

# SOME REMARKS ON "ESR DATING OF BONES"

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Bones and teeth constitute an important component of archaeological and Pleistocene geological deposits. They not only allow the determination of the palaeoenvironment from the known ecological ranges of the organisms, but they may allow us to determine both the relative (paleontological) and absolute ages of these deposits. The latter possibility has been, until recently, largely limited to the use of  $^{14}\text{C}$  in the dating of either the collagen fraction of bone, or the carbonate fraction of the bone mineral. Many attempts have been made, however, to use other techniques to date bones ranging in age well beyond the 50 ka time limit normally accepted for radiocarbon. In particular, uranium series dating has been used on both bones and teeth, with varying degrees of success (see for example, discussion on the U-series dates of the bones from Del Mar and Sunnyvale: Bischoff & Rosenbauer, 1981; 1982; Bada & Finkel, 1982). In addition some relative dating methods seem to give promising results on bones, such as amino acid racemization (Bada & Protsch, 1973; DeLumley et al., 1977; Hille et al., 1981) or the determination of elemental concentrations of uranium (Oakley, 1980) or nitrogen and fluorine (Eisenbarth & Hille, 1977; Hille et al., 1981; Molleson, 1981).

More recently, it has been shown that tooth enamel can be dated by electron spin resonance (ESR) (Grun & Invernati, 1985; Grun, 1985; Grun et al., 1987). Having demonstrated that ESR is applicable to tooth enamel when appropriate methods are used for determining both the accumulated dose and the time-dependent dose-rate of radiation (Grun et al., 1987), we should now inquire whether it is indeed possible to apply these methods to bone, and in general what are the prospects for the ESR dating of this ubiquitous material. In fact, the method has already been used by other workers on whole bone (Ikeya, 1982; Ikeya & Miki, 1980; 1981a&b; Mascarenhas et al., 1982; Yokoyama et al., 1981; 1982), and this paper is also a critique of these previous attempts. It should also be apparent that many of the problems in ESR dating of bone will also constitute problems for U-series dating, which will not be specifically discussed here.

## COMPARISON OF BONE AND ENAMEL

It is first important to note the anatomical, physical, and mineralogical differences between these two types of tissues, both in their living state, and as fossilized material.

Living bone is a composite material, constructed of a mineral phase intergrown with a complex of tissues consisting principally of proteins, and dominantly of one protein: collagen. In living bone, the inorganic phase is very poorly crystallized. Table 1 shows the proportions of these components in bone and dentine, and contrasts them with enamel which contains very little organic (non-mineral) matter and initially contains larger crystals than does bone. Furthermore, enamel contains no amorphous phase.

**Table 1:****Composition of enamel, dentine and bone (after Driessens, 1980)**

		Enamel	Dentine	Bone
organic compounds	(%)	0.4-0.8	≈20	≈25
water	(%)	3.2-3.6	≈10	≈25
mineral phase	(%)	96-97	≈70	≈50
<b>MINERAL PHASE:</b>				
hydroxyapatite	(%)	100	≈50	≈50
crystal size	(Å)	260x300x680	30x500x500	50x400x400 & 40x40xNx660
amorphous phase	(%)	0	≈50	≈50

Approximate sign indicates large variations in analyses.

As seen in Table 1, about 40% of the inorganic portion of bone and dentine consists of spherical aggregates of amorphous Ca phosphate with an approximate formula of  $\text{Ca}_9(\text{PO}_4)_6$  (Brown & Chow, 1976). It is noteworthy that during the inorganic precipitation of hydroxyapatite [ $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ], these amorphous phosphates occur as precursors of the final mineral phase (Eanes et al., 1976). It has been shown by Williams & Sallis (1982) that these amorphous calcium phosphates can be transformed directly into hydroxyapatite. Other minerals in bone are fluorapatite  $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$  and octacalcium phosphate  $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$  (Brown & Chow, 1976); the latter is also not found in enamel.

Soon after death (within a few minutes) the ultrastructure of bone begins to change, a process which steadily continues long after death, and is still going on in buried fossil bone many millennia or hundreds of millennia after death. The major processes which characterize this postmortem transformation of bone appear to be:

- 1.) increase in crystal size
- 2.) crystallization of all amorphous Ca phosphate
- 3.) dehydration
- 4.) denaturation and biodecomposition of protein and other organic constituents.
- 5.) chemical change of the mineral phase, largely through uptake of ions from ground water, such as U, F. (see, for example, Henderson et al, 1983; Badone and Farquhar, 1982; Molleson, 1981)

Other more drastic changes that can take place include replacement of the bone mineral (apatite) by other phosphates or other non-phosphate minerals (eg calcite); dissolution of significant amounts of the bone mineral; and filling of the pore space in bone that survives in the ground for more than a few million years; such bone is referred to as "mineralized".

Unfortunately, at the present time we have only a very poor understanding of the details of these processes. A thorough review of the literature has revealed only a handful of papers written over the past 20 years that are devoted to mineralogical or chemical changes in buried bone.

On the other hand, much less change is expected during fossilization of enamel

due to its initially larger crystal size, absence of amorphous phase, and lack of organic matter. Thus, for example, Wyckoff et al. (1963) note no visible changes in 100 Ma old tooth enamel, but a little alteration of the associated dentine. However, Brophy & Hatch (1962) observe definite recrystallization of Pleistocene tooth enamel.

