Simantjutak, H.T. 2011. Available at: http://ogan-community.blogspot.fr/2012/04/goa-harimau-part-1-gua-harimau.html
Souza, C. & W.G. Solheim II. 1976. New area of rock paintings in Irian Jaya, Indonesian New Guinea, in K.K. Chakravarty (ed.) *Rock art of India*: 182-95. New Delhi: Arnold-Heinemann.
Sukkham, A., P.S.C. Tacon & N.H. Tan. 2011. Rock art of Phrayanaga (Viking) Cave, southern Thailand: the illustration of ancient vessels. Available at: http://www.themua.org/collections/items/show/1214.

Isotope Geochemistry in Archaeology

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Introduction

Isotope geochemistry is an important scientific technique that has made a significant contribution to archaeological research. Isotope techniques measure the relative abundance of a number of nuclides of the same (or derivative) element as a means of investigating a variety of natural processes. Both stable (H, O, C, N, Ca, Sr, Cu, Pb, S) and unstable (U, Th, K, Ar) isotope systems are analyzed as part of archaeological investigations.

Isotopes (often referred to as a nuclide in the singular) are variants of a particular element, which share the same number of protons but have varying numbers of neutrons. Isotopes are referred to as stable or unstable, depending on whether they undergo radioactive decay. Some nuclides are primordial, meaning they have existed since the beginning of the universe, while others are the product of the decay of other elements. Isotopes of the same element generally share the same chemical behavior.

Stable isotopes can be applied to studying a variety of processes with their applicability to specific problems depending on the mechanism by which one nuclide becomes naturally enriched or depleted. The basis of the application of some stable isotopes is that the variation in their atomic mass leads them to behave differently during processes such as evaporation, precipitation, freezing, photosynthesis, and incorporation into the body. Another approach is based on taking advantage of the varying abundance of some stable isotopes within different geological units to allow proveniencing of various materials. This can only be achieved if the isotope ratios remain unchanged after incorporation into the sample.

Unstable isotopes are most commonly used as a geochronological tool for establishing the age of materials such as organics, calcium carbonates, and igneous rocks. Unstable nuclides that have either too many or too few neutrons spontaneously transform by beta decay, alpha decay, or spontaneous nuclear fission. The decay speed can be calibrated to time and is usually expressed as a "half-life." On the basis of a known decay rate and original abundance ratio, the comparison of the relative abundance of a stable nuclide to an unstable nuclide can provide an age estimation of the material studied. In the case of radiocarbon dating, the abundance of ^{14}C in the sample is compared to modern levels of ^{14}C.

Isotope analysis can be performed directly on archaeological materials or on geological materials to provide a context for archaeological sites. A particular advantage of using isotopic methods in archaeological investigations is that it provides quantifiable information that can be compared to the material culture record.

Definition

Isotope geochemistry is the measurement of the relative abundance of different species of the same element that have the same number of protons but varying numbers of neutrons. A wide range of elements and materials can be analyzed to provide insights into age, diet, mobility, climate, and provenience with important implications for archaeology.

Key Issues/Current Debates/Future Directions/Examples

A wide (and increasing) number of isotope systems can be applied to archaeological questions. This entry introduces each isotope system that has been applied in archaeological research and discusses the rationale for its use.

Hydrogen has two stable isotopes: ^{1}H and ^{2}H (often known as deuterium). Isotope results for this element are usually reported as δD that represents $^{2}H/^{1}H$ compared to the Vienna Standard Mean Ocean Water standard. This method, which is suitable to the analysis of collagen, has been used to determine paleoclimate (Leyden et al. 2006) and diet (Reynard & Hedges 2008) for archaeological samples. This technique works on the basis that hydrogen isotope ratios of precipitation vary according to climate and geography. Hydrogen in plant tissues, particularly from shallow-rooted plants, is generally sourced from leaf water derived from growing season precipitation. There is no fractionation of hydrogen during water uptake by terrestrial plants and the δD composition of herbivore tissue correlates to that of their diet, providing a time-averaged composition over their lifetime. δD values are fractionated with trophic level, with an increase of 30–50 ‰ from herbivores to omnivores and 10–20 ‰ from omnivores to herbivores, and are not influenced by other parameters, such as those which influence $\delta^{15}N$ (Reynard & Hedges 2008). As a result, this method can be used for sample provenience (using existing maps of δD), to examine changes in precipitation regime or to measure trophic level.

