

URANIUM-SERIES DATING OF MARLY SEDIMENTS: APPLICATION TO JAROSZÓW FOSSIL LAKE (SW Poland)

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Abstract: A U-series ($^{230}\text{Th}/\text{U}$) study was carried out on the carbonate sediments from the fossil lake of Jaroszów (SW Poland). Six marly samples of unit 5 have been dated with isochron method. Two procedures for obtaining sub-samples have been investigated, the Successive Leaching (SL) and the Full Leaching (FL). It appears that with SL method thorium isotopes are subjected to isotope fractionation. On the other hand, FL method presents no significant isotopic fractionation and gives a wide range of values for isotopic ratios, which is very convenient for plotting isochrons. A simple graphical representation of sample sub-sets was created to detect isotopic fractionation. Even though FL procedure is efficient, results are not in agreement with stratigraphy. Three possible explanations can be given for these stratigraphic inconsistencies: (1) detrital contamination, (2) open system, and (3) mixing of carbonates of different ages.

1. INTRODUCTION

Located in the SW of Poland (Fig. 1), Jaroszów is a fossil lake lying between two fluvial series and it is said to be a Weichselian deposit. Krzyszkowski *et al.*, 1999, carried out the first investigation with dating methods. These authors (Krzyszkowski *et al.*, 1999; Krzyszkowski *et al.*, 2001) have divided all the lacustrine deposit into 8 lithological units. However, it is never possible to find those 8 layers on the same cross-section. Samples have been taken from different profiles for ^{14}C , TL and U-series dating. Unit 5, the only suitable for U-series dating was sampled on six locations along a log of the profile (Fig. 2). Sediments of this unit are constituted of unconsolidated and homogeneous marls of different colours (grey or white rich carbonate marl). The chemical composition (Krzyszkowski *et al.*, 1999; Krzyszkowski *et al.*, 2001) of this unit is uniform with predominance of CaCO_3 (40 to 100%) and presence of silica, ferrous compounds and sulphurs. According to the same source, mineralogical composition is dominated by calcite with some gypsum and sometimes kaolinite, illite and quartz. In the previous study, apart from U-series dating, two other methods (^{14}C and TL) have been used to give the chronology of all the deposits. Ages obtained on unit 5 by ^{14}C , TL and U-series dating have shown discrepancies (Table 1). Moreover, $^{230}\text{Th}/\text{U}$ ages are not reproducible (Table 1, Fig. 2). The aim of this present work was to account for the lack of reproducibility of U-series dating and to find the origin of inconsistencies between ^{14}C , TL and U-series dating.

2. PREVIOUS DATING RESULTS

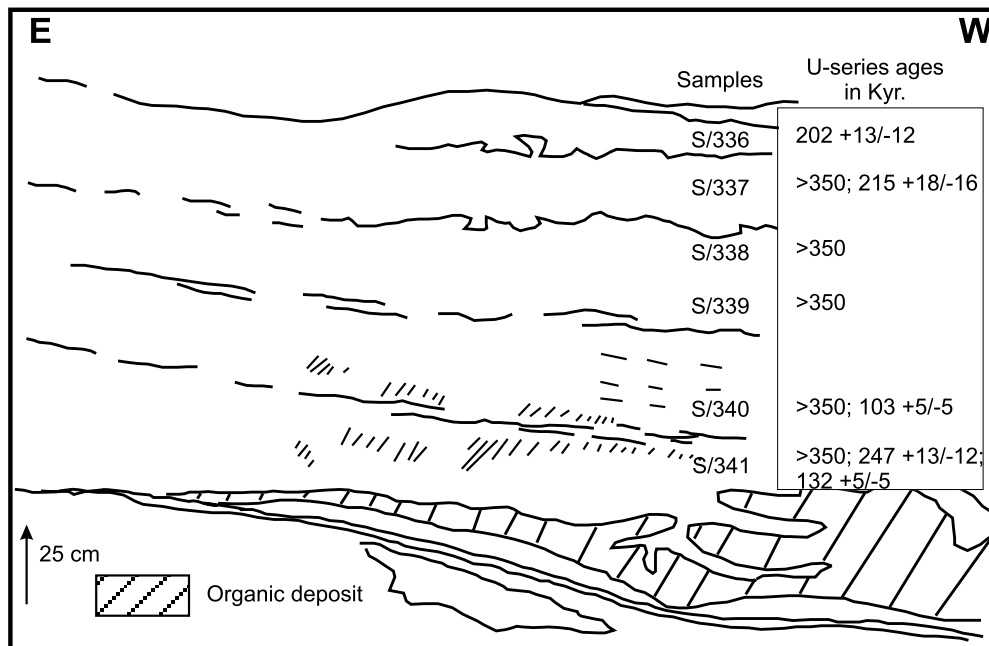
Three absolute dating methods were used to set the chronology of the deposit. Material was sampled as follows (Krzyszkowski *et al.*, 1999; Krzyszkowski *et al.*, 2001): ^{14}C samples have been taken from almost all sections of the lacustrine deposit, TL samples are coming from section E/96. Both ^{14}C and TL dates were obtained in the Department of Radioisotopes, Silesian University of Technology (Poland). The two sets of samples (Table 1) dated with $^{230}\text{Th}/\text{U}$ method were analysed for the first set (I) at



Fig. 1. Map of Poland with Jaroszów fossil lake localisation.

Table 1. Radiometric dating results of Krzyszkowski *et al.*, 1999 investigations. ? indicates an approximate localisation for TL samples.

Sample number	Ages in kyr		
	U-series	¹⁴ C	TL
S/336	202	34.9 ± 0.21	
S/337	>350; 215	34.1 ± 0.2	
S/338	>350	38.1 ± 0.3	123 ± 19?
S/339	>350	35.4 ± 0.6	
S/340	>350; 103±5	30.2 ± 1.0	
S/341	>350; 247 ; 132±5	38.2 ± 0.3	40 ± 6?

**Fig. 2.** Cross-section of unit 5 with samples localisation and U-series ages after Krzyszkowski *et al.*, 1999. Some of the samples have been dated two or three times.

Bergen University (Norway) and for the second set (II) at the U-series Laboratory of the Polish Academy of Sciences in Warsaw (Poland). ²³⁰Th/U samples are coming from section E/95A.

For the same sample, different methods have given completely different ages (such as sample S/338: ²³⁰Th/U Age > 350 ka, ¹⁴C Age = 38.1±0.3 ka and TL Age = 123±19 ka). As showed in **Table 1**, two first problems are the age disagreement between methods and the lack of concordance (for each method) of dating results with stratigraphy. ¹⁴C dates range from 30.2 ka to 38.2 ka (close to the limit of the method), TL dates range from 40 ka to 123 ka and U-series dates range from 103 ka to more than 350 ka (upper limit of the method). Stratigraphic correlation of samples S/338 and S/341 dating with TL has been performed based on the altitude level of the sample in the lithological unit because they do not belong to the same profile.

