the dentine had experienced U leaching;
3. different uptake models should be assumed for the two different tissues;
4. other diagenetic effects due to fossilization have produced the different ages.

Infrared spectroscopy has been used to study changes in crystallinity and electron microscopy to look for recrystallization [52]. In our preliminary study, older samples came from open air sites, while the younger teeth were taken from caves. As noted by Grün, open air sites more likely experience environmental change, especially erosion and increased water percolation which potentially favor changes in U uptake rates, thus making RU models more likely [41]. Further investigation into dentine dating parameters, including its α-efficiency, signal lifetime, and U uptake models, will extend these results to other sites and, if systematic changes are found, possibly to other age ranges.

Acknowledgements It is an honor to have been invited to contribute to this tribute to Prof. Sergio Mascarenhas. In 2018, Dr. Skinner spent time in Brazil on a Fulbright fellowship. Prof. Mascarenhas was kind enough to invite her to his 90th birthday party. Aside from the pleasure of meeting him, it was a revelation to see the wide variety of supporters whose professional and personal lives he had affected (including some very, very young, and charming, attendees).

Contributions

Author Contributions Dr. Anne Skinner performed some calculations and is responsible for the writing of the manuscript. Dr. Joyce Lundberg performed some analyses. Dr. Bonnie Blackwell and Dr. Joel Blickstein passed away during the final preparation of this manuscript. However, their contributions both experimental and theoretical were crucial to it.

Other Contributions Samples were provided by Eric Delson (Senèze), M. R. Séronie-Vivien (Pradayrol), Kevin Kuykendall (Makapansgat) and L. V. Golovanova and V. B. Doronichev (Mezmaiskaya, Matuska and Treugol'naya). Jean Johnson and Alice Pidruczny performed the NAA analyses at McMaster University; students from Williams College and the RFK Science Research Institute assisted with the sample preparation; Jon Florentin prepared the final artwork.

Funding The National Science Foundation for grants ILI 915111 (ARS); SBR 9709912, SBR 9896289, and SBR 9904376 (ARS and BABB). A Mellon Foundation sabbatical leave grant to JIBB, Williams College, McMaster Nuclear Reactor, RFK Science Research Institute, and the ESR Foundation.

Declarations

Conflict of Interest The authors declare no competing interests.

References

1. W.J. Rink, Rad. Meas. **27**, 975 (1997)
2. A.R. Skinner, In Encyclopedia of Geology, 2nd Ed. Ed. By Alderton, D and Elias, S.A. (Academic Press, New York, 2020) Vol 6, p. 153
3. R. Grün, Am. J. PhysAnthropol. 2006; Suppl. **43**, 2 (2006)
4. R. Joannes-Boyau, Geochronometria. **40**, 322 (2013)
5. R. Grün, P.B. Beaumont, J. Hum. Evol. **40**, 467 (2001)
6. R. Grün, J. Maroto, S. Effins, C. Stringer, S. Robertson, L. Taylor, G. Mortimer, M. McCulloch, J. Hum. Evol. **50**, 347 (2006)
7. R. Grün, H.P. Schwarcz, J.M. Chadam, Nucl. Tracks. Rad. Measur. **14**, 237 (1988)
8. C. Falguères, Quat. Sci. Rev. **22**, 1345 (2003)
9. R. Grün, Ancient. TL. **18**, 1 (2000)
10. M. Duval, C. Falguères, J.-J. Bahain, Quat. Geochron. **10**, 412 (2012)
11. T. De, A. Romanyukha, F. Trompier, B. Pass, P. Misra, Appl. Mag. Res. 44 (2012). https://doi.org/10.1007/s00723-012-0379-9 (2012)

