

Evaluating the precision requirements for isotope ratio determination of archaeological materials using LA-TOF-ICP-MS

Increasing Ratio Precision

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High precision isotopic determination of archaeological materials using laser ablation ICP-MS remains an elusive goal. While practical, nearly non-destructive, rapid and cost effective, isotope ratio measures using LA-ICP-MS suffer from transient effects, laser-induced fractionation, and generally lower precision than other methods of sample introduction. However, in contrast to high precision measurement requirements in biological systems, lower levels of analytical precision may still meet threshold levels for isotopic discrimination in archaeological materials, depending on the specificity of the research questions. We here report on our efforts to reduce the spread of replicate isotopic measurements of archaeological materials using pre and post-

laser sample treatment, and evaluate the degree to which lower levels of precision affect group attribution in specific cases.

Some recent attention on the desirability of using laser ablation sample introduction for the fingerprinting and compositional analysis of archaeological materials has touted the rapid, low cost and minimally destructive result possible with laser ablation techniques (1). It is unfortunate that the strides made in multi-element compositional group formation have not permeated into the realm of isotope ratio analyses on some of the same material types. Isotope ratio analysis of biologically available heavy elements such as strontium are useful indicators of marine and terrestrial diet or for distinguishing migrants within populations by the difference in strontium isotope ratios in bones and teeth, which are a consequence of soil and groundwater isotope differences in natal regions (2, 3). Alternatively, lead isotope analysis is useful to the archaeologist because lead is a widely used mineral in additive technologies such as prehistoric glasses and frits as well as ceramic glazes, and it is used as an alloying agent in ancient metallurgy (4, 5).

Of primary interest in this study is the effort to increase the precision of isotopic measurement using inductively coupled plasma time of flight mass spectrometry (ICP-TOF-MS) and to determine if variation in absolute accuracy, relative to well-characterized NIST standard reference materials, is a function of fractionation in the laser ablation chamber, sample transport, or merely a mass bias artifact of instrumental operating conditions and other adjustable parameters in the time of flight mass spectrometer. Several authors have argued the merits of improving isotopic ratio techniques in ICP-MS (6, 7, 8), but most have come at the problem from disciplines where ultra-precise ratio measures are not only desirable, but critical to understanding biological uptake and incorporation of radionuclides, or isotopic fractionation of exotic particles in analytical chemistry. Taken as a whole, this literature can be divided into two main camps. The first is concerned largely with sample introduction mechanisms (7, 9, 10), and the concomitant effort to understand the effect of sample introduction relative to precision and possible fractionation of the ion stream, whether liquid or gas sample carrier is used. The second camp has focused its efforts on describing the instrumental parameters and physics of ion counting in different mass analyzers (8, 11), in an effort to estimate precision limits and to explain the deviation from expected isotopic ratios that affect instrumental accuracy. Both of these literatures are technical and perhaps esoteric outside of the realm of analytical chemistry, but they provide us some expectations for experimental procedure that we can test for our own real world samples and projects.

Isotope ratios for archaeology

In the remainder of this chapter, we describe some of our lab's efforts to increase the precision and accuracy for replicate measurements of the isotopes of two elements of particular interest to archaeologists, lead (Pb) and strontium (Sr). Over the past 30 years, lead and strontium isotope ratios have been measured with thermal ionization mass spectrometry (TIMS). Elemental salts are deposited on a filament heated to produce ionized particles, which are then sent into a mass spectrometer where they are detected by multiple Faraday cups arrayed such that ions of several masses are collected simultaneously. TIMS is capable of high precision isotope discrimination, but the instruments tend to be large and expensive, and extensive sample preparation is required prior to sample introduction. Newer ICP-MS-based technologies like multi-collector ICP-MS (especially laser ablation) circumvent some of the sample preparation issues while exploiting the precision of simultaneous mass discrimination, but they are still limited by the number and configuration of ion collectors.

Archaeologically, isotope ratio measures provide a means to identify the location of origin of artifacts or osteological remains. However, ambiguity of provenance based on isotopic signatures may be partially resolved by incorporating trace element signatures that improve the likelihood of source identification. One example currently under study is the comparative analysis of isotope ratios and potential discriminator elements, such as the simultaneous collection of strontium or lead isotope ratio data and differential concentration of rare earth elements within large samples of archaeological skeletal remains (12).