A full report of the older ²³⁰Th/U results is described here because it was beyond the scope of the Krzyszkowski *et al.*, 2001 paper. **Table 2** presents U-series data for unit 5. It shows that the third problem is non-reproducibility of U-series results. For example, sample S/341 gives three ages (132 ka, 247 ka and more than 350 ka) for the same standard procedure (Ivanovich and Harmon, 1992) when

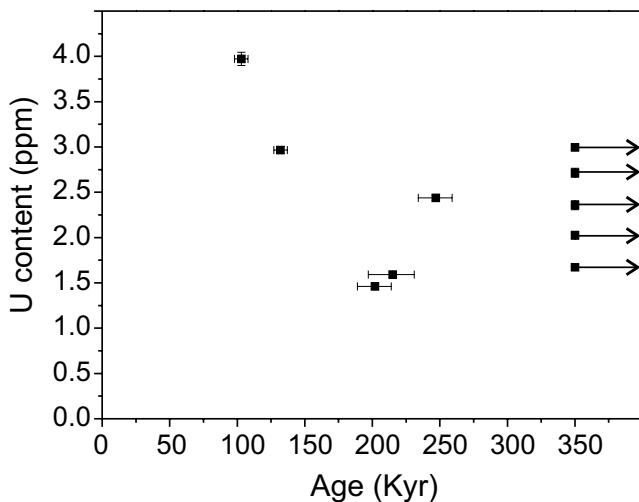
three separate analyses are carried out. Concentration of uranium is high (1.5 to 4 ppm) but common for this kind of deposit and ²³⁰Th/²³²Th activity ratios are ranging from 28 to 150. Generally, a ratio ≤ 20 indicates a detrital contamination with more than 5% of detritus. As ²³⁰Th/²³²Th activity ratios of Jaroszów marly sediments are > 20 it seems that no correction is needed but, whereas it is well known that pure carbonate ratios are much higher, isochron method was intended to check upon the age inconsistencies of isolated samples.

In regards to previous results, it looks as if there were no relation between the U content and the age of the sample (**Fig. 3**). In addition, repeated analyses for fractions of a bulk sample do not give concordant U activities.

As seen in **Fig. 4A**, the isotopic ratio ²³⁴U/²³⁸U is rather a constant, but on a few occasions it is slightly lower and in this case, the U content is bigger. Such behaviour is not compatible with a preferential leaching of ²³⁴U because in this case, the age should be older which is not true here. One can think about an accumulation of uranium with a lower ²³⁴U/²³⁸U ratio. This scenario is compatible with samples S/340 and S/341 because they have a higher U content and a smaller ²³⁰Th/U ratio (**Fig. 4A**), which means a younger age. There is no relation between the

Table 2. Activity ratios and other data after Krzyszkowski et al., 1999 (Unit 5).

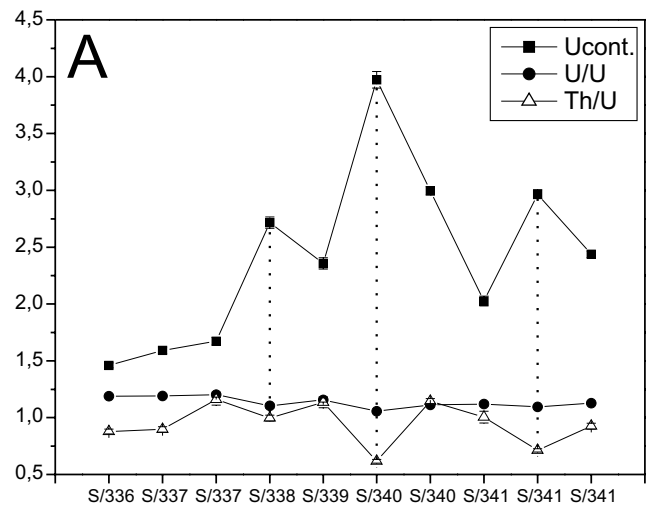
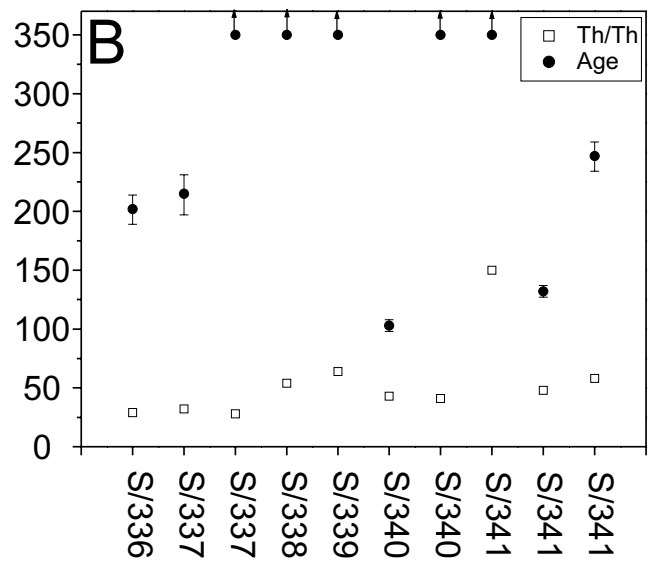
Sample	Sample set	U conc. (ppm)	Activity ratios			Age(kyr)
			$^{234}\text{U}/^{238}\text{U}$	$^{230}\text{Th}/^{234}\text{U}$	$^{230}\text{Th}/^{232}\text{Th}$	
S/336	II (1998)	1.460 ± 0.023	1.190 ± 0.010	0.878 ± 0.021	29	202
S/337	I (1995)	1.592 ± 0.028	1.191 ± 0.015	0.896 ± 0.024	32	215
S/337	II	1.673 ± 0.033	1.203 ± 0.021	1.161 ± 0.05	28	>350
S/338	II	2.716 ± 0.050	1.104 ± 0.018	0.996 ± 0.026	54	362
S/339	II	2.357 ± 0.049	1.156 ± 0.19	1.135 ± 0.048	64	>350
S/340	II	3.972 ± 0.073	1.056 ± 0.007	0.617 ± 0.016	43	103±5
S/340	II	2.996 ± 0.036	1.112 ± 0.008	1.146 ± 0.022	41	>350
S/341	I	2.026 ± 0.043	1.120 ± 0.017	1.004 ± 0.052	150	>350
S/341	II	2.966 ± 0.040	1.096 ± 0.006	0.713 ± 0.014	48	132±5
S/341	II	2.437 ± 0.028	1.127 ± 0.006	0.925 ± 0.026	58	247

**Fig. 3.** Uranium content as a function of the age.

value of $^{230}\text{Th}/^{232}\text{Th}$ and the age (**Fig. 4B**). As for a set of samples of the same age, a low $^{230}\text{Th}/^{232}\text{Th}$ does not necessarily mean an older sample as it is usually stated in literature. In addition, a similar level of contamination for analogous samples can give two completely different ages. No clear relation exists between $^{230}\text{Th}/^{234}\text{U}$ and the U contents for samples S/336 and S/337, although an apparent inverse relation exists for all other samples (**Fig. 4A**). There is heterogeneity of U distribution within the stratigraphy and sometimes within one unit and heterogeneity in the detrital contents within one lithological unit.

