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Testing LA-ICP-MS analysis of archaeological bones with different diagenetic histories for paleodiet prospect

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ABSTRACT

LA-ICP-MS is a powerful technique requiring minimal sample preparation and providing high spatial resolution which may offer the possibility of analysing trace elements in targeted pristine areas of archaeological bone sections. This would provide invaluable information about an individual's life if combined with the geochemical composition of the teeth from the same individual. However, there is no consensus regarding the calibration to be used for LA-ICP-MS analysis of bone, which is a highly complex organo-mineral tissue. In this study, we tested different calibration approaches (NIST and USGS glass series, synthetic phosphate glass and synthetic phosphate pellet from USGS) on a modern bone. The best method was applied to three Precolumbian skeletons (Lerma Valley, Mexico). These individuals show different degrees of preservation (crystallinity, calcite, F and organic matter content) which have been previously explored at the intra-skeletal level. A bone sample with exceptional preservation from the Dogon Country (Mali) was analysed for comparison.

Based on BSE SEM images and element distribution of the bone sections obtained via LA-ICP-MS mapping, quantification of Ca, P, Li, Zn, V, U, Na, Mg, Sr and Ba was performed using LA-ICP-MS spot analysis on areas displaying varying concentration profiles and histological preservation. Although avoiding sampling at the external margin of the bone sections may minimize diagenetic Li, Zn, V, U, Sr and Ba, it was not possible to discriminate biological from diagenetic Sr adsorbed onto the bone crystallites of the best preserved Precolumbian skeleton, whose low crystallinity favored adsorption efficiency. In contrast, the well preserved Dogon sample, as well as the most altered Precolumbian skeletons provided Sr and Ba content roughly similar to concentrations obtained using bulk analysis. LA-ICP-MS can therefore not substitute solution analysis for paleodiet prospect, especially for bones in relatively early state of diagenetic transformations.

1. Introduction

Reconstructing dietary habits of past populations exploring the geochemical composition of their skeletons is an approach that emerged in the 1960s (Toots and Voorhies, 1965). Almost 40 years later, this method is routinely included in a wide variety of archaeological projects (Pestle et al., 2014; Makarewicz and Sealy, 2015).

Carbon and nitrogen stable isotope ratios recorded in bone collagen (and sulphur to a lesser extent), as well as carbon, strontium and oxygen isotope values archived in tooth enamel, constitute the preferred and increasingly used tools for deciphering past diet and mobility. This derives from the fact that the evaluation of diagenetic impact on bone collagen stable isotope values is made using "simple" criteria, namely %C, %N, C/N and collagen yield (van Klinken, 1999). Tooth enamel is less susceptible to diagenetic alteration than bone mineral (Hollund et al., 2013), because of its lower amount of organic material and higher crystallinity (LeGeros, 1991; Kohn et al., 1999), making it a more suitable material for dietary and mobility interpretation from isotopic data (Price et al., 2002).

Bone mineral (bioapatite) also archives the dietary habits of individuals but, up to date, there is no perfect proxy for assessing the complete integrity of its geochemical composition. Some pre-treatments are usually applied for leaching diagenetic contaminants (Sillen, 1986), such as calcite, whose presence impacts bone biological $\delta^{13}C$ and $\delta^{18}O$ values (Balter et al., 2002). Another way to overcome the diagenetic problem is to use a combination of analytical techniques i.e. XRD (X-Ray Diffraction) and FTIR (Fourier-transform infrared spectroscopy), to assess the preservation of the biological signal registered in the mineral

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part of bones (Adamiano et al., 2013; Salesse et al., 2014; Somerville et al., 2016).

Therefore, there are fewer studies relying on the trace element composition of the mineral part of bones. Archaeological investigation would benefit, however, from additional proxies. For instance, Sr/Ca and Ba/Ca can provide information about trophic level (Burton et al., 1999; Balter, 2004), geographic origin (Burton et al., 2003; Cucina et al., 2011) and introduction of specific food component in the diet (Maurer et al., 2011; Lösch et al., 2014). Environmental exposure to heavy metals, (i.e., Pb, Hg) and As can also be recorded in bones and teeth (Degryse et al., 2004; Stadlbauer et al., 2007; Farell et al., 2013; Avila et al., 2014; Swift et al., 2015; Guede et al., 2017; Rasmussen et al., 2017).

As bones record the dietary habits of the last years of an individual's life as opposed to teeth (excepted dental calculus), that account for childhood habits, combining the investigation of both tissues with the certainty that a biological signal can still be retrieved, can therefore reveal invaluable information regarding past populations habits.

In this paper, we investigate how to use LA-ICP-MS to routinely analyse archaeological bones for such purposes. Amongst several analytical advantages, such as minimal sample preparation, high spatial resolution and fast analysis, Laser Ablation coupled to ICP-MS has the potential of analysing a wide range of chemical elements in targeted areas of a bone section. It therefore offers the possibility of analysing bone and teeth areas that might be less affected by diagenetic processes (Koenig et al., 2009), with high sensitivity, while minimizing the damages to the skeletons caused by the analyses.

2. Research question and strategy

LA-ICP-MS is used broadly in scientific areas such as, earth sciences, environmental chemistry, nanotechnology, medicine, forensics and archaeology (Sylvester, 2008; Hare et al., 2013; Almirall and Trejos, 2016; Amerstorfer et al., 2016; Dussubieux et al., 2016; de S. Pessôa et al., 2017).

Rigorous quantitative analysis of samples requires concomitant analysis of CRMs, whose physical and chemical matrix resembles that of the samples analysed (Limbeck et al., 2015; Miliszkiewicz et al., 2015; Lin et al., 2016), especially when matrix dependence is more important using LA system with 213 nm wavelength (used in this study) as compare to 193 nm (Guillong et al., 2003).

Although a large number of CRMs are available on the market for geological samples, non-silicates as well as biological tissues lack appropriate matrix-matched certified reference materials for accurate quantification of their TE content (Becker and Dietze, 1999; Hare et al., 2012; Hare et al., 2013; Pozebon et al., 2014; Limbeck et al., 2015; Luo et al., 2017; Pozebon et al., 2017). Although there is no perfect match for bones, a CaP glass was prepared by Klemme et al. (2008). It was used for analysing teeth with LA-MC-ICP-MS (Müller and Anczkiewicz, 2016) but was never applied to bone trace elements measurement. Instead, NIST glass SRM610 and 612 are commonly used for analysing bone samples, either as fragments or pelleted. Recent calibration strategies also consist of homogenising hydroxyapatite spiked with the elements of interest and pressed into pellets for use as external standards (Stadlbauer et al., 2007; Ugarte et al., 2011; Han et al., 2015; Amerstorfer et al., 2016; Praamsma and Parsons, 2016).

External calibration is also mostly applied in conjunction with normalization to an internal standard (ISTD), which must be a major element homogeneously distributed within the sample, and previously measured using another instrument. Although Ca is commonly used, there is no consensus regarding the choice of the internal reference, and some authors used either Mg (Scharlotta et al., 2013) or P (Amerstorfer et al., 2016) in order to see variation in bone Ca content.

Therefore, there is no universal method to quantify TE content in biological materials (Limbeck et al., 2015) and more specifically, in bone.

In addition, bone is a highly complex organo-mineral compound, and the presence of organic matrix not only affects the ablation rate (Praamsma and Parsons, 2016) but may also influence trace element content as observed from the comparison between bulk and LA-ICP-MS analysis of aragonitic bivalve shells (Schöne et al., 2010). Besides, pretreatments such as leaching with weak acids are usually applied to archaeological bone samples before bulk analysis in order to remove the secondary calcite precipitated in the bone porosity. Therefore, how would data obtained from LA-ICP-MS compare to bulk analysis, when LA-ICP-MS analysis is directly performed on selected areas of the bone sections?

In order to investigate these issues, we propose a two-step approach for analysing bones using LA-ICP-MS: 1) to control signal accuracy and understand what is exactly measured, and 2) to know if LA-ICP-MS can be used as an alternative to ICP-MS for further studies on diet and mobility. In the first step, a modern cow bone and a well preserved archaeological sample from the Dogon population (Mali, 17th–20th cent. CE, Maurer et al., 2017) are analysed using a set of CRMs available on the market, in order to examine the impact of organic matter on the trace element (TE) content and to find out which of the CRMs and ISTDs suits best the analysis of bones using LA-ICP-MS. In the second step, we apply the technique to archaeological bones previously analysed using ICP-MS (Maurer et al., 2011), and purposely selected for their specific diagenetic trend and intensity (see 3.2).

3. Material

3.1. For testing the different calibration approaches using LA-ICP-MS

Experiments using different calibration approaches were conducted on a modern juvenile cow bone collected from the local butcher in Évora (Portugal). The modern bone was boiled for 1 h in milliQ water in order to help removing adhering tissues. After drying, the trabecular bone and the periost were removed using a diamond saw. While one piece was cut to be analysed as a bone fragment, around 500 mg of bone was powdered using a dremel with a diamond burr.

A femur from the Dogon population (Bandiagara, Mali, Maurer et al., 2017) was analysed as a control sample for testing the different calibration strategies and as a well preserved reference for investigation of the archaeological skeletons.

3.2. For validating the analysis of archaeological bones using LA-ICP-MS for paleodietary reconstruction

Bone samples from the Chupicuaro population (Mexico, 600 BCE–200 CE) were used to test the approach on archaeological samples, whose diagenetic trajectories, as well as dietary habits, were previously investigated (Maurer et al., 2011).

Six skeletons were examined at the intra-skeletal level in Maurer et al. (2011), in order to know whether it was possible to extract a biological signal from their bones, and more specifically, to observe the ingestion of hydrothermal products, present in their environment and compatible with their nowadays dietary habits. Amongst these 6 skeletons, S1, S6 and S9 were selected for the present study because they constitute 3 specific cases of diagenetic impact. S1 seemed to be the best preserved skeleton (Table 1) showing low crystallinity, high organic content and no secondary calcite precipitated in the bone porosity. In contrast, S9 was highly affected by diagenesis probably due to the numerous skeletal pathologies that weakened the bones antemortem. Its bones yielded the highest Ca/P, with one bone outside of biological range, the highest Y, Ce and La content, as well as a concentration of fluoride of around 1%. Bones from skeleton S6 were also very affected by diagenetic processes probably by leaching in groundwater with varying degrees of preservation depending on the part of the skeleton. Its skeleton yielded medium crystallinity and organic matter content, but presented the highest secondary calcite and uranium

Table 1
Diagenetic features of the Chupicuaro bone samples chosen for LA-ICP-MS analysis. Data are from Maurer et al. (2011).