In contrast to multi-collector TIMS or ICP-MS based instruments, the GBC Optimass orthogonal Time of Flight ICP-MS installed in our lab utilizes a single discrete dynode ion detector (ETP Pty. Ltd., Ermington, Australia). Instead of measuring the characteristic mass/charge of an ion as a consequence of its deflection along a magnetic flight tube, time of flight mass spectrometry measures the characteristic flight time of an ion as it traverses a parabolic flight path with an effective 1.4 meter flight distance. Traversing this distance allows temporal separation of ions by mass/charge (13), and renders essentially synchronous signal counting over the entire mass spectrum. Synchronous data acquisition has the potential to vastly improve transient signal discrimination. Transient signals are produced by sampling spatially or temporally heterogeneous materials, and generally are the rule rather than the exception in laser ablation sample introduction. While not central in the present context, the ability to discern heterogeneity within the sample matrix or from surface contamination in real time allows correction and resampling, and offers insights to the problem of 'noisy data'. More importantly in the present context, the

ability to sample the ion stream very rapidly can be exploited to achieve improvements in isotope ratio analyses.

Analytical parameters

The purposes of this paper are to report on our efforts to evaluate the real world precision of laser ablation time of flight ICP-MS (LA-TOF-ICP-MS) replicate measurements on NIST standards and archaeological materials, and to explore the sources and magnitudes of mass bias and/or mass fractionation in our instrumental setup. Some authors (7, 14) have speculated on the causes of laser induced fractionation in laser ablation sample introduction systems. While not fully understood, laser-induced fractionation seems to be a complex interaction at the ablation site of laser energy differentially heating and volatilizing sample particles, resulting in a heterogeneous distribution of elements and isotopes across ablated particle size.

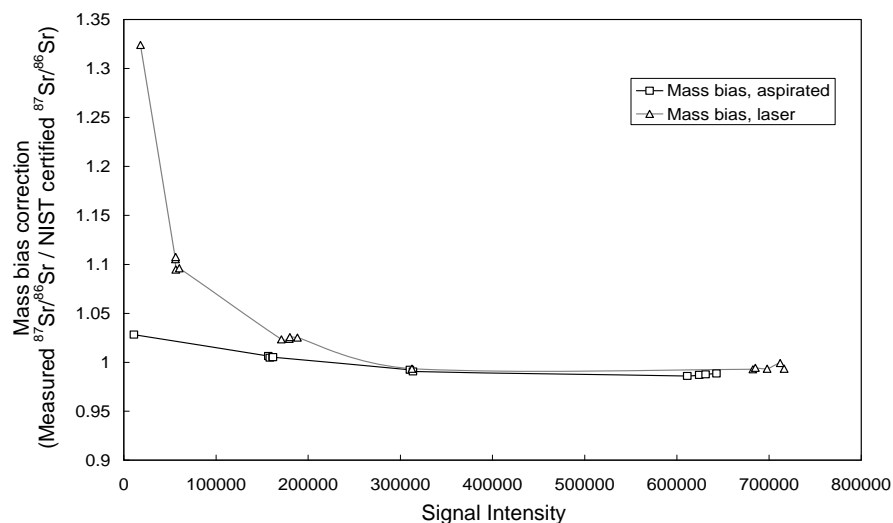


Figure 1. Comparison of mass bias by sample introduction type.

To test for the possibility of laser-induced fractionation, we compared NIST standards in the TOF with both laser and nebulizer aspirated solutions (Figure 1). Our results indicate that while a small amount of bias correction difference exists between laser and aspirated sample introduction at lower signal intensities, no significant difference in isotopic ratios between ablated and

aspirated samples exists when signal intensities are maintained at 300,000 cps and higher.

To mitigate laser induced fractionation at different laser energies, we operated the laser at 100% of maximum output energy on all samples (Table 1), and modulated the argon and aerosolized sample entering the plasma torch using a simple tabletop rotometer. Controlling the gas flow with the rotometer allows us to standardize the measured signal intensity across samples of widely variable concentrations without altering plasma or detector settings, which might introduce conditions generating differential mass bias.