In conclusion, one can say that in the view of ^{14}C , TL and $^{230}\text{Th}/\text{U}$ dating results, it appears difficult to tell which method is reliable or not. For this reason, this new study was carried out (1) to account for the problem of the origin of inconsistencies of U-series dating results and (2) to explain controversial results between dating methods on the lacustrine sediments of Jaroszów.

For the U-series inconsistencies dating results on unit 5, three possibilities were envisaged. (1) Detrital contamination such as clay minerals or sand which are common detritus in lake sediments, (2) Open system to U and/or Th and (3) Mixing of carbonates (authigenic or not) with different ages.

**Fig. 4A.** Variations of the U content, $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{234}\text{U}$ activity ratios as a function of the sample. Errors bars are within the symbol size.**Fig. 4B.** Variations of the age and $^{230}\text{Th}/^{232}\text{Th}$ as a function of the sample.

3. ISOCHRON METHOD

Basic assumption in $^{230}\text{Th}/\text{U}$ dating method is that the material being dated is free of Th and only contains U at the time of deposition. This is possible because uranium is very soluble in natural waters and is co-precipitated during carbonate precipitation, contrary to Th which is insoluble in groundwater and is adsorbed at the surface of detrital minerals (silicates, iron hydroxides, quartz, etc.). In this way, $^{230}\text{Th}/^{234}\text{U}$ isotopic ratio at the time of deposition of the authigenic carbonates equals zero. Then the concentration of ^{230}Th in the authigenic carbonate is just a question of time elapsed since deposition and the age of the sample can be calculated using the equation (Kaufman and Broecker, 1965):

$$\frac{^{230}\text{Th}}{^{234}\text{U}} = \frac{^{238}\text{U}}{^{234}\text{U}} (1 - \exp(-\lambda_{230}t)) + \frac{\lambda_{230}}{\lambda_{230} - \lambda_{234}} (1 - \frac{^{238}\text{U}}{^{234}\text{U}}) (1 - \exp(-(\lambda_{230} - \lambda_{234})t)) \quad (3.1)$$

Where λ 's are a decay constants and t is the time.

The major problem arising with impure authigenic carbonates is that of detritus which contributes U and Th to the leachate during acid treatment. As a result, when sediments are impure, we do not measure only authigenic ^{230}Th coming from ^{234}U decay but also ^{230}Th coming from detritus.

In that case, the question is: How to determine isotopic composition of the authigenic carbonate?

Different correction methods have been developed in U-series dating to deal with detrital contamination. The purpose of all correction methods is to subtract from the total measured activities of ^{230}Th , ^{234}U and ^{238}U , those portions, which have originated in detritus. A review of several correction methods can be found in Kaufman (1993). One of those methods, an isochron solution was first proposed to date fossil shells (Osmond *et al.*, 1970) to estimate ages of marine terraces. Ever since, several attempts with isochron methods have been made.

Isochron method is based on the assumption that sediments are made up of two components: (1) chemically precipitated calcite free of Th at the time of deposition; and (2) detritus which are not inert during acid treatment, releasing some U and Th to the leachate.

A common isochron dating method with exception of those requiring dissolution of the detritus (e.g. Ku and Liang, 1984) is the leachate alone (L/L) method (Schwarz and Latham, 1989). A series of coeval samples each assumed to be a variable mixture of authigenic and 'detrital' ^{230}Th is analysed. The observed ^{230}Th , ^{234}U , and ^{238}U isotope activities are normalised to the ^{232}Th activity which comes from the detritus and then plotted $^{230}\text{Th}/^{232}\text{Th}$ versus $^{234}\text{U}/^{232}\text{Th}$ and $^{234}\text{U}/^{232}\text{Th}$ versus $^{238}\text{U}/^{232}\text{Th}$ according to the Rosholt scheme (Rosholt, 1976). In the case of a non-authigenic thorium contamination, isochrons will be defined by a straight line, the slope of which gives the corrected activity ratios. These corrected ratios allow

calculating the corrected age of the carbonate using the equation of Kaufman and Broecker (1965). This method is often used with heterogeneous samples such as contemporaneous speleothems with different levels of contamination, which are easily macroscopically differentiable in a few sub-samples of diverse carbonate/detritus ratio. Data used in this method are obtained from leachates of two or more samples. Each of these samples must be a mixture in different proportions of a single type of authigenic carbonate and a single type of detritus. This method assumes that the activities of ^{230}Th , ^{234}U and ^{238}U of detritus are different for all samples but are coming in solution in the same proportion to ^{232}Th for all leachate fractions.

Unfortunately for homogeneous samples (samples which have the same macroscopic aspect along a profile or a part of it), it is impossible to obtain sub-samples with different proportions of carbonates and detritus. Thus, the L/L method is inappropriate for obtaining a wide range of activity ratios and therefore dating homogeneous samples.

Two procedures (requiring the same assumptions as L/L method) for marl samples were envisaged here:

Successive Leaching (SL)

The successive leaching is a method commonly used to date dirty calcites.

About 50 to 100g of sample is weighed, crushed, sieved and homogenised. Visible organic matter (roots, piece of plant) is handpicked up. The crushed sediment is then wetted with water in a beaker. Diluted acid (0.1M HCl) is added slowly to the sample. After few minutes, just before the reaction stops, the sample is filtered. The part of sample remaining is now leached with a stronger acid.

In this way, different fractions are obtained. Each of these fractions is spiked with a $^{232}\text{U}/^{228}\text{Th}$ solution and treated as a normal calcite sample (Ivanovich and Harmon, 1992).

Full Leaching (FL)

This is a variation of the L/L method we use to obtain the mixtures (authigenic carbonate/detritus) needed. One sample is pre-treated as for successive leaching (crushed, sieved, and homogenised). This sample is then divided into small sub-samples of identical weight. Sub-samples are spiked and then the carbonate fraction is totally dissolved in acidic solutions of different strengths. Strength of the acid used is the same as in SL procedure (e.g. 0.1M HCl, 0.5M HCl, 1M HCl, 1M HNO₃, 3M HNO₃, and 6M HNO₃). Volume of the acid used is double of that necessary to dissolve the weight of a corresponding carbonated sub-sample to be sure that all the calcite is dissolved. Great care is given to keep the same laboratory procedure (acid strength, stirring time) all along the study, because it seems that results are very sensitive to the laboratory procedure applied.

4. RESULTS

Errors are 1σ 's based on counting statistics. Large error bars are due to the small α -activity of ^{232}Th in samples and sometimes for samples analysed with SL, to very low activities for both ^{230}Th and ^{232}Th . Both SL and FL activity ratios results were plotted using the Rosholt scheme (Rosholt, 1976), where the slope of $^{234}\text{U}/^{232}\text{Th}$ versus $^{238}\text{U}/^{232}\text{Th}$ gives the corrected $^{234}\text{U}/^{238}\text{U}$ activity ratio and $^{230}\text{Th}/^{232}\text{Th}$ versus $^{234}\text{U}/^{232}\text{Th}$ the corrected $^{230}\text{Th}/^{232}\text{Th}$ activity ratio for the authigenic carbonate. If all the requirements about close system and isotopic fractionation are fulfilled, data points should lie along a straight line of positive slope and show a good linearity. Fitting the line was made by classical linear regression (least square method) without considering error to avoid low weighting of samples with very low ^{232}Th activity (Schwarcz and Latham, 1989; Przybylowicz *et al.*, 1991).

