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Uranium–thorium dating method and Palaeolithic rock art

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ABSTRACT

Dramatic progress was seen in ^{14}C-dating with the introduction of accelerator mass spectroscopy (AMS) which made possible the direct dating of prehistoric artworks painted or drawn with charcoal. However, in the case of engravings and red paintings, only indirect methods can be used that allow us to date deposits that have covered the works over time (TL, U/Th, oxalates, etc.).

The uranium/thorium dating method gives reliable and relatively precise results in the case of massive speleothems, because the sampling is carried out at the heart of the material where the hypothesis of a closed system (that is, no exchange with the outside environment) is justified in most cases. Unfortunately, the situation is quite different in the case of thin layers of calcite that overlie Palaeolithic cave drawings. The conditions under which calcite forms depend largely on the hydrologic activity, which has greatly varied over the course of the Upper Palaeolithic and Holocene. In many cases, we can see that the growth of speleothems stopped during much of the Upper Palaeolithic. Consequently the ages obtained are minimum ages (terminus ante quem) which are frequently much younger than the real ages of the underlying artworks.

Moreover, a much more serious but rarely considered source of error contradicts the assumption of a closed system. In thin layers of carbonate deposits and in damp media, the uranium incorporated into the calcite during its crystallization may be partially eliminated because of its solubility in water. Uranium leaching causes an artificial increase of the age that may reach considerable proportions (e.g. a negative hand in a cave in Borneo was dated to 27,000 years by U/Th whereas its ^{14}C age was only 8–10,000 cal BP; Plagnes et al., 2003).

Due to these two contradictory sources of error, the dates given by the U/Th method may prove to be younger or older, with deviations that are much larger than the standard deviations given by laboratories. As a result it is nearly impossible and very dangerous to base archaeological reasoning on U/Th ages of Palaeolithic artworks, so long as the dates are not confirmed by an independent method, dating the carbonates in the same samples by ^{14}C being the best means of detecting anomalies.

The application of the U/Th method for the dating of prehistoric rock art is still experimental. Technical improvements (for less damageable sampling) and fundamental research on the causes of errors are needed.

1. Introduction

Numerical chronology is of paramount interest for archaeologists, particularly in the case of rock art which is an essential way of understanding the hunters-gatherers societies and the cultural links among human groups during the Upper Palaeolithic. In the last twenty years, the direct dating of organic pigments by ^{14}C-AMS has completely renewed the study of cave art, but red paintings and engravings remain out of reach. This is why the interest is now

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focussed on indirect methods, such as the uranium/thorium technique allowing the dating of calcite deposits covering the artworks.

The method is not new. The use of the disequilibrium between ^{234}U and ^{230}Th was first proposed for the dating of corals and it was subsequently applied to cave speleothems. In the case of massive stalagmites, samples are taken along the axis of growth and they are generally in good correlation with ^{14}C dating, confirming that calcite in the centre of stalagmites (i.e. isolated from the outside by deep layers of carbonates) does not exchange with the environment and can be considered as a closed system.

The hypothesis of a closed system is required for the application of uranium/thorium disequilibrium to rock art dating. Calcite incorporates some uranium when it crystallizes (because uranium compounds are soluble in water), but no thorium compounds which are insoluble. At this moment, the meter is set to zero. With time, ^{230}Th begins to appear due to the decay of ^{234}U and the activity ratio of the two elements may be used to determine the time elapsed since the calcite deposit.

However, several sources of error may seriously undermine the use of this method for the dating of cave art. First, calcite may have grown long after the artwork was made, which leads to underestimation of the ages of artworks. Second, calcite may behave as an open system. In that case, uranium removal or thorium input could lead to overestimation of the age. Let us examine, through specific examples, the effects of these two factors.