	S9		S6		S1	
conclusion from Maurer et al., 2011 based on diagenetic tracers	**most altered skeleton** highest Ca/P = 2.28 highest F amount = 0.99 ± 0.14% highest crystallinity CI = 0.28 ± 11		**contact with groundwater** high calcite amount important Mg depletion = 0.14% high intraskeletal variability of F concentrations = 0.61 ± 43%		**best preserved skeleton** highest organic matter content = 27% lowest crystallinity CI = 0.07 ± 0.08 lowest calcite amount highest Mg content = 0.26%	
samples chosen for LA-ICP-MS analysis	**right humerus RH**	**right tibia RT**	**right femur RF**	**right ulna RU**	**right tibia RT**	**right humerus RH**
[Sr] ppm	2028	2590	1504	2183	2978	3902
[F] %	0.75	1.16	0.23	1.07	0.34	0.53
CI	0.31	0.26	0.22	0.19	0.11	0.1
OM %	15	14	16	19	26	22
calcite	0.26	0.22	0	0.48	0	0

content, as well as the highest variability in fluoride concentrations.

From each of these three skeletons, 2 bones were selected for this study: right tibia (RT) and right humerus (RH) from skeleton S1, right ulna (RU) and right femur (RF) from skeleton S6, and right humerus (RH) and right tibia (RT) from skeleton S9 (Table 1).

4. Method

All the samples, the modern cow bone, the Dogon femur as well as the Chupicuaro bones, were embedded in epoxy resin. They were then polished using SiC sandpaper sheets of different grain sizes before being analysed by SEM and LA-ICP-MS. In addition, an aliquot of the powder collected from the modern cow bone was analysed by ICP-MS, while another aliquot was pressed as a pellet, without binder, for SEM-EDS and LA-ICP-MS measurements.

4.1. SEM analysis for quantifying bone major element content and providing microphotographs of the bone samples

A variable pressure Scanning Electron Microscope HITACHI S-3700N coupled to an Energy Dispersive X-Ray spectrometer (Bruker XFlash 5010 Silicon Drift Detector SDD) was used for quantitative analysis of the bone samples at the Laboratory HERCULES (Portugal). Accelerating voltage was 20 kV. Three areas of around 200 to 400 µm2 were used for quantitative analysis of the Chupicuaro samples, while for the samples used for testing the different calibration approaches, one area was selected. Data can be found in Appendix A (modern and Dogon samples) and in Appendix B (Chupicuaro and Dogon bones). The bone samples were not carbon coated for quantitative analysis (Hadjipanteli et al., 2014). Phi-Rho-Z correction (Goldstein et al., 1992) was applied as ZAF correction provided inaccurate results (Vajda et al., 1998) especially under-estimating P content of around 2%. Analyses included C and O in the measurements. Average concentrations of Ca, Mg and P were used as internal standards for quantifying LA-ICP-MS intensities.

Bone samples embedded in epoxy were also studied using electronic imaging (secondary electrons SE and back scattered electrons BSE) with a ZEISS SUPRA 55VP Scanning Electron Microscope (SEM) coupled to an Energy Dispersive X-ray (EDX) microanalysis system (Bruker QUANTAX EDS system including a QUAD silicon drift detector SDD) at University of Paris VI. Accelerating voltage was 15 kV and working distance 15 mm. Samples were carbon-coated to reduce charging effect. SEM scans are provided in Appendices C–I.

4.2. ICP-MS for bulk analysis of the modern bone

The modern cow bone sample used for testing different calibration strategies applied in LA-ICP-MS analysis was analysed for its bulk elemental composition in Ca, P, Na, Mg, Sr, Ba, Zn, Li, V and U using an Agilent 8800 ICP-MS Triple Quad. Around 100 mg of the powdered raw sample was digested on a hot plate using 1.6 mL ultrapure 65% HNO_3 for 2 h in acid-cleaned teflon beakers before being transferred to acid-cleaned teflon flasks adjusted to 50 mL with milliQ water. NIST SRM bone ash 1400 was used for control quality, and recovery of all elements analysed was within 100 ± 10%. The quantification limit was 10 times the detection limit, the calculation of which was made based on 11 replicates of the blank and of one external standard used for calibration curve. External calibration was prepared using a multi-elemental solution from High Purity Standards, diluted in ultrapure 2% HNO_3. The bulk elemental composition of the modern bone was used as a reference by which to compare data obtained from LA-ICP-MS.

4.3. LA-ICP-MS

The bone fragments embedded in epoxy (the modern bone, the Dogon sample as well as the Chupicuaro bones) and the pelleted modern bone were measured using an Agilent 8800 ICP-MS Triple Quad coupled to a CETAC LSX-213 G^{2+} laser ablation system.

Measurements were performed with MS/MS scan type in No Gas mode, using a RF power of 1550 W, RF matching of 1.3 V, a sample depth of 4 mm, dilution gas (Ar) of 0.65 L/min and Plasma Gas (Ar) of 15 L/min. The equipment was calibrated and tuned prior to analysis with the certified reference material NIST 612. Elemental fractionation was monitored and optimized using $^{238}U/^{232}Th$ ratio (≅101%) and oxide formation was evaluated using $^{248}ThO/^{232}Th$ ratio (< 0.3%). ^{43}Ca, ^{44}Ca, ^{31}P, ^{23}Na, ^{24}Mg, ^{88}Sr, ^{137}Ba, ^{66}Zn, ^{7}Li, ^{51}V and ^{238}U were analysed.

Pre-ablation of the sample was performed in order to clean the sample surface and thus avoid possible handling contaminations. Element quantification was performed using spot analysis. Three to four spots were ablated from each bone area (see concentrations in Appendices A and B). Spot size was 100 µm, using 60% energy, with a frequency of 20 Hz. The total acquisition time was set to 80 s, including 15 s of blank acquisition and 20 s of wash out. Cps intensities were converted to ppm concentrations with Glitter® data reduction Software, using CaO and testing MgO and P_2O_5 as internal standards and previously converted from Ca, Mg and P concentrations acquired with SEM-EDS.

Several external calibrations were tested. Single-point calibrations were made using MAPS4 (synthetic calcium phosphate pellet from USGS), synthetic glass from NIST SRM612 and SRM610 (Jochum et al., 2011), as well as synthetic phosphate glass STDP-150 and STDP-1500 (Klemme et al., 2008). The approach of Dudgeon et al. (2015) was also applied, using multiple-point calibration based on a set of NIST and

USGS glasses TB-1G, NKT-1G, GSE-1G, GSD-1G, GSC-1G, BIR-1G, BHVO-2G, BCR-2G, NIST 616, NIST 614, NIST 612, NIST 610 (Jochum and Stoll, 2008; Jochum et al., 2011).

Semi-quantitative mapping of element distribution was also performed within the bone sections and was conducted by ablating lines of 50 µm diameter, with 40 µm spacing, using 60% energy and a scan rate of 110 $\mu m \cdot s^{-1}$. Concentrations obtained from spots analysis were used for conversion of counts per second to concentration values, for each line of ablation, by applying simple linear regression. The conversion of concentrations to images, and background subtraction were done using iQuant2 software, developed by the Institute of Technology of Tokyo and University of Kyoto.

5. Results and discussion

5.1. Which Certified Reference Material (CRM) and which Internal Standard (ISTD) should be used for bone LA-ICP-MS data quantification?

The concentrations of Ca, P, Na, Mg, Sr, Ba and Zn measured using LA-ICP-MS to analyse the modern bone and the archaeological Dogon sample used for evaluating the CRMs, can be found in Appendix A and are represented in Fig. 1. They are presented as a percentage of recovery of the concentrations obtained from the same samples analysed with ICP-MS (solution analysis) without any previous pre-treatment (i.e., 100% recovery in Fig. 1). For the Dogon bone, the difference between solution analysis with and without organic matter (ashed) is also presented (data from Maurer et al., 2017). Bone Li, V and U content were also analysed. However, they were close or below the quantification limit for the experimental samples analysed by ICP-MS, and were therefore not included in the following discussion (see Appendix A).

For quantifying isotope intensities acquired via LA-ICP-MS to elemental concentrations, ^{44}Ca, ^{31}P, ^{23}Na, ^{24}Mg, ^{88}Sr, ^{137}Ba, ^{66}Zn intensities were normalized to an internal standard (ISTD) using Glitter software (see Method, 4.3). In the literature, Ca is mostly used as internal reference for analysing bones and teeth (Farell et al., 2013; Han et al., 2015; Praamsma and Parsons, 2016) but some authors preferred Mg (Scharlotta and Weber, 2014) or P (Amerstorfer et al., 2016; Tanaka et al., 2017) in order to consider variations in bone Ca concentrations. Ca, Mg and P content were therefore tested as ISTDs and previously measured by SEM-EDS (Appendix A). In order to validate this approach, data obtained by SEM-EDS were first inspected.