Laser Ablation Device	New Wave UP213 Nd:YAG
Wavelength	213 nm
Energy	0.6 mJ
Spot size	100 μm
Fluence	7.35 J cm^{-2}
Rep rate	20 Hz
Depth/pass	5 μm
Scan speed	50 $\mu\text{m/s}$
ICP-MS	GBC Optimass 8000 TOF ICP-MS
Detector	discrete dynode electron multiplier
RF power	700 W
Plasma Ar gas flow rate	10.0 l min^{-1}
Auxiliary Ar gas flow rate	0.5 l min^{-1}
Sample Ar gas flow rate	1.2 l min^{-1}
Data acquisition mode	time resolved, 1 second/acquisition

Table 1. Instrument parameters for this experiment

Mass bias—the condition in which ions of different masses are sampled by the detector at frequencies varying from their expected proportions—is thought to be a result of space-charge effects in the high pressure region immediately downstream of the plasma torch (15).

In the TOF-ICP-MS, space-charge produces varying effects on different isotopic masses, as ions with higher atomic masses maintain higher inertia (16). This results in an increased transmission efficiency of heavier ions and an increase in scattering of the lighter ions from the axial path as they encounter the high pressure region between the plasma flame and the ion optics. This effect should be more noticeable for lighter ion isotope species, because of the relatively smaller ratio of mass to mass difference between adjacent isotopes.

Our experiments have demonstrated that, irrespective of the magnitude of mass bias when counting isotopes, by standardizing the time-resolved signal intensity within the linear portion of the mass bias count rate curve, mass bias corrections have small variations with respect to rather larger signal differences.

On the other hand, at high signal intensities approaching 50 million analog counts per second, saturation of the detector results in suppression of actual counts for the most abundant isotope, producing a spurious mass bias correction. While the 256 ion counting channels of the detector software are theoretically capable of measuring 64 million counts per second without ion stacking (13), our empirical result shows that significantly lower count rates can result in ratio suppression on certain isotopes. Consequently, our strategy was to generate count rates that inhabited the flattest portion of the mass bias correction curve, without detector saturation. Problematically, isotope ratios that were far from percentage equilibrium (e.g., $^{204}\text{Pb}/^{206}\text{Pb}$) may exhibit both problems: too low count rate for ^{204}Pb to generate the flattest linear mass bias correction, and too high for ^{206}Pb , causing partial detector saturation. A similar problem was found for $^{84}\text{Sr}/^{88}\text{Sr}$ and $^{86}\text{Sr}/^{88}\text{Sr}$, which precludes these invariant ratios from being used as an internally-standardized mass bias correction for the measured $^{87}\text{Sr}/^{86}\text{Sr}$ (17).

Experimental procedure

Pb isotopes

We began our experiment by taking fused glass beads impregnated with NIST Common Lead Isotopic Standard SRM 981 and making successive passes over the bead surface with the laser, continuously ablating over a pre-ablated raster pattern. To control the ion count rate, we utilized the tabletop rotometer to adjust the argon sample gas flow up or down to normalize the count rate at the detector to around 5-10 million counts per second. At this count rate, we achieve the greatest linear stability of the isotope ratio $^{207}\text{Pb}/^{206}\text{Pb}$. Using this data as our isotopic ratio mass bias correction, we analyzed several archaeological lead glasses and glazes previously analyzed by Robert Brill (Corning Museum of Glass) using TIMS (Figure 2).

