Isotope imaging of ultra-traces by LA-fs HR-ICP-MS for U-series dating (U/Th) of archaeological biominerals: how far can we go?

Isotope imaging of ultra-traces by LA-fs HR-ICP-MS for U-series dating (U/Th) of archaeological biominerals: how far can we go?

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Abstract. To overcome the problems associated with the traditional U-series dating protocol (large amount of sample required, possible contamination during preparation and consideration of sample contamination in the past), we present a new approach using isotope mapping of radioelements produced by femtosecond laser ablation coupled with high resolution mass spectrometry (LA-fs HR-ICP-MS). This protocol, developed and validated on different carbonate supports, has been applied to a series of archaeological biominerals (shells, teeth, calcitic crusts). A high resolution of a few micrometres has been achieved, as well as a significant improvement of the sensitivity. This allows to obtain U/Th ages with minimal sampling (< 1mg), even though only ultra-traces of uranium (sub-ppb) are present. The isotope mapping approach also allows a real study of the material, highlighting areas potentially contaminated with detrital thorium, but also areas that have experienced leaching. The potential of this method and its limitations are discussed.

1. Introduction

Today, paleodosimetric methods such as luminescence or Electron Spin Resonance dating, are widely used to date Middle and Upper Pleistocene remains. However, these methods usually lead to a precision limited to 10-15 % of the age and are dependent on parameters that are sometimes difficult to accurately determine (i.e. moisture during burial time, complex taphonomy and problems of signal resetting, etc.) which can impact on their accuracy.
Conversely, other radiometric methods are often neglected as it is the case for the U-series methods, particularly the U/Th method, because of the difficulty to obtain reliable ages on samples which

experienced through time post-depositional processes (variations in the U content, leaching of isotopes, …). The U/Th method is based on the imbalance between uranium 238 (^{238}U), incorporated during the formation of the calcitic material, and one of its daughters, thorium 230 (^{230}Th), produced over time by radioactive decay. Although this method was theorized in the 1950's and is, in principle, applicable to a wide variety of archaeological remains such as shells, biominerals, hydroxyapatite, and also to a wide range of carbonates, its current use in archaeology is limited for three main reasons. Firstly, the chemical protocol used for sample preparation (i.e. dissolution with acids and introduction of double spikes, before the radioelements are separated using ion exchange resins) requires several tens or even hundreds of mg of sample with an increased risk of contamination when small or low uranium samples are processed. Secondly, due to this dissolution, the potential incorporation and/or leaching of exogenous radioelements are difficult to take into account, and may require several subsamples, thus increasing the amount of material needed for dating. Finally, the detection limits of the instruments traditionally used for measurements make it difficult to study materials containing only traces or even ultra-traces of uranium, typically a few ppb or less.
In recent years, significant efforts have been made to develop an approach that combines a laser for sample ablation, and an ICPMS to detect the radioelements relevant for U/Th dating [1,2]. However, today, accurate U/Th dating of bio-carbonates by LA-ICP-MS is limited to samples with a high radioelement content [3]. We explore here the new possibilities offered by recent instrumental developments to push the detection limits while achieving a spatial resolution of about ten microns. These improvements can open the U/Th dating by LA-ICP-MS to previously neglected archaeological materials: ostrich eggshells, snail shells, teeth, calcitic crusts.

2. LA-fs HR-ICP-MS coupling

To achieve these objectives, we use a femtosecond laser coupled with a high resolution ICPMS to produce maps of the radioelements and isotopes. The laser is a 257 nm femtosecond laser ablation system delivering 360 fs pulses (Lambda 3, Nexeya SA/Amplitude System, Bordeaux, France). It has 2 galvanometric mirrors allowing a fast scanning of the beam on the surface of the sample, which, combined with the very high-firing rate of the shots (from 1 Hz to 100 kHz), allows to increase the ablation rate [4]. The ultra-short pulse of this laser allows a clean and precise ablation of the material, with very limited thermal effects, thus considerably reducing the biases, notably in mass, often induced during ablation by conventional nanosecond lasers.

This femtosecond laser is coupled to an ICP-MS Element Xr Jet Interface (Thermo Fisher Scientific, Bremen, Germany). This single-sector field mass spectrometer has the specificity of a double focusing of the ions: this offers a better sensitivity and a background noise reduced by a factor of 10 compared to conventional ICP-MS systems, but it also leads to better detection limits and more accurate and reproducible measurements of the isotopic ratios [5, 6, 7].