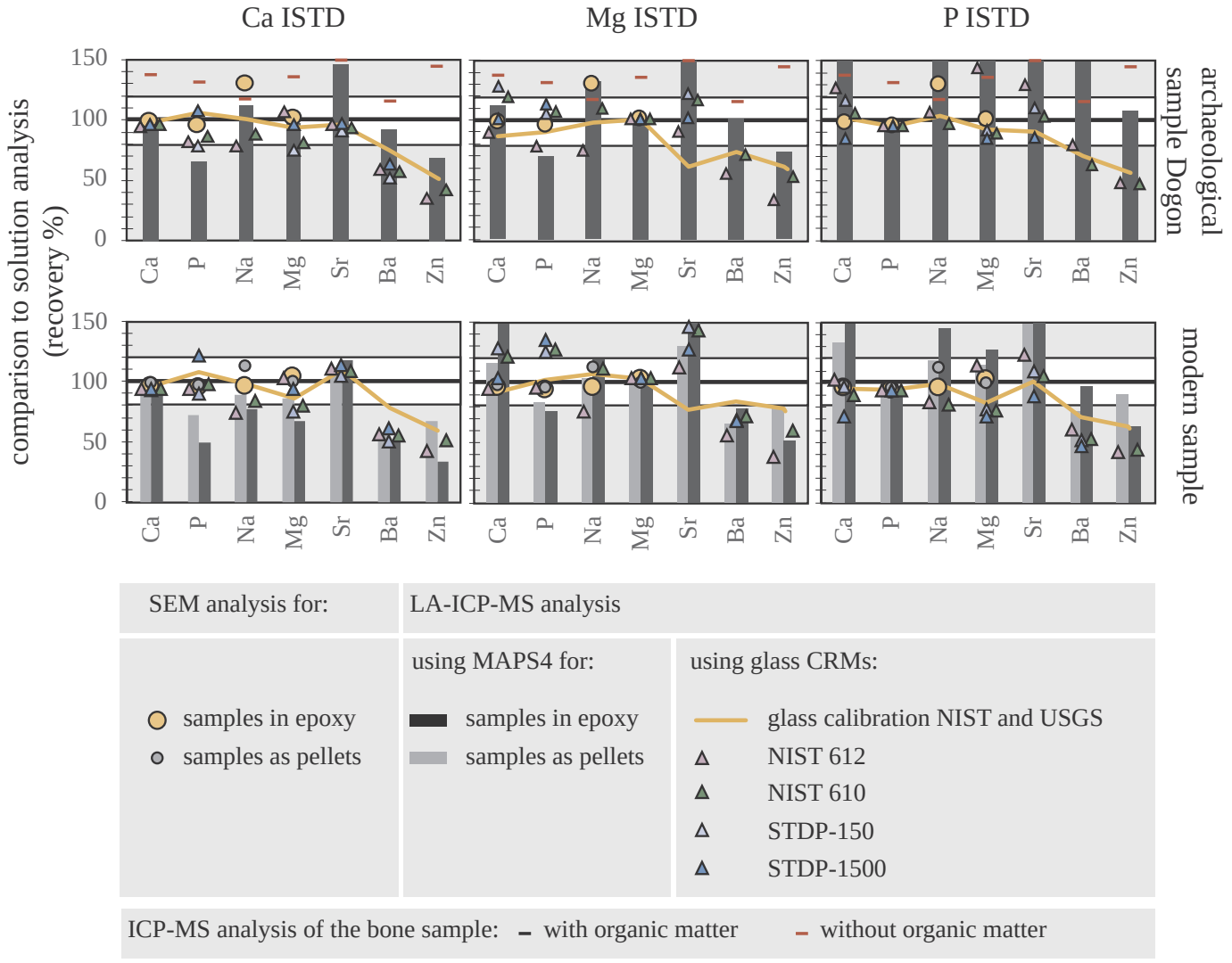

Fig. 1. Comparison in bone Ca, P, Na, Mg, Sr, Ba and Zn concentrations quantified with different external standards (MAPS4 pellet or glass CRMs) in bone either pelleted (modern sample) or embedded in epoxy (modern sample and archaeological Dogon bone). The comparison is provided for Ca, Mg and P used as internal standards. Ca, P, Na and Mg measured by SEM-EDS are also displayed. Bone element concentrations are normalized to concentrations obtained in solution analysis. For the Dogon sample, element concentrations analysed in solution after ashing pre-treatment are also reported (data from Maurer et al., 2017).

5.1.1. Bone Ca, Mg and P content analysed by SEM-EDS versus ICP-MS

For the modern bone and the Dogon sample, the concentrations of the major elements measured by SEM-EDS very closely matched those obtained in solution mode, except for Na content of the Dogon sample (analysed in epoxy) which was higher (130%) when analysed by SEM-EDS (Fig. 1). These results show that SEM-EDS can be employed in reliably analysing bone Ca, P and Mg as ISTDs for LA-ICP-MS. As Ca, P and Mg concentrations obtained via solution analysis of the previously ashed Dogon bone sample (Maurer et al., 2017) display an offset of around 130% to the untreated sample (with organics, this study), Ca, P and Mg concentrations of the modern and Dogon sample analysed by SEM-EDS and subsequently, by ICP-MS, well reflect the presence of organic matter which dilutes (i.e., decreases) their concentrations. Therefore, stoechiometric Ca concentrations of the highly mineralized enamel tissue can be used as an ISTD for quantifying element intensities acquired using LA-ICP-MS. When applied to dentine (Guede et al., 2017) or bone, however, this would induce a bias related to organic dilution (Dudgeon et al., 2015).

5.1.2. Bone Ca, P, Na, Mg, Sr, Ba and Zn content analysed by LA-ICP-MS versus ICP-MS

While major elements Ca, P, Na and Mg in bones can be analysed using SEM-EDS, our objective was to know whether it would be possible to measure them accurately using LA-ICP-MS in conjunction with some trace elements (e.g., Sr, Ba and Zn) for the same sampling location (spots of 100 µm).

Data obtained with the CRMs tested were different (Fig. 1). In comparison to concentrations obtained using ICP-MS, the measured concentrations of Ca, P, Na, Mg, Sr, Ba and Zn content in the modern bone analysed by LA-ICP-MS and quantified using MAPS4, were much better for the pelleted sample compared to the sample in epoxy resin (Fig. 1) regardless of whether Ca, Mg or P were used as ISTDs. These results show that MAPS4 is not a good candidate for analysing bone samples as fragments. Although MAPS4, as a calcium phosphate, matches the chemical composition of bones, MAPS4 is a commercial pressed powder pellet, with a different physical texture to bone fragments, which will affect the ablation, transport, vaporization, atomization and ionization of the sample (Limbeck et al., 2015).

Therefore, calibration based on pure hydroxyapatite pellets spiked with elements of interests to build calibration curves (Stadlbauer et al., 2007; Amerstorfer et al., 2016; Praamsma and Parsons, 2016) may also not be a good calibration strategy for quantifying element concentrations of bone fragments, which constitutes one of the main interests using LA-ICP-MS over ICP-MS.

In contrast to MAPS4, the single-point calibrations based on NIST glasses 612 and 610, and on the synthetic phosphate glasses, STDP-150 and STDP-1500, as well as the multiple-point calibration (Dudgeon et al., 2015) based on NIST and USGS glass series (see Method, 4.3) generally provided improved concentrations for the bone fragments for all ISTDs, i.e., closer (80 to 120%) to those acquired via ICP-MS (Fig. 1). Normalizing data to Ca should, however, provide the most accurate bone P, Na, Mg, Sr, Ba and Zn content. Indeed, more variability within the different CRMs was observed when using Mg or P as ISTD, especially regarding Sr concentrations, which is the one of the key elements for dietary reconstructions (Sillen and Kavanagh, 1982; Sponheimer et al., 2005). However, Ca, Mg and P used as ISTDs provided similar trends in concentrations for the experimental samples.

Zn and Ba could not be accurately measured, as they consistently displayed lowest amounts (30% to 60%, up to 80% when applying the glass calibration) when quantified by LA-ICP-MS, for all of the CRMs used, and all ISTDs applied. Although elemental fractionation during ablation and transport was reported for Zn (Longerich et al., 1996; Ugarte et al., 2011), this cannot explain the pattern observed for Ba as it behaves similarly to Ca, used as an ISTD, during ablation (Longerich et al., 1996). Also, the discrepancy between LA-ICP-MS and solution analysis for Ba quantification cannot derive from the presence of bone organics, as similar pattern ($Ba_{LA\text{-}ICP\text{-}MS} < Ba_{ICP\text{-}MS}$) was observed for tooth enamel (Dolphin et al., 2012). Instead, Ba must be more sensitive to matrix effect, as proved by the increased recovery obtained using the glass calibration.

Overall, these results show that MAPS4 can be used to analyse pelleted bone samples but cannot provide reliable data for bone fragments. In contrast, for the multiple-point and single-point glass calibration provided for most of the elements (excepted Ba), the concentrations are much more in agreement with those measured by solution analysis. This shows that using CRMs with a similar physical texture to the samples seems to prevail over having a similar chemical composition, as assessed by the phosphate glasses that provided very similar concentrations to the NIST 612 and 610, yet having very different chemical composition (Klemme et al., 2008; Jochum et al., 2011).

Although the multiple-point glass calibration provided better recovery for Ba content, considering the limited space of the HelEx cell, the increase in time of analysis applying the multiple-point calibration and the fairly similar recovery to that of the single point calibration, we chose to apply NIST612 and NIST610 in conjunction with STDP-1500, for analysing archaeological Chupicuaro bones using LA-ICP-MS. Using these three CRMs with varying composition, allows for cross checking and the validation of data. In addition, considering the higher variability in bone Mg content of the archaeological samples (average of 22%) analysed by SEM-EDS (Appendix B), Ca (with an average variability of 7%) was applied as an ISTD for quantification of element concentration of the archaeological samples (see 5.2.3). Although variability of P content of the Chupicuaro samples analysed by SEM-EDS was low (6%), its utilisation as ISTD is not recommended because of mass spectral interference (with $^{14}N^{16}OH^{+}$) and its high ionization potential (10.486 eV) which makes it difficult to analyse with LA-ICP-MS (Hayashi et al., 2002).

5.2. Application to archaeological bones

The ultimate goal of this study was to know if, by using LA-ICP-MS to analyse archaeological bones, it would be possible to obtain TE concentrations comparable with bulk solution analysis, and to potentially retrieve a biological signal locked in some areas preserved from diagenetic alteration (Koenig et al., 2009). While a series of pre-treatments are usually conducted before bulk analysis, such as leaching with weak acids and ashing, laser ablation is, however, directly performed on the polished bone surface which may yield diagenetic contaminants such as calcite, commonly found in bone porosity and previously observed on XRD diffractograms of the Chupicuaro skeletons (Maurer et al., 2011). Therefore, the three Chupicuaro skeletons used in this study (see Table 1), consisting of 2 bones each, were thoroughly examined by SEM-BSE before ablation in order to examine the presence versus absence of diagenetic minerals and the distribution thereof, within the archaeological bone tissues. The Dogon femur sample was concomitantly analysed as a well preserved bone reference.