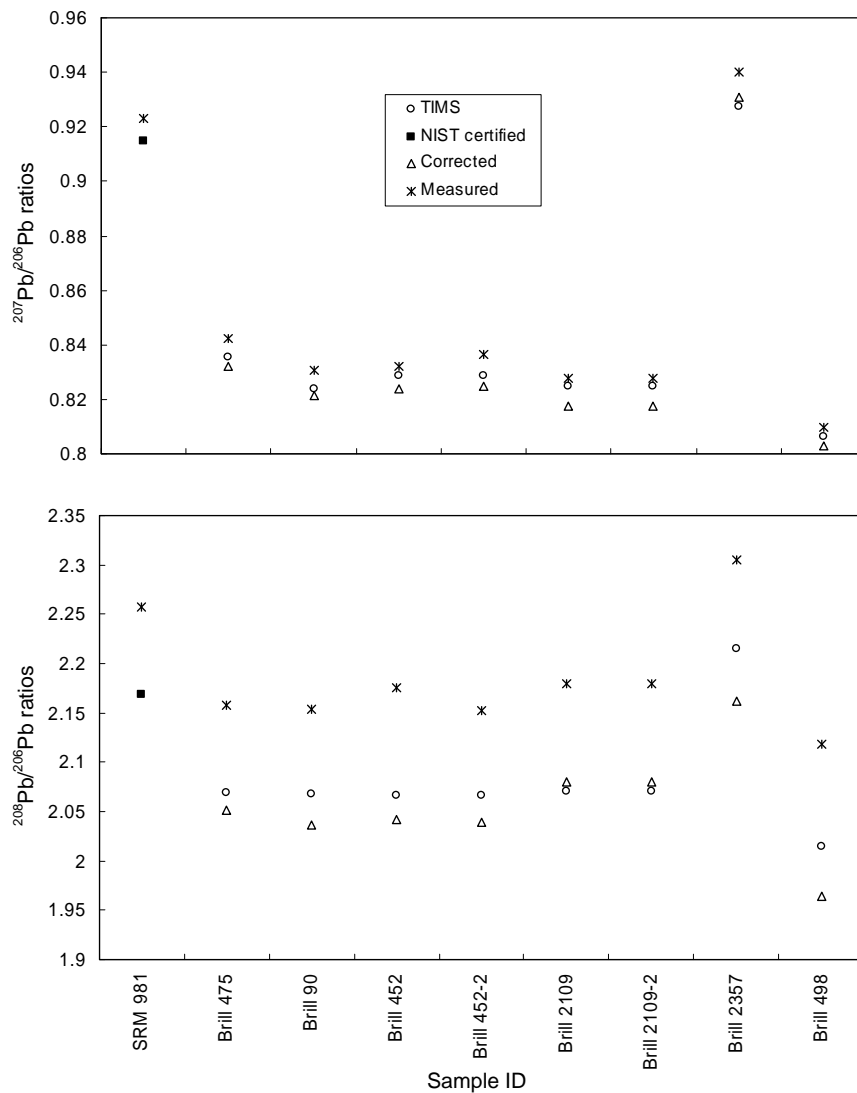


Figure 2. Comparison of TIMS and time of flight ICP-MS Pb isotope ratios from Brill glasses.

Our results indicate that at standard count rates across lead glasses with a range of lead oxide weight percents, we are able to closely approximate the TIMS-reported $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios, after correcting for mass bias

using NIST SRM 981 standard isotopic lead. As anticipated, the mass bias correction for the $^{208}\text{Pb}/^{206}\text{Pb}$ ratio was of greater magnitude than the $^{207}\text{Pb}/^{206}\text{Pb}$, an indication that space-charge effects were of greater magnitude for isotopes two mass units apart than for adjacent masses.

Sr isotopes

A similar set of experiments was performed to test our ability to precisely characterize strontium isotopes. For the archaeological chemistry of biological remains, strontium isotopes are useful for testing dietary hypotheses and for examining differences in place of birth and place of residence. To test the precision of strontium isotope ratio measurement using TOF-ICP-MS, we made glass fusion beads using NIST Strontium Carbonate Standard SRM 987 and examined the effect of varying concentrations of strontium on our precision. Unlike the measurement of lead isotope ratios in pottery glazes or metal artifacts, strontium concentration occurs at lower levels in biological tissues, usually from about 10 to 1000 parts per million (19). While this concentration is well within the analytical range of high precision aspirated liquid ICP-MS, it is generally too low to achieve high precision isotope ratio measures using laser ablation, due to lower ion counting rates.

One technique to remedy this problem involves taking several hundred independent, one second 'snapshot' measures of strontium isotope ratios and averaging the individual ratio measures to build higher statistical precision. The method has two important advantages: first, it makes use of the TOF-ICP-MS ability to simultaneously measure multiple masses and generate isotope ratios 'on the fly'; and second, plots of the one second instantaneous isotope ratio deviations from expected ratios can be visually checked for laser ablation artifacts or sample contamination during data acquisition. It is expected that this method will help identify the source of 'noisy' data that sometimes affect isotope ratio determinations using TIMS or other averaged sample introduction methods.