2. Causes of underestimation of the ages

It has been shown in several cases that secondary deposits of carbonates in caves are strongly dependent on climatic conditions. The rate of speleothem growth may be very fast or almost zero depending upon temperature, precipitation, vegetation and other environmental factors. For instance, in one Austrian cave there was almost no growth of a flow stone between 190 and 75 ka, except for a short interval between 135 and 125 ka during which time growth was extremely rapid (Scholz and Hoffmann, 2008). In the northern Alps, the growth of stalagmites was intermittent during the period 65–35 ka with four periods of arrested growth (Moseley et al., 2014). Genty and coworkers (Genty et al., 2004, 2005; Genty, 2008) observed that speleothems did not grow in the Chauvet cave (Ardèche) between 25 and 16 ka (Genty et al., 2004) and in Villars cave (Dordogne) between 31.5 and 16.5 ka (Genty, 2008). In contrast, in El Pindal cave (Asturias, Spain), the growth of stalagmites was observed between 25 and 11.6 ka, except for a short period of time between 18.2 and 15.4 ka during which speleothem growth completely ceased, probably due to extremely cold and dry conditions (Moreno et al., 2010). During the Holocene, growth rates seem to have been more regular (Lauritzen and Lundberg, 1999). Thus, there is no general rule and each case should be considered in relation to its own specific characteristics.

Nevertheless, the frequently observed interruption of calcite deposition during a part of the Upper Palaeolithic may explain why U/Th dates on calcite are often much younger than the real age of the underlying rock art, a fact generally recognized under the euphemistic term "minimum age" or terminus ante quem. This was recently demonstrated in the case of Chauvet cave. The ^{36}Cl dating of surfaces exposed to cosmic rays has shown that the collapse of the overhang was complete before 21 ka (Sadier et al., 2012). However the growth of a stalagmite on the internal rockfall began only 11,500 years ago (Genty et al., 2005) showing the absence of speleothem formation during about ten millennia.

3. Causes of overestimation of the ages

The U/Th ages may be overestimated for at least two reasons. The first one is widely recognized because it is easily identified and may be corrected. The second one, much more difficult to detect, is rarely taken into account in spite of its important consequences.

One of the possible reasons leading to age overestimation is the presence of thorium trapped in calcite during crystallization. As thorium is presumed to be insoluble, it would have to be imbedded in solid particles of detrital material such as silt or clay. In such particles, both isotopes of thorium, ^{230}Th and ^{232}Th, are assumed to be present in their natural proportions. Therefore, the presence of ^{232}Th, which does not belong to the ^{238}U family, reveals the importance of this contamination and the fraction of ^{230}Th not coming from ^{234}U decay may be subtracted. When the ratio $^{230}Th/^{232}Th > 20$, the correction is negligible. When the correction to be applied is more significant, the dates should be considered with caution or they should be rejected because they strongly depend on the chosen value for the initial proportion of the two isotopes. Values varying between 0.746 ± 0.2 (Moseley et al., 2013) and 1.5 ± 0.5 (Gozlar et al., 2000) are used, and it has been shown that the values vary in different layers of the same stalagmite (Cai et al., 2005b).

Correction for detrital thorium-containing particles is standard practice for specialists. However, there is another source of error, much more confusing because it is captious and difficult to detect. This derived from the opening of the system after the deposition of calcite. This cause of error is well known in the case of corals, but much more difficult to detect in the case of speleothems (Scholz and Hoffmann, 2008). The possibility of such error is seldom mentioned in spite of well-documented examples.

According to the kinetics of decay of the radioactive elements in the ^{238}U family, each element should reach a stationary state when the rates of formation and disappearance become equal, a situation known as secular equilibrium. For instance, the $^{230}Th/^{234}U$ activity ratio tends asymptotically toward a limit equal to 1 after approximately 500 ka. This applies only if there is no chemical exchange with the exterior (i.e. it is a closed system). It is therefore interesting to note that $^{230}Th/^{234}U$ activity ratios that are much higher than 1 have been observed for speleothems, which can be explained only by uranium removal or ^{230}Th input caused by the opening up of the system.

U/Th analyses of 130 speleothems coming from 28 caves in Northern Italy were studied in order to reconstruct the palaeoclimate (Borsato et al., 2003). In one third of the analyses, $^{230}Th/^{234}U$ activity ratios were higher than 1, whereas the $^{234}U/^{238}U$ remained close to 1, an observation that can only be explained by the opening of the system. Post-depositional phenomena are particularly frequent when the conditions that prevailed during speleothem formation have changed: water circulating in the internal porosity of the speleothem may cause dissolution, reprecipitation and recrystallization leading either to uranium removal or ^{230}Th input.

