L'Homme de Néandertal, vol. 1, LA CHRONOLOGIE, Liège, 1988, pp. 11 à 16

URANIUM-SERIES DATING OF CONTAMINATED CALCITE DEPOSITS

by

Henry P. SCHWARCZ * and N. CESAR *

The use of uranium-series (henceforth, U-S) dating in archaeology has allowed archaeometrists to extend the time scale of human cultural and biological evolution beyond the limits of ^{14}C dating. Using the U-S method it is possible to date certain types of deposits ranging in age up to a maximum limit of 350,000 years. The datable materials include (ranked approximately in order of their suitability for dating): coral, stalagmitic calcite, travertine, molluscan carbonate, tooth enamel, bone, marl, calcrete, and organic matter (peat, wood). The best materials that are commonly found in an archaeological context generally consist of relatively pure, chemically precipitated calcite. "Pure" in this instance principally refers to the amount of matter that was incorporated in the deposit in the form of detritus. The presence of this extraneous detrital component interferes with the dating process in two ways: 1) it may contain organic matter or clay minerals which interfere with the chemical extraction of uranium (U) and thorium (Th) from the sample, and thereby decreses the precision of the date; 2) the detritus may contribute to the sample, at the time of its deposition, a component of ^{230}Th that imparts an apparent finite age to the sample. While that "unsupported" ^{230}Th decays away in time, it will continue to make the apparent age of the sample greater than its true age, up to the age limit of the dating method. This problem has been discussed in various papers on U-S dating, e.g., SCHWARCZ (1980).

This second problem is particularly serious in archaeological sites where the calcite deposit has formed as a stratum in a sequence of detrital deposits, for example in the filling of a cave. Fortunately it is always possible to recognize the presence of the detrital contaminant because the ^{230}Th is accompanied by ^{232}Th, a long-lived isotope of Th that is ultimately derived from the weathering of crustal rocks, and is commonly associated with clay minerals. During the U-S dating of a calcite sample, both Th isotopes will be detectible by alpha spectrometry, if present. The abundance of ^{232}Th can be used as a measure of the *initial* concentration of ^{230}Th in the sample (most of which may have, by now, decayed away due to the 75,000 y half life of this isotope).

Various methods have been devised to "correct" for this detrital contaminant, making use of the ^{232}Th activity. The most widely used method in use at present is a graphical technique in which a plot of the ratios of isotope activities is used to obtain the parameters necessary for the age equation: $^{230}Th/^{232}Th$ vs $^{234}U/^{232}Th$ and $^{238}U/^{232}Th$ vs $^{234}U/^{232}Th$. If the data form linear arrays on these diagrams then the slopes of the lines are

---

* Dept. of Geology, McMaster University, Hamilton, Ontario, Canada, L85 4MI.

equal, respectively, to $^{230}Th/^{234}U$ and $^{234}U/^{238}U$ ratios. The samples whose analyses are plotted must satisfy the following criteria: a) they must be mixtures of a uniform, pure, chemically precipitated calcite mixed in varying proportions with a uniform, homogeneous detrital "phase" (e.g., mud, silt, clay); we shall henceforth call this mixture "dirty calcite"; b) there must be no isotopic or chemical fractionation of Th or U during the analysis procedure, so that the isotope activity ratios of the minor amounts of detrital Th and U that are taken into solution should be the same in each of the analysed aliquots. The fact that the samples lie on a single line is a *de facto* proof of (a); there is no easy way to demonstrate (b). If these two conditions are satisfied, then the respective slopes give the isotope ratios for the chemically precipitated calcite component of the mixture. These ratios, in turn, are used to determine the age of the sample as described in SCHWARCZ (1980).

There have been two different approaches in using this method: 1) in the method of KU and LIANG (1984) only two points are used to determine the slope, namely, a point for the insoluble residue (R) and a point for the soluble "leachate" (L) (Figure 1 a; 2) in the method used by SZABO and STERR (1978) and this author (e.g., SCHWARCZ and SKOFLEK, 1982) the plotted points consist of analyses of a number of replicate leachate solutions, obtained by the analysis of several aliquots of the same calcite deposit. It is understood that the all these aliquots were deposited at the same time (coeval), and that there is some natural variation in the proportions of detritus to calcite, which results in a variation in the isotope ratios of the leachates (Figure 1 b).