This particular combination allows to produce maps of the isotopes relevant for U/Th dating (^{238}U, ^{235}U, ^{234}U, ^{230}Th and ^{232}Th), while necessitating less than 1 mg of material [8].

3. Results and perspectives

The strength of our approach lies in the advanced technologies used, both for the laser ablation sampling and the ICP-MS measurement, but also in the possibility of analysing the images produced and making a precise selection (with a resolution of about 15 µm) of the areas free of contaminants (^{232}Th) and preserved from post-depositional processes (recrystallisation, leaching of radioelements).

Each step of the process was optimised for the needs of this ultra-traces imaging, and the whole process was validated on different materials, namely speleothems and corals. This allowed to assess the precision and accuracy of our methodology, but also to take into account the various biases induced by the measurement.

We now present applications of our methodology to different biominerals and show that isotope imaging helps to overcome the current limitations of the U/Th method based on the traditional protocol, in particular to identify the state of preservation of the studied materials. For this purpose, the free ImageJ software program has been used to develop a series of functions to quickly and efficiently process the isotope maps (Fig.1 A-D). Isotope ratio images can be computed, highlighting regions particularly contaminated by detrital thorium (^{232}Th) (Fig.1 B); these areas are then selected with the software and excluded before continuing with the next steps of the analysis (Fig.1 C). Variations in isotope ratios also allow the identification of areas that have potentially been affected by leaching (Fig.1 E). Finally, the post-analysis processing of these images allows actual resampling and sub-sampling of the material, without the need for further experiments (Fig.1 F).

The results presented here are based on analyses of teeth, shells and microscopic calcitic fragments from various iconic Middle Paleolithic archaeological sites, notably in the Near East and South Africa. The obtained images allow a better understanding of the dynamics of uranium or thorium incorporation and to focus only on carefully selected microscopic areas, what is essential to obtain consistent dates.
These analysis were performed on very small quantities of material (typically a few mg or less), and despite the low counting statistic (that can be as low as 1 count per second or less, which only represent few attograms for ^{230}Th), the precision on the ages is equivalent to those obtained with the paleodosimetric methods usually applied for dating these sites.

This presentation will therefore highlight the potential of ultra-trace isotope mapping for heritage materials, in particular dating for the U/Th method. The limitations of this new approach will also be considered in order to discuss the place of this methodology in relation to existing U/Th protocols and other dating methods.