As the uranium concentration was not significantly lower in closed systems than in open systems, the authors of the above study do not favour the hypothesis of U removal. An input of ^{230}Th seems more probable as, contrarily to what is usually claimed, ^{230}Th is not rigorously insoluble, particularly when occurring as salts of organic acids such as fulvic and humic acids. The introduction of a very small quantity of ^{230}Th, not correlated with the incorporation of detrital thorium, may be responsible for $^{230}Th/^{234}U$ activity ratios that are greater than 1. The same phenomenon probably also takes place when this ratio is lower than one, causing an overestimation of the ages. This would explain why the ages of speleothems grown during MIS 5e were found to be 30–40 ky too old (Borsato et al., 2003).

A spectacular confirmation of ^{230}Th solubility was given by Whitehead et al. (1999). A 'contemporary' straw stalactite (i.e. less than a century old that could be assimilated to "zero age") was sampled in a cave of New Zealand and gave a U/Th age of 3520 ± 170 a. As ^{232}Th was virtually absent, thorium could not come from detrital particles, but was incorporated as soluble salts, probably organic ones. This study demonstrates that soluble ^{232}Th may be coprecipitated with calcite at the very moment of its formation giving it a false age of a few thousands of years. We cannot reject the hypothesis that ^{232}Th, present in the limestone of the cave, continues to percolate through the porosity and to accumulate during the growth of the speleothem leading to increasingly erroneous ages.

^{230}Th/^{234}U activity ratios that are higher than 1 are not exceptional. In an Egyptian cavern, 32 samples from 8 speleothems were analyzed (Dabous and Osmond, 2000; Railback et al., 2002). Nine of them presented ^{230}Th/^{234}U activity ratios between 1.5 and 15, these values being impossible in the hypothesis of a closed system (Fig. 1). The authors interpret their results by a phenomenon of recrystallization facilitating uranium leaching; this is in keeping with the fact that the highest ^{230}Th/^{234}U activity ratios correspond to the lowest uranium concentrations. Similarly, the growth of a flow stone in an Austrian cave ceased at 190 ka and began again at 135 ka. During this interval, dates were impossible to calculate due to the loss of uranium (Scholz and Hoffmann, 2008).

4. Attempts of dating rock art by U-series

In spite of the difficulties mentioned above, U/Th dating has become an important tool in many domains (palaeoclimate reconstruction, sea level fluctuations, ^{14}C calibration, etc.). In the domain of rock art, it is not surprising that the method has stimulated a great deal of research in the hope of going beyond the limits of ^{14}C. However the problems on rock surfaces are acute. The thin layers of calcite that form over the prehistoric paintings or engravings are often subjected to water flow that favours the leaching of soluble compounds. The large surface/volume ratio can be another aggravating factor. Given the causes of errors giving minimum ages (periods of no growth of calcite, the difficulty of dating only the lowermost layer of calcite in contact with the painting) and those giving exceedingly old ages (uranium leaching or ^{230}Th input), the margin of uncertainty is so wide as to severely limit the archaeological benefit.

In the present state of the technique, U/Th dating of rock art should not be accepted when unconfirmed by another independent dating method. The most straightforward method to use is ^{14}C dating of the carbonates in the same sample as this is commonly applied for the calibration of the radiocarbon time scale. Such cross-dating has been carried out in the case of a stencilled handprint in a cave in Borneo (Plagnes et al., 2003). The handprint was covered by a calcite drapery that was dated both by U/Th and ^{14}C. Samples were taken close to the pigment and at the outer edge of the drapery.

^{14}C dating of carbonates is not exempt from difficulties because carbonates contain a fraction of "dead carbon" (i.e. carbon no longer containing ^{14}C). As this fraction is generally unknown, an approximation is required, which increases the uncertainty. Using a minimum value of 5% and a maximum value of 20% of dead carbon, the radiocarbon ages in the Borneo case vary from 8000 to 10,000 cal BP. The precision is not good, but importantly the dates are in good agreement for the inner and the outer edges of the drapery. For the sample in contact with the pigment, that represents the beginning of calcite growth, the U/Th age is perfectly coherent. However, the sample taken at the outer edge of the drapery, which should normally be younger, gave an age of 27,000 years! (Fig. 2). The authors interpret this aberrant result by a partial dissolution of uranium that was probably washed out by the classical phenomenon of leaching. This interpretation is in keeping with the absolute concentration of uranium which was much lower at the outer limit of the drapery than at the inner edge.