Successive leaching

Three series of six sub-samples have been analysed with the SL method. **Table 3** shows activity ratios obtained for sub-samples originated from samples S/336, S/338 and S/341. Isochrons obtained with SL method are plotted in **Fig. 6**. Column A contains the graph representations of $^{234}\text{U}/^{232}\text{Th}$ versus $^{238}\text{U}/^{232}\text{Th}$. In column B, the graph representations of $^{230}\text{Th}/^{232}\text{Th}$ versus $^{234}\text{U}/^{232}\text{Th}$ are plotted.

It is interesting to notice (**Table 3**, **Fig. 5**), that there is a divergence of behaviour of $^{230}\text{Th}/^{232}\text{Th}$ and $^{234}\text{U}/^{238}\text{U}$ activity ratios with the variation of acid nature and strength. During all acid treatment, $^{234}\text{U}/^{238}\text{U}$ ratio is a constant (within error range) but the behaviour of the $^{230}\text{Th}/^{232}\text{Th}$ ratio is remarkable. This ratio is not decreasing with the acid strength as expected (a stronger acid should leach more ^{232}Th from detritus) but growing, excepting three sub-samples. This may be due to a quicker leaching of ^{232}Th over ^{230}Th , or similar leaching of these two isotopes with preferentially re-adsorption of ^{230}Th on the remain-

ing sediment. Then adding acid takes an effect of leaching this re-adsorbed ^{230}Th . $^{230}\text{Th}/^{234}\text{U}$ is also growing with acid strength as the U contents (**Table 3**).

“U-isochrons”: $^{234}\text{U}/^{232}\text{Th}$ versus $^{238}\text{U}/^{232}\text{Th}$

All “U-isochrons” are characterised by a positive slope and a very good linearity (**Fig. 6**, column A). It looks as though all requirements for isochron dating during the successive leaching of the sample are satisfied for U.

“Th-isochrons”: $^{230}\text{Th}/^{232}\text{Th}$ versus $^{234}\text{U}/^{232}\text{Th}$

“Th-isochrons” (**Fig. 6**, column B) show a major problem as they are characterised by a poor linearity. This linearity is probably due to isotopic fractionation or adsorption of leached Th on the sample residue or the beaker.

One can compute an age from these isochrons. Nevertheless, for sample S/336, the regression coefficient is $r = 0.583$ which has no significance. Therefore, there is no

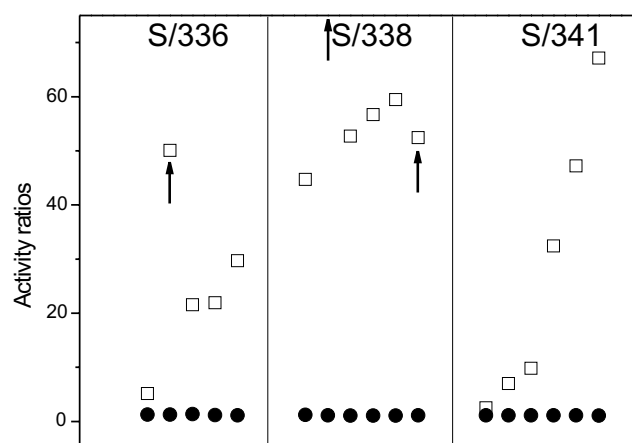


Fig. 5. Behaviour of $^{230}\text{Th}/^{232}\text{Th}$ (empty square) and of $^{234}\text{U}/^{238}\text{U}$ (full circle) during successive leaching. Arrows indicates samples who don't follow the pattern of Th/Th ratio.

Table 3. Activity ratios and U content of samples (SL method).

Sample	Lab. No.	Conc. U (ppm)	$^{234}\text{U}/^{238}\text{U}$	$^{230}\text{Th}/^{234}\text{U}$	$^{230}\text{Th}/^{232}\text{Th}$	Acid
S/336	W 484	0.121 ± 0.007	1.298 ± 0.075	0.009 ± 0.004	$5.16 \pm ?$	0.5M HCl
	W 485	0.116 ± 0.007	1.296 ± 0.077	0.033 ± 0.008	$50.11 \pm ?$	1M HCl
	W 486	0.110 ± 0.007	1.361 ± 0.082	0.074 ± 0.012	$21.59 \pm ?$	1M HNO_3
	W 487	0.137 ± 0.009	1.207 ± 0.068	0.251 ± 0.029	22 ± 13	3M HNO_3
	W 488	0.602 ± 0.033	1.143 ± 0.037	1.462 ± 0.042	29.7 ± 3.0	6M HNO_3
S/338	W 301	0.269 ± 0.013	1.233 ± 0.045	0.215 ± 0.013	45 ± 19	0.1M HCl
	W 302	0.138 ± 0.007	1.148 ± 0.059	0.014 ± 0.006	$177.4 \pm ?$	0.5M HCl
	W 303	0.331 ± 0.009	1.121 ± 0.027	0.395 ± 0.013	53 ± 13	1M HCl
	W 304	0.311 ± 0.011	1.211 ± 0.028	0.031 ± 0.004	$56.7 \pm ?$	1M HNO_3
	W 305	0.892 ± 0.027	1.112 ± 0.017	1.169 ± 0.017	59.5 ± 5.0	3M HNO_3
	W 306	1.096 ± 0.029	1.138 ± 0.015	1.156 ± 0.014	52.4 ± 3.3	6M HNO_3
S/341	W 543	0.138 ± 0.006	1.135 ± 0.041	0.005 ± 0.002	2.5 ± 2.2	0.1M HCl
	W 544	0.151 ± 0.007	1.128 ± 0.039	0.031 ± 0.005	7.0 ± 3.2	0.5M HCl
	W 545	0.110 ± 0.007	1.139 ± 0.064	0.025 ± 0.006	9.8 ± 9.8	1M HCl
	W 546	0.175 ± 0.010	1.131 ± 0.051	0.056 ± 0.008	32 ± 28	1M HNO_3
	W 547	0.201 ± 0.011	1.131 ± 0.044	0.083 ± 0.009	47 ± 40	3M HNO_3
	W 548	0.314 ± 0.016	1.108 ± 0.035	0.125 ± 0.009	67 ± 40	6M HNO_3