### ESR SPECTRA OF BONE AND ENAMEL

The ESR-Spectra for bone and teeth are essentially the same. The radiation sensitive signals at  $g = 2.0018$  and  $g = 1.9976$  are certainly due to the mineral phase of bone and teeth (Houben, 1970; Ostrowski et al., 1971; 1974) and have been attributed to a  $\text{CO}_3^{\cdot-}$  radical (Cevc et al., 1972; Sato, 1979; Caddie et al., 1985); this was, however, doubted by other authors (Peckauskas & Pullman, 1978; Van Willigen et al., 1980; Bacquet et al., 1981; Geoffroy & Tochon-Danguy, 1982). Doi et al. (1979 a&b; 1980, 1981) attributed the signals at  $g=2.0023$  and  $1.9976$  to  $\text{CO}_3^{\cdot-}$  and postulated a different but unknown center for the dominant  $g=2.0018$  line. However, irradiation and annealing behaviour of the lines  $g=2.0018$  and  $1.9976$  suggest strongly that these belong to the same center (Grun et al, 1987).

Ikeya (1985) suggested, that fluorine uptake might lead to a decrease of ESR-sensitivity (and underestimation of AD) since his laboratory tests showed a decrease of ESR intensity with increasing F concentration. F-ions replace the OH-group in the hydroxyapatite lattice. Assuming that the ESR signal in fossil teeth and bone represent a  $\text{CO}_3^{\cdot-}$  center this uptake of fluorine should only affect, if at all, the signal from  $\text{CO}_3$  ions at the OH sites (up to 11% of the total, Elliott et al., 1985). It is generally questionable, whether a continuous decrease of available traps would lead to an underestimation of AD, as long as this partial destruction of traps affects the "filled" and "unfilled" traps to the same extent. It is not likely, that fluorination leads to a recombination of trapped electrons followed by creation of new (and empty) traps with the same magnetic characteristics. It is more likely that fluorination will simply lead to a slight decrease in the sensitivity of the hydroxyapatite crystal.

The ESR signal of the amorphous phase seems to be identical to that of hydroxyapatite, but shows a low thermal stability (20% remaining after storage for 40h at room temperature: Houben 1970). Since the stable ESR signals of enamel, bone and synthetic hydroxyapatite are identical (Ostrowski, 1974), it is rather likely that the stable ESR-signals of bones originate within the hydroxyapatite crystals (unstable components might be generated by collagen, proteins or surface interactions of small sized hydroxyapatite crystals; Ostrowski et al, 1974).

Assuming that indeed the main ESR signal is due to  $\text{CO}_3^{\cdot-}$ , we must note that  $\text{CO}_3$  can occur in the hydroxyapatite lattice substituting for either a  $\text{PO}_4$  or two OH ions (where it constitutes about 11% in human tooth enamel; Elliot et al., 1985). According to Doi et al. (1980) the resulting ESR signals are not measurably different.

The ESR spectra of bone are additionally complicated by the fact that they may display fairly intense signals from free-radicals of amino acids or other organic compounds. This problem is greater in bone than in teeth, due to the higher

organic content of the former. The  $g$ -value of the "alanine" free-radical is not very far removed ( $g=2.0036$ ) from that of the 2.0018 signal for the bone/tooth mineral itself, and will interfere in determinations of AD by the additive dose method, due to the great sensitivity of the free-radical to irradiation.

TL-dating on bone and enamel has also been attempted (e.g., Cristodulides & Fremlin, 1971; Driver, 1979). The method seems to be promising but the TL-spectra seem to be strongly interfered by chemiluminescence effects. Another problem is that the second glow curve of tooth enamel and probably bone as well is affected by decomposition of the organic matter.

#### URANIUM UPTAKE

One serious problem occurring in the dating of both bones and enamel is the accumulation of uranium (Charalambous & Papastefanou, 1977; Molleson, 1981; Henderson et al., 1983). Two different U-accumulation models have been proposed (see Ikeya, 1982; Grun et al., 1987): early uranium uptake (henceforth EU) where the present-day content of uranium is assumed to have been accumulated soon after burial; and continuous, linear U-uptake (LU), in which the content of uranium is approximated by a linear function of time. Since there is generally no independent indication as to which model should be applied for a sample under investigation, two ages are generally calculated.

In considering U-uptake, it is important to appreciate the various mechanisms by which this may occur. In general, U is present in soil as an insoluble  $U^{4+}$  species, possible bound on or in some silicate or oxide mineral. Soluble uranyl ions are produced by oxidation, and can then travel through soil water to be taken up by bones or teeth. The uptake can occur either by:

- a) reduction of the  $U^{6+}$  back to insoluble  $U^{4+}$
- b) adsorption of uranyl ions by humic matter formed during decomposition of collagen, etc.
- c) uptake of either  $U^{4+}$  or  $U^{6+}$  by the apatite crystals
- d) physical trapping of U-bearing minerals in the pore-spaces of the bone.

It can be seen that U-uptake is likely to be greater in bone than in teeth, as is shown also by the much higher concentrations of U in the former (see Szabo, 1982; Seitz & Taylor, 1974). Also, as the bone constantly recrystallizes and as its large initial content of organic matter decreases through time, the rate of uptake is likely to change markedly, making it very difficult to model this process. On the contrary, enamel does not recrystallize as much, due to its larger initial crystal size, and should experience much less uptake by organic matter. Nevertheless, both teeth and bones are seen to increase their U content through time. Furthermore, Badone & Farquhar (1982) found that the U concentration in bones can actually go through a maximum, possibly due to loss of organic-bound U.