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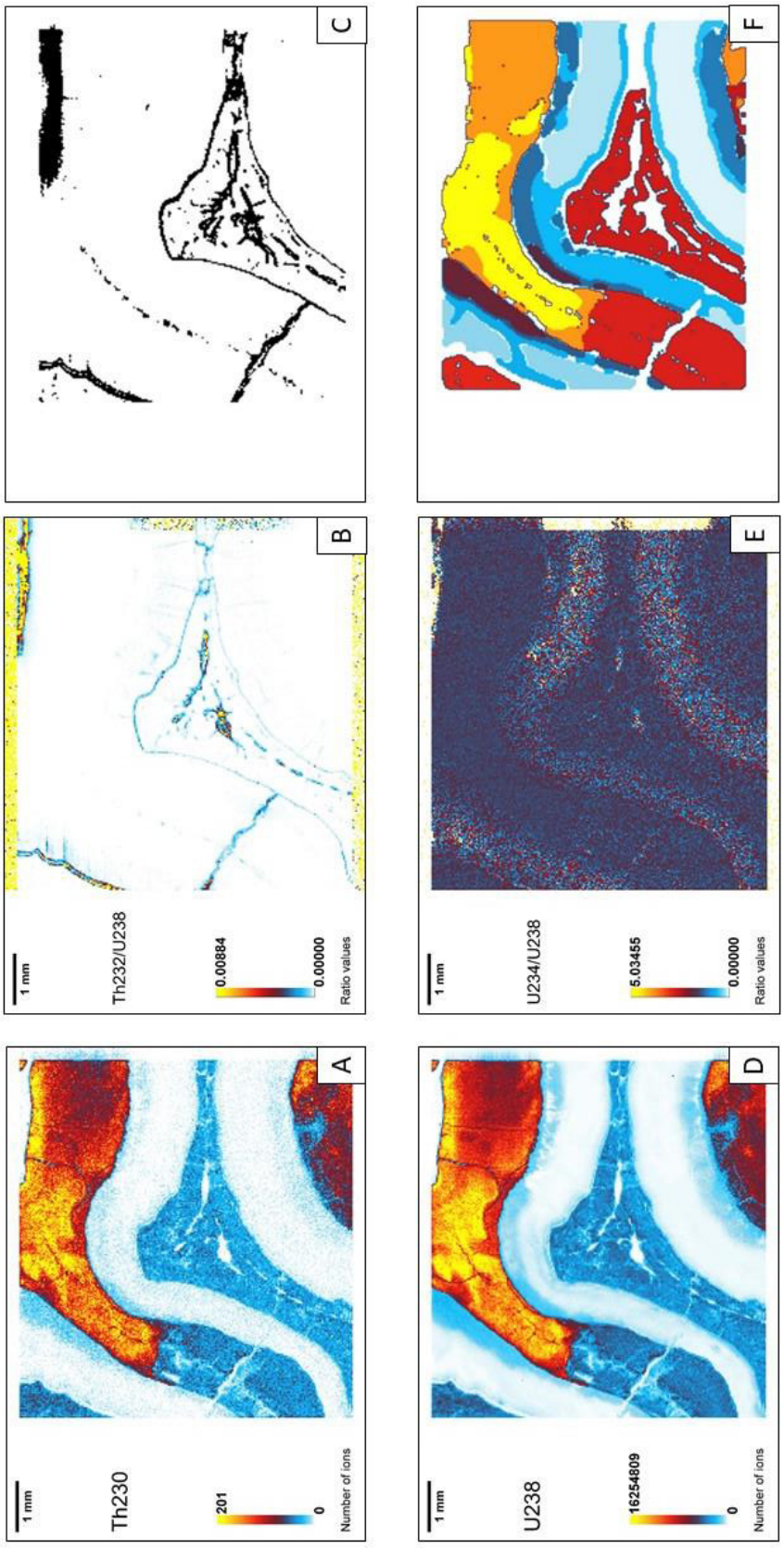

Figure 1: Mapping of an auroch tooth from the Nesher Ramla site, Israel. Resolution 15µm. Obtained by fs-LA HR-ICPMS. Maps (A, D) are given in number of detected ions. The ratios (B, E) are isotopic ratios. C: Pixels with a high ^{232}Th content are identified and excluded from the next steps of the images analysis. F : the colors correspond to areas with different mean $^{234}U/^{238}U$ mean ratios.

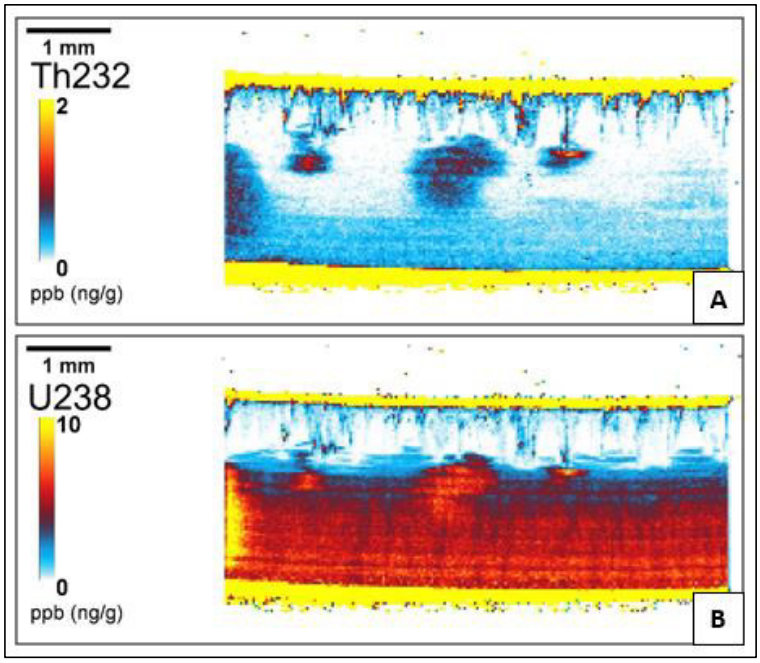

Figure 2: Mapping of the slice of an ostrich eggshell from Misliya Cave, Israel. Resolution 30µm. Obtained by fs-LA HR-ICPMS. Maps (A, B) are given concentration (ppb) of each isotope, normalized with ^{43}Ca.