We tested this data acquisition method by first ablating bracketing concentration standard glasses that had been determined from previous measurements. All the samples in this analysis had total strontium elemental concentrations between 95 and 350 parts per million strontium. We then collected 150-300 one second ion count packets for ^{84}Sr , ^{86}Sr , ^{87}Sr and ^{88}Sr , plus the instantaneous ratio of each isotope to ^{86}Sr (Figure 3).

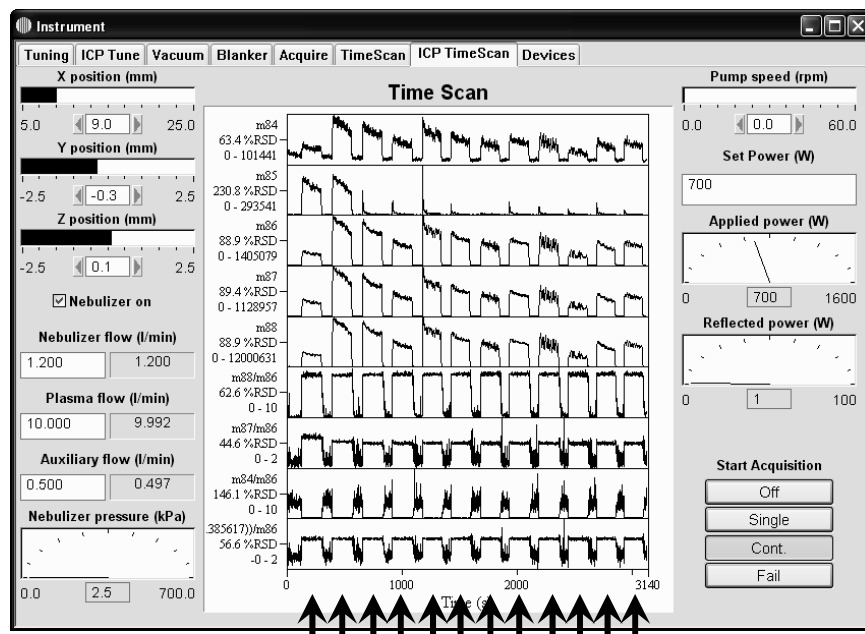


Figure 3. Timescan packets for dental enamel Sr isotope sampling. Arrows indicate individual samples (standards and teeth).

After examining the calibration curve for mass bias correction between the bracketing standards, and culling measurements arising from instrument noise or regions of sample contamination, all remaining one second count packets were averaged and bias corrected. This ‘on the fly’ sampling method, made possible by the simultaneous counting of the entire mass spectrum, enables us to quickly determine the region on the sample with the highest elemental concentration, so that isotope ratio precision and accuracy can be optimized. It also permits rapid identification of regions of matrix variability, because aberrant transient signals are easily identified as spikes of analyte signal intensity on the graphical display. TOF-ICP-MS technology is perfectly suited to laser ablation sample introduction, in that it makes best use of the transient signal that is volatilized by the laser beam, and can be temporally matched to the scan and pulse rate of ablation for systematic data acquisition.

Results from archaeological samples

Pb isotopes in glass beads

We tested this method for lead isotope ratio measurement using archaeological glass trade beads from central California. These beads were used as trade goods between fort traders and Native Americans all over the western United States (19, 20). Central Californian Indian groups had manufactured and used shell and stone beads for centuries prior to the arrival of Europeans and quickly adopted the brightly colored glass beads as prestige and trade items. Linking the characteristic compositions of the beads found in both historic European forts and Native American archaeological sites is one method to determine the level of interaction between these groups. Specific recipes are believed to have been used by European bead workshops, and the addition of isotopic compositional data is a potentially powerful way to tie the chemical data to specific manufacturing regions.