5.2.1. Observations with SEM-BSE

The Dogon femur sample, as expected, did not display any bacterial attack nor any precipitation in the bone porosity (Appendix C). However, SEM-BSE images provided for the Chupicuaro bones from skeletons 1, 6 and 9 (Fig. 2, Appendices H–I, F–G, D–E, respectively) were in agreement with conclusions drawn from the previous analysis of histological features of these skeletons and with their diagenetic history deduced from the mineralogical, structural and geochemical analysis made at the intra-skeletal level (Table 1, Maurer et al., 2011). Without any exception, all of the samples observed by SEM presented relatively high degrees of bacterial attack typically found in terrestrial environments (Fernandez-Jalvo and Andrews, 2016; Pesquero et al., 2017). The bacterial colonies appeared to either be sectioned longitudinally or cross-sectioned and were surrounded by rims of hyper-

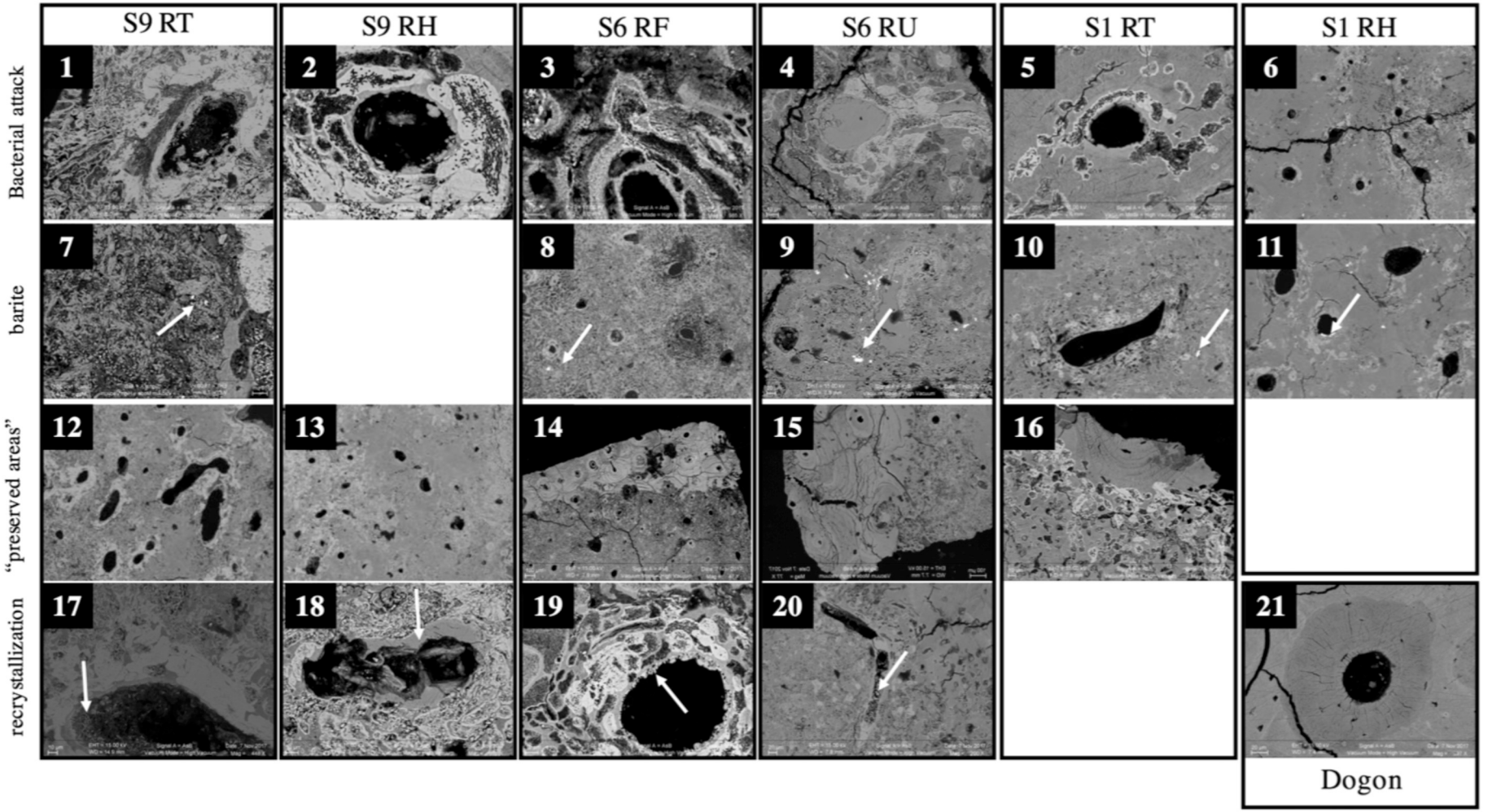

Fig. 2. SEM microphotographs of the Dogon femur (21) and the Chupicuaro samples (1–20), S9 right tibia (RT) and right humerus (RH), S6 right femur (RF) and right ulna (RU) and S1 right tibia (RT) and right humerus (RH).

Bacterial attack surrounding the haversian canals was observed for all the Chupicuaro bones (1–6). The presence of barite was evidenced for the Chupicuaro skeletons (7–11). Calcite precipitated within the haversian canals (4,17–18) was observed. In the porosity of sample S6RF, calcium phosphate was recrystallized (19) while microspheres of calcium phosphate were detected in the porosity of sample S6RU (20). Apart from the Dogon sample which shows no evidence of bacterial attack (21), the Chupicuaro samples show only few bone unaltered (12–16).

mineralized zones. However, the distribution and intensity of bacterial attack varied within the three skeletons analysed. Bones from skeleton S9, considered as the most diagenetically altered (see Table 1), displayed almost no area of unaltered bone. Besides calcite previously observed on XRD diffractograms (Maurer et al., 2011), fibrous aragonite was found in the bone porosity (Fig. 2). Spots of barite were also observed in the right tibia of skeleton S9 while it was not detected by previous XRD analysis. Bones from skeleton S6 displayed bacterial attack all over the section excepted in the adjacent region to the periost. This particular feature, associated with large calcite crystals infilling the bone voids (Fig. 2) are concordant with the immersion of skeleton S6 in water for some time (see Table 1). Although calcite was detected by XRD analysis (Maurer et al., 2011), the presence of significant amounts of barite spread in the right ulna especially, was only revealed by SEM-BSE analysis (Fig. 2). Additionally, microspheres of calcium phosphate observed in the bone porosity of skeleton S6 indicated recrystallization process. Finally, bones from skeletons S1, considered as the best preserved of the Chupicuaro skeletons (see Table 1), although attacked by bacteria, as was previously observed on thin sections (Maurer et al., 2011), unexpectedly displayed significant amounts of barite precipitated within the porosity of the right humerus specifically, while no exogenous mineral was observed on XRD diffractograms (Maurer et al., 2011).

The presence of barite is not surprising in hydrothermal environments; however, its occurrence within the archaeological Chupicuaro skeletons may constitute a bias to LA-ICP-MS analysis.

5.2.2. Mapping bone TE concentrations using LA-ICPMS

Semi-quantitative trace element mapping of the bone sections using LA-ICP-MS was conducted in order to see whether the distribution of trace elements within the section could be related to their histological preservation, and also to choose targeted areas, with different element concentrations, with an attempt to retrieve areas preserving antemortem composition (Koenig et al., 2009). The Dogon femur section was used as a reference for a preserved sample.

For most of the elements analysed (Ca, P, Na, Mg, Sr, Ba, Zn), the Dogon femur exhibited relatively homogeneous concentrations within its section (Fig. 3). The Chupicuaro bone sections however, displayed very heterogeneous distribution for all of these elements (Fig. 3).

Amongst the six Chupicuaro bone sections mapped, the right ulna of skeleton S6 exhibited a particular distribution of concentrations for all elements analysed. Indeed, the external part of S6RU is depleted in Ca, P, Na, Mg and Li, and enriched in Sr, Ba, V and Zn, with a clear difference to the bone core. These different concentrations clearly match the transition between the parts of the bone exempt from bacterial attack with those destroyed by bacteria (Fig. 2). Although less striking, a relatively similar pattern was observed for the right femur of skeleton S6. Therefore, LA-ICP-MS mapping in combination with SEM images enables one to reconstruct the diagenetic history of this skeleton, providing the evidence of its immersion in water (see Table 1) which prevented bacterial attack in the immerged part of the bones (Turner-Walker and Jans, 2008; Booth, 2016) while leaching Ca, Na, Mg and Li, and adding Sr, Ba, U, V and Zn to the bone in contact with water. This confirms previous results from the mineralogical and geochemical intra-skeletal study (Maurer et al., 2011).

Likewise, heterogeneity in trace elements distribution in bones from skeleton S9 was not surprising, considering several diagenetic indicators (see Table 1) that argues for a very poor preservation state of this skeleton. In bones from skeleton S9, higher concentrations of Ca, P, Na, Mg, Sr and Ba seem to be found in the core of the samples, which correspond in part, to areas less attacked by bacteria.

In contrast, Skeleton S1 considered as the best preserved skeleton (Table 1), also displayed heterogeneous element distribution although more attenuated (Fig. 3). Sr especially showed a clear distribution, for both the right tibia and the right humerus, with higher concentrations close to the periost area and lower concentrations in the bone core and towards the medullar cavity. In the case of bones from skeleton S1, the lowest Sr concentrations seem to be localized in areas preserved from bacteria.

The concentration profiles obtained for the elements under investigation can help elucidate the complex diagenetic processes that affected the skeletons (Koenig et al., 2009; Decrée et al., 2018), although they can be inherent to ante-mortem conditions of the skeletons themselves (i.e., pathologies, Bell, 1990). The skeletons investigated in this study followed different diagenetic trajectories (Maurer et al., 2011), as displayed by their different element distribution patterns. However, they present a common trend for V and Zn distribution, encountered with higher concentrations close to the periost. This profile clearly shows that V and Zn diffuse through the bone via direct contact with the soil and progressively diffuse through the bone cortex in the direction of the medullar cavity.