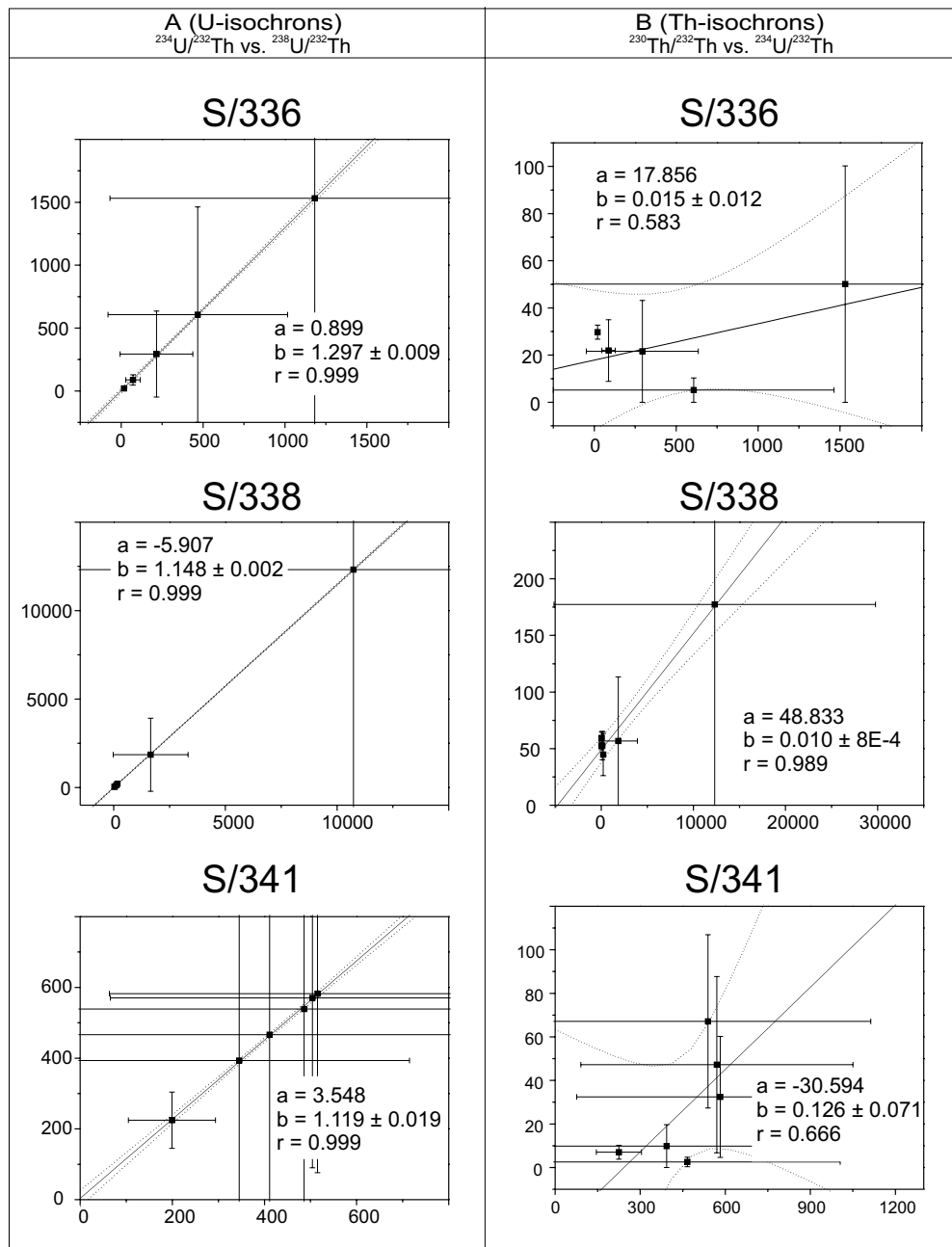


Fig. 6. Successive Leaching (SL) isochrons. The slope b represents the corrected activity ratio for the pure calcite.

clear relation between the isotopes and the age. On the other hand, sample S/338 presents an apparent good linearity ($r = 0.989$), which is an artefact caused by one outlier (coming from the leaching by 0.5M HCl). Without this point, $r = 0.281$ and the isochron is meaningless.

Finally, sample S/341 presents a poor linearity and a negative intercept. This intercept is a proof of incorrectness, because the intercept of the Th-isochron should always be positive since it represents the actual $^{230}\text{Th}/^{232}\text{Th}$ activity ratio of the sample detritus.

These results let us think that isotopic fractionation occurs during acid treatment only with Th isotopes and that eventually it is not always possible to detect it in regard of the slope of the isochron. A check of the intercept is recommended. Eventually in the case of a positive

intercept and if doubt still subsist, a simple graphical representation of sample sub-sets is useful (see appendix).

Full leaching

A new leaching procedure is proposed here: the Full Leaching (FL) method (see procedure above). A series of coeval sub-samples (of the same age and the same calcite/detritus ratio) coming from a *homogenous* sample is dissolved in different acids. Acid solutions are the same as in SL method. Carbonates are totally dissolved. It means that we avoid possible isotopic fractionation during calcite dissolution. With this approach, we avoid the possibility for an isotope to be leached quickly/preferably by an acid than another isotope. Because in the case of the SL method, activity ratio observed are not related to

the sample but only to a part of it. The complete dissolution of the calcite during FL method allows us to check for the isotopic fractionation during calcite dissolution that probably happens with successive leaching. Yet, possibilities of isotopic fractionation during the leaching of the detritus still persist. **Table 4** gives the activity ratios obtained for all samples analysed for FL and the isochrons are plotted in **Fig. 7**. Similarly to SL method, graph representations of $^{234}\text{U}/^{232}\text{Th}$ versus $^{238}\text{U}/^{232}\text{Th}$ are plotted in column A and in column B graph representations of $^{230}\text{Th}/^{232}\text{Th}$ versus $^{234}\text{U}/^{232}\text{Th}$.

“U-isochrons”: $^{234}\text{U}/^{232}\text{Th}$ versus $^{238}\text{U}/^{232}\text{Th}$

As for SL method, the slope of ‘U-isochrons’ represents the corrected $^{234}\text{U}/^{238}\text{U}$ -activity ratio. Isochrons (**Fig. 7**, column A) show a positive slope and a very good

linearity (except sample S/339 whose value of r , close to unity is linked to an outlier). It means FL method fulfils all requirements of the isochron dating for uranium.

“Th-isochrons”: $^{230}\text{Th}/^{232}\text{Th}$ versus $^{234}\text{U}/^{232}\text{Th}$

All the “Th-isochrons” (**Fig. 7**, column B) but sample S/337, show a positive slope and a good enough linearity, even if the fit of the data points for the U-isochrons is much better (maybe caused by a slight thorium fractionation or re-deposition). The linearity for Th-isochron S/339 is, as for the U-isochron, an artefact caused by one outlier. Despite the apparent suitability of FL method for dating homogeneous samples one should pay attention to the fact that intercepts for samples S/339 and S/340 are negative. This is a clue that probably there is something wrong with the sample.

Table 4. Activity ratios and U content of samples (FL method).