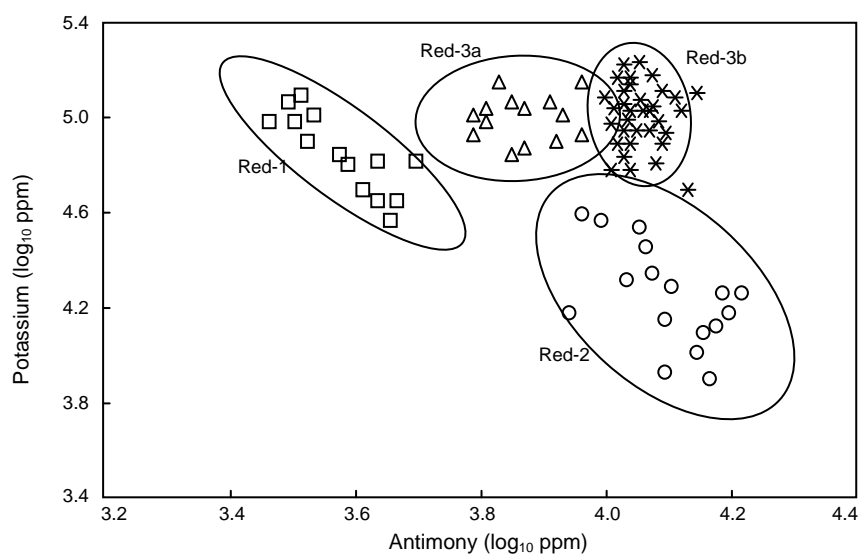


Figure 4. Provisional compositional groups among red beads determined on a plot of potassium and antimony.

Multiple compositional groups recognized in the data are illustrated on a bivariate plot of log-transformed potassium and antimony (Figure 4). These groups are believed to represent different recipes and, consequently, different regions of manufacture. We compared the $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios to see if similar group discrimination could be determined (Figure 5). Two groups, Red-1 and Red-2, are visible in this plot. The other groups defined elementally, Red-3a and Red-3b, do not show unique isotope ratio profiles, and the group identified as Red-3a shows an undesirable spread along both isotopic axes. Further analysis is required to understand whether this bead group is isotopically heterogeneous but of similar elemental recipe, or if the beads themselves are compositionally heterogeneous. Since the beads are considered to be aesthetically beautiful—as well as important—historical artifacts, large scale bulk analyses derived from crushing and vaporizing whole collections of beads is not an option for compositional determination and sourcing. For this reason, LA-TOF-ICP-MS may be the most appropriate tool for rapid elemental and isotopic characterization within this class of artifacts.

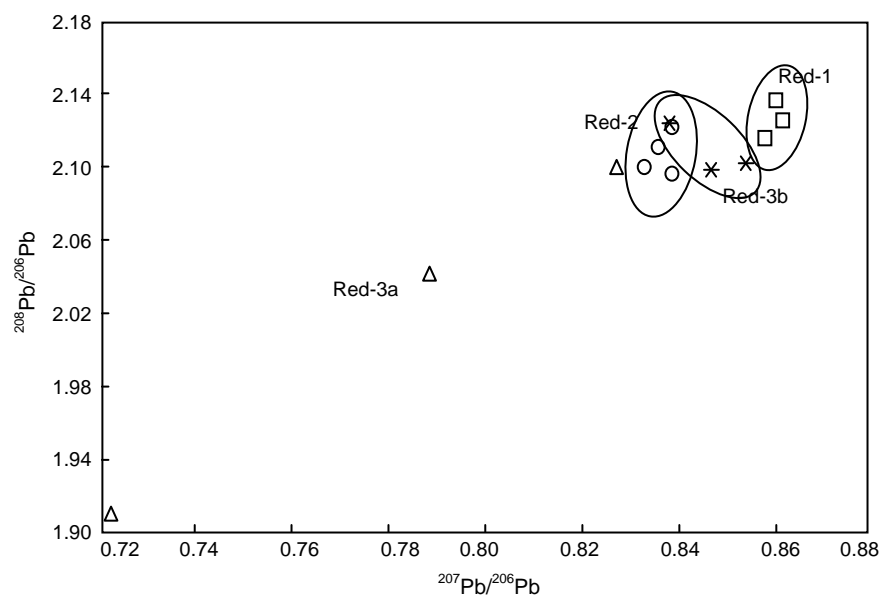


Figure 5. Possible group identification determined from a plot of $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$.