Amongst the elements mapped, U displayed a skeleton-specific concentration gradient. Bones from S6 clearly showed higher concentrations in U close to their external part. More specifically, there is a region of high U concentrations in the right ulna of S6 where bacteria started to invade the bone. This could reflect a region of recrystallization towards the part of the bone that was not immersed in water and therefore where recrystallization occurred more rapidly (Reiche et al., 2003). In contrast to S6, bones from skeletons S9 and S1 display different diffusion profiles of U which indicate reduced interaction between bone and pore water (Koenig et al., 2009) in comparison to S6. Finally, higher Ba concentrations in the porosity of S1RH and randomly distributed in S6RU were in agreement with the barite detected on SEM images (Fig. 2).

Some studies investigated trace element profiles in bones and teeth (Millard and Hedges, 1996; Kohn, 2008; Kohn and Moses, 2013; Müller et al., 2019) which have implications for fossilization rate, mineralization, paleoenvironmental or dietary reconstruction. Models based on diagenetic experiments made on modern bones show that trace element profiles observed in fossil bones must result from recrystallization process, rather than intrabone diffusion (Kohn and Moses, 2013). Besides, fossil bones, enamel and dentine have different trace element profiles due to the nature of their tissue structure (Hinz and Kohn, 2010). In this study, the different diagenetic histories of the three skeletons affected their bone tissues differently (see 3.2, Maurer et al., 2011) which similarly resulted in different trace element profiles within the bone sections of each skeleton.

If some bone areas have been exempted from recrystallization, although no evidence of such process was found for S1, they may have preserved the so-called biological signal used for paleodietary interpretations (Koenig et al., 2009). In order to know if this signal could directly be deduced from LA-ICP-MS, as a substitute to bulk analysis, fast quantification of the elements analysed was performed using LA-ICP-MS spot analysis (Fig. 4) on different areas chosen according to the elemental distribution maps.

5.2.3. Quantifying bone elemental content using LA-ICP-MS versus ICP-MS

According to the experimental approach, trace element concentration acquired via LA-ICP-MS analysis depends on the OM content (Fig. 1). Therefore, data obtained by LA-ICP-MS from the three Chupicuaro skeletons was compared to data acquired via ICP-MS (Li, V, Zn, Sr, Ba and U), colorimetry (P) and ICP-AES (Ca, Mg, Na) measurements (from Maurer et al., 2011) – referred to as solution analysis or bulk, in the following discussion – normalized to their organic matter content (analysed as weight loss %, Maurer et al., 2011) in order to overcome the dilution effect of the organic matrix. Measurements using solution analysis involved bone pre-treatments: acetic acid to remove the secondary carbonates (although this treatment was not applied to the Dogon sample) and bone ashing to remove their organic content prior to the digestion of the samples. The concentrations of the Chupicuaro samples can be found in Appendix B. Comparison between LA-ICP-MS and solution analysis are displayed in Fig. 5.

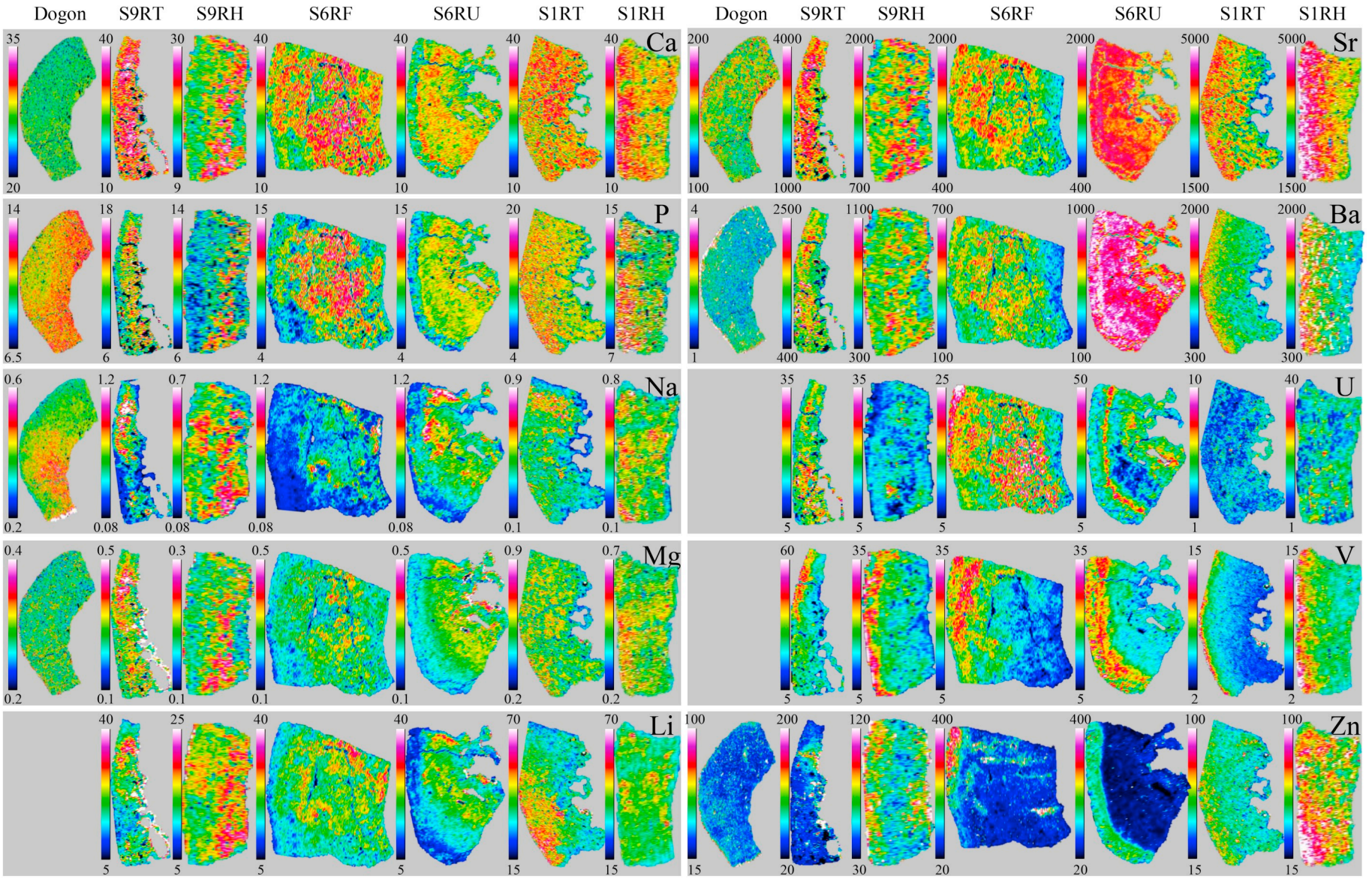

Fig. 3. Spatially resolved analysis of the Dogon femur and the Chupicuaro samples, S9 right tibia (RT) and right humerus (RH), S6 right femur (RF) and right ulna (RU) and S1 right tibia (RT) and right humerus (RH). Color scale varies according to the concentrations obtained for Ca, P, Na, Mg, Li, Sr, Ba, U, V and Zn. Li, V and U concentrations are not provided for the Dogon sample as they were below the quantification limit (see Appendix A). As each image was treated separately, color scale applies specifically to each bone sample and is not comparable between samples. Lowest and highest concentrations are therefore reported for each sample (bottom and top of color scale). Values are provided in % for Ca, P, Na and Mg, and in ppm for Li, Sr, Ba, U, V and Zn. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

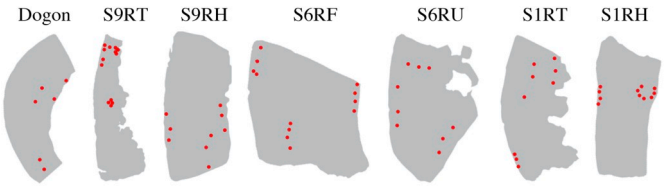

Fig. 4. Sampling spot location for LA-ICP-MS quantification.

Ca, P, Na, Mg, Sr and Ba concentrations of the Dogon sample analysed with LA-ICP-MS as a reference for well preserved bone, were constantly within ± 20% of the amounts acquired via bulk analysis. This validates the comparison based on the normalization to organic matter content estimates obtained via ashing of the samples. The Chupicuaro samples however, already showing features of post-mortem modifications (Table 1), display inconsistent element concentrations when analysed with LA-ICP-MS with regards to bulk analysis.

Three main trends were observed: Ca, P and Li content of the Chupicuaro bones analysed by LA-ICP-MS were mostly within the range ± 20% of the concentrations previously measured with solution analysis. The second trend applied to bone Zn, V and U content which, for most of the samples, were much lower when analysed by laser ablation than as bulk. Although elemental fractionation during ablation affects Zn but not V and U (Longerich et al., 1996), the presence of organic matter in the ablated samples seems to hamper accurate recovery of U, whose affinity for organics is known (Volesky and Holan, 1995), as well as metals which may be bound, in part, to organic molecules, such as Zn (Gómez-Ariza et al., 2004) and probably V. Finally, bone Na, Mg, Sr and Ba content of the Chupicuaro skeletons did not display any consistent offset between LA-ICP-MS analysis and bulk measurements. The absence of offset between the two techniques for the well preserved Dogon sample rather argues for diagenetic processes instead of matrix effect due to the LA system wavelength (213 nm) used in this study (Guillong et al., 2003; Jochum et al., 2012).

The offset between LA-ICP-MS measurement (and, *a fortiori* SEM-EDS) and bulk analysis observed in Ca content of the Chupicuaro samples, was correlated to their weight loss (Table 1), although data were normalized to organic content. Biases related to SEM-EDS precision, Ca variability within the bone (Appendix B) and organic matter content estimates might be responsible for the observed offset. However, P concentrations of the Chupicuaro skeletons did not follow exactly the same trend as Ca. Interestingly, S9 and S6 which showed recrystallization processes (Fig. 2) also displayed the highest average offset in P content for S9RT and S6RF between LA-ICP-MS and solution analysis, resulting in Ca/P outside of the biological range 2–2.3 (Trueman and Tuross, 2002), especially close to the external margin of the bones (Appendix B). Although Ca/P ratios of the other Chupicuaro samples were within the biological range, all bone fragments analysed exhibited high discrepancies between LA-ICP-MS and solution analysis for Na, Mg, Sr and Ba content, but not for all intra-bone locations sampled. As offsets were not consistent between the three skeletons and not even between two different bones from the same individual, they can only originate from the samples themselves and thus, their diagenetic state.

