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Uranium–thorium dating method and Palaeolithic rock art

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A B S T R A C T

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

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