12. P. Fattibene, A. Carosi, V. DeCoste, S. Onori, S., Rad. Prot. Dosimetry. **120**, 216 (2006)
13. P. Fattibene, F. Callens, Appl. Rad. Isot. **68**, 2033 (2010)
14. B. Pass, J.E. Aldrich, P.L. Scallion, Calcifi. Tissue. Int. **46**, 166 (1990)
15. F. Trompier, D.D. Tikunov, A. Ivannikov, I. Clairand, Rad. Prot. Dos. **120**, 191 (2006)
16. J. d D. Tereul, A. Alcolea, A. Hernández, A.J.O. Ruiz, Arch. Oral. Biol. **60**, 768 (2015)
17. B.J. Brenann, W.J. Rink, E.M. Rule, H.P. Schwarcz, W.V. Prestwich, Ancient. TL. **17**, 45 (1999)
18. J-L. Bada, Earth. Planet. Sci. Lett. **55**, 292–298 (1981)
19. N.W. Rutter, B.A.B. Blackwell, In: Dating Methods for Quaternary Deposits. Ed. by N.W. Rutter, N.R. Catto (Geological Association of Canada, St. John's, Geotext 2, 1995) p. 125
20. B.A.B. Blackwell, N.W. Rutter, W.M. Last In: G. A. Goodfriend, M.J. Collins, M.L. Fogel, J.F. Wehmiller, In Perspectives in Amino Acid and Protein Geochemistry, Ed. By G. A. Goodfriend, M.J. Collins, M.L. Fogel, J.F. Wehmiller,(Oxford University Press, Oxford 2000). p. 88
21. A.R. Skinner, B.A.B. Blackwell, S. Martin, J.I.B. Blickstein, L.V. Golovanova, V.B. Doronichev, Appl. Rad. and Isot. **62**, 219 (2005)
22. B.A.B. Blackwell, A.R. Skinner, J.I.B. Blickstein, L.V. Golovanova, V.B. Doronichev, M.R. Séronie-Vivien, in *Sourcebook of Paleolithic Transitions: Methods, Theories, and Interpretations*. ed. by M. Camps, P. Chauhan (Springer, Heidelberg, Germany, 2009), p. 93
23. B.A.B. Blackwell, S. Liang, L.V. Golonova, V.B. Doronichev, A.R. Skinner, J.I.B. Blickstein, Appl. Rad. sot. **6**, 237 (2005)
24. A.N. Molod'kov, Quat. Sci. Rev. **20**, 1051 (2001)
25. C.S. Churcher, Palaeontol. Afr. **36**, 97 (2000)
26. L.V. Golovanova, V.B. Doronichev, eds., Matuska Cave. (Ostrovityanin, St. Petersburg, 2006) 1–194 (2006)
27. E. Delson, M. Faure, C. Guérin, A. Aprile, J. Argant, B. Blackwell, Courier Forschunginstitut Senckenberg **256**, 275 (2006)
28. M. Ikeya, *New Applications of Electron Spin Resonance* (World Scientific, Singapore, 1993), p. 244
29. E. Bular, *Fit software* (University of Istanbul, Istanbul, 1991)
30. B. Grassi, G.M. La Veccia, S. Manera, A. Salvini, A. Zenoni, Determination of trace elements in metallic materials by neutron activation analysis. J. Phys. Conf. Ser. **41**, 288 (2006)
31. M.S. Tite, *Methods of Physical Examination in Archaeology* (Seminar Press, London and New York, 1972), p. 273
32. R. Grün, Quat. Int. **1**, 65 (1989)
33. V.E. Arana-Chavez, L.F. Massa, Int. J. Biochem. Cell. Biol. **36**, 1367–1373 (2004)
34. S. Nakashima, Org. Geochem. **19**, 421 (1992)
35. J.-J. Bahain, C. Falguères, J.-M. Dolo, P. Antoine, P. Auguste, N. Limondin-Lozouet, J.-L. Locht, A. Tuffreau, H. Tissoux, S. Farkh, Quat. Geochron. **5**, 371 (2010)
36. B.A.B. Blackwell, A.R. Skinner, P. Brassard, J.I.B. Blickstein, Advances in ESR Applications **18**, 77 (2002)
37. A.R. Skinner, B.A.B. Blackwell, D.E. Chasteen, J.M. Shao, Quat. Sci. Rev. (Quat Geochronol) **20**, 1027 (2001)