S9 and S6 for instance, which showed significant recrystallization of calcite and calcium phosphate in their bone porosity (Fig. 2), presented “anomalies” in their Na content, when analysed with LA-ICP-MS, while the two bones from skeleton S1, considered to be the best preserved of the Chupicuaro series (Table 1) yielded Na content very similar to that measured as bulk. However, all of the bones from the three Chupicuaro skeletons showed much higher Mg content when analysed with LA-ICP-MS in comparison to bulk analysis. Amongst the six bone samples analysed, S9RH, S6RF, S1RT and S1RH showed a Mg enrichment of around 170% compared to solution analysis. These samples have all been leached with acetic acid prior to sample digestion, which was not the case for the Dogon sample. This enrichment could therefore be attributed to Mg leaching during pre-treatment, considering that around one third of Mg is located on a surface pool of bone apatite and is therefore rapidly exchangeable (Alfrey and Miller, 1973). Interestingly skeletons S9RT and S6RU showed the lowest and highest, respective Mg enrichment, which would therefore be related to their advanced diagenetic state compared to S1. Yet, the two bones from skeleton S1 exhibited the most surprising higher offset in Sr concentrations between measurements conducted using LA-ICP-MS and bulk analysis. Diagenetic uptake of Sr is known (Hedges, 2002). This skeleton yielded the lowest crystallinity (CI = 0.1, Table 1) while bones from S9, with the highest crystallinity (CI = 0.3, Table 1), presented similar Sr concentrations using LA-ICP-MS and bulk analysis. Adsorption of strontium onto bone crystallites with high specific area (Decrée et al., 2018), i.e., low crystallinity (Farlay et al., 2010), could explain this offset. The same pattern was also observed for Ba content measured in S1RT while S1RH displayed the lowest Ba concentrations using LA-ICP-MS in comparison to solution analysis. Interestingly, barite was detected in the porosity of S1RH (Fig. 2). Bulk analysis of S1RH may therefore have included some Ba from the precipitated barite, which would create the offset between solution analysis and LA-ICP-MS. As barite was not detected in S1RT, the fact that Ba follows the same trend as Sr argues in favor of a concomitant Ba and Sr adsorption onto bone crystallites.

Overall, the six Chupicuaro samples analysed using LA-ICP-MS showed varying element concentrations depending on the area ablated. As expected, for many elements such as Li, Zn, V, Sr and Ba, a clear diagenetic enrichment was observed at the external margin of the bone sections (Fig. 5), which could therefore be avoided for dietary reconstructions. Unfortunately, a biological signal in the least altered skeleton S1 was completely lost because its low crystallinity favored adsorption of Sr and Ba onto bone crystallites. While pre-treatments before conducting bulk analysis may have leached adsorbed Sr and Ba, LA-ICP-MS cannot make the distinction with biological concentrations as revealed by the comparison between LA-ICP-MS and solution analysis. This would impair any tentative of dietary reconstruction, while mobility could still be deciphered by performing Sr isotope measurement with LA-MC-ICP-MS to discriminate biological Sr (Scharlotta et al., 2013).

6. Summary and conclusions

Although there is no universal method for the quantification of elemental content using LA-ICP-MS, NIST612 and 610, in association with the synthetic phosphate glass STDP-1500 constitute reliable CRMs for quantifying bone P, Mg, Na, Sr, Ba, Li, Zn, V and U content, in combination with Ca used as an internal standard (previously measured by SEM-EDS), due to its low variability in archaeological bones. This strategy was used to analyse selected archaeological Chupicuaro samples whose diagenetic history was well known, in order to know whether data obtained from LA-ICP-MS are similar to bulk analysis and if a biological dietary signal could be locked in some preserved areas of the bone sections. Prior to LA-ICP-MS analyses, the Chupicuaro samples were inspected by SEM-BSE to check for the presence of secondary minerals, recrystallization and histological damage mediated by bacterial attack. These diagenetic features, combined with spatial analysis of element concentrations, acquired via LA-ICP-MS mapping, were in agreement with the diagenetic history previously ascribed to each skeleton, based on a mineralogical and geochemical analysis conducted at the intra-skeletal level (Maurer et al., 2011). Using the element distribution maps, quantification of bone P, Mg, Na, Sr, Ba, Li, Zn, V and U concentrations of the Chupicuaro samples was performed via LA-ICP-MS using sampling spots in bone areas presenting varying element concentrations. The comparison to bulk analysis was made by normalizing element content analysed via LA-ICP-MS, to the organic content (% weight loss) of each bone sample. Although avoiding sampling at the external margin of the bone sections may minimize diagenetic Li,

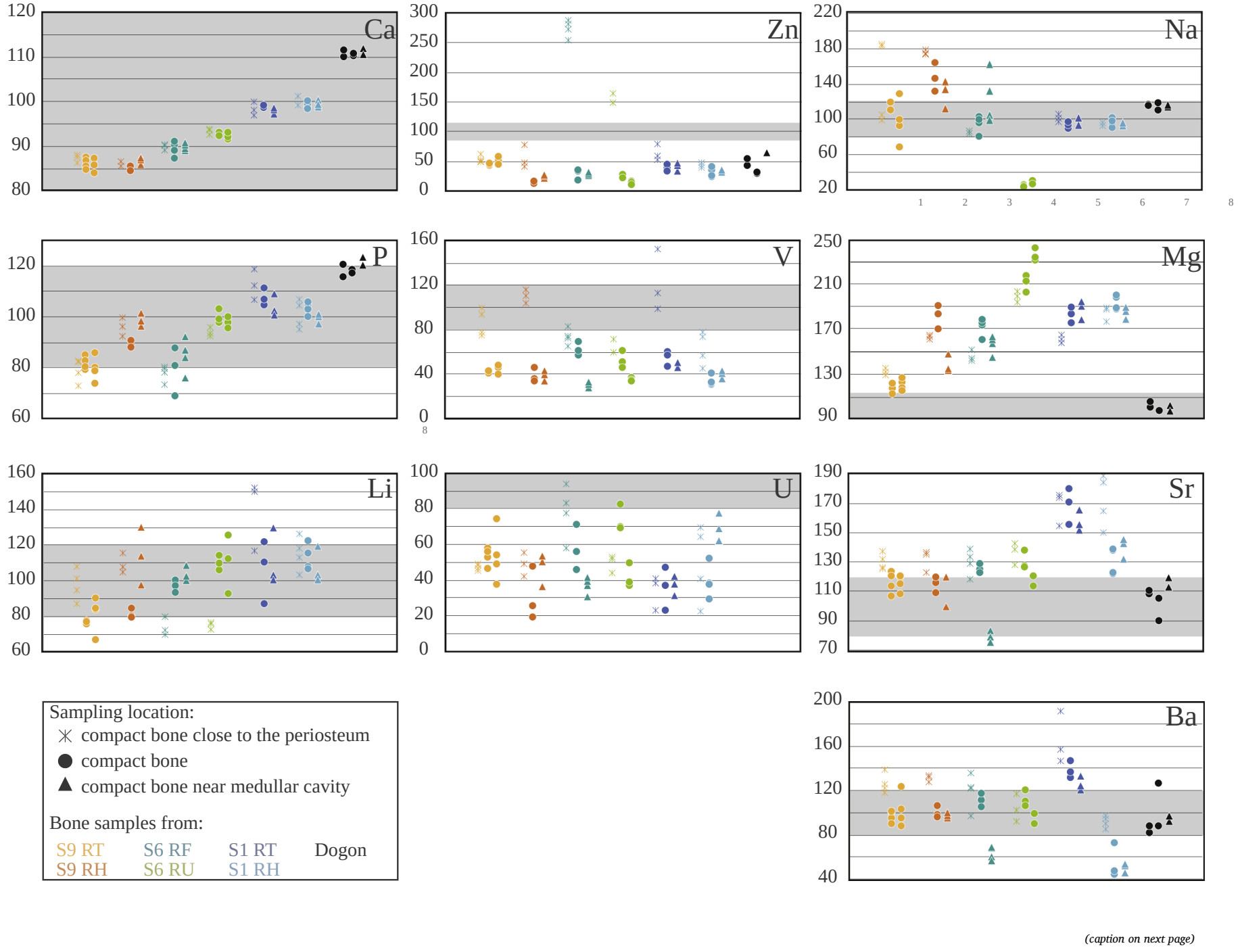

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Fig. 5. Percent recovery of bone elemental content (Ca, P, Li, Zn, V, U, Na, Mg, Sr and Ba) analysed using LA-ICP-MS compared to concentrations obtained using solution analysis. Data acquired via bulk measurements were corrected for the dilution effect of organic matter. The grey zone indicates comparable (± 20%) concentrations using both analytical methods. Concentrations are provided for each bone analysed and according to the sampling location (compact bone near the periost, bone cortex and compact bone near medullar cavity). For elemental quantification, ^{43}Ca was used as internal standard. CRMs NIST 612 and STDP-1500 were used for respective quantification of: Ca, Li, Zn, V, U, Na, Sr, Ba and P, Mg.

Zn, V, U, Sr and Ba, it was not possible to discriminate biological from diagenetic Sr adsorbed onto the bone crystallites of the best preserved skeleton, the low crystallinity of which favored adsorption efficiency. Therefore, according to this study, for past diet reconstruction, bone LA-ICP-MS analysis as such cannot be used as an alternative to solution analysis whose pre-treatment requirements (i.e., leaching with acetic acid) removed adsorbed Sr. These results open prospective for further investigations using similar approach to see whether similar patterns are observed in other geoecosystems, and therefore inherent to early diagenetic states, or if conclusion drawn from this study are specific to the hydrothermal environment in which the Chupicuaro populations lived and were buried.

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References

Adamiano, A., Fabbri, D., Falini, G., Belcastro, M.G., 2013. A complementary approach using analytical pyrolysis to evaluate collagen degradation and mineral fossilisation in archaeological bones: the case study of Vicenne-Campochiaro necropolis (Italy). J. Anal. Appl. Pyrolysis 100, 173–180.

