Improvement Of The U-Th Method For Dating Of Impure Calcite Having A Large Amount Of Clay And Very Low Uranium Content

Samer Farkh, Nafez Harb, Katia Haddad, Zaher Zeaiter, Samir Farkh

Abstract: The U-Th method, also called series method of uranium, is improved by a new experimental protocol and successfully applied to the impure calcite (with uranium concentration <0,05 dpm/g) which was previously difficult to be dated accurately. Our experiments performed on 15 calcite samples taken from France and Morocco, have highlighted the importance of this methodological improvement by enabling: (i) the elimination of 100 % of clay residues, (ii) the reduction of calcite quantity necessary to the chemical manipulation from 20g to 5g, (iii) the analysis of calcite samples poor in uranium and on the other hand rich with clay and (iiii) the reduction of the lower limit of the U-Th method from 10 Kyrs to 6 Kyrs. The optimization of U-Th method in this work provided a better dating of the accurate age of calcite. Thus, this technique is important for the chemical analysis of stalagmite floors of different caves in the region of the Near East.

Keywords: Calcite, U-Th method, Dating, Sample cleaning, Clay residues, Uranium, Cave floors.

INTRODUCTION

The U-th method combined with ESR method (Bahain et al., 2010) aims to date the accurate age of mammals teeth affected by water leaching and with delayed uranium incorporation. This allows specifying the age of calcites deriving from limestone tufa (Boudad et al., 2003, Antoine et al., 2006) and from speleothems (Farkh, 2004; Michel et al., 2013; Pons-Branchu et al., 2014) which behave in a closed system. In the case of forming stalagmite floors in archeological layers, an excess of thorium deriving from clay can be noted. This could limit the effectiveness of the method (Shen, 1985) especially when the concentration of uranium is low such the case of stalagmite floors of Karain site in Turkey, where the uranium concentration is less than 0.05 dpm/g (Tab.1). Furthermore, the drilling in floors does not allow the extraction of sufficient calcite quantity to analyze and which must be at least 20g. To overcome, these two problems affecting the application and the analysis of the U-Th method, it was important to modify the experimental procedure described by Shen and adapt it to the impure calcite samples under the delicate conditions which leave residues during the chemical manipulation. These residues, essentially clay, represent a serious limitation. In the case where the residue is around 3%, which does not influence the age measuring of the sample, Shen dissolved it with concentrated hydrochloric and hydrofluoric acids. However this is a difficult and long procedure. The challenge was to find a solution for such residue. This is why we adopted a cleaning method which allows to overcome the difficult part of using concentrated acids.

- *Samer Farkh , Zaher Zeaiter, associate professors, Lebanese University, Faculty of Sciences (I), Beirut, Lebanon. E-mail: farkhsamer@yahoo.fr*
- *Nafez Harb, Katia Haddad, Samir Farkh, associate professors, Lebanese University, Faculty of Sciences (III), Beirut, Lebanon.*

The new method made the experimental protocol easy to use. It was described by Kaufman and Broecker (1965), Ku and Broecker (1967), Ku (1976) and Shen (1985). Bischoff and al (1988) have applied it to fossil teeth and introduced it to the laboratory of Prehistory (M.N.H.N.) at Paris in 1989. The principal objective of this work was to apply the cleaning method, first to the impure calcite samples rich in uranium till the samples poor in uranium obtained from different sites in France and Morocco. Second to the impure calcite samples of stalagmite floors from Karain site having a very small quantity of uranium and which were previously difficult to analyze. The evaluation of the amount of uranium and clay residue present in some of the calcite samples was assessed by a standard infrared spectroscopy.