Sample	Lab. No.	Conc. U (ppm)	$^{234}\text{U}/^{238}\text{U}$	$^{230}\text{Th}/^{234}\text{U}$	$^{230}\text{Th}/^{232}\text{Th}$	Acid
S/336	W 453	1.342 ± 0.022	1.159 ± 0.021	1.018 ± 0.018	36.7 ± 2.8	0.1M HCl
	W 454	1.559 ± 0.030	1.194 ± 0.020	0.870 ± 0.144	28.4 ± 1.9	0.5M HCl
	W 455	1.325 ± 0.018	1.192 ± 0.014	0.971 ± 0.011	28.5 ± 1.2	1M HCl
	W 456	1.292 ± 0.016	1.201 ± 0.014	1.017 ± 0.011	29.2 ± 1.3	1M HNO ₃
	W 457	1.461 ± 0.020	1.177 ± 0.015	1.003 ± 0.013	27.2 ± 1.3	3M HNO ₃
	W 458	1.336 ± 0.022	1.217 ± 0.017	0.978 ± 0.013	26.0 ± 1.3	6M HNO ₃
S/337	W 549	1.579 ± 0.029	1.207 ± 0.015	0.953 ± 0.012	30.7 ± 1.5	0.1M HCl
	W 550	1.598 ± 0.023	1.192 ± 0.015	1.190 ± 0.014	33.7 ± 1.6	0.5M HCl
	W 551	1.538 ± 0.026	1.180 ± 0.016	1.175 ± 0.015	29.7 ± 1.4	1M HCl
	W 552	1.672 ± 0.027	1.158 ± 0.015	1.135 ± 0.014	30.0 ± 1.4	1M HNO ₃
	W 553	1.651 ± 0.038	1.188 ± 0.027	1.191 ± 0.024	34.5 ± 2.8	3M HNO ₃
	W 554	1.627 ± 0.035	1.250 ± 0.028	1.161 ± 0.024	27.2 ± 2.0	6M HNO ₃
S/338	W 330	2.218 ± 0.048	1.149 ± 0.022	0.928 ± 0.017	64.7 ± 7.0	0.1M HCl
	W 331	2.170 ± 0.038	1.150 ± 0.020	1.088 ± 0.018	64.0 ± 5.7	1M HNO ₃
	W 332	2.322 ± 0.041	1.119 ± 0.019	1.090 ± 0.017	45.2 ± 3.4	6M HNO ₃
	W 577	2.085 ± 0.017	1.124 ± 0.017	1.002 ± 0.015	53.4 ± 4.1	0.1M HCl
	W 578	1.977 ± 0.032	1.153 ± 0.018	1.152 ± 0.017	43.5 ± 2.8	0.5M HCl
	W 579	2.175 ± 0.034	1.095 ± 0.016	1.176 ± 0.016	50.3 ± 3.4	1M HCl
	W 580	2.011 ± 0.036	1.100 ± 0.017	1.199 ± 0.017	48.2 ± 3.3	1M HNO ₃
	W 581	2.652 ± 0.038	1.132 ± 0.015	1.110 ± 0.014	50.3 ± 3.1	3M HNO ₃
	W 582	1.925 ± 0.031	1.174 ± 0.018	1.119 ± 0.016	68.4 ± 5.6	6M HNO ₃
S/339	W 591	1.920 ± 0.050	1.143 ± 0.024	1.120 ± 0.022	76.8 ± 9.0	0.5M HCl
	W 592	1.953 ± 0.041	1.184 ± 0.021	1.139 ± 0.018	59.6 ± 5.0	1M HCl
	W 594	1.994 ± 0.034	1.203 ± 0.016	1.122 ± 0.014	58.7 ± 3.8	3M HNO ₃
	W 595	2.883 ± 0.043	1.127 ± 0.013	1.044 ± 0.011	54.7 ± 3.1	6M HNO ₃
	W 867	2.238 ± 0.119	1.131 ± 0.032	1.112 ± 0.030	58.9 ± 8.4	14M HNO ₃
S/340	W 538	2.652 ± 0.053	1.105 ± 0.015	0.939 ± 0.013	40.3 ± 2.5	0.5M HCl
	W 539	2.404 ± 0.063	1.154 ± 0.016	0.979 ± 0.013	39.4 ± 2.4	1M HCl
	W 540	2.546 ± 0.032	1.124 ± 0.011	0.977 ± 0.010	38.3 ± 1.7	1M HNO ₃
	W 541	2.544 ± 0.043	1.138 ± 0.017	1.006 ± 0.014	40.9 ± 2.7	3M HNO ₃
	W 542	2.469 ± 0.050	1.158 ± 0.017	0.942 ± 0.014	32.2 ± 2.0	6M HNO ₃
W341	W 525	1.302 ± 0.027	1.106 ± 0.018	0.975 ± 0.016	41.0 ± 3.1	0.1M HCl
	W 526	2.125 ± 0.059	1.132 ± 0.024	0.823 ± 0.018	47.9 ± 5.3	0.5M HCl
	W 527	2.568 ± 0.058	1.069 ± 0.021	0.740 ± 0.015	44.4 ± 4.7	1M HCl
	W 528	2.430 ± 0.062	1.100 ± 0.022	0.761 ± 0.016	68.3 ± 8.9	1M HNO ₃
	W 529	2.629 ± 0.064	1.113 ± 0.020	0.718 ± 0.014	59.2 ± 6.7	3M HNO ₃
	W 530	2.264 ± 0.058	1.075 ± 0.021	0.897 ± 0.018	56.5 ± 6.1	6M HNO ₃