Alfrey, A.C., Miller, N.L., 1973. Bone magnesium pools in uremia. J. Clin. Invest. 52, 3019–3027.

Almirall, J.R., Trejos, T., 2016. Applications of LA-ICP-MS to forensic science. Elements 12, 335–340.

Amerstorfer, F., Fischerauer, S.F., Fischer, L., Eichler, J., Draxler, J., Zitek, A., Meischel, M., Martinelli, E., Kraus, T., Hann, S., Stanzl-Tschegg, S.E., Uggowitzer, P.J., Löffler, J.F., Weinberg, A.M., Prohaska, T., 2016. Long-term in vivo degradation behavior and near-implant distribution of resorbed elements for magnesium alloys WZ21 and ZX50. Acta Biomater. 42, 440–450.

Avila, A., Mansilla, J., Bosch, P., Pijoan, C., 2014. Cinnabar in Mesoamerica: poisoning or mortual ritual? J. Archaeol. Sci. 49, 48–56.

Balter, V., 2004. Allometric constraints on Sr/Ca and Ba/Ca partitioning in terrestrial mammalian trophic chain. Oecologia 139, 83–88.

Balter, V., Saliège, J.-F., Bocherens, H., Person, A., 2002. Evidence of physico-chemical and isotopic modifications in archaeological bones during controlled acid etching. Archaeometry 44, 329–336.

Becker, J.S., Dietze, H.-J., 1999. Determination of trace elements in geological samples by laser ablation inductively coupled plasma mass spectrometry. Fresenius J. Anal. Chem. 365, 429–434.

Bell, L.S., 1990. Palaeopathology and diagenesis: an SEM evaluation of structural changes using backscattered electron imaging. J. Archaeol. Sci. 17, 85–102.

Booth, T.J., 2016. An investigation into the relationship between funerary treatment and bacterial bioerosion in European archaeological human bone. Archaeometry 58, 484–499.

Burton, J.H., Price, T.D., Middleton, W.D., 1999. Correlation of bone Ba/Ca and Sr/Ca due to biological purification of calcium. J. Archaeol. Sci. 26, 609–616.

Burton, J.H., Price, T.D., Cahue, L., Wright, L.E., 2003. The use of barium and strontium abundances in human skeletal tissues to determine their geographic origins. Int. J. Osteoarchaeol. 13, 88–95.

Cucina, A., Tiesler, V., Sierra Sosa, T., Neff, H., 2011. Trace-element for foreigners at a Maya port in Northern Yucatan. J. Archaeol. Sci. 38, 1878–1885.

Decrée, S., Herwartz, D., Mercadier, J., Mián, I., de Buffrénil, V., Leduc, T., Lambert, O., 2018. The post-mortem history of a bone revealed by its trace element signature: the case of a fossil whale rostrum. Chem. Geol. 477, 137–150.

Degryse, P., Muchez, P., De Cupere, B., Van Neer, W., Waelkens, M., 2004. Statistical treatment of trace element data from modern and ancient animal bone: evaluation of Roman and Byzantine environmental pollution. Anal. Lett. 37, 2819–2834.

Dolphin, A.E., Dundas, S.H., Kosler, J., Meyer Tvinnereim, H., Geffen, A., 2012. A comparison of techniques for measuring the trace element content of human teeth: laser ablation ICP-MS versus solution ICP-MS of micromilled enamel. International Journal of Analytical and Bioanalytical Chemistry 2, 189–195.

Dudgeon, J., Tromp, M., Peterson, D., Hanks, B.K., 2015. Investigating biogenic versus diagenetic trace element incorporation in archaeological mineralized tissues with LA-ICP-MS. In: Dubussieux, L., Goliko, M., Gratuze, B. (Eds.), Recent Advances in Laser Ablation ICP-MS for Archaeology. Natural Science in Archaeology Springer, Berlin, Heidelberg, pp. 323–341.

Dussubieux, L., Golitko, M., Gratuze, B., 2016. Recent Advances in Laser Ablation ICP-MS for Archaeology, Natural Science in Archaeology. Springer, Berlin.

Farell, J., Amarasiriwardena, D., Goodman, A.H., Arriaza, B., 2013. Bioimaging of trace metals in ancient Chilean mummies and contemporary Egyptian teeth by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS). Microchem. J. 106, 340–346.

Farlay, D., Panczer, G., Rey, C., Delmas, P., Boivin, G., 2010. Mineral maturity and crystallinity index are distinct characteristics of bone mineral. J. Bone Miner. Metab. 28, 433–445.

Fernandez-Jalvo, Y., Andrews, P., 2016. In: Delson, E., Sargis, E.J. (Eds.), Atlas of Taphonomic Identifications. Vertebrate Paleobiology and Paleoanthropology Series. Springer.

Goldstein, J.I., Newbury, D.E., Echlin, P., Joy, D.C., Romig Jr., A.D., Lyman, C.E., Fiori, C., Lifshin, E., 1992. Scanning Electron Microscopy and X-Ray Microanalysis. A Text for Biologists, Materials Scientists, and Geologists. Plenum Press, New York, pp. 1992), 1–820.

Gómez-Ariza, J.L., Garcia-Barrera, T., Lorenzo, F., Bernal, V., Villegas, M.J., Oliveira, V., 2004. Use of mass spectrometry yechniques fort he characterization of metal bound to proteins (metallomics) in biological systems. Anal. Chim. Acta 524, 15–22.

Guede, I., Zuluaga, M.C., Ortega, L.A., Alonso-Olazabal, A., Murelaga, X., Pina, M., Gutierrez, F.J., 2017. Analyses of human dentine and tooth enamel by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) to study the diet of medieval Muslim individuals from Tauste (Spain). Microchem. J. 130, 287–294.

Guillong, M., Horn, I., Günther, D., 2003. A comparison of 266 nm, 213 nm and 193 nm produced from a single solid state Nd:YAG laser for laser ablation ICP-MS. J. Anal. At. Spectrom. 18, 1224–1230.

Hadjipanteli, A., Kourkoumelis, N., Speller, R., 2014. Evaluation of CT-DEA performance on Ca/P ratio assessment in bone apatite using EDX. X-Ray Spectrom. 43, 286–291.

Han, P., Zhou, Y., Lu, S., Lloyd, T., Friis, T., Moromizato, K., Allen, C., Xiao, Y., 2015. Utilisation of bovine bone pellet as a matrix-matched reference material for calcified tissues in LA-ICP-MS application. Journal of Analytical and Bioanalytical Techniques S13.

Hare, D., Austin, C., Doble, P., 2012. Quantification strategies for elemental imaging of biological samples using laser ablation-inductively coupled plasma-mass spectrometry. Analyst 137, 1527.

Hare, D.J., Lear, J., Bishop, D., Beavis, A., Doble, P.A., 2013. Protocol for production of matrix-matched brain tissue standards for imaging by laser ablation-inductively coupled plasma-mass spectrometry. Anal. Methods 5, 1915–1921.

Hayashi, H., Ohe, I., Tanaka, T., Hiraide, M., 2002. Dtermination of traces of phosphorus in steels by laser ablation/low pressure helium ICP-MS. Anal. Sci. 18, 1387–1389.

Hedges, R.E.M., 2002. Bone diagenesis: an overview of processes. Archaeometry 44, 319–328.

Hinz, E.A., Kohn, M.J., 2010. The effect of tissue structure and soil chemistry on trace element uptake in fossils. Geochim. Cosmochim. Acta 74, 3213–3231.

Hollund, H.I., Arts, N., Jans, M.M.E., Kars, H., 2013. Are teeth better? Histological characterization of diagenesis in archaeological bone–tooth pairs and a discussion of the consequences for archaeometric sample selection and analyses. Int. J. Osteoarchaeol. https://doi.org/10.1002/oa.2376.

Jochum, K.P., Stoll, B., 2008. Reference materials for elemental and isotopic analyses by LA-(MC)-ICP-MS: successes and outstanding needs. In: Sylvester, P. (Ed.), Laser Ablation ICP-MS in the Earth Sciences: Current Practices and Outstanding Issues. Mineralogical Association of Canada, Short Course Series Volume 40. Quebec, Canada, 147–168. (GeoReM 2902).

Jochum, K.P., Weis, U., Stoll, B., Kuzmin, D., Yang, Q., Raczek, I., Jacob, D.E., Stracke, A., Birbaum, K., Frick, D.A., Günther, D., Enzweiler, J., 2011. Determination of reference values for NIST SRM 610—617 glasses following ISO guidelines. Geostand. Geoanal. Res. 35, 397–429.

Jochum, K.P., Scholz, D., Stoll, B., Weis, U., Wilson, S.A., Yang, Q., Schwalb, A., Börner, N., Jacob, D.E., Andrea, M.O., 2012. Accurate trace element analysis of speleothems

