Using and interpreting isotope data for source identification

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Isotopes have been widely used for source identification since the early twentieth century. Recent advances in analytical techniques have increased the precision and the accuracy of isotope analysis. As a result, the use of isotopes has spread to several fields (e.g., ecology, food chemistry, archaeology, environmental health and pollution, and forensic sciences).

This review examines the principal uses of stable-isotope analyses for tracing origins or sources, along with statistical methods employed for data interpretation, in recent papers (2007–09) dealing essentially with food authentication, ecology, environmental pollution and other applications, including geology, police forensics, hydrology and archaeometry. The main elements analyzed were H, C, N, O, S, Sr and Pb.

For isotope-data interpretation, statistical methods appear to depend essentially on the field, the objectives of the study and the number of parameters. They were not often stated explicitly because the studies were exploratory and aimed primarily at assessing the relevance of the analytical techniques used to identify sources. We critically discuss the adequacy of these methods.

Keywords: Data interpretation; Fingerprinting; Statistical methods; Source identification; Stable isotope

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1. Introduction

Isotopes are atoms of a chemical element with different numbers of neutrons, and most elements have more than one isotope. Many isotopes are radioactive and some of those are used for dating. Stable isotopes may be radiogenic (produced by the decay of radioactive isotopes) or may be present since the formation of the Earth (e.g., ^{204}Pb) [1]. They do not decay over geological time-scales and are widely used for source identification and fingerprinting, which rely on mass fractionation of elements or differences from the original material [2–4].

Mass fractionation is very small but measurable enrichment in the lighter, more mobile, isotope of light elements (e.g., H, C, N, O and S). It is caused by many natural processes (e.g., evaporation, condensation, crystallization, ion exchange, diffusion, photosynthesis or respiration) and is often stated relative to an international standard of known composition:

$$\delta\% = ((R_{sam} - R_{std})/R_{std}) * 1000 \qquad (1)$$

where R_{sam} is the isotope ratio (IR) of the sample (e.g., $^{13}C/^{12}C$, $^{15}N/^{14}N$, or $^{18}O/^{16}O$) and R_{std} is an international standard IR [e.g., V: Pee Dee Bee; O, H: Vienna standard mean ocean water (VSMOW)]. Table 1 indicates the abundance ratios and reference standards for some environmental isotopes

For some heavier elements (Hf, Nd, and sometimes Sr), other transformations are used to amplify abundance differences, e.g., ε:

$$\varepsilon = ((R_{sam} - R_{CHUR})/R_{CHUR}) * 10000) \qquad (2)$$

with: R_{sam}: Isotope ratio of sample (i.e. $^{143}Nd/^{144}Nd$); $^{143}Nd/^{144}Nd_{CHUR} = 0.512638$; CHUR: chondritic uniform reservoir. ε is used to amplify processes related to planetary evolution, and is the difference between the isotopic composition at the time of crystallization of the sample and the isotopic composition in a hypothetical chondritic meteorite or bulk Earth reservoir.

For heavy elements (e.g., Pb and Sr), fractionation is insignificant compared to the original IRs because the nuclides have high mass compared to the mass differences of the isotopes. In this case, stable IRs depend essentially upon the origin of the ore body and can be used for

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Table 1. Abundance ratios and reference standards for main environmental isotopes [3]

Isotope	Ratio	Reference standard	Abundance ratio of the standard
^{2}H	^{2}H/^{1}H	V- SMOW	1.5575×10^{-4}
^{3}He	^{3}He/^{4}He	Atmospheric He	1.3×10^{-6}
^{6}Li	^{6}Li/^{7}Li	L - SVEC	8.32×10^{-2}
^{11}B	^{11}B/^{10}B	NBS 951	4.04362
^{13}C	^{13}C/^{12}C	V - PDB	1.1237×10^{-2}
^{15}N	^{15}N/^{14}N	Atmospheric N_2	3.677×10^{-3}
^{18}O	^{18}O/^{16}O	V - SMOW, or V - PDB	2.0052×10^{-3} 2.0672×10^{-3}
^{34}S	^{34}S/^{32}S	CDT	4.5005×10^{-2}
^{37}Cl	^{37}Cl/^{35}Cl	SMOC	0.324
^{87}Sr	^{87}Sr/^{86}Sr	Absolute ratio, or various materials	-

identifying the source of a material or characterizing its transportation history (e.g., ^{208}Pb/^{207}Pb) [5].

Developments in analytical chemistry [mass spectrometry (MS)] have led to improved precision and accuracy, allowing the measurement of small isotopic differences, thus making isotope analysis a powerful tool for source identification [6] in various fields. Isotopes were largely employed in analyses of trace elements, in addition to biochemical, geological and physical parameters. With the increasing number of parameters and samples measured, the need for appropriate statistical tools for data interpretation is becoming even more crucial.

Published reviews on stable-isotope analysis [6–9] focused on specific fields without discussing the statistical methods for data interpretation and visualization. After a brief overview of the principal uses of stable-isotope analysis for fingerprinting purposes, this review discusses the statistical methods used to interpret the data in recent years (2007–09).

2. Principal uses of stable-isotope analysis

2.1. Ecology

Along with greater interest in ecology and ecosystems, stable-isotope analysis is emerging as a useful tool in ecological studies to investigate origins and food webs from insects to birds and fish [6]. Organisms moving between different food webs carry the isotopic composition of previous feeding groups.

Light, stable isotopes H, C, N and O were widely used for studying food sources and trophic levels, mainly in marine ecosystems, allowing ecosystem-based management [10]. C and N stable isotopes were used, as they provide better understanding of benthic systems and food-web structures [11–13]. They strongly reflect the diet of animals. Isotope deviations are enriched from prey to consumer by 3.4‰ for δ^{15}N and 1‰ for δ^{13}C [11]. Carbon IRs can indicate the plant group that constitutes the basic diet (C_3 or C_4), whereas nitrogen IRs provide information about the trophic level of animals. Hydrogen (δ^{2}H) and oxygen (δ^{18}O) IRs are also useful to trace animal origins and migration flows because they vary along geographical gradients [14]. Tissues (e.g., hair, feathers and nails) hold an isotopic signature depending on the location where the tissue was synthesized, {e.g., Hobson and Wassenaar [15] established that δ^{2}H values of bird feathers and butterfly wings were strongly correlated with the water in the region where the tissue was produced}. Ehleringer et al. [14] developed and tested a model to predict the geographic origin of humans based on H and O isotopic compositions of their scalp hair.

Studies of migration and food webs used to be based on direct observation, stomach-content analyses; however, these methods were inappropriate for small organisms {e.g., bivalves, songbirds and insects [15]}. Starting with papers demonstrating high correlation between hydrogen IR in animal tissue and regional precipitation or latitude [14] and correlation between locality and C and N isotopic signatures [12,16], this area of research has included many more species.

However, some limitations must be mentioned. First, animal tissues do not exactly reflect the diet of isotopic signatures because of fractionation, which varies widely between regions and species, thus preventing us from applying a general fractionation factor [17]. Second, isotopic signatures of animal tissue (e.g., feathers) reflect the isotopic signature of the food and water ingested in a specific period, whereas the geographical reference for isotopic signatures (e.g., water) is generally a value averaged over a year, or more [17].

2.2. Food authentication

With the increase in global trade and free markets, food is becoming more regulated. This has increased the need for new methods and techniques that can discriminate between foods of different origins, sources or farming systems. Stable-isotope measurements for food authentication were first introduced within the European wine industry to ensure authenticity of wine provenance and to detect adulteration [18,19]. They have been extended