The above study shows that the U/Th dating method can lead to aberrant results if the possibility of an open system is ignored. For this reason, it is absolutely necessary to control the results by an independent method and to document the absolute concentration of uranium for each measurement, which can help to detect anomalous data.

The necessity of a correlation between U/Th and other dating methods is indirectly illustrated by a recent study of a series of 50 dates obtained in Palaeolithic caves in the Cantabrian Region of Spain (Pike et al., 2012). The dates range from approximately 0 to 41 ka (Fig. 3). Two-thirds of the dates are much younger than expected and point to the Holocene, which is a consequence of the "terminus ante quem" principle. Among these 'too-recent" dates, there is one from Covalanas cave that is coherent with a former measurement made by another team (Bischoff et al., 2003). Though slightly different, the two results both fall in the Holocene, showing no correlation with the underlying painting. This may be due to accelerated calcite growth at the end of the last glaciation. It is also possible that the analyzed layer of calcite was not directly in contact with the painting.

On the graph in Fig. 3, four dates are much older than the others. Instead of considering these values as possible outliers, the authors

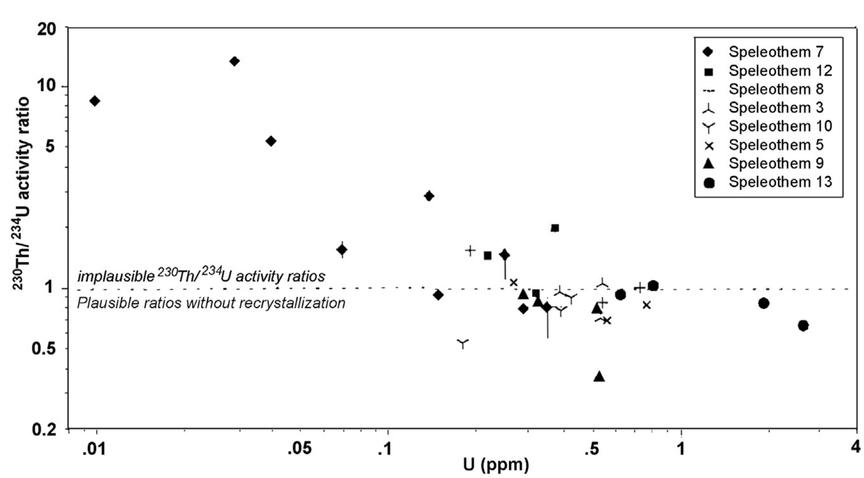
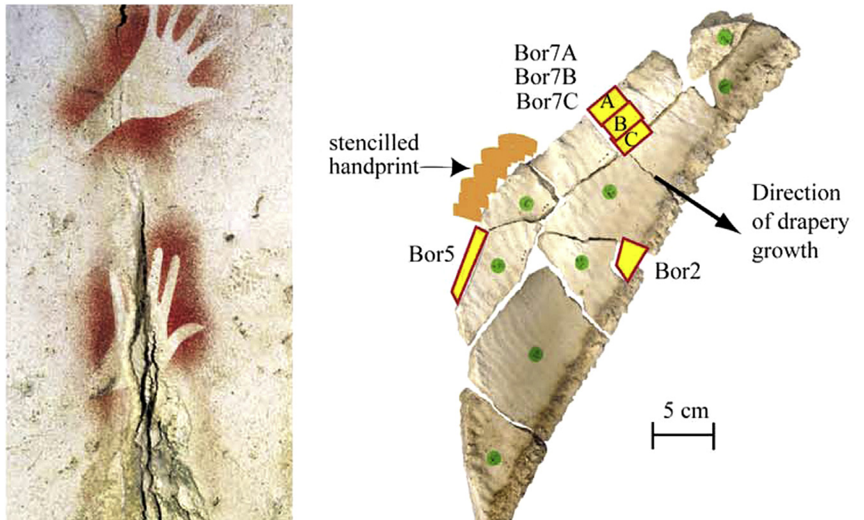


Fig. 1. Logarithmic plot of ^{230}Th/^{234}U activity ratios as a function of uranium concentrations of 32 samples from 8 speleothems from Waddi Sannur Cavern, Egypt (after Railsback et al., 2002).