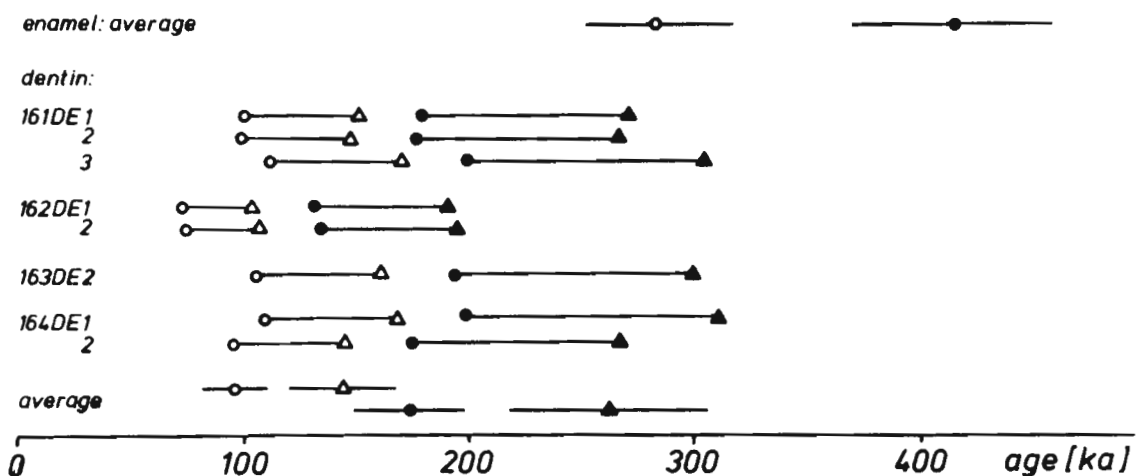
Note, however, that the problem of U uptake by bone (as opposed to enamel) is a serious one in the dating of enamel as well. This is because a large part of the beta-ray dose accumulated by the enamel arises from U in the adjacent layers of dentine or cementum. Therefore, it is important to understand the U-uptake process in this case, as well.

## AN EXPERIMENTAL TEST

In order to get a clearer idea of the difference in behaviour of enamel and bone, we have done ESR analyses of enamel and associated dentine from the Bilzingsleben archaeological site. The dentine/cement is taken to behave like bone, which it resembles histologically. Table 2 and Fig. 1 show the calculated ages for these samples. The details of sample preparation, signal processing and age calculation and measured values of the enamel samples are given in Grun et al. (1987) and Schwarcz et al. (1987).

Independent U-series and ESR results on the surrounding travertine and the geomorphological history of this site imply an age at least as old as that corresponding to oxygen isotope stage 9 (303-339 ka, Imbrie et al., 1984), but more likely attributable to stage 11 (362-423 ka). As can be seen from Fig. 1, the LU-enamel ages agree with stage 11 and the EU-enamel ages with stage 9. It is hoped that improvements in our modelling of the U-uptake history via studies of U-series disequilibria (Grun & Schwarcz, in preparation) will resolve the uncertainty in the age of the enamel samples.

All age-results on the dentine are, however, far too young compared with the expected age of the site even when calculated for a 100% Rn-loss (which was not assumed in the enamel calculations). U-series studies show, that the  $^{230}\text{Th}/^{234}\text{U}$  ratios of enamel are lower than the ratios in the attached dentine or cement layers. This indicates that uranium concentration has risen faster in the dentine/cement than in the enamel. This finding would imply, that the dose rate for the enamel should be calculated according a mixed model, but it also suggests that the LU-uptake model is more appropriate for enamel and the EU-model (or some approximation to it) for dentine. This, however, increases the discrepancy in ESR ages between the enamel and dentine, and does not account for the low dentine ages compared to the independent U-series and geological estimates.



**Figure 1.** ESR age results on tooth enamel and dentine from the Bilzingsleben archaeological site  
 circles: no Rn-loss  
 triangles: 100% Rn-loss  
 open: ages according early U-uptake (EU)  
 black: ages according linear U-uptake (LU)

**Table 2:**  
**Results of the chemical and ESR analyses on dentine samples from Bilzingsleben archaeological site**

No.	AD	U-cont		H <sub>2</sub> O		Sediment			Dose-rates		EARLY U-ACCUM.		LINEAR U-ACCUM.	
		[ppm]	DENT	SED	U	Th	K	Cos.	Sed	int. D-r	AGE	int.D-r	AGE	
161 DE1	865	26.9	5	15	1.92	4	0.60	75	552.8	a:	8182.8	99.4	4304.5	179
										b:	5292.7	149	2691.4	269
161 DE2	909	29.1	5	15	1.92	4	0.60	75	552.8	a:	8789.9	97.6	4625.0	176
										b:	5706.2	146	2904.9	265
161 DE3	982	26.5	5	15	1.92	4	0.60	75	552.8	a:	8374.0	110	4403.9	199
										b:	5321.2	169	2698.6	304
162 DE1	834	42.18	6	15	1.71	3	0.63	75	496.8	a:	11165.6	71.7	5906.5	130
										b:	7683.5	102	3939.8	189
162 DE2	860	42.32	6	15	1.71	3	0.63	75	496.8	a:	11290.2	73.2	5982.7	133
										b:	7750.2	105	3969.5	194
163 DE2	1373	40.82	5	15	1.71	3	0.59	75	488.6	a:	12691.3	105	6697.5	192
										b:	8133.5	161	4147.4	299
164 DE1	1553	43.49	4	15	2.08	3	0.67	75	541.4	a:	13846.6	108	7316.6	198
										b:	8843.9	167	4506.9	310
164 DE2	1335	44.40	4	15	2.08	3	0.67	75	541.4	a:	13497.2	95.5	7125.9	174
										b:	8816.7	144	4502.7	267