While both methods (a) and (b) seem to give satisfactory age data, it would be desirable to have some independent confirmation that the methods are both theoretically and experimentally valid. The present paper is intended to partially satisfy that need; a more complete version of this discussion is in preparation (SCHWARCZ and PRZYBYLOWICZ, 1988).

The theoretical proof was in effect presented by KU and LIANG (1984) who derived an equation for the slope of a line through the leachate (L) and residue (R) points as described above. It can be easily shown that their equation also applies to the case of an array of leachate points from several aliquots of dirty calcite. The equations are as follows:

$$\left(\frac{^{230}Th}{^{232}Th}\right)_L = \left(\frac{^{230}Th}{^{234}U}\right)_C \left(\frac{^{234}U}{^{232}Th}\right)_L + \left[\left(\frac{^{230}Th}{^{232}Th}\right)_R - \left(\frac{^{230}Th}{^{234}U}\right)_C \left(\frac{^{234}U}{^{232}Th}\right)_R\right] \qquad (1)$$

$$\left(\frac{^{234}U}{^{232}Th}\right)_L = \left(\frac{^{234}U}{^{238}U}\right)_C \left(\frac{^{238}U}{^{232}Th}\right)_L + \left[\left(\frac{^{234}U}{^{232}Th}\right)_R - \left(\frac{^{234}U}{^{238}U}\right)_C \left(\frac{^{238}U}{^{232}Th}\right)_R\right]] \qquad (2)$$

where L refers to leachate and C refers to the chemically precipitated calcite component of the mixture. These equations confirm that the graphs as defined above (and shown in Figure 1) yield lines with slopes as stated above. The age of deposition of the dirty calcite can then be obtained from these slopes.

In order to test experimentally whether this method does in fact provide a good estimate of the age of the calcite, we have analysed artificial mixtures of detritus and calcite, where the age of the calcite was independently known. The calcite component consisted of a homogenized sample of a pure calcitic stalagmite from a cave in West Virginia (Lew's Last Climb). The detritus consisted of a homogenized sample of the mud that surrounded the base of the stalagmite and which had been deposited during one or more floodings of the cave by a stream, during the time that the stalagmite was growing. In spite of the presence of large amounts of mud in the cave, the stalagmite itself was extremely pure, and the amount of initial ^{230}Th present in it was negligible (as judged from the very high ^{230}Th/^{232}Th in the stalagmite at present). The age of the stalagmite was found to be 13 ± 1 ka, by ^{230}Th/^{234}U dating.

We prepared mixtures consisting of the following weight fractions of mud: 0.1 (2), 0.3; and 0.5. The mixtures dissolved in 2N nitric acid, filtered, and the leachates were then analysed following the procedures described by GASCOYNE *et al.* (1978). The analyses were then plotted and a linear regression was used to determine the ^{230}Th/^{234}U and ^{234}U/^{238}U ratios. From these the age was determined: 12 ± 2 ka, indistinguishable from the age of the pure calcite (Figure 2; only the graph for ^{230}Th/^{234}U determination is presented; the ^{234}U/^{238}U ratio generally does not vary appreciably as a function of detrital contamination and the graph for the determination of this ratio is not shown). As expected, the ^{232}Th activity in the leachates increased with increasing proportion of detritus, although there was not a good linear relation between these variables. In a continuation of this study we are also analysing the residues to test the method of Ku and Liang.

It thus appears, on the basis of this test (and as confirmed by other data which will be reported later) that the leachates alone provide a satisfactory sample for age determination. The main advantage of this method is that it avoids the necessity of completely dissolving the silicate residue, which commonly contains small traces of U-rich detrital minerals (zircon, sphene, etc.) that can only be dissolved completely in strong acid, with great difficulty. Incomplete dissolution of these minerals might lead to fractionation of the U or Th isotopes. The attack with mild acid (2N nitric) used in the leachate method probably does not remove a significant part of the U or Th from these resistant minerals, and therefore the incompleteness of the dissolution may be less problematic. In any case, we cannot claim to understand in great detail the chemical basis for the present method, but it appears to work.