MATERIALS AND METHODS

Cleaning technique:

The simple and effective cleaning technique, used for the first time, is detailed as follows: The first stage was to know how to clean an impure calcite sample. First, we started to clean the most compact part of the sample where a low porosity is visible. The processed sample must be weighted each time to assess the cleaning efficiency with respect to its size. To obtain a good result, one preserves only the purest part of the rough sample. All the visible impurities (surface encrusting, clay, manganese and iron oxide inclusions brown, black and red, respectively) are to be eliminated by a dentist strawberry as much as possible. Unfortunately, the dust that was released from the cleaning makes the part intended for the analysis invisible. To avoid this confusion, we washed the sample with ethanol which gets evaporated very quickly especially with the frequent use of the strawberry. It is to be noted that this stage is very important in the cleaning of calcite, related to the fact that it makes it possible to easily eliminate the impurities without increasing the weight of the sample. The same operation was repeated several times until the complete elimination of all non-white parts of the sample. Finally, we measured the weight of the cleaned sample before heating it for two hours at 500°C (Shen, 1985).
The second stage was to analyze several impure calcite samples varying from being very rich in uranium to very poor in uranium, in order to be able to control the application of the

U-Th method on samples that are very low in uranium and clay. The results obtained are represented in table 2.

Infrared spectroscopy:
This method is considered as none or low destructive. It is used in archeological analysis and for the quantification of substances constituents. Analysis of two selected samples was carried out as previously described (Slimane et al., 2002).

RESULTS AND DISCUSSION

The cleaning of impure calcite sample, step that seemed essential for better analysis, was made carefully. For best results, only the purest part of the raw sample was kept. We did not use the water while washing calcite, where the dust fills the sample, to avoid increasing its weight. Indeed, the use of ethanol seemed simple to do and its use was crucial in cleaning calcite because it

Table 1: Calcite samples of Karain cave

Karain calcite	Uranium (dpm/g)
KRF2	0,020
KRF1	0,036
KRA8	0,035
KRA7	0,036
KRA6	0,034

Table 2: Impure calcite samples with various uranium contents

Sample	^{238}U (dpm/g)	$^{234}U/^{238}U$	$^{230}Th/^{232}Th$	$^{230}Th/^{234}U$	Age (kyrs)
MA0201T	5.896	**2.773** ± 0.015	>100	**1.076** ± 0.027	**263** +22/-19
MA0304T	6.021	**2.690** ± 0.008	>100	**0.912** ± 0.030	**177** +12/-11
MA0202T	1.608	**4.659** ± 0.025	>100	**0.249** ± 0.006	**30** ± 0.8
MA0203T	1.551	**5.042** ± 0.056	>100	**0.164** ± 0.006	**19** ± 0.7
MU0203C	0.299	**1.443** ± 0.032	>100	**0.377** ± 0.026	**50** ± 4
MU0204C	0.162	**1.440** ± 0.035	>100	**0.888** ± 0.032	**193** +20/-17
ST3-III	0.357	**1.011** ± 0.022	>100	**0.099** ± 0.009	**11.3** ± 1.1
ST2-III	0.620	**1.023** ± 0.021	>100	**0.056** ± 0.005	**6.2** ± 0.6
EXT2-3	0.387	**1.057** ± 0.022	>100	**0.064** ± 0.005	**7.2** ± 0.6
Mettamis03	0.408	**1.052** ± 0.014	>100	**1.032** ± 0.024	**>350**
Caours03	0.090	**1.224** ± 0.035	>100	**0.753** ± 0.028	**142** +12/-11
Val.Seine03T	0.062	**1.184** ± 0.055	>100	**1.165** ± 0.075	**>350**
JU0303C	0.051	**1.007** ± 0.054	>100	**1.151** ± 0.064	**>350**
JU0101C	0.077	**1.046** ± 0.037	>100	**0.388** ± 0.019	53 ± 4
JU0302C	0.051	**0.973** ± 0.051	>100	**1.202** ± 0.064	>350
All samples presented no residues					