Units	[Gy]	[ppm]	[wt.%]	[ppm]	[%]	[mGy/ka]	[mGy/ka]	ka	[mGy/ka]	ka
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Notes.

a: 0% Radon loss      b: 100% Radon loss.

Considering the various differences between enamel and bone as discussed above, we can propose various hypotheses to account for this difference. First, if bone continuously recrystallizes while it is buried, then the ESR signal stored in newly formed crystals will be much "younger" than the age of burial, as the crystals themselves will have formed continuously since that time. The creation of new traps leads to an increase of ESR sensitivity, which in turn causes an underestimation of AD when using the additive dose method. Secondly, as the bone is altered by decomposition of the organic matrix, it becomes more porous and two processes can occur: a) trapping of U-bearing colloidal particles from the soil water; b) increased exposure of the newly recrystallized apatite to U-bearing water. Both of these processes will tend to lead to sub-linear U-uptake (ie accelerating through time), and will produce ages that are anomalously young. One can equally well imagine other situations where the U content passes through a maximum (as observed by Seitz and Taylor, 1974; Badone & Farquhar, 1982), which would cause underestimates of the integrated dose rate. In general therefore, we expect to observe rather erratic results in ESR dating of bone.

The question arising is, why "good agreements" have been observed by other workers between ESR results and supposed geological or archaeological age. It appears that in most cases the ESR "ages" were not determined but the dose rate was assumed (Ikeya & Miki, 1980; 1981a&b; Mascarenhas et al., 1982): about 10 mGy/a for open sites and 1-2 mGy/a for caves. For a 100 ka sample, a mean dose rate of 10 mGy/a and of 1 mGy/a would be produced internally by about 4 and 40 ppm U respectively, assuming  $k=0.1$  (or 8 and 80 ppm with linear U-accumulation). For a 500 ka sample, 2.5 ppm U is sufficient to produce a mean dose rate of 1 mGy/a due to the fact that its daughters have grown into equilibrium. But in any case we must assume that bones accumulate U over time (although the precise

mechanism is unknown) leading again to an increasing dose rate with time. Therefore, it is rather dangerous to assume a constant dose rate for a specific type of locality. Indeed, the U-concentration in bones within one site and even in one stratigraphic layer can vary greatly, even over one order of magnitude (Hennig & Grun 1983; Seitz and Taylor, 1974).

In those cases where the dose rate for bones was determined from the U-concentrations (e.g. Yokoyama et al., 1981; 1982) severe age underestimations were observed.

### CONCLUSIONS

Given the complexity of the diagenetic processes affecting fossil bone (including the complexity of its U-uptake history), it is, in our opinion, impossible at this time to perform ESR dating on bones. If extensive basic studies of bone-fossilization and further laboratory experiments are first carried out, then it may be possible to find optimal conditions and types of bone for which ESR ages can be applied. Furthermore, careful comparisons between such ESR ages and other independent estimates of age as have been done here, must be carried out. In the meantime, the term "ESR-dating of bones" should be avoided.

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#### **PR** Reviewers comments (Barnaby Smith)

This paper clearly shows the problems which can arise when ESR (or TL) dating is attempted on a complex material such as bone. The samples were presumably crushed for measurement, which may have further complicated the picture. Rae and Ivanovich (*Applied Geochemistry*, **1**, pp 419 -426, 1986) have had success dating fossil bones by uranium series when only the outer 0.5 to 2 mm was used. This portion of the bone generally had the highest uranium content and gave ages in agreement with control dates whereas total cross-sections gave anomalously young ages. The surface layers therefore appear to better approximate a closed system. Choosing these for ESR analyses would allow more accurate alpha (and probably beta) dose calculations, but the problems of recrystallization may still remain. Another point which has not been raised in the paper is the possibility of systematic errors in the fitting of the ESR growth curve. Presumably the saturation level is high enough for the form of the curve fitting to make little difference and therefore not account for the massive discrepancy.

#### **Authors' Response**

We did not mention the possibility of taking samples from the outside in order to investigate a closed system for U-uptake, since there are still some objections against it (work by Pavlish and Farquhar at the Univ. of Toronto).

# INTERNAL RADIOACTIVITY IN QUARTZ AND FELDSPAR GRAINS

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## INTRODUCTION

When Fleming (1970) proposed the quartz inclusion dating technique for pottery, he assumed that quartz grains contained no internal radionuclides and thus could be regarded as non-radioactive dosimeters in a radioactive clay matrix. Later Sutton and Zimmerman (1976) found that quartz contains trace amounts of uranium and thorium and they estimated that the alpha dose contribution from internal sources could amount to 5% of the total dose.