As a further demonstration of the utility of this method, we shall present some new results on the dating of dirty calcite from a cave in Ialy. A complete report on this study is in preparation (SCHWARCZ, BIETTI and GRÜN, 1987). The samples come from the cave Grotta Guattari located at the base of Monte Circeo, 100 km SE of Rome. The cranium of a "classical" Neandertal hominid was discovered there in 1950. The skull lays on the upper surface of a sequence of detrital deposits. Also present on the same surface were many bones of large mammals (horse, etc.) as well as large, rounded cobbles of rock. The skull, bones and cobbles were all encrusted with a coating of calcite. On cutting through a sample of this crust, we found that it consisted of several layers; we have carefully removed the outer layers and peeled off the innermost calcite layer which was partly contaminated with detritus. Four aliquots of this layer were analysed by uranium-series. The data are shown in Figure 3. The individual analyses of each aliquot of dirty calcite can, of course, also be used to obtain an age. These estimates are shown in Table 1, compared with the age as obtained from the slopes of the lines in Figure 3, determined by linear regression. Based on the latter technique, the age of the innermost calcite crust appears to be 51 ± 3 ka (where the error is based on the error in the slope). Note that the ages based on individual analyses are all *younger* than the slope-based estimate.

Other applications of the leachate method have been presented earlier by us (e.g. SCHWARCZ and SKOFLEK, 1982; SCHWARCZ and LATHAM, 1986; BLACKWELL and SCHWARCZ, 1986). It appears that this method can also be applied to samples in which the calcite component makes up only a small fraction of the total rock, such as a calcrete zone in a soil, or a calcite cemented sandstone. One should, however, note that the method assumes that the only acid-leachable carbonate component present in the rock is the chemically precipitated calcite whose age is sought. The detrital contaminant (sand, silt, etc.) may however also contain particles of limestone which also would dissolve during analysis.

This limestone component would generally have an apparently infinite age and would therefore give the leachate an anomalously great age. Furthermore, limestone typically does not contain any ^{232}Th and the presence of this material would therefore not be revealed by the analyses of isotope activity, themselves.

Acknowledgments: samples of calcite and dirt were provided by S. Worthington. Dr. A. Bietti and Prof. A. Segre assisted the senior author in collecting samples from Grotta Guattari. This research was supported by a grant from the Social Sciences and Humanities Reseach Council of Canada.

REFERENCES cited

BLACKWELL B. and SCHWARCZ H.P., 1986. Absolute age of the lower travertine at Ehringsdorf, DDR. *Quaternary Res. 25*: 215-222.

GASCOYNE M., SCHWARCZ H.P. and FORD D.C. , 1978. Uranium series dating and stable isotope studies of speleothems: Part I. Theory and techniques. *Proc. Brit. Cave Res. Assoc. 5* : 91 - 111.

KU T.-L. and LIANG Z.-C., 1984. The dating of impure carbonates with decay-series isotopes. *Nuclear Instr. and Methods 223* : 563-571.

SCHWARCZ H.P., 1980. Absolute age determination of archaeological sites by uranium series dating of travertines. *Archaeometry 22* : 3 - 24.

SCHWARCZ H.P. and SKOFLEK I., 1982. New dates for the Tata, Hungary, archaeological site. *Nature 295* : 590 - 591.

SCHWARCZ H.P. and LATHAM A.G., 1984. Uranium series age determinations of travertines from the site of Vertesszollos, Hungary. *Jour. Archeol. Sci. 11* : 327 - 336.

SZABO B. and STERR H., 1978. Dating caliches from southern Nevada by ^{230}Th/^{232}Th versus ^{234}U/^{232}Th versus ^{238}U/^{232}Th isochron-plot method. *U.S. Geological Survey, Open File Report* 78-701.