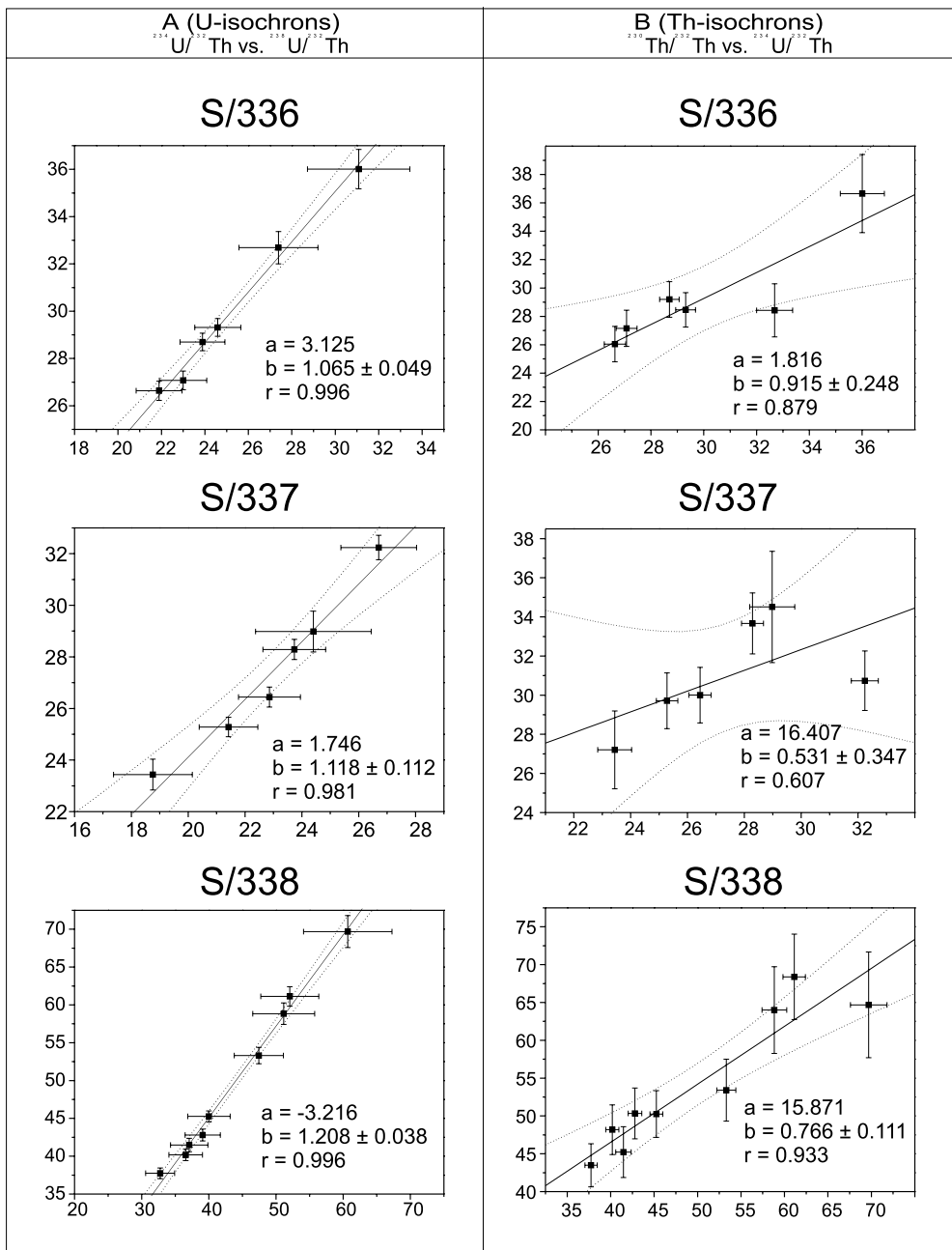


Fig. 7. Full Leaching (FL) isochrons.

5. DISCUSSION

In the view of results obtained with SL it is clear that this method has to be discarded since it is impossible to obtain correct 'Th-isochrons'. The reason can be a strong isotope fractionation occurring during acid treatment as shown by the sub-isochron test (**Fig. 8**). Explanations about the sub-isochron test can be found in the appendix.

As a solution to this problem, a new procedure was used, the Full Leaching (FL) method. FL method allows us to obtain a significant range of values for the activity ratios and to plot isochrons. No clear isotopic fractionation was observed in the view of the results of the sub-isochron test.

An age has been calculated for four of the six samples studied with FL method (**Table 5**). Isochron ages like isolate ages are not in agreement with the stratigraphy of

the deposit. It means that despite the correction for detrital contamination, it is impossible to have a correct chronology of the deposit.

As consequence, the marl sediments from Jaroszów are not suitable for U-series dating. The causes then can be: (1) an open system or (2) a mixing of carbonates.

In the case of an open system, several possibilities can be envisaged:

- Uranium leaching, which is very likely to happen because U is very soluble. Ages will appear older. As shown before (**Fig. 4a**) a preferential leaching in that sediment is not compatible with our results.
- Thorium leaching will cause ages to be younger, but Th is nearly insoluble and this situation is unlikely to happen.
- Leaching of both U and Th is possible, but in this case, the age will be a function of the Th/U ratio leached.

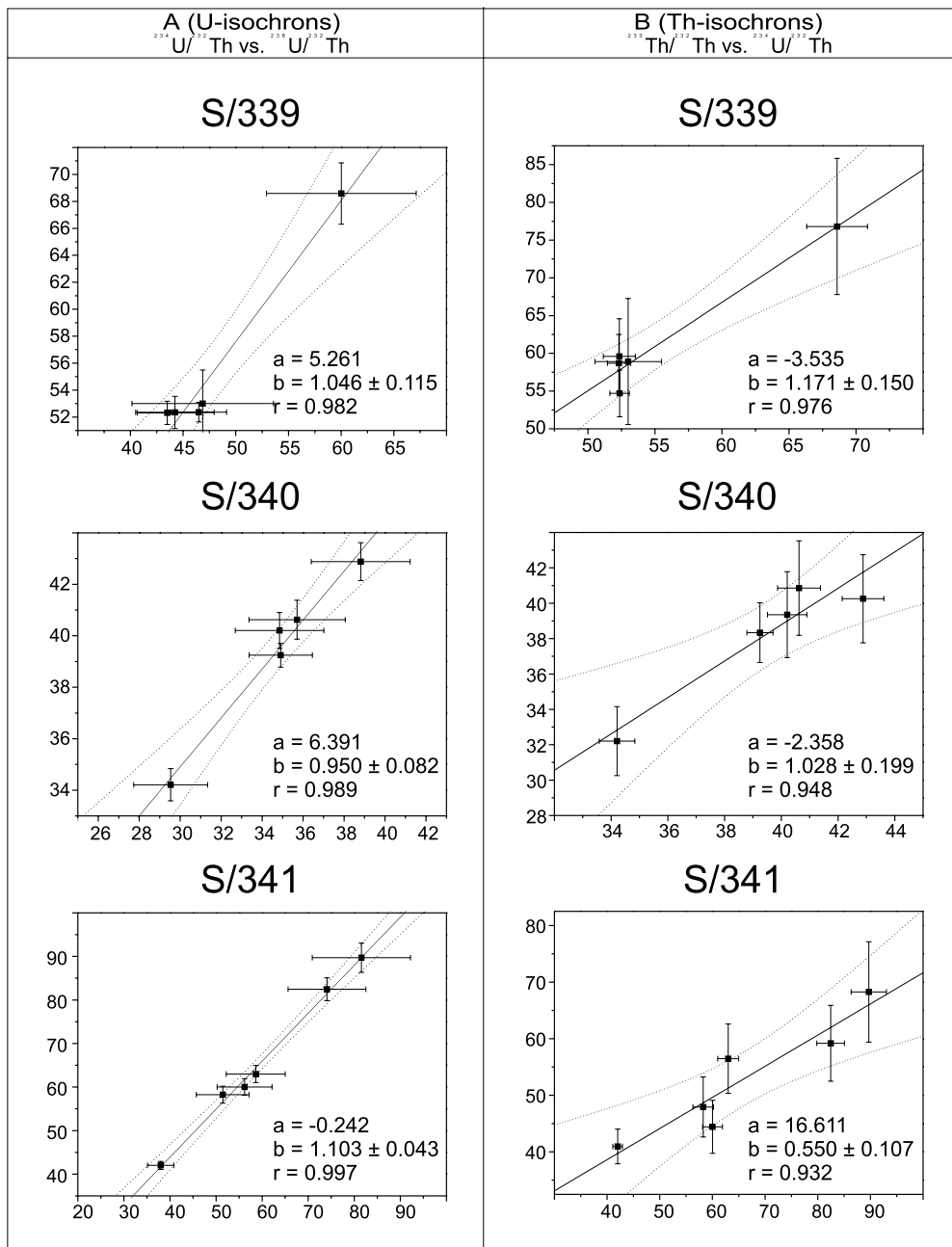


Fig. 7 cont.
FL isochrons continued.