distinguished the pure part from the impure part and being a solvent that evaporates quickly, it did not have an influence on the weight of the sample. Here the repeated weighting of the sample was necessary to know if we had to increase the cleaning steps taking into account the size of the sample. Using this method of cleaning, we were able to analyze 15 samples by the U-Th method, with different uranium contents ranging between 0.05 and 6 dpm. The results showed its effectiveness (table 1). All samples do not show clay residue. We also lowered the amount of calcite used in chemical handling from 20g to 10g and from 10g to 5g which is the new limit for a significant measurement. This last step was very important for the analysis of Karain samples where the amount of 5g (instead of 20g needed in the classic procedure) was sufficient. No residues were detected for all tested samples, something which was not performed by Shen's method (1985) and with an error in determining the age of about 10%. This is certainly because of the improvement of the cleaning mode that we have applied. Therefore, regardless of the uranium content and despite the small amount of calcite used, the result was always satisfactory and the error is kept at this same percentage for too recent ages to about 6 Kyears instead of 10 Kyears for the classic method. Samples listed in bold in Table 2 were taken from travertine rich in uranium from the region of Morocco (Boudad et al., 2003). We used them to test the effectiveness of our cleaning technique by applying infrared spectroscopy analysis to samples (MA0201T and MA0202T) to reassure the absence of clay residue. Both spectra reveal two major peaks corresponding to calcite and aragonite with a total neglect of the clay (Fig. 1).

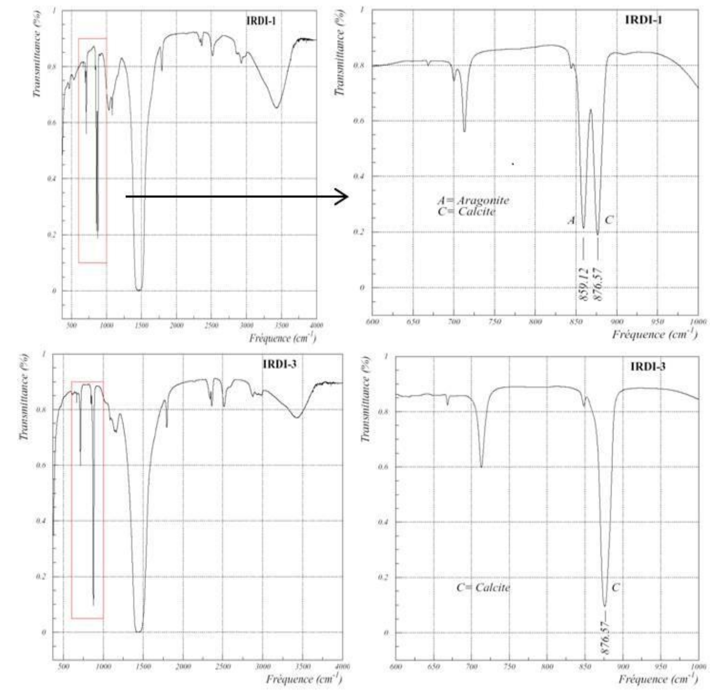

Figure 1: *Infrared spectroscopy spectrums of MA0201T (Irdi-1) and MA0202T (Irdi-3)*

CONCLUSION

Calcite which are substances more or less abundant in caves, are now regarded as sensors to assess the condition and estimate the age of these natural geological sites. The improvement we have made to the U-th method helped overcome several problems in the chemical manipulation of calcite contributing in a fundamental way to the determination of the age. Our improved U-th method has (i) made chemical analysis optimal with an almost complete absence of residues in samples, (ii) decreased the amount of calcite used in chemical handling from 20g to 5g and (iii) reduced the lower limit of the U-Th method from 10000 years to 6000 years with the same % of error on age. The technique adopted in this work is intended to be applied to calcite samples taken from stalagmite cave floors "Karain" in Turkey, the "Jeita" cave in Lebanon and travertines seen near these caves. Thus, this study can be extended to other caves in order to reconstruct paleoclimatic conditions that prevailed during the Quaternary period in this region of the Near East.

ACKNOWLEDGMENTS

We thank the team of Geochronology Laboratory of Prehistory of MNHN in Paris where calcite samples were analyzed. We also sincerely thank the Laboratory of Geology MNHN for infrared analysis. We also thank the Lebanese University for the support that has brought us.