Sr isotopes in human dental enamel

As part of an ongoing research project to document the dietary and health status of the prehistoric population of Easter Island, dental samples were analyzed to determine our ability to discern marine versus terrestrial dietary groups on this small island (12). As an extension of a previous project to determine archaeological signatures of migration using total biologically incorporated strontium (21), we analyzed $^{87}\text{Sr}/^{86}\text{Sr}$ in a sample of skeletal remains representing coastal and inland populations. This preliminary effort attempted to generate $^{87}\text{Sr}/^{86}\text{Sr}$ ratios with precisions commensurate with data generated by TIMS. Following the methods outlined above, several hundred one second ‘snapshot’ measures of $^{87}\text{Sr}/^{86}\text{Sr}$ were collected in timescan mode, as well as the more traditional short interval, time-averaged integration method, and precision estimates calculated. Both results were compared to typical data created by TIMS, to assess the magnitude of precision differences between instrumental methods.

Precision estimates of our replicate measurements are shown below, along with average $^{87/86}\text{Sr}$ (Table 2). Compared with precision estimates for published TIMS data and our standard laser ablation time of flight protocol (comprised of an average of five, five second integrations) we can see that our timescan protocol reduces the standard error of replicate measures by around 80%. This standard error is still about three times the average reported standard error of the TIMS measurements, but demonstrates the increased precision achievable with increased sampling.

LA-tof-ICP-MS (replicate integrations)	LA-tof-ICP-MS (time scan)	TIMS (Univ. Wisconsin)
0.71034 +/- 0.0211	0.71034 +/- 0.0027	0.70843 +/- 0.0008
0.71034 +/- 0.0105	0.71034 +/- 0.0015	0.70788 +/- 0.0008
0.71034 +/- 0.0059	0.70824 +/- 0.0019	0.71259 +/- 0.0008
0.71034 +/- 0.0030	0.71191 +/- 0.0064	0.70856 +/- 0.0007
0.70414 +/- 0.0120	0.70474 +/- 0.0021	0.70821 +/- 0.0007
0.70919 +/- 0.0122	0.70856 +/- 0.0029	0.71869 +/- 0.0008
0.70109 +/- 0.0120	0.71240 +/- 0.0018	0.70872 +/- 0.0007
	0.71183 +/- 0.0018	0.70848 +/- 0.0007
	0.71468 +/- 0.0021	0.72279 +/- 0.0008
	0.71280 +/- 0.0018	0.73342 +/- 0.0007
	0.71208 +/- 0.0015	0.70867 +/- 0.0007

Table 2. Precision estimates for $^{87/86}\text{Sr}$, by instrument and technique.

It is anticipated that more experimentation using longer counting intervals will reduce the spread of replicate measures even more. However, it is not known whether discrete sampling techniques will equal the precision of bulk-averaged multi-collector mass spectrometer measurements like TIMS without some effort to average a heterogeneous sample prior to introduction to the ICP-MS torch. Presently, we believe the remaining noise in our strontium isotope determinations is due to: 1) inherent instability in the TOF measurements, presumably related to Poisson-distributed counting statistics and, 2) micro-spatial heterogeneity within the material being ablated. The latter may be explained by dietary variation during enamel mineralization, or micro-structural diagenetic variation (22). Both hypotheses impact the conclusions offered here, and as such deserve further exploration to assess the magnitude of their effect on our measurements. Additional research on samples measured by laser ablation time of flight ICP-MS, with validation by TIMS or other traditional high precision technologies will help determine whether LA-TOF-ICP-MS can address archaeological questions with the required degree of precision and accuracy to make verifiable statements about prehistoric migration and diet of animals and people.

Conclusion

While we think we have arrived at the right combination of sample introduction and system and ion counting parameters, it remains an empirical challenge to produce reliable isotope measurements using LA-TOF-ICP-MS. Adjusting for an appropriate instrumental count rate is key to approaching accurate measures, and averaging many multiples of replicates is effective at reducing the spread of the data points to achieve a precision that may be sufficient to assign samples to particular source groups or to identify migrants within populations. Unfortunately, the data required to prove the technology sufficient for the current application is essentially a moving target, because questions about the archaeological record are continually being asked at smaller scales, and answers that may render a meaningful interpretation of human prehistory today may not do so tomorrow. We are continually striving to compare more samples from different locales with the expectation that we can make meaningful distinctions between samples in most cases. We will continue to analyze artifacts previously characterized by TIMS and multi-collector ICP-MS to amass a database of isotope variability to compare our conclusions and validate our methods and results.

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