Oxygen has three stable isotopes: ^{16}O, ^{17}O, and ^{18}O. Results are commonly reported as $\delta^{18}O$ which reflects the ratio of ^{18}O to ^{16}O compared to a known isotope standard such as Standard Mean Ocean Water. Oxygen isotopes are fractionated by a variety of processes with the heavier ^{18}O being preferentially precipitated or frozen and the lighter ^{16}O being preferentially evaporated. Oxygen isotope analysis of tooth enamel can be focused on the oxygen atoms from either the phosphate or carbonate portion, although phosphate is traditionally favored as it is considered more resistant to post-burial diagenesis.

The oxygen isotope analysis of marine carbonates or ice cores allows the global ice volume to be estimated through time. This led the Quaternary to be divided into Marine Isotope Stages, which provide a broad framework for climate variation between glacial and interglacial periods. These changes are driven by Milankovitch cyclicity, in which the eccentricity, obliquity, and precession of the Earth's orbit vary on a regular timescale. The Marine Isotope Stage changes have had a significant effect on plant, animal, and hominin biogeography. The oxygen isotope composition of mammal tooth and bone reflects the $\delta^{18}O$ of ingested water and macronutrients in food (Sponheimer & Lee-Thorp 1999). Ingested water has a composition similar to meteoric water, which is sensitive both to temperature and precipitation. The water in shallow-rooted plant stems and roots reflects meteoric water, although the value from leaves is enriched in ^{18}O. The effect of mammalian diet and physiology on isotope composition is poorly understood, although the relative proportion of oxygen derived from food or water may be significant. Overall, oxygen isotope analysis is a very commonly applied technique in archaeological research that has frequently been used as a proxy for climate or diet.

Carbon isotopes, reviewed by Lee-Thorp (2002), can be applied to archaeological biogenic minerals to determine the nature of vegetation included in diet. The method works on the basis that ^{13}C is strongly discriminated against during photosynthesis; however, the degree to which this occurs varies between different photosynthetic pathways. The C3, C4, and CAM photosynthetic pathways have distinctly different levels of ^{13}C, with C4 plants ranging between 9 ‰ and −16 ‰ and C3 plants ranging between −22 ‰ and −34 ‰. C4 plants are principally grasses which are predominant in areas with higher levels of solar radiation. The carbon isotope composition of biominerals such as bone, teeth, and shell will reflect the plant material in diet. Carbon isotopes have also been applied to determine the proveniencing of

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archaeological marble. Carbon isotope composition may also reflect the degree of marine resources within an individual's diet, as there is a significant difference in the isotopic composition of dissolved ocean bicarbonate and atmospheric carbon dioxide which is reflected in plant values (Richards & Trinkaus 2009).

Radiocarbon dating, a derivative of carbon isotope analysis, measures the amount of ^{14}C (which has a half-life of 5730 years) in a sample and compares this value to the level in modern systems. The dating technique, which is suitable for organic materials, is ubiquitous in archaeology due to its relatively low cost and accurate and precise results. More effective sample pretreatment methodologies and the use of accelerator mass spectrometry instruments has recently allowed a wider range of materials and smaller samples to be analyzed. The principal disadvantage of this method is that the amount of ^{14}C becomes too small for statistically robust analysis after ~40,000 years. Dates from radiocarbon are usually presented as "years before present" (BP) in which 1952 is taken to be present or as "calibrated years before present" (Cal BP). Calibrated years before present recognizes that the level of atmospheric ^{14}C has varied over time which is adjusted using a calibration curve constructed based on samples dated by other methods, such as dendrochronology or stratigraphy.

Nitrogen has two stable isotopes, ^{14}N and ^{15}N, the analysis of which in terms of archaeological studies is reviewed by Hedges and Reynard (2007). ^{15}N is progressively concentrated at higher trophic levels as shown by an increase in $\delta^{15}N$ values of 3–5 ‰ for each iteration. Nitrogen may also provide insights into weaning behavior (Schurr 1998). Bone and teeth are amenable to analysis for nitrogen isotope composition. There are however a number of complicating factors, including effects from temperature and aridity, which mean that nitrogen isotope results must be interpreted within geographic context.

Calcium isotopes, reviewed by Reynard et al. (2010), are utilized in archaeological investigations on the basis that they reflect some parameters of an individual's diet including trophic level and level of dairy consumption. Calcium isotope results are usually reported as $\delta^{44/42}Ca$ or $\delta^{44/40}C$. There appears to be a significant fractionation between diet and bone but little fractionation between diet and soft tissues.

