



Best practices for calibrating and reporting stable isotope measurements in archaeology



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ABSTRACT

The use of isotopic measurements in archaeological research has increased rapidly over the past ~25 years, owing largely to the proliferation of the instruments required to produce these measurements relatively quickly and cheaply. Unfortunately, the understanding of how to adequately calibrate and report these isotopic data has not kept pace. We surveyed nearly 500 archaeological research papers published within the past 25 years that presented original isotopic data. We found that, generally, the majority of studies do not provide adequate information regarding how isotopic measurements were calibrated, nor how analytical uncertainty (precision and accuracy) was assessed. We review and present recommendations for data analysis, calibration, and reporting to aid archaeological researchers who use isotopic measurements and practices. We present a simple method for quantifying standard analytical uncertainty using data that would be provided by most laboratories.

1. Introduction

Isotope ratio mass spectrometry (IRMS) is used widely in archaeological¹ studies to address a variety of questions. Beginning in the late 1990s, the direct interfacing of rapid and automated combustion techniques (e.g., elemental analyzers connected via continuous-flow to IRMS systems) for analyzing bulk organic materials decreased analytical costs and dramatically increased the number of analyses that could feasibly be performed in a given study. Prior to that time relatively few isotopic studies had been conducted in archaeology, and each study produced at most a few dozen measurements. In recent years, an abundance of studies has been conducted, producing thousands of measurements (Fig. 1). Given the now widespread availability of technology to produce isotopic measurements quickly and cheaply, it is important to examine how these measurements are being reported. This is particularly important in archaeology as the researchers primarily responsible for disseminating the results in publications are often not directly involved in obtaining the raw measurements and transforming them into calibrated δ - (delta) values. Moreover, results obtained from commercial laboratories may lack the relevant details or be difficult to interpret with respect to analytical uncertainty, particularly for scholars with a limited understanding of isotope ratio mass spectrometry. A decade ago, Jardine and Cunjak (2005) commented on the increase in laboratories providing isotopic measurements and

recognized the potential of a widening knowledge gap between IRMS operators and ecologists disseminating these data. We have noticed a similarly widening knowledge gap in archaeology, particularly as it relates to the reporting of analytical methods and uncertainty. While a number of studies have attempted to examine within- and among-laboratory variation in isotopic measurements, the emphasis has been on sample preparation specifically (e.g., Guiry et al., 2016; Jørkov et al., 2007; Sealy et al., 2014), or more generally on measurements produced by different laboratories (e.g., Pestle et al., 2014). Little attention has been paid to the effects of data calibration or the quantification of measurement accuracy, precision, and overall uncertainty.

The purpose of this paper was fourfold. First, we sought to evaluate the reporting of stable carbon and nitrogen isotopic measurements and their associated uncertainties in the archaeological literature. To do this, we performed a review of relevant literature, focusing on data reporting, calibration methods and quality control (accuracy and precision). The results of this survey suggested that a review of methods and strategies for reporting isotopic data would be useful to archaeologists utilizing IRMS in their research. As such, the second purpose of the paper was to review data reporting and quality control methods and present them in a manner accessible to researchers who are reporting isotopic measurements but not generating the measurements themselves. Third, on the basis of our literature survey and review of

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¹ For the purposes of this discussion, we use the terms 'archaeological' and 'archaeology' as catch-alls for isotopic studies in both archaeology and physical anthropology.

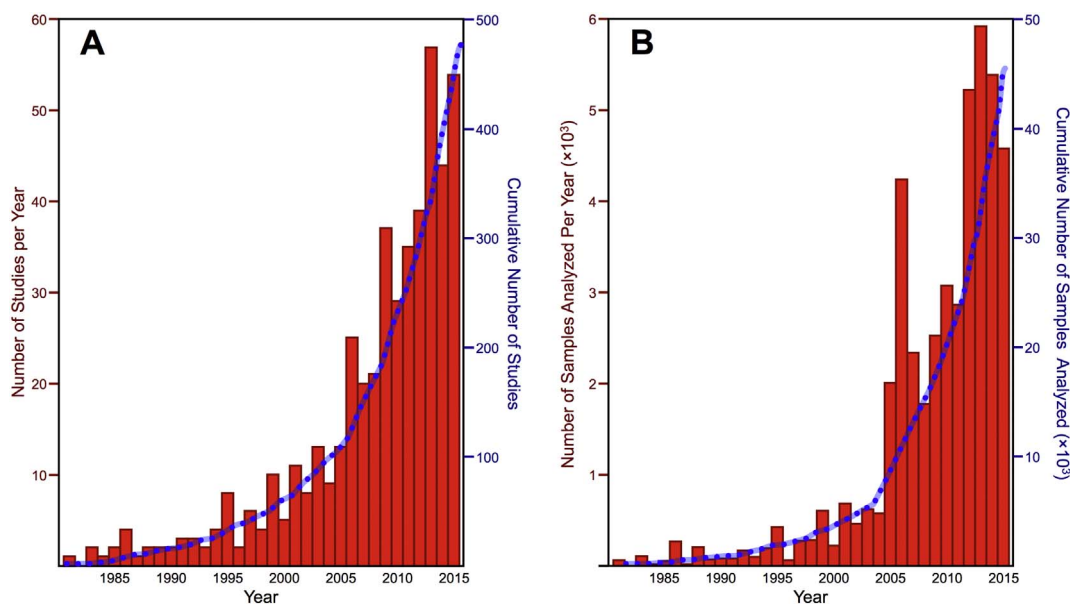


Fig. 1. (A) Number of studies included in the survey per year (primary axis) and cumulative number of studies (secondary axis). (B) Number of isotopic measurements (in thousands) presented in the papers included in the survey per year (primary axis) and cumulatively (secondary axis).