38. A.R. Skinner, N.D. Chasteen, J.M. Shao, G.A. Goodfriend, B.A.B. Blackwell, Quat. Int. **135**, 13 (2005)
39. B. Blackwell, H.P. Schwarcz, App. Rad. Isot. **44**, 243 (1993)
40. B.A.B. Blackwell, A.R. Skinner, J.I.B. Blickstein, Quat. Sci. Rev. **20**, 1031–1039 (2001)
41. B.A.B. Blackwell, B.A.B., A.R. Skinner, J.I.B. Blickstein, S. Lebel, Geoarchaeology **16**, 719–761 (2001)
42. R. Grün, Rad. Measur. **44**, 472 (2009)
43. E. Ben Arous, C. Falguères, O. Tombret, M.A. El Hajraout, R. Nespoulet, Quat. Int. **556**, 58 (2020)
44. C. Falguères, J.-J. Bahain, A. Pérez-Gonzâlez, N. Mercier, M. Santonja, J.-M. Dolo, J. Arch. Sci. **33**, 149 (2006)
45. C. Falguères, J.-J. Bahain, C. Tozzi, G. Boschian, J.-M. Dolo, N. Mercier, H. Valladas, Y. Yokoyama, Quat. Geochron. **3**, 390 (2008)
46. C. Falguères, J-J. Bahain, J. Bischoff, A. Pérez-Gonzâlez, A. I. Ortega, A. Ollé, A. Quilles, B. Ghaleb, D. Morena, J-M. Dolo, Qingfen Shao, J. Vallverdú, E. Carbonell, J.M. Bermúdez de Castro, J.L. Arsuga, J. Hum. Evol. **65**, 168 (2013)
47. F. Han, S. Chengkai, J.-J. Bahain, J. Zhao, M. Lin, S. Xing, G. Yin, Quat. Int. **400**, 195 (2016)
48. M. Richard, C. Falguères, E. Pons-Branchu, L. Foliot, P.M. Guillem, R. Martínez-Valle, A. Eixea, V. Villaverde, Quat. Geochron. **49**, 283 (2019)
49. H. Valladas, N. Mercier, L.K. Ayliffe, C. Falguères, J.-J. Bahain, J-M. Dolo, L Froget, J.-L. Joron, H. Masaoudi, J-L. Reyss, M-H. Moncel. Quat. Geochronol. **3**, 377 (2008)
50. R. Grün, L. Taylor, Ancient. TL. **14**, 21 (1996)
51. F. Han, J.-J. Bahain, C. Deng, E. Boëda, Y. Hou, G. Wei, W. Huang, T. Garcia, Q. Shao, C. He, C. Falguères, P. Voinchet, G. Yin, Quat. Int **434**, 75 (2017)
52. I. Reiche, C. Vignaud, M. Menu, Archaeometry **44**, 447 (2002)
53. J.H. Scott, N.B.B. Symons, *Introduction to Dental Anatomy*, 8th edn. (Churchill Livingstone, Edinburgh, 1977), p. 464
54. Eastoe, J.E. 1964. In: Bones and Teeth: Proceedings of 1st European Symposium (Oxford, 1963), Ed. By H.J.J. Blackwood (Pergamon, New York, 1964) p. 269
55. Frost, H.M., 1980. In:, ed. Fundamental and Clinical Bone Physiology, Ed By M.R. Urist (Lippencott, Philadelphia, 1980) p. 208
56. Hare, P.E., 1980. In Fossils in the Making, ed by A.K. Behrensmeyer, A.P. Hill, (Chicago U. Press, Chicago, 1980) p. 208
57. J. A. Ogden, In: Fundamental and Clinical Bone Physiology. ed. by M.R. Urist (Lippencott, Philadelphia, 1980) p. 108
58. R.B. Parker, H. Toots, J.W. Murphy, Geochim. Cosmochim. Acta. **38**, 1317 (1974)
59. J.D. Pasteris, D.Y. Ding, Am. Mineralo. **94**, 53 (2009)
60. J. M. Shackleford, J.M., Am. J. Phys. Anthropol. **25**, 291 (1966)
61. X.W. Su, F.Z. Cui, Mat. Sci. Eng. **C7**, 19 (1999)
62. J.T. Triffit, In Fundamental and Clinical Bone Physiology Ed. by M.R. Urist. (Lippencott, Philadelphia, 1980) p. 45
63. J.C. Marquet, M.R. Séronie-Vivien, Quaternaire. **27**, 111 (2016)
64. C. Guerin, Quaternaire. **18**, 23 (2007)
65. J.F. Pastre, E. Debard, S. Nomade, H. Guillou, M. Faure, C. Guérin, E. Delson, Quaternaire **26**, 225 (2015)