The application of strontium isotopes as a provenience tool in archaeology is summarized by Bentley (2006). Strontium has four naturally occurring isotopes including ^{84}Sr, ^{86}Sr, ^{87}Sr, and ^{88}Sr of which the relative abundance of these isotopes is invariant and they are essentially stable on archaeological time scales. The analysis of the strontium isotope composition of archaeological materials can provide important information about the mobility of a range of mammals, including humans. The basis of this method is that, prior to any post-burial diagenesis, the Sr^{87}/Sr^{86} ratio of bone and teeth reflects the geological environment from which food and water were sourced while these biominerals were forming. Teeth are particularly amenable to tracing the geographic origins of humans as they mineralize during the first 12–13 years of life and do not subsequently change strontium composition after this time. Strontium isotope analysis can be used to determine if individuals are local or nonlocal by comparison to the isotopic composition in and around their burial location. In order to quantify the extent of faunal mobility, the strontium isotope composition of biominerals from fossil samples needs to be compared with a regional map of values obtained either from local faunal material or from analysis of the bioavailable component of strontium from plants, regolith, or bedrock. Knudson et al. (2010) recently introduced the use of $\delta^{88/86}Sr$ as a measurement of trophic level, on the basis that ^{86}Sr is preferentially incorporated into biological systems.

Copper isotopes have been infrequently utilized in archaeological research; however, potential exists for this method to be utilized as a tool for metal provenience studies (Gale et al. 1999). The stable isotopes ^{63}Cu and ^{65}Cu are usually measured relative to the copper isotope composition of the NIST SRM 976 standard and are reported as $\delta^{65}Cu$. Copper isotopes have not been widely utilized in the past because of the challenge of overcoming problems of incomplete ionization using traditional TIMS instruments, a short coming made redundant by the use of plasma source ionization and multi-collector instruments. Copper isotopes (in combination with iron isotopes) have been used in archaeological bone to discriminate between sexes, on the basis that male bone iron is depleted in ^{56}Fe and enriched in ^{65}Cu relative to female (Jaouen et al. 2012).

Lead isotopes, reviewed by Stos-Gale and Gale (2009) are used as a provenience tool in archaeological investigations. Four stable lead isotopes exist (^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb) of which all except ^{204}Pb represent the ultimate product of element decay chains from uranium or thorium. The ratio of these isotopes varies between ore bodies and is not affected by anthropogenic processing, allowing them to be used to define the source of archaeological metals. Lead isotope ratios are most commonly reported as ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb, and ^{208}Pb/^{204}Pb. Lead is present in a range of archaeological metals including silver, copper, bronze, and brass. Lead may also substitute for calcium in biominerals such as teeth, bone, and ivory with its composition reflecting the isotopic composition of the geological environment where these materials formed.

Sulfur isotopes, reviewed for archaeological applications by Richards et al. (2003), provide information about both the provenience of biominerals and the relative contribution of freshwater and marine materials to diet. There are four stable isotopes of sulfur (^{32}S, ^{33}S, ^{34}S, ^{36}S), and archaeological investigations usually report measurement of the two most abundant isotopes (^{32}S and ^{34}S) as δ^{34}S with reference to the meteorite standard Canyon Diablo Troilite. The δ^{34}S of bedrock locally, in combination with rivers and precipitation, controls this value in soil and water and hence plants and animals. The offset between sulfur source and isotopic composition in consumer is very small. There is a significant variation between δ^{34}S values of marine (+17 ‰ to +21 ‰) and terrestrial (−7 ‰ to +8 ‰) plants (Privat et al. 2007).

The uranium series technique (which utilizes the isotopes ^{234}U, ^{238}U, and ^{230}Th) is used to date both biological and geological calcium carbonate materials. This technique can provide minimum ages for samples up to an upper limit of ~500,000 years. The basis of this method is that carbonate materials are free from ^{230}Th when formed; however, it will accumulate over time due to the decay of uranium. As ^{230}Th is itself unstable, it will also decay until dating is no longer possible when these isotopes reach secular equilibrium. U-series dating has been widely applied to "closed system" samples such as corals and speleothems in which uranium is present at the time of formation and has also been used for "open system" biominerals such as bone or teeth which contain no premortem uranium. Open system samples are particularly prone to postformation accumulation of ^{234}U, which is enriched compared to ^{238}U in surface waters and groundwaters. The use of laser ablation systems allows domains of different ages to be located with spatially resolved analysis in the same sample, which have been demonstrated to yield very heterogenous age results for open system samples (Grün et al. 2008). Uranium series can also be used to enhance the accuracy of electron spin resonance dating of tooth enamel by constraining the uranium uptake history of these samples. This approach can dramatically improve the age estimations of this method, particularly in samples with high uranium concentration (Grün et al. 1988).