When the alkali feldspar technique was proposed (Mejdahl and Winther-Nielsen, 1982), it was obvious that the beta dose contribution from inherent potassium had to be included and methods for estimating it were developed. We have now found that the dose contributions from inherent U, Th and Rb must also be taken into account and procedures for estimating these are discussed in the following.

## POTASSIUM AND RUBIDIUM

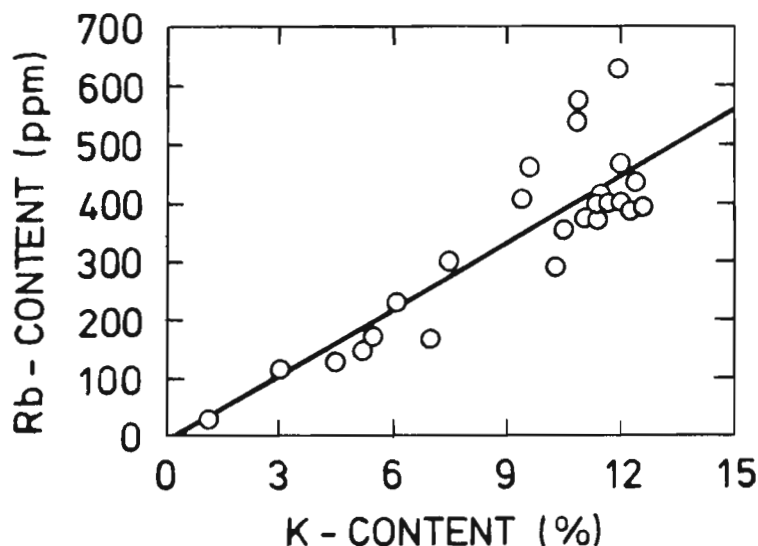
Our mineral separation technique (Mejdahl 1985a) yields two fractions of alkali feldspars: K-feldspar (10-12% K) and Na-feldspar (5-6% K). The K content is determined by beta counting using a multiscaler system (Bøtter-Jensen and Mejdahl, 1985) and the beta dose contribution from K-40 is calculated from absorption and conversion data given by Mejdahl (1979) and Nambi and Aitken (1986).

The assessment of the beta dose contribution from Rb-87 in a clay matrix was considered by Warren (1978). On the basis of the close geochemical association of Rb with K he suggested the use of a K:Rb ratio of 200:1 when the Rb content has not been measured. In inclusion dating the beta dose contribution from external Rb is negligible because of the low beta energy ( $E_{av} = 0.104$  MeV), but even a 0.1 mm grain will receive the full dose from internal Rb. The dose rate from 1% of Rb is 4.68 Gy/ka (Nambi and Aitken 1986).

We have measured the K and Rb content of 27 samples of feldspar extracted from pottery, burnt stones and sediments; Fig. 1 shows the Rb content as a function of the K content. A rather strong correlation of Rb with K is apparent with a K:Rb ratio of about 270:1. The regression line has the equation.

$$\text{Rb (ppm)} = -9.17 + 38.13 \text{ K (\%)}$$

For grains in the range 0.1 - 0.3 mm the above content ratio corresponds to a dose ratio of 3.4:1, that is, the contribution from Rb is about 30% of that from K.



*Figure 1. Rb content as a function of K content for alkali feldspars from archaeological materials and sediments.*

**Table 1:** Measured (NAA) and estimated (eq. 1) Rb dose rates (D-r) for those points in Fig. 1 for which the deviation from the regression line gives rise to a total dose rate error exceeding 0.5%.

Sample No.	Mat'l	K	Rb			Rb D-r	Tot. D-r	Tot. Error
			Meas.	Est.	Diff.			
R-840708, FN35	B	10.3	288	384	-96	0.045	5.31	0.8
R-831804, FN58	B	7.0	171	258	-86	0.040	5.76	0.7
R-832009, FK1-2	B	10.9	74	406	168	0.078	8.53	0.9
R-832105, FK13	S	11.4	372	426	-54	0.025	1.94	1.3
R-842201, FK35	C	9.6	459	357	102	0.047	5.34	0.9
R-854301, FK13	S	12.6	394	471	77	0.036	4.50	0.8
R-854409, FK13	B	11.9	628	445	183	0.085	9.34	0.9
UNITS		%	ppm	ppm	ppm	Gy/ka	Gy/ka	%

**Notes.**

Diff. is the difference between measured and estimated values.

Material (Mat'l); B = burnt stone, C = ceramics, S = sediment.

Because routine measurements of Rb would be difficult, it is desirable to utilize the correlation of Rb with K and it is therefore of interest to estimate the error ensuing from deviations from the regression line in Fig. 1.

Measured and estimated Rb values are given in Table 1 for those samples for which the deviation gives rise to a total dose rate error exceeding 0.5%. It can be seen that the total dose rate error is smaller than 1% in all cases except that of sample R-832105 which consists of sand from a frost wedge cast (Kolstrup and Mejdahl 1986). The error that would have resulted from neglecting the Rb contribution varies from 1 to 4% for all samples except R-832105 for which it is 9%. A total dose rate as low as 1.33 Gy/ka (1.48 Gy/ka including the Rb contribution) was encountered for cover sand from Jutland (Mejdahl 1985b).

The largest difference in Table 1 (168 ppm) together with this dose rate would result in a total error of 5% while the error resulting from neglecting the Rb contribution would be 20%.