	^{14}C calib age (dcf 5%)	^{14}C calib age (dcf 20%)	U/Th age	[U] ppm
Bor5	9,900-9,480	8,190-7,840	9,870	0.10797
Bor2	9,900-9,480	8,190-7,840	27,320	0.0572

Fig. 2. Cross-dating by U/Th and ^{14}C of a stencilled hand in Borneo (after Plagnes et al., 2003).

have concentrated their attention on them, because they open a debate on the "oldest Palaeolithic art". The possibility that these dates are overestimated due to an open system is not mentioned, although numerous cases have been documented in the literature. Several authors reacted immediately, questioning the reliability of these very old dates and the likelihood of the hypothesis that Neandertals could be the authors of the first parietal art (Bednarik, 2012; Clottes, 2012). In our opinion, such a discussion of Neandertal art is premature due to the high uncertainty surrounding these dates.

In some cases, two measurements were made in the depth of the calcite layer and the dates were found in the expected order, which was considered to be proof that calcite behaves as a closed system (Pike et al., 2012). However, the results are only qualitative, and the possibility that each date was somewhat affected by uranium leaching and/or ^{230}Th input cannot be excluded.

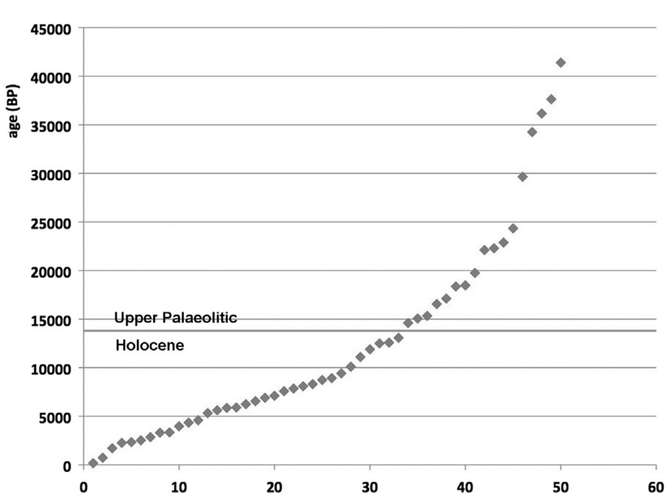


Fig. 3. Distribution of 50 U/Th dates obtained in Cantabrian Palaeolithic caves (after Pike et al., 2012).

A more precise sampling protocol was implemented by Aubert et al. (2007) in East Timor using laser ablation MC-ICPMS (multi-collector-inductively coupled plasma mass spectroscopy). A core sample "excavated" through the calcite layer overlying the paintings was later subdivided by laser ablation into layers about 100 μm thick to obtain a microstratigraphy. A thin layer of pigment imbedded in the deposit could be bracketed between 24 and 29.3 ka (Fig. 4A). Though the possibility of ageing due to an open system cannot be ruled out, this new technique has the advantage of avoiding the bias that comes from averaging the age of calcite that has been deposited over extended periods of time.

Recently, U/Th dating of paintings at Sulawesi (Indonesia) was performed using the same technique of laser ablation MC-ICPMS (Aubert et al., 2014). Dates in the range of 35–40 ka were obtained for the lowest sublayer of calcite less that 1 mm thick overlying several hand stencils (Fig. 4B). These dates are considered as "minimum ages", but the same reservation as above should be applied. In the absence of correlation with another dating technique, the possibility of an open system cannot be totally excluded. The fact that the ages are found in the expected order is insufficient.

5. A major drawback: invasive sampling over prehistoric rock art

The significant damage caused by sampling, conducted by scraping with a scalpel or drilling with a carbide drill bit (Pike et al., 2012) is a matter of grave concern (Fig. 5). The alternative technique of core sampling with a rotating diamond sawblade is probably also very invasive, as the excavated section is very large (up to 200 mm^2, corresponding to circular pits of 16 mm diameter) (Aubert et al., 2014). In recognizing this destruction, the "Decorated Caves" section of the French Commission of Historical Monuments has recently prohibited "the sampling of calcite for purposes of U/Th dating in the perimeter of decorated areas" (decision taken on 2013/10/24). Given the uncertainties of the U/Th method outlined above, a serious discussion needs to take place among physical scientists, archaeologists, conservation specialists and authorities concerning the costs and benefits of such sampling.