Table 5. Corrected activity ratios and corresponding ages

Sample	$(^{230}\text{Th}/^{234}\text{U})_0$	$(^{234}\text{U}/^{238}\text{U})_0$	Isochron Age (kyr)
Successive Leaching			
S/336	0.015 ± 0.012	1.297 ± 0.009	-
S/338	0.010 ± 0.001	1.148 ± 0.002	-
S/341	0.126 ± 0.071	1.119 ± 0.019	-
Full Leaching			
S/336	0.92 ± 0.25	1.065 ± 0.049	Min. 117
S/337	0.53 ± 0.35	1.12 ± 0.11	81^{+130}_{-59}
S/338	0.78 ± 0.11	1.208 ± 0.038	147^{+54}_{-59}
S/339	1.17 ± 0.15	1.05 ± 0.12	-
S/340	1.03 ± 0.20	0.950 ± 0.082	-
S/341	0.55 ± 0.11	1.103 ± 0.043	85^{+29}_{-59}

- All opposite cases (addition of U or/and Th) are also possible. One of these scenarios, the accumulation of U with a low $^{234}\text{U}/^{238}\text{U}$ ratio is likely to have happened because has showed before, samples with lowest $^{234}\text{U}/^{238}\text{U}$ ratio have higher U contents.

The check for open system is rather difficult but can be tested by plotting $^{234}\text{U}/^{238}\text{U}$ versus $^{230}\text{Th}/^{238}\text{U}$ according to Ivanovich and Harmon (1992). Unfortunately, this checking does not work with impure carbonates. Nothing in this case is evident. The plot of the U activities in function of the deep of the profile is very useful to check for mobilisation or deposition of U and Th. **Fig. 4a** correspond to such a kind of representation. As no trend is detectable for the U contents within the profile, there is no material proof for an open system.

Because ^{14}C , TL and U-series dating methods have shown discrepancies of ages within the stratigraphy it is hard to believe that the system has been open for all the isotopes engaged in these methods.

More likely, a mixing of carbonates with different isotopic ratios might have happen, though such a mixing is hardly detectable but with microscopical (e.g. SEM) or micromorphological study. A microscopical study can provide some useful information if there are corroded carbonate grains. In this case, U mobilisation is probable. Monger *et al.*, 1998, carried out such an approach. They showed that the ^{14}C discrepancies were due to dissolution or transport of the carbonates in the profile.

Another approach could be to look for the stable isotopes along the profile. It could give information if there is any heterogeneity in the stable isotope composition, which is likely to happen with a mixing of carbonates.

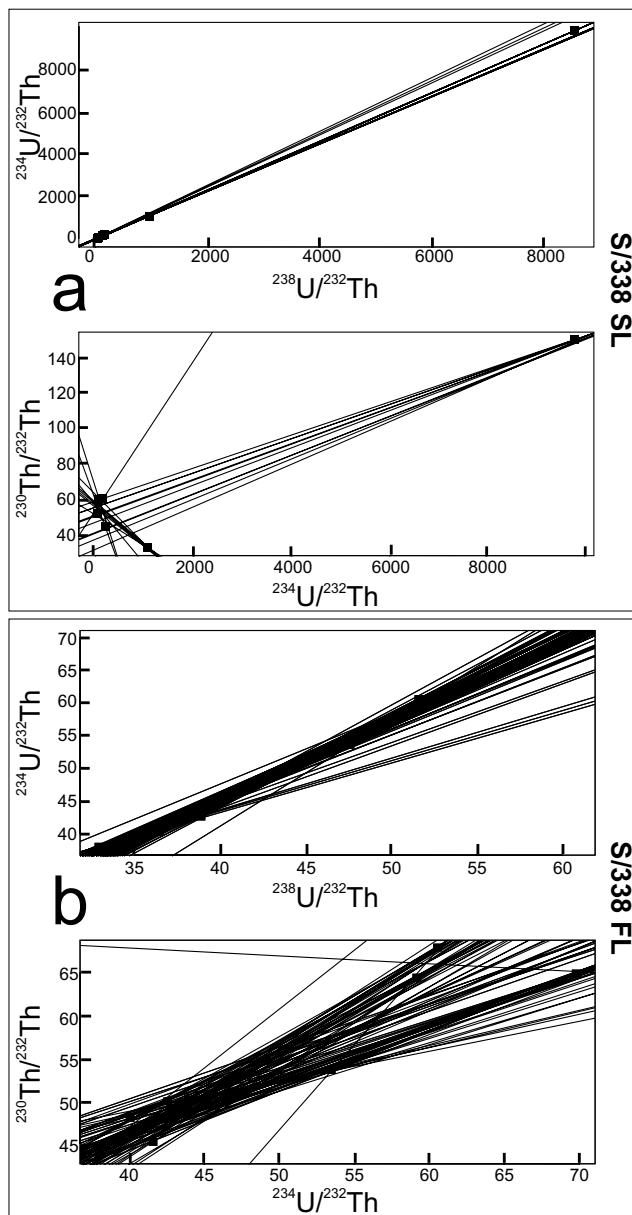


Fig. 8. Sub-isochron test. Part a. represents the test for SL of sample S/338. Part b. represents the test for FL of sample S/338.

CONCLUSION

This study has shown that using the Successive Leaching (SL) is a poor method to date impure carbonates, because of a strong isotopic fractionation during acid treatment. This problem can be avoided by using the Full Leaching (FL) method. Unfortunately, no valid results were found because the sediments of Jaroszów seem to have been either an open system or mixing of carbonates with different isotopic ratios, where the latter is more probable to have occurred during the aging process.

The result of this study is that marly sediments from Jaroszów are not suitable for U-series dating; the question about Jaroszów chronology is still open.

APPENDIX

If there is no isotope fractionation, at the time of dissolution, all data points are lining up along a straight line. As a test for isotope fractionation, we used to plot all possible sequences of three points for each isochrons. If one compares the slopes of all the sub-sets for one sample, they should give us the same corrected activity ratio (within the error range) if there is no isotopic fractionation.

The number of possible sub-sets (without repetition) of data is given according to the following relation:

$$C_n^p = \frac{n!}{(n-p)!p!}$$

Where n is the number of data and p the number of point used to plot the sub-isochrons.

As our isochrons are built with 5, 6, and 9 points, combinations for plotting sub-sets of three data points are respectively: 10, 20, and 84.

In **Fig. 8a** are plotted sub-isochrons for the SL of sample S/338. No detectable isotope fractionation with U isotopes is detected. On the contrary, ten of twenty sub-isochrons plotted in the $^{230}\text{Th}/^{232}\text{Th}$ versus $^{234}\text{U}/^{232}\text{Th}$ diagram are out of the error limits of the original isochron. We consider it as a proof of isotopic fractionation of the Th isotopes.

Fig. 8b is the same representation for FL of sample S/338. No U-sub-isochrons are beyond the confidence bend of the original isochron. And only three of eighty-four for the Th-sub-isochrons. This is less than 1 sigma standard deviation; no fractionation seems to occur with the Full Leaching method.

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