and biogenic calcium carbonates by LA-ICP-MS. Chem. Geol. 318–319, 31–44.
Klemme, S., Prowatke, S., Münker, C., Magee, C.W., Lahaye, Y., Zack, T., Kasemann, S.A., Cabato, E.J.A., Kaeser, B., 2008. Synthesis and preliminary characterisation of new silicate, phosphate and titanite reference glasses. Geostand. Geoanal. Res. 32, 39–54.
Koenig, A.E., Rogers, R.R., Trueman, C.N., 2009. Visualizing fossilization using laser ablation–inductively coupled plasma–mass spectrometry maps of trace elements in Late Cretaceous bones. Geology 37, 511–514.
Kohn, M.J., 2008. Models of diffusion-limited uptake of trace elements in fossils and rates of fossilization. Geochim. Cosmochim. Acta 72, 3758–3770.
Kohn, M.J., Moses, R.J., 2013. Trace element diffusivities in bone rule out simple diffusive uptake during fossilization but explain in vivo uptake and release. PNAS 110, 419–424.
Kohn, M.J., Schoninger, M.J., Barker, W.W., 1999. Altered states: effects of diagenesis on fossil tooth chemistry. Geochim. Cosmochim. Acta 63, 2737–2747.
LeGeros, R.Z., 1991. Calcium Phosphates in Oral Biology and Medicine. Monographs in Oral Science 15. Karger, Paris.
Limbeck, A., Galler, P., Bonta, M., Bauer, G., Nischkauer, W., Vanhaecke, F., 2015. Recent advances in quantitative LA-ICP-MS analysis: challenges and solutions in the life sciences and environmental chemistry. Anal. Bioanal. Chem. 407, 6593–6617.
Lin, J., Liu, Y., Yang, Y., Hu, Z., 2016. Calibration and correction of LA-ICP-MS and LA-MC-ICP-MS analyses for element contents and isotopic ratios. Solid Earth Sciences 1, 5–27.
Longerich, H.P., Jackson, S.E., Günther, D., 1996. Laser ablation inductively coupled plasma mass spectrometric transient signal data acquisition and analyte concentration calculation. J. Anal. At. Spectrom. 11, 899–904.
Lösch, S., Moghaddam, N., Grossschmidt, K., Risser, D.U., Kanz, F., 2014. Stable isotope and trace element studies on gladiators and contemporary Romans from Ephesus (Turkey, 2nd and 3rd ct. AD) – implications in diet. PLoS ONE 9, e110489.
Luo, R., Su, X., Xu, W., Zhang, S., Zhuo, X., Ma, D., 2017. Determination of arsenic and lead in single hair strands by laser ablation inductively coupled plasma mass spectrometry. Sci. Rep. 7, 3426.
Makarewicz, C.A., Sealy, J., 2015. Dietary reconstruction, mobility, and the analysis of ancient skeletal tissues: expanding the prospects of stable isotope research in archaeology. J. Archaeol. Sci. 56, 146–158.
Maurer, A.-F., Gerard, M., Person, A., Barrientos, I., del Carmen Ruiz, P., Darras, V., Durlet, C., Zeitoun, V., Renard, M., Faugère, B., 2011. Intra-skeletal variability in trace elemental content of Precolumbian Chupicuaro human bones: the record of post-mortem alteration and a tool for paleodietary reconstruction. J. Archaeol. Sci. 38, 1784–1797.
Maurer, A.-F., Person, A., Zazzo, A., Sebilo, M., Balter, V., Le Cornec, F., Zeitoun, V., Dufour, E., Schmidt, A., de Rafélis, M., Ségalen, L., Bedaux, R., 2017. Geochemical identity of pre-Dogon and Dogon populations at Bandiagara (Mali, 11th–20th cent. AD). J. Archaeol. Sci. Rep. 14, 289–301.
Miliszkiewicz, N., Walas, S., Tobiasz, A., 2015. Current approaches to calibration of LA-ICP-MS analysis. J. Anal. At. Spectrom. 30, 327–338.
Millard, A.R., Hedges, R.E.M., 1996. A diffusion-adsorption model of uranium uptake by archaeological bone. Geochim. Cosmochim. Acta 60, 2139–2152.
Müller, W., Anczkiewicz, R., 2016. Accuracy of laser-ablation (LA)-MC-ICPMS Sr isotope analysis of (bio)apatite – a problem reassessed. J. Anal. At. Spectrom. 31, 259–269.
Müller, W., Nava, A., Evans, D., Rossi, P.F., Alt, K.W., Bondioli, L., 2019. Enamel mineralization and compositional time-resolution in human teeth evaluated via histologically-defined LA-ICP-MS profiles. Geochim. Cosmochim. Acta 255, 105–126.
Pesquero, M.D., Bell, L.S., Fernandez-Jalvo, Y., 2017. Skeletal modification by microorganisms and their environments. Hist. Biol. https://doi.org/10.1080/08912963.2017.1371713.
de S. Pessôa, G., Lopes Júnior, C.A., Madrid, K.C., Arruda, M.A.Z., 2017. A quantitative approach for Cd, Cu, Fe and Mn through laser ablation imaging for evaluating the translocation and accumulation of metals in sunflower seeds. Talanta 167, 317–324.
Pestle, W.J., Crowley, B.E., Weirauch, M.T., 2014. Quantifying inter-laboratory variability in stable isotope analysis of ancient skeletal remains. PLoS ONE 9, e102844.
Pozebon, D., Scheffler, G.L., Dressler, V.L., Nunes, M.A.G., 2014. Review of the applications of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) to the analysis of biological samples. J. Anal. At. Spectrom. 29, 2204–2228.
Pozebon, D., Scheffler, G.L., Dressler, V.L., 2017. Recent applications of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) for biological sample analysis: a follow-up review. J. Anal. At. Spectrom. 32, 890–919.
Praamsma, M.L., Parsons, P.J., 2016. Calibration strategies for quantifying the Mn content of tooth and bone samples by LA-ICP-MS. Accred. Qual. Assur. 21, 385–393.
Price, T.D., Burton, J.H., Bentley, R.A., 2002. The characterization of biologically available strontium isotope ratios for the study of prehistoric migration. Archaeometry 44, 117–135.
Rasmussen, K.L., Skytte, L., D'imporzano, P., Thomsen, P.O., Søvsø, M., Boldsen, J.L., 2017. On the distribution of trace element concentrations in multiple bone elements in 10 Danish medieval and post-medieval individuals. Am. J. Phys. Anthropol. 162, 90–102.
Reiche, I., Favre-Quattropani, L., Vignaud, C., Bocherens, H., Charlet, L., Menu, M., 2003. A multi-analytical study of bone diagenesis: the Neolithic site of Bercy (Paris, France). Meas. Sci. Technol. 14, 1608–1619.
Salesse, K., Dufour, E., Lebon, M., Wurster, C., Castex, D., Bruzek, J., Zazzo, A., 2014. Variability of bone preservation in a confined environment: the case of the catacomb of Sts Peter and Marcellinus (Rome, Italy). Palaeogeogr. Palaeoclimatol. Palaeoecol. 416, 43–54.
Scharlotta, I., Weber, A., 2014. Mobility of middle Holocene foragers in the Cis-Baikal region, Siberia: individual life history approach, strontium ratios, rare earth and trace elements. Quat. Int. 348, 37–65.
Scharlotta, I., Goriunova, O.I., Weber, A., 2013. Micro-sampling of human bones for mobility studies: diagenetic impacts and potentials for elemental and isotopic research. J. Archaeol. Sci. 40, 4509–4527.
Schöne, B.R., Zhang, Z., Jacob, D., Gillikin, D.P., Tütken, T., Garbe-Schönber, D., McConnaughey, T., Soldati, A., 2010. Effect of organic matrices on the determination oft he trace element chemistry (Mg, Sr, Mg/Ca, Sr/Ca) of aragonitic bivalve shells (Arctica islandica) – comparison of ICP-OES and LA-ICP-MS data. Geochem. J. 44, 23–37.
Sillen, A., 1986. Biogenic and diagenetic Sr/Ca in Plio-Pleistocene fossils in the Omo Shungura Formation. Paleobiobiology 12, 311–323.
Sillen, A., Kavanagh, M., 1982. Strontium and paleodietary research: a review. Am. J. Phys. Anthropol. 25, 67–90.
Somerville, A.D., Sugiyama, N., Manzanilla, L.R., Schoeninger, M.J., 2016. Animal management at the ancient metropolis of Teotihuacan, Mexico: stable isotope analysis of leporid (cottontail and jackrabbit) bone mineral. PloSONE 11, e0159982.
Sponheimer, M., Ruiter, D.D., Lee-Thorp, J., Späth, A., 2005. Sr/Ca and early hominin diets revisited: new data from modern and fossil tooth enamel. J. Hum. Evol. 48, 147–156.
Stadlbauer, C., Reiter, C., Patzak, B., Stingeder, G., Prohaska, T., 2007. History of individuals of the 18th/19th centuries stored in bones, teeth, and hair analyzed by LA–ICP–MS—a step in attempts to confirm the authenticity of Mozart's skull. Anal. Bioanal. Chem. 388, 593–602.
Swift, J., Cupper, M.L., Greig, A., Westaway, M.C., Carter, C., Santoro, C.M., Wood, R., Jacobsen, G.E., Bertuch, F., 2015. Skeletal arsenic of the pre-Columbian population of Caleta Vitor northern Chile. J. Archaeol. Sci. 58, 31–45.
Sylvester, P., 2008. Matrix effects in LA–ICP–MS. In: Laser Ablation–ICP–MS in the Earth Sciences, Cyrrent Practices and Outstanding Issues. Paul Sylvester Editor, Short Course Delivered in Association with Goldschmidt 2008, Vancouver, B.C., 19–20 July, 2008, pp. 67–76.
Tanaka, Y-k., Yajima, N., Okada, M., Matsumoto, T., Higuchi, Y., Miyazaki, S., Yamato, H., Hirata, T., 2017. The effect of Mg and Sr on the crystallinity of bones evaluated through Raman spectroscopy and laser ablation-ICPMS analysis. Analyst 142, 4265–4278.
Toots, H., Voorhies, M.R., 1965. Strontium in fossil bones and the reconstruction of food chains. Science 149, 854–855.
Trueman, C.N., Tuross, N., 2002. Trace elements in recent and fossil bone apatite. In: Kohn, M.J., Rakovan, J., Hugues, K.M. (Eds.), Phosphates: Geochemical, Geobiological and Materials Importance. 48. Mineralogical Society of America, pp. 489–521.
Turner-Walker, G., Jans, M., 2008. Reconstructing taphonomic histories using histological analysis. Palaeogeogr. Palaeoclimatol. Palaeoecol. 266, 227–235.
Ugarte, A., Unceta, N., Pecheyran, C., Goicolea, M.A., Barrio, R.J., 2011. Development of matrix-matching hydroxyapatite calibration standards for quantitative multi-element LA-ICP-MS analysis: application to the dorsal spine of fish. J. Anal. At. Spectrom. 26, 1421–1427.
Vajda, E.G., Skedros, J.G., Bloebaum, R.D., 1998. Errors in quantitative backscattered electron analysis of bone standardized by energy-dispersive X-ray spectrometry. Scanning 20, 527–535.
Van Klinken, G.J., 1999. Bone collagen quality indicators for palaeodietary and radiocarbon measurements. J. Archaeol. Sci. 26, 687–695.
Volesky, B., Holan, Z.R., 1995. Biosorption of heavy metals. Biotechnol. Prog. 11, 232–250.