The K-Ar/Ar-Ar technique is used to date igneous rocks, with a particularly focus on tuffs in archaeological investigations. Unstable ^{40}K, which decays with a half-life of 1.2 x 10^{10} years to form ^{40}Ar, is abundant in volcanic minerals and glasses. All argon is excluded from the samples by high temperatures associated with igneous processes, and so, all ^{40}Ar present in these minerals must derive from radioactive decay. This argon cannot escape from the crystals as long as the sample is not reheated. In K-Ar dating, the relative abundance of ^{40}K and ^{39}Ar is measured directly, and in Ar-Ar dating, neutron activation is used to form ^{39}Ar by neutron capture on ^{39}K. The extension of this method beyond the limits of radiocarbon and the presence of many tuffs have made this technique important for determining the chronology of the East African Rift region.

A range of instrumental approaches are utilized within the discipline of isotope geochemistry. Light elements such as H, O, C, and N are measured using gas source isotope ratio mass spectrometry. In this method, the material of interest is converted to a gas, ionized, and the relative abundance of the elements relative to a standard of known composition by using magnetic analyzer. Heavy elements such Ca, Sr, Cu, Pb, S, U, and Th are usually measured using thermal ionization mass spectrometry (TIMS) or multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS). In TIMS analysis, samples are heated leading to ionization before being focused into beams by an electromagnet. The more recently developed technique of MC-ICPMS allows the measurement of a greater range of isotopes and has a significantly higher sample throughput compared to TIMS. Direct sampling methods such as laser ablation analysis and ion microprobe allow spatially resolved, minimally invasive, high-resolution sampling of a range of materials and has the added advantage of avoiding the need for chemical sample preparation facilitating high sample throughput.

In the future, isotope geochemistry is likely to be applied far more frequently in archaeology due to the greater availability of analytical instruments and the higher throughput of samples, made possible by MC-ICPMS and direct sampling. Additionally, isotope systems that have not been applied in archaeological research may yield interesting results in the future.

Cross-References

- ▶ Archaeological Chemistry: Definition
- ▶ Archaeometry: Definition
- ▶ Bone Chemistry and Ancient Diet
- ▶ Bone: Chemical Analysis
- ▶ Chemical Survey of Archaeological Sites
- ▶ Dating Techniques in Archaeological Science
- ▶ Electron Spin Resonance (ESR) Dating in Archaeology
- ▶ Environmental Reconstruction in Archaeological Science
- ▶ Isotopic Studies of Foragers' Diet: Environmental Archaeological Approaches
- ▶ Isotopic Studies of Husbandry Practices
- ▶ Molluscs (Isotopes): Analyses in Environmental Archaeology
- ▶ Provenance Studies in Archaeology
- ▶ Radiocarbon Dating in Archaeology
- ▶ Zooarchaeology by Mass Spectrometry (ZooMS)

References

Bentley, R. A. 2006. Strontium isotopes from the earth to the archaeological skeleton: a review. *Journal of Archaeological Method and Theory* 13(3): 135-87.

Gale, N.H., A.P. Woodhead, Z.A. Stos-Gale, A. Walder & I. Bowen. 1999. Natural variations detected in the isotopic composition of copper: possible applications to archaeology and geochemistry. *International Journal of Mass Spectrometry* 184(1): 1-9.

Grün, R., M. Aubert, R. Joannes-Boyau & M.H. Moncel. 2008. High resolution analysis of uranium and thorium concentration as well as U-series isotope distributions in a Neanderthal tooth from Payre (Ardeche, France) using laser ablation ICP-MS. *Geochimica et Cosmochimica Acta* 72(21): 5278-90.

Grun, R., H.P. Schwarcz & S. Zymela. 1987. Electron-spin-resonance dating of tooth enamel. *Canadian Journal of Earth Sciences* 24(5): 1022-37.

Hedges, R.E.M. & L.M. Reynard. 2007. Nitrogen isotopes and the trophic level of humans in archaeology. *Journal of Archaeological Science* 34(8): 1240-51.

Jaouen, K., V. Balter, E. Herrscher, A. Lamboux, P. Telouk & F. Albarède. 2012. Fe and Cu stable isotopes in archeological human bones and their relationship to sex. *American Journal of Physical Anthropology* 148(3): 334-40.

Knudson, K.J., H.M. Williams, J.E. Buikstra, P.D. Tomczak G.W. Gordon & A.D. Anbar. 2010. Introducing δ88/86Sr analysis in archaeology: a demonstration of the utility of strontium isotope fractionation in paleodietary studies. *Journal of Archaeological Science* 37: 2352-64.