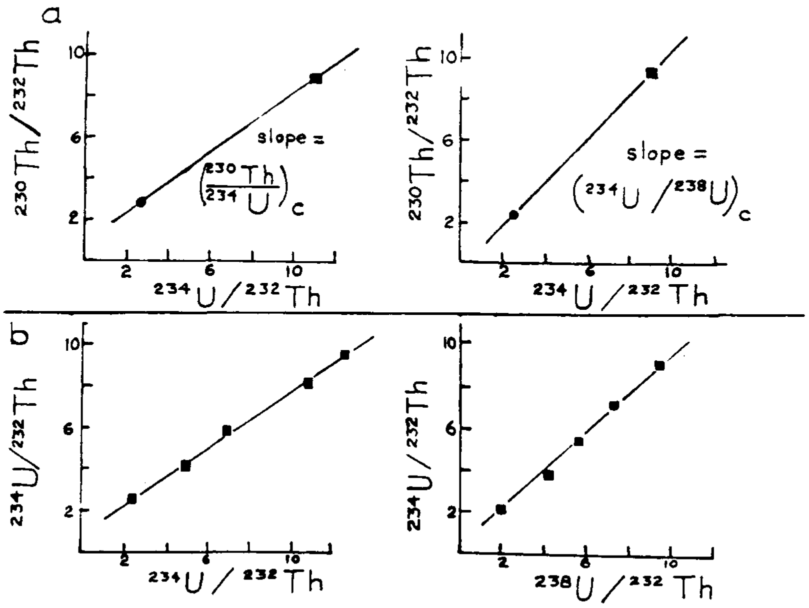

FIGURE 1

Isochron plots for determination of isotope ratios of the chemically precipitated (leachable) carbonate component in dirty calcite: a) Method of KU and LIANG (1984); (■) = leachate; (●) = residue; b) Leachate-only isochron (this paper); all points represent leachates from coeval samples with varying proportions of detritus.

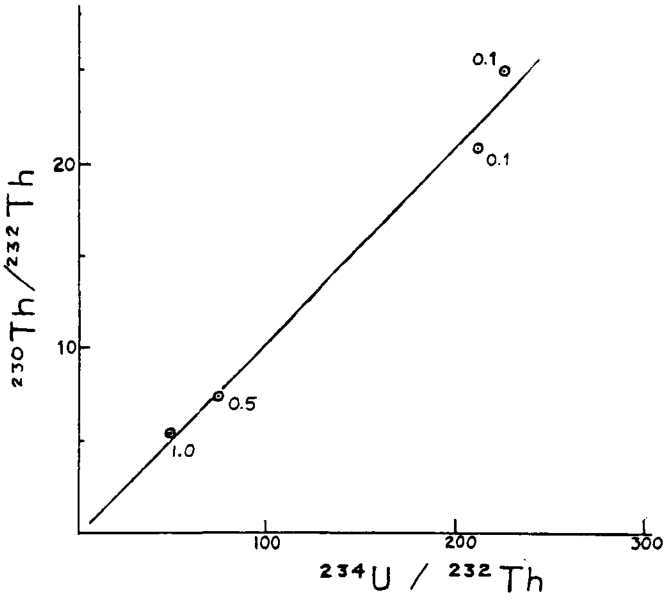

FIGURE 2

Isochron plot (Th-U only) for artificial mixtures of pure calcite (Age = 13 ± 1 ka) and associated detritus, from cave in West Virginia, USA. "0.1" = weight fraction of detritus in mixture. Slope corresponds to age of 12 ± 1 ka.

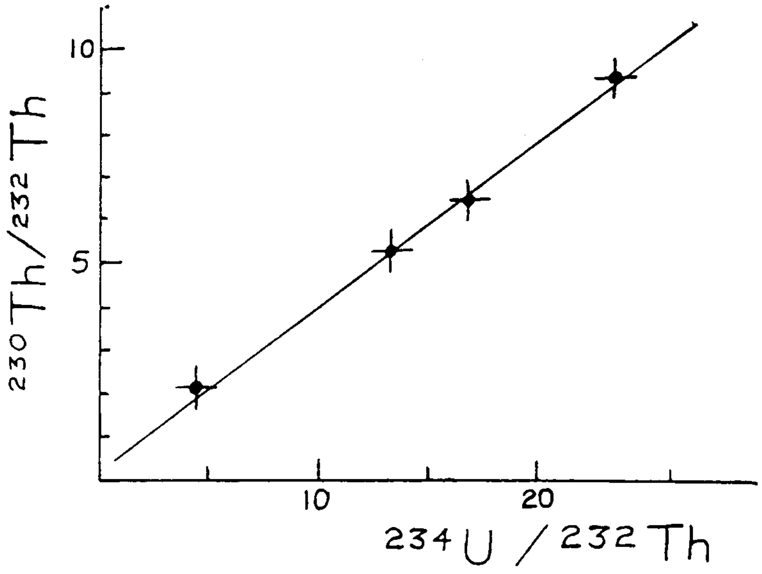

FIGURE 3

Isochron plot (Th-U only) for calcite layers covering bones at Monte Circeo, Italy. Slope corresponds to age of 51 ± 3 ka.