The conclusion from the results presented here is that the contribution from internal Rb in alkali feldspar grains must be taken into account and can be calculated with sufficient accuracy from equation (1).

#### URANIUM AND THORIUM

The U content of all grain fractions dated in our laboratory is measured routinely by means of the delayed neutron counting technique (Kunzendorf et al., 1980). Results for a number of quartz and feldspar samples are given in Fig.2. The U content was below 0.5 ppm for most of the samples, but in a few of them values above 1 ppm were found.

The Th content of about 30 samples was measured by means of neutron activation analysis. Because it is not feasible to measure Th routinely, the relation of Th to U was studied. A marked difference between sediments and heated archaeological samples was seen. The results for sediments are discussed first.

The Th measurements included ten sediment samples, one quartz and nine K-feldspar. The U and Th contents for these were less than 0.4 and 1 ppm respectively. Fig. 3 shows a plot of Th vs U. A linear regression line with the equation.

$$\text{Th (ppm)} = 0.004 + 2.36 \text{ U (ppm)}.$$

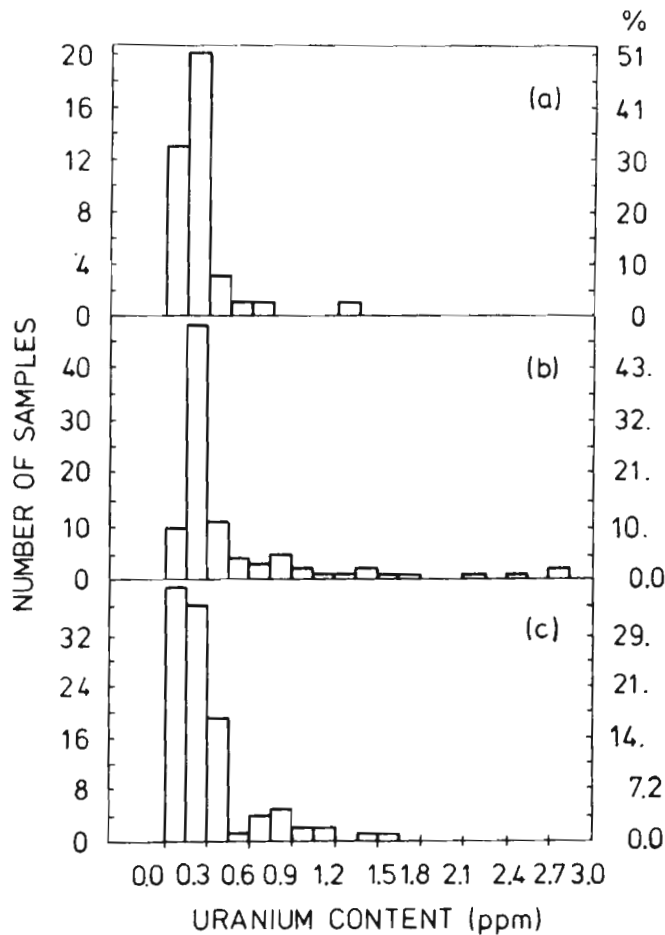
was fitted to the points. From the equation, the Th:U ratio is about 2.36:1, corresponding to an alpha dose-rate ratio of 0.63:1 using conversion factors from Nambi and Aitken (1986). The beta dose rates are small compared with those from alpha particles; they are considered in a later section.

Because the points in Fig. 2 scatter considerably, it is important to estimate the errors resulting from deviations from the regression line. Resulting dose-rate errors for those points that deviate most are given in Table 2. In calculating the effective alpha dose to feldspar an a-value of 0.2 was assumed, based on results for three sediment samples measured by Ann Wintle (personal communication).

The total error resulting from the scatter of the points in Fig. 2 is smaller than 1% except for fsample no. R-832105 for which it is 11.2%. The error that would have resulted from neglecting the alpha dose contributions from U and Th is about 10%. It is obvious, therefore, that these contributions cannot be neglected for coarse-grained feldspars from sediments with a low external dose rate.

The U and Th contents in grains from archaeological samples are considerably higher than those in sediment samples. A plot of Th vs. U for ten samples is shown in Fig. 3. Linear regression for these points yields the equation:

$$\text{Th (ppm)} = 0.826 + 0.783 \text{ U (ppm)}$$



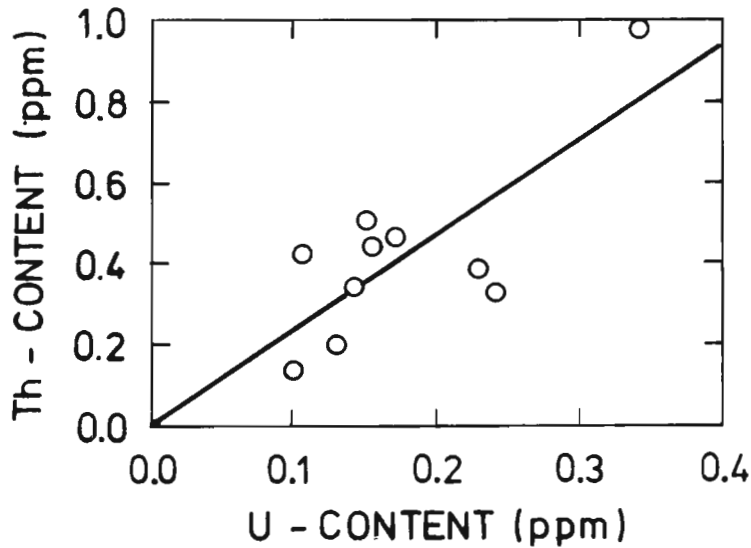
*Figure 2* Uranium content in quartz and feldspar samples. a) quartz, 39 samples, b) sodium feldspar, 93 samples, and c) potassium feldspar, 110 samples.