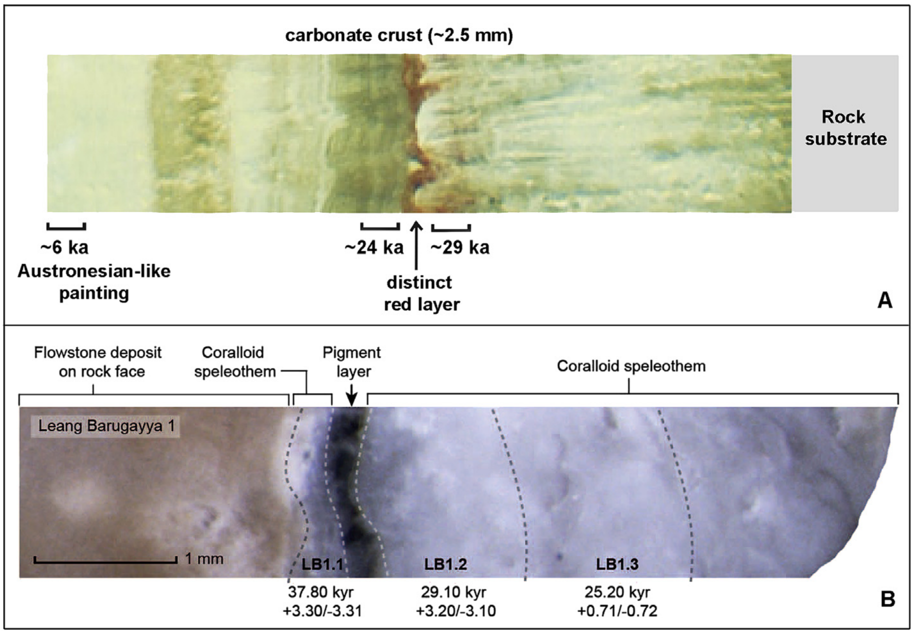


Fig. 4. Microstratigraphy of calcite samples covering prehistoric paintings. A. Timor: a pigment layer was bracketed between 24 and 29 ka (after Aubert et al., 2007); B. Sulawesi (Indonesia): a hand stencil was bracketed between 29 and 38 ka (after Aubert et al., 2014).

6. Cross-dating with other techniques

The possibility that calcite behaves as an open system should always be kept in mind, because it is very difficult to demonstrate that exchange did not occur. Even the common method of isochron diagrams does not permit us to exclude the possibility of an open system when detrital contamination is important (Geyh, 2001). A very small loss of uranium or input of ^{230}Th could lead to dates older by several thousands of years. This may hamper archaeological reasoning, particularly in the case of artwork production.

A correlation with ^{14}C dating of the same carbonate should always be done, since it does not require a supplementary sample. The difficulty is due to the fraction of dead carbon (dcf) incorporated in speleothem that can vary between 9 and 21% according to sites and locations in the sites (Genty et al., 1999) and may even vary along the same stalagmite (Cai et al., 2005a). The presence of dead carbon makes the ages older but the effect remains relatively limited (between 760 and 1900 years for extreme dcf values), so that the comparison of the ages obtained by U/Th and ^{14}C on the same sample may help to detect aberrant results. As a general rule, when the U/Th age is found to be significantly older than the calibrated ^{14}C age, an open system should be suspected. In the same vein, the uranium concentration should always be given in publications, as it is an important parameter in order to estimate the possibility of uranium removal.

The protactinium-231 (^{231}Pa) dating method may be used to check the results obtained by U/Th dating of calcite. ^{231}Pa belongs to the disintegration family of ^{235}U. It is thus completely independent of ^{230}Th and ^{238}U/^{234}U and may be useful to assess the reliability of U/Th dating using so-called concordia diagrams (based on the concordance of ^{231}Pa and ^{230}Th ages) (Cheng et al., 1998). The same hypotheses as in the case of thorium are required (absence of Pa at time zero and closed system). Up until to now, the method has been used mainly in the case of corals (Mortlock et al., 2005), much less in the case of cave speleothems, and not at all for rock art dating because the concentration of Pa is much lower than that of Th. However, developments along these lines are in progress (Dorale et al., 2004).