REFERENCES

[1] J.J. Bahain, C. Falguères, J.M. Dolo, P. Antoine, P. Auguste, N. Limondin-Lozouet, J.L. Locht, A. Tuffreau, H. Tissoux, S. Farkh, “ESR/U-series dating of teeth recovered from well-stratigraphically age-controlled sequences from Northern France,” Quaternary Geochronology, 5 , 2-3 , pp. 371-375. 2010.

[2] J.L. Bischoff, R.J. Rosenbauer, A. Tavoso, H. de Lumley, “A test of uranium-series dating of fossil tooth enamel: results from Tournal cave France,” Applied Geochemistry, Vol. 3, pp. 145-151. 1988.

[3] L. Boudad, L. Kabiri, S. Farkh, C. Falguères, L. Rousseau, J. Beauchamp, E. Nicot, G. Cairanne, “Datation par la méthode U/Th d'un travertin quaternaire du Sud-Est marocain: implications pendant le Pléistocène moyen et supérieur,” C.R. Géoscience, 335, pp. 469-478. 2003.

[4] A. Kaufman and W.S. Broecker, “Comparison of ^{230}Th and ^{14}C ages for carbonate materials from lakes Lahontan and Bonneville,” Journal of Geophysical Research, 70, pp. 4039-4054. 1965.

[5] T.L. Ku, “The uranium series methods for age determination,” Ann. Rev. Earth. Planet. Sc., 4, pp. 347-379. 1976.

[6] T.L. Ku and W.S. Broecker, “Uranium, thorium and protactinium in a manganese nodule,” Earth and Planetary Sciences letters, Vol. 2, Issue 4, pp. 317-320. 1967.

[7] P. Antoine, N. Limondin-Lozouet, P. Auguste, J.L. Locht, B. Galheb, J.L. Reyss, E. Escude, P. Carbonel, N. Mercier, J.J. Bahain, C. Falguères, P. Voinchet, “Le tuf de Caours : mise en évidence d'une séquence emienne et d'un site paléolithique associé,” Quaternaire, 17, 4, pp. 281-320. 2006.

[8] E. Pons-Branchu, R. Bourrillon, M. Conkey, M. Fontugne, C. Fritz, D. Garate, A. Quilès, O. Rivero, G. Sauvet, G. Tosello, H. Valladas, R. White, “U-series dating of carbonate formations overlying Paleolithic art: interest and limitations,” Bulletin de la Société préhistorique française, 111 (2). pp. 211-224. 2014.

[9] S. Farkh, “Contribution à la datation des niveaux moustériens de la grotte de Karaïn (Antalya, Turquie) par les méthodes des séries de l'uranium (U-Th) et la résonance de spin électronique (ESR): méthodologie et paléoclimatologie,” Thèse du Muséum National d'Histoire Naturelle et Université Pierre et Marie Curie (Paris VI). 2004.

[10] S. Guanjun, “Datation des planchers stalagmitiques de sites acheuléens en Europe par les méthodes des déséquilibres des familles de l'uranium et contribution méthodologique,” Thèse du Muséum National d'Histoire Naturelle et Université Pierre et Marie Curie (Paris VI). 1985.

[11] S. Hachi, F. Fröhlich, A. Gendron-Badou, H. de Lumley, C. Roubet, S. Abdessadok, “Figurines du Paléolithique supérieur en matière minérale plastique cuite d’Afalou Bou Rhummel (Babors, Algérie). Premières analyses par spectroscopie d’absorption Infrarouge,” L'Anthropologie, Volume 106, Issue 1, pp. 57-97. 2002.

[12] V. Michel, G. Shen, C.C. Shen, C.C. Wu, C. Vérati, S. Gallet, M.H. Moncel, J. Combier, S. Khatib, M. Manetti, “Application of U/Th and 40Ar/39Ar Dating to Orgnac 3, a Late Acheulean and Early Middle Palaeolithic Site in Ardèche, France,” PLoS ONE, 8(12): e82394. doi:10.1371. 2013.