Compared with sediments the Th content relative to U is smaller in the archaeological samples and there is no proportionality. The reason might be that the grains have been enriched preferentially in U during firing of the materials. Not included in Fig. 3 are three samples that gave somewhat abnormal results; these are listed in Table 3. The samples in table 3 are burnt stones from an area in Sweden just north of Uppsala.

The errors that would result from using the regression line in Fig. 3 are listed in Table 4 for the three samples in Table 3 and those in Fig. 3 that show the largest deviation from the regression line. It can be seen that the errors are negligible except for the three samples from Table 3. Two of these give a total error of 3.5% which is just acceptable within the general uncertainty of about 6%. The errors that would result from neglecting the Th contribution are 5 and 7% in the two cases and about 2% for the other samples.

The question of zoning remains to be considered. Because U and Th tend to accumulate in cracks in the grains, the distribution is likely to be inhomogeneous. We have not yet carried out any zoning studies, but Sutton and Zimmerman (1978) found in their study of 1 mm quartz grains from a granite fireplace rock that most of the radioactivity has agglomerated in large areas ( $\sim 50 \mu\text{m}$ ) that had low luminescence efficiencies. In such cases the alpha dose rate will be overestimated. Another effect resembling that of zoning in individual grains arises from the occurrence of red-coloured grains appear to contain more U and Th and have less

luminescence efficiency than lighter grains and, consequently, the alpha dose rate will be over-estimated in a sample containing a mixture of light and red grains.



*Figure 3. Th content as a function of U content for quartz and feldspar from sediments.*

**Table 2.:** Errors in Th alpha dose rate and total dose rate for those points in Fig. 3 that deviate most from the regression line

Sample No.	Meas. (NAA)	Est. (eq.2)	Diff. error	Th D-r	Tot. D-r	Tot. error
R-841604	0.38	0.55	-0.16	0.024	3.98	0.6
R-841605	0.98	0.81	0.17	0.025	3.92	0.6
R-841608	0.42	0.25	0.17	0.025	4.63	0.5
R-832105	0.51	0.36	0.15	0.022	1.90	1.2
R-832401	0.33	0.57	-0.24	0.035	5.04	0.7
UNITS	ppm	ppm	ppm	Gy/ka	Gy/ka	%

**Notes.**

The samples listed are potassium feldspar from sediments. An alpha efficiency factor of 0.2 was assumed. Conversion factor from Nambi and Aitken (1986). Diff. is the difference between measured and estimated value

**Table 3:** U and Th concentration for three samples of burnt stones not included in Fig. 4.

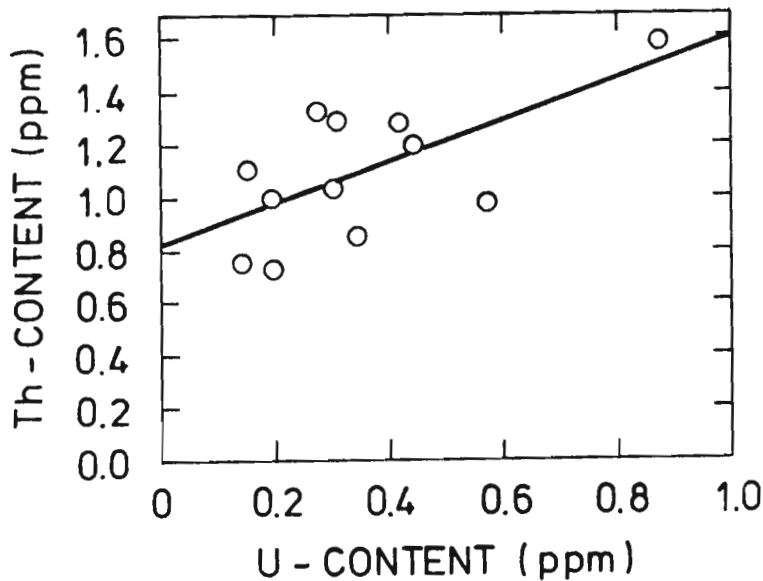
Sample No	U (ppm)	Th (ppm)
R-853604, K1-2	1.13	0.98
R-853612,FK1-2	0.83	4.77
R-853632, FN58	0.40	2.41

**Table 4.:** Errors in Th alpha dose rate and total dose rate for the samples in Table 3 and those points in Fig. 3 that deviate most from the regression line.