It is also possible to correlate U/Th dating with thermoluminescence (TL). This was attempted in La Garma cave (Cantabria) some years ago (González Sainz, 2003). U/Th ages and TL ages were obtained for the same calcite cord overlying a red ibex painting (Fig. 6). The values obtained with the two techniques are statistically compatible (at 2σ) because of the large standard deviations. In

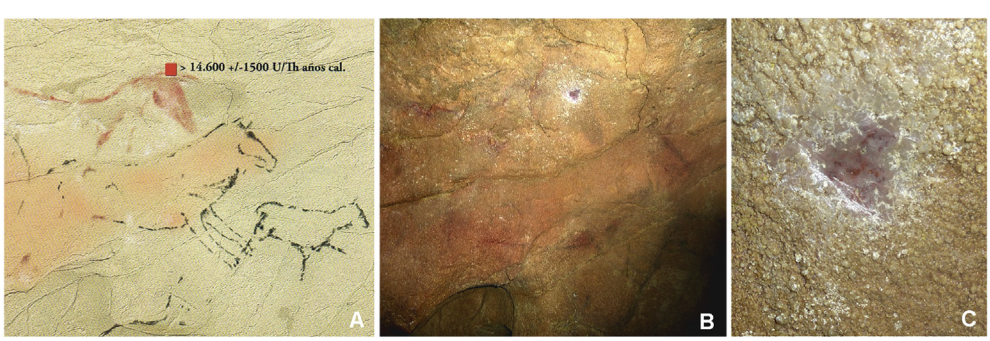


Fig. 5. Example of the damage caused by calcite removal for U/Th dating in Tito Bustillo cave (Asturias, Spain). A. Tracing of the panel (after de Balbín Behrmann and Alcolea González, 2013); B. zone of sampling; C. detail of the sample.

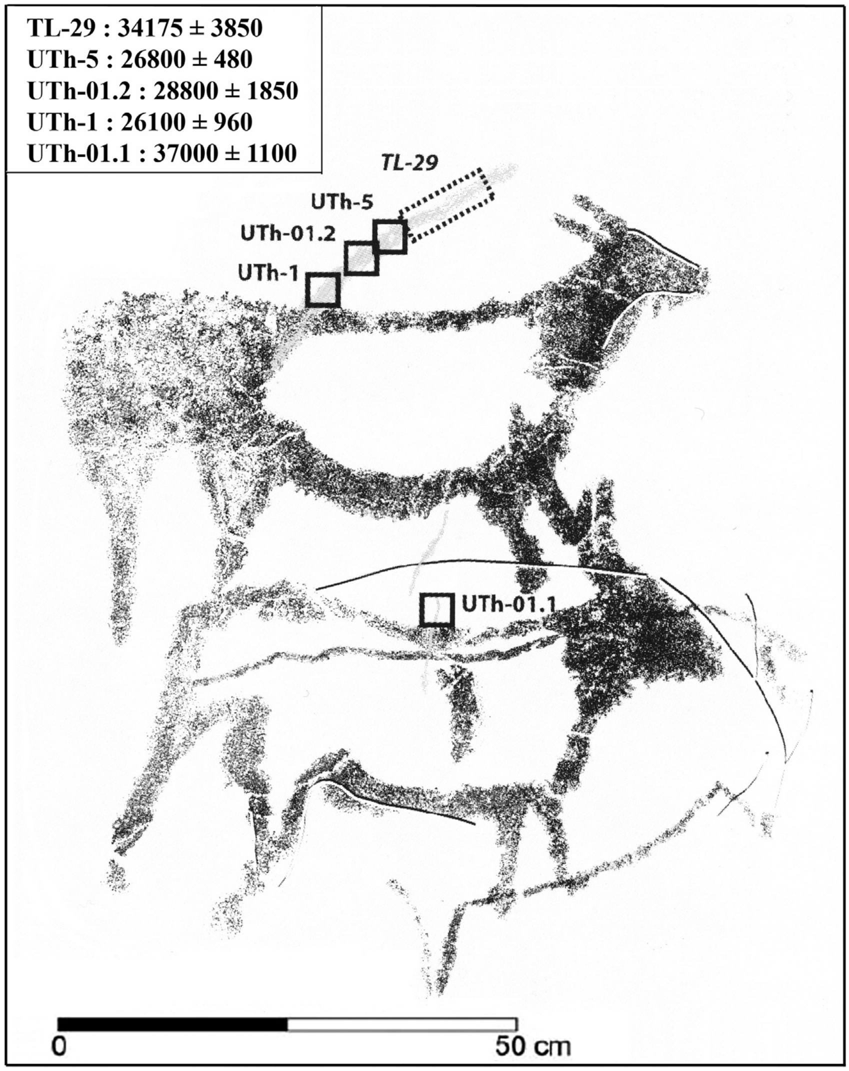


Fig. 6. Dating by U/Th and thermoluminescence (TL) of a calcite cord overlying a red caprid in La Garma cave (Cantabria, Spain) (after González Sainz, 2003).

this case, an open system is not likely as the U/Th ages are younger that the TL age, but the large gap between the two techniques prevents the archaeologist from building a clear chronological schema.