Lee-Thorp, J. 2002. Two decades of progress towards understanding fossilization processes and isotopic signals in calcified tissue minerals. *Archaeometry* 44(3): 435-46.

Leyden, J.J., L.I. Wassenaar, K.A. Hobson & E.G. Walker. 2006. Stable hydrogen isotopes of bison bone collagen as a proxy for Holocene climate on the Northern Great Plains. *Palaeogeography, Palaeoclimatology, Palaeoecology* 239(1–2): 87-99.

Privat, K.L., T.C. O'Connell & R.E.M. Hedges. 2007. The distinction between freshwater- and terrestrial-based diets: methodological concerns and archaeological applications of sulphur stable isotope analysis. *Journal of Archaeological Science* 34(8): 1197-204.

Reynard, L.M. & R.E.M. Hedges. 2008. Stable hydrogen isotopes of bone collagen in palaeodietary and palaeoenvironmental reconstruction. *Journal of Archaeological Science* 35: 1934-42.

Reynard, L.M., G.M. Henderson & R.E.M. Hedges. 2010. Calcium isotope ratios in animal and human bone. *Geochimica et Cosmochimica Acta* 74(13): 3735-50.

Richards, M.P. & E. Trinkaus. 2009. Isotopic evidence for the diets of European Neanderthals and early modern humans. *Proceedings of the National Academy of Science* 106: 16034-9.

Richards, M.P., B.T. Fuller, M. Sponheimer, T. Robinson & L. Ayliffe. 2003. Sulphur isotopes in palaeodietary studies: a review and results from a controlled feeding experiment. *International Journal of Osteoarchaeology* 13(1-2): 37-45.

Schurr, M. R. 1998. Using stable nitrogen-isotopes to study weaning behavior in past populations. *World Archaeology* 30(2): 327-42.

Sponheimer, M. & J. Lee-Thorp. 1999. Oxygen isotopes in enamel carbonate and their ecological significance. *Journal of Archaeological Science* 26: 723-8.

Stos-Gale, Z.A. & N.H. Gale. 2009. Metal provenancing using isotopes and the Oxford archaeological lead isotope database (OXALID). *Archaeological and Anthropological Sciences* 1: 195-213.

Further Reading

Dickin, A.P. 2005. *Radiogenic isotope geology*. Cambridge: Cambridge University Press.

Pollard, M., C. Batt, B. Stern & S.M.M. Young. 2007. *Analytical chemistry in archaeology*. Cambridge: Cambridge University Press.

Isotopic Studies of Foragers' Diet: Environmental Archaeological Approaches

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Introduction

The introduction of stable isotopes into archaeological research began in the 1970s and revolutionized the ways in which several key issues are studied, including early hominin diets, subsistence and spatial organization of forager societies, and individual life histories (Price & Burton 2011; Schwarcz & Schoeninger 2011). Isotopic analysis of bones, teeth, and other organic tissues is a tool for the quantitative reconstruction of past human diets, providing an archaeological measure of subsistence that complements studies in zooarchaeology and archaeobotany.

Isotopic research is based on the premise that "you are what you eat", in other words, that the isotopic composition of an organism's tissues is a function of the composition of its diet. Nevertheless, isotopic values do not have direct dietary meaning and need to be analyzed in an environmental context. The isotopic values for the vegetal and animal foods potentially available for forager populations in a given environment, known as the "isotopic ecology," provide the context for the interpretation of past foragers' diets.

Definition

The different chemical elements that constitute all organic tissues (e.g., carbon, nitrogen, oxygen) are defined by the number of protons in their nucleus, which varies among elements and is unique to each of them. For example, carbon has six protons, nitrogen seven, and oxygen eight. An isotope is a variety of a chemical element defined by the number of neutrons in its nucleus. For instance, carbon has three isotopes used in archaeology: ^{12}C, ^{13}C, and ^{14}C, possessing six, seven, and eight neutrons in the nucleus, respectively (Fig. 1). These carbon isotopes have different atomic masses that condition whether isotopes are stable, like ^{12}C and ^{13}C, or radioactive, like ^{14}C. Stable isotopes do not change in abundance through time after an organism dies, whereas radioactive isotopes decay at a constant rate and are therefore useful as a radiometric-dating tool.

Stable isotope values are a ratio between the heavier and the lighter isotope of each element ($^{13}C/^{12}C$, $^{15}N/^{14}N$). Since absolute abundances of these isotopes are very small, this ratio is