Sample No.	Th Content			Th D-r	Tot. D- r	Tot. Error
	Meas. (NAA)	Est. (eq.3)	Diff. error			
R-840713, FN58	0.74	0.98	-0.24	0.04	5.33	0.7
R-831804, FN58	0.98	1.27	-0.29	0.04	5.76	0.7
R-832009, FK1-2	1.30	1.06	0.23	0.03	8.53	0.4
R-853604, FK1-2	0.98	1.71	-0.73	0.11	8.38	1.3
R-853612, FK1-2	4.77	1.48	3.29	0.49	13.94	3.5
R-853622, FN58	2.41	1.14	1.27	0.19	5.30	3.5
R-834410, FN35	0.86	1.09	-0.24	0.04	6.11	0.6
R-854406, FK1-2	1.33	1.04	0.29	0.04	8.76	0.5
UNITS	ppm	ppm	Gy/ka	Gy/ka	%	%

**Notes.**

All samples are alkali feldspar from burnt stones. An alpha efficiency factor of 0.2 was assumed and the conversion factor was taken from Nambi and Aitken (1986). Diff. is the difference between measured and estimated values.



*Figure 4. The content as a function of U content for feldspars from archaeological materials.*

### BETA DOSE FROM U AND TH IN QUARTZ AND FELDSPAR GRAINS

The beta dose rate from U and Th in quartz and feldspar grains can be estimated from the absorbed fraction values listed by Mejdahl (1979). The dose rates that would result from 1 ppm of U and Th for various grain sizes are listed in Table 5. It is clear from Fig. 2 that the U content is less than 1 ppm for most samples. From eqs. (2) and (3) the Th content corresponding to 1 ppm U is 2.4 ppm or less. Since the total dose rate is usually at least 1 Gy/ka, the contribution from beta radiation emitted by internal U and Th will be negligible in nearly all cases. In those cases where higher internal contents of U and Th were found, the total dose rate was also correspondingly higher.

**Table 5:** Beta dose rates for 1 ppm internal concentration of U and Th in quartz and feldspar grains.

Grain diameter (mm)	Dose rate (Gy/ka)	
	U	Th
0.1	0.014	0.004
0.3	0.028	0.007
0.5	0.039	0.009
1.0	0.059	0.013
5.0	0.114	0.023

**Notes.**

Absorbed fractions taken from Mejdahl (1979).

The beta particles from U and Th will be counted along with those from K in our technique for estimating the K content of feldspar grains (Bøtter-Jensen and Mejdahl 1985). In order to investigate the interference of the beta particles from U and Th we measured the apparent K content of the U and Th standards NBL 105 ( $10 \pm 1$  ppm U) and NBL 109 ( $104 \pm 3$  ppm Th + 3.7 ppm U). We found that 1 ppm U and 1 ppm Th would correspond to apparent K contents of 0.15% and 0.04%, respectively. The corresponding infinite-matrix dose rates calculated from these apparent K-contents are 0.122 Gy/ka and 0.033 Gy/ka which correspond rather well to the values 0.147 Gy/ka and 0.029 listed in Nambi and Aitken (1986). However, because the absorbed fractions for K are considerably smaller than those for U and Th, one would not estimate the beta dose from U and Th to smaller grains correctly by counting the beta particles along with those from K.

The result of the counting of beta particles from U and Th with those from K in the K determination will be the inclusion of 25-80% of the beta dose from U and Th, depending on the grain size. This can be regarded as an advantage but one of little practical consequence because, as mentioned above, the beta dose contribution from internal U and Th is negligible.

### CONCLUSION

Our studies of the Rb content of feldspar grains and U and Th contents of quartz and feldspar grains have shown that the dose rate contribution from these sources is significant and must be taken into account.

Rb appears to be rather well correlated with K, and the contribution can be included with sufficient accuracy by assuming a K:Rb ratio of 270.1 corresponding to a dose rate ratio of 3.4:1.

The U content of all our samples is measured routinely by delayed neutron



counting, but routine measurements of the Th content is not feasible. We therefore studied the relation of Th to U. For sediments approximate proportionality was found with a Th:U ratio of 2.36:1. For heated archaeological samples there was a linear relation, but not proportionality. The conclusion is that these relations allow determination of Th with sufficient accuracy from the known content of U. In all cases studied the beta dose contribution from U and Th was negligible.

It should be emphasized that the results are preliminary. NAA studies of a larger number of samples are planned in order to provide a broader base for the conclusions.

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#### PI. Reviewer's Comments(S R Sutton)

These important measurements on internal radioactivity in quartz and feldspar represent primarily good news with regard to practical dating. The Rb contribution in alkali feldspars appears to be the greatest contribution, up to 20% of the total dose-rate, however, the geochemical coherence of K and Rb allows the internal Rb dose-rate to be predicted with sufficient accuracy from the K content alone. Alpha doses from internal U and Th tend to be lesser contributions, up to 10%. Consequently, the approach of using a typical Th/U ratio to estimate the Th content of these grains from their U content, as suggested by Mejdahl, is adequate. U and Th beta doses were negligible in the samples studied. These results suggest that internal dose-rates in quartz and feldspar can be estimated with sufficient accuracy from their K and U contents.

It is difficult to predict the universal nature of these conclusions, since the samples studied were presumably restricted to Scandanavian materials. Individual samples from other geologic provenances may have greater internal dose-rate contributions, and, therefore, greater total dose-rate errors, than those reported here. Ceramics may be highly variable in this regard since the inclusions and the clay typically derive from different geologic sources, ie quartz and feldspar with relatively high radioactivity can be incorporated in low radioactivity clay and vice versa.

#### Author's Response:

It is true that all samples were from Scandanavia, and, therefore, the results are not directly applicable in other parts of the world without further studies. However, I should think that the mineral properties governing the uptake of uranium and thorium would be more or less the same everywhere.

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Compiled by Ann Wintle