7. Conclusions

Uranium–thorium dating has proved its usefulness for the reconstruction of palaeoclimate, the assessment of sea level changes and ^{14}C calibration. In the case of samples taken along the growth axis of large stalagmites, far removed from the surface, chemical exchanges are probably absent and closed-system behaviour is expected. However, even in such cases, we have seen that open systems may be observed (Railsback et al., 2002; Borsato et al., 2003). Loss of uranium or input of ^{230}Th leads to anomalously old ages and sometimes to the impossibility to calculate an age when $^{230}Th/^{234}U > 1$.

For the application of U/Th dating to rock art, difficulties are still greater. Thin layers of calcite with low surface/volume ratio are particularly exposed to run off water and hence to uranium lixiviation. The fact that different samples taken in the thickness of the layer provide ages in the expected order is not enough to exclude an open system: loss of uranium may have occurred during the whole period of calcite growth leading to overestimation of the ages of each layer in the sample, but this possibility is widely disregarded by specialists.

Another drawback acts in the opposite direction. Time elapsed between the artwork and the beginning of calcite growth is unknown and may be very long, particularly during the Upper Palaeolithic, which leads in many cases to dates that are meaningless for the archaeologists.

These two opposite effects give an extremely wide range of uncertainty providing a weak base upon which to build scientific reasoning. If the preservation of this invaluable heritage is taken into consideration, as it should always be, the damage caused to prehistoric artworks by sampling appears too high a cost with respect to the information gained.

Thus, in the present state of the technique, the application of the U/Th method should be regarded as experimental as far as rock art dating is concerned. Fundamental geochemical studies are needed, concerning the formation and diagenesis of speleothems, particularly in the case of thin veils of calcite. Given the important consequences of open systems, a better knowledge of the influence of crystallinity, porosity, and texture on the mechanism of uranium removal or thorium input is necessary.

To establish the reliability of the ages given by U/Th, an experiment of great scientific interest would be to date calcite covering well-dated prehistoric artworks. For instance, many Magdalenian paintings have been dated by ^{14}C and they are easily identified by their stylistic features. In some cases, stalactites have grown on top and could be U/Th dated. A good example could be an indisputably Magdalenian bison covered by a dense network of stalactites in the Réseau Clastres (Ariège) (cf. Fig. 67 in Clottes, 1995).

In any case, before deciding to take calcite samples overlying a prehistoric artwork, thorough preliminary studies should be undertaken, away from the decorated areas, to determine whether sampling could really be useful. A petrographic study of microscopic thin-sections could help to detect diagenetic processes capable of leading to a loss of uranium and thus avoid destructive and fruitless sampling. It is also important to determine the periods of calcite growth in each particular case. This could be done by measuring the ages along the axis of growth of a massive stalagmite from the same gallery, in order to detect possible hiatuses in speleothem growth (Moreno et al., 2010; Moseley et al., 2014). All these factors should be studied locally before deciding if calcite overlying prehistoric artwork is worth sampling, as the results may be quite different from one cave to another and even on different panels of the same cave. The final decision should be taken by archaeologists and conservators, balancing the scientific interest with the interests of preservation.

Except for the conservation problem, it is clear that the laser ablation MC-ICPMS technique should be preferred because it allows us to bracket the age of the painting between a minimum and a maximum age relatively close to each other. Unfortunately this requires a relatively large “coring” of the wall that may drastically limit the feasibility and the expansion of this kind of sampling.

There is no doubt that technical progress is expected in the future, allowing smaller samples to be dated with less damage. On the other hand, cross-dating of U/Th with other techniques appears inescapable, because it is the best way to know whether the calcite has behaved as a closed system. ^{14}C dating of the carbonate in the same sample should be done systematically to help to detect aberrant values, and Pa/U should be associated to U/Th whenever possible.

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