concepts, as well as previously-published International Union of Pure and Applied Chemistry (IUPAC) guidelines (Coplen, 2011), we make a series of recommendations for reporting isotopic data in archaeology. Finally, on the basis of international documents outlining the quantification of standard measurement uncertainty (Joint Committee for Guides in Metrology, 2008; Magnusson et al., 2012), we present a method for determining analytical uncertainty that can be easily derived using a simple set of equations in an Excel spreadsheet. To illustrate examples related to calibration and analytical uncertainty, we have included an example IRMS dataset (Appendix A) that is referenced throughout the paper.

2. Review of key concepts

2.1. Calibration (also referred to as normalization)

Isotopic δ -values are not absolute abundance measurements. Rather, they are relative differences between a sample and an internationally agreed-upon standard (Eq. 1)²:

$$\delta = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \quad (1)$$

where R = the ratio of the heavy to light isotope (e.g., $^{15}\text{N}/^{14}\text{N}$). The standard mentioned in Eq. (1) is a real or hypothetical international reference material with an accepted value that defines the scale of isotopic measurement for each element. Originally, this standard was PDB (PeeDee Belemnite, a calcareous fossil) for carbon, air N_2 (AIR) for nitrogen, CDT (Canyon Diablo Troilite) for sulfur, and SMOW (Standard Mean Ocean Water) for hydrogen and oxygen (Coplen, 2011; Coplen et al., 2006; Mariotti, 1983). The original samples of PDB, CDT and SMOW have now been exhausted, so the carbon, sulfur, hydrogen and oxygen scales are now reported to VPDB (Vienna PeeDee Belemnite), VCDT (Vienna Canyon Diablo Troilite) and VSMOW (Vienna Standard Mean Ocean Water), respectively (Coplen, 1994; Coplen, 2011; Coplen et al., 2006).

EA (Elemental Analyzer) IRMS systems (or other automated ‘online’ systems) generate raw values using a single-point calibration relative to

a laboratory working gas; the isotopic composition of the working gas is arbitrary (Paul et al., 2007). Even if the ‘true’ δ value for the reference gas is inputted into the EA software, the isotopic composition of the gas can change over time (Paul et al., 2007). To properly calibrate these raw measurements to internationally-accepted δ -scales, standard reference materials (SRMs) with known isotopic values (previously calibrated to VPDB, AIR, or VSMOW) must be interspersed among samples in each analytical session (or ‘run’) and then used to calculate a two-point calibration curve (Carter and Fry, 2013; Werner and Brand, 2001). The use of a two-point curve is crucial; by anchoring the raw isotopic values with calibration standards at both the high- and low-ends of the range, δ -values for unknown samples can be shifted and stretched to fit onto the international δ -scales. The laboratory working gas therefore does not need to be calibrated as it only provides an arbitrary comparator for the sample isotope ratios. The calibration of the isotopic measurements occurs entirely after a given analytical session is complete and the raw measured isotopic compositions of the standards can be compared to their known δ values. An example of a two-point calibration curve generated using USGS40 and USGS41 is presented in Appendix A for two different analytical sessions.

Internationally-certified SRMs are preferred for calibration, and can be obtained from organizations such as the IAEA (International Atomic Energy Agency), NIST/NBS (National Institute of Standards and Technology, formerly the National Bureau of Standards), and USGS (United States Geological Survey). These standards have previously been calibrated to the appropriate isotopic measurement scale, and have internationally accepted values assigned to them. Calibration standards should have isotopic values that bracket the high and low ends of the measurement range (Paul et al., 2007). For example, the internationally-accepted SRMs USGS40 and USGS41 are amino acids with $\delta^{13}\text{C}$ values of -26.39 and $+37.63$ ‰ and $\delta^{15}\text{N}$ values of -4.5 and $+47.6$ ‰, respectively; these values are near or beyond the high and low end of the range of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values expected for the vast majority of plant and animal tissues (Qi et al., 2003). Internal or in-house SRMs (i.e., standards developed locally and not internationally certified) are less desirable as calibration standards, but are very useful as check standards (see below). If internal SRMs are used as calibration standards, it is necessary to specify their accepted values, and how these values were obtained (Coleman and Meier-Augenstein, 2014). Guidelines for developing in-house standards can be found in Carter

² Note that Eq. (1) is not multiplied by 10^3 as per Note 9 in Coplen (2011).

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