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Heritage Science

REVIEW

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Isotopes in cultural heritage: present and future possibilities

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Abstract

This paper is focused on methodology and scientific interpretations by use of isotopes in heritage science—what can be done today, and what may be accomplished in the near future? Generally, isotopic compositions could be used to set time constraints on processes and manufacturing of objects (e.g. the ^{14}C technique). Furthermore, isotopic compositions (e.g. Sr and Pb isotopes) are useful for tracing the origin of a component or a metal. The concepts isotope and isotopic fractionation are explained, and the use of stable respectively radioactive isotopes is exemplified. Elements which today have a large potential in heritage research are reviewed, and some recent and less known applications from the literature are summarized. Useful types of mass spectrometers are briefly described, and the need for reliable standards as well as accurate measurements and corrections is stressed. In future, further chemical elements may be utilized for isotope studies in heritage science, and possible candidates are discussed. The paper may in particular be valuable to readers less acquainted with the use of isotopic measurements. The many examples from referenced papers and also results from the authors' studies in this field may inspire imaginative and inquisitive scientists to try new applications utilizing isotope data in heritage science.

Keywords: Isotopes, Standards, Dating, Measurement, Mass spectrometer, Archaeology, History, Art

Brief history and introduction

Some 100 years ago, the knowledge concerning the composition of atoms was elucidated by brilliant scientists such as Ernest Rutherford, J. J. Thomson, Marie Curie, Henri Bequerel, Niels Bohr, F. W. Aston, Frederick Soddy and many others [1]. Much of the early work was concentrated on radioactivity. During studies on the radioactive decay of uranium and thorium, a confusing discovery was that there seemed to be several kinds of thorium atoms which decayed at different rates. The American chemist T. W. Richards showed in 1913 that lead produced from the decay of uranium had a different atomic weight as compared with "ordinary" lead from lead ore. Soddy showed that a radioactive element may have different atomic masses although with identical chemical properties. Francis W. Aston showed with his so-called mass spectrograph that neon gas is composed of two different kinds of atoms, having atomic weights around 20 respectively 22. The different atoms were named "isotopes" after the Greek name which means "the same place" (i.e. in the Periodic Table of Elements). Many of the scientists were rewarded with a Nobel Prize in chemistry or physics: J. J. Thomson (1906), Ernest Rutherford (1908), Marie Curie (1911), Niels Bohr (1922), Frederick Soddy (1921), Francis Aston (1922), Harold Urey (1934) and James Chadwick (1935).

Today, the concept isotope is well known to the scientific world, and numerous applications have for almost a century been used in science. Geologists were among the first to use this technique when attempting to date rocks. Among the earliest works is a helium isotope study [2] where uranium minerals were dated, which a few years later was followed by a radiogenic Pb study aimed to date the mineral uraninite [3]. Some decades later, isotopes were used also in other fields, e.g. medicine and archaeology. In 1943, Georges de Hevesy was awarded a Nobel Prize for his isotopic methods to trace chemical reactions and processes in the human body. Still most important in archaeology is the well-known radiocarbon dating

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technique [4], for which Willard F. Libby in 1960 received the Nobel Prize in Chemistry. Today's archaeologists can benefit from a number of scientific techniques to investigate excavated objects [e.g. 5–8], among them various isotopic techniques. Isotope measurements are also applied in many other fields such as forensics, food and beverage industry, environmental sciences, history, heritage science, and also utilized to detect forgeries in art. The present paper gives examples of factors controlling isotopic compositions and gives prominence to chemical elements which are apt to applications in heritage science research, today and in the future. A brief description of useful measuring instruments is included.

Fundamentals of isotopes

Each element is built of atoms. However, for most elements their atoms may have different masses, and the variants are called *isotopes*. The isotopic distribution for a specific element is almost uniform in the lithosphere and atmosphere. However, small variations of the isotopic compositions of certain elements in nature do occur, and isotope studies are concerned with the interpretations of such variations. These variations are due to two mechanisms: (i) isotopic fractionation—which essentially is due to the breaking of physical bonds of different strengths; and (ii) radioactive decay—whereby one unstable (parent) isotope spontaneously disintegrates and eventually results in a stable (daughter) isotope. The first mechanism concerns stable (non-radiogenic) isotopes and is above all important for light elements, as will be explained below.

Most chemical elements in nature exist with two or more isotopes. The various isotopes of each element have the same number of protons (Z), but this is not true for the number of neutrons (N) or the mass ($M=Z+N$). For example, carbon (always with $Z=6$) has three isotopes: the two stable isotopes ^{12}C (with six neutrons) and ^{13}C (seven neutrons), and (with only about one part per trillion) the radioactive (non-stable) isotope ^{14}C (with eight neutrons), often denoted C-14. Tin is outstanding with its ten stable isotopes. On the other hand, 20 elements exist in nature with only one stable isotope. Among these elements are gold and phosphorus, which is unfortunate since both are important to archaeologists and museum curators. It should also be added that no element with an atomic number $Z>83$ is stable, i.e. containing only stable isotopes. There are basically two ways of applying isotopic techniques: one to track the background of objects or human remains (origin, provenance, diet, migration), and another for dating of investigated objects or sites. Some isotope systems have been utilized for many decades, while others have only recently been tested or used for certain applications. The stable isotopes of carbon have a unique archaeological potential, since analyses of carbon isotopes allow evaluations of both provenance and diet pattern. A brief summary of isotope systems and their possible use in heritage science is presented in Table 1.

Stable isotopes and isotopic fractionation

Local variations in the proportions of stable isotopes of an element are brought about by *isotopic fractionation.* Each element's isotopes have identical chemical properties, whereas physical properties such as melting and boiling points display very slight differences. This is the basis for isotopes of different elements to behave differently during natural processes, and therefore the ratio of these isotopes changes or "fractionates". As early as 1931, Harold Urey discovered the deuterium isotope (^{2}H or "D") and demonstrated discrepancies in vapor pressure among the isotopes of gaseous elements. Accordingly, evaporation, condensation, rain, snow, melting, crystallization, adsorption, diffusion etcetera may give rise to a small but (sometimes) measurable isotopic differentiation [9]. For example, "ordinary" water, H_2O, boils at 100.00 °C at 1 bar, while "heavy" water, D_2O, has a boiling point of 101.42 °C. Complicated biochemical processes may also induce a slight isotopic fractionation, for example in photosynthesis, during the synthesis of amino acids or lipids, and processes in bacteria [10–16]. In these processes, the isotopic fractionation is due to physical processes such as diffusion. Occasionally, so called mass-independent fractionation (MIF) can be important in e.g. biochemical reactions as shown for a number of light elements [17]. Generally, a light element induces larger isotopic fractionation because the relative difference in mass between its isotopes is greater than for a heavy element. For instance, deuterium (D, ^{2}H) is twice as heavy as ^{1}H, i.e. 100% heavier, while ^{181}Ta is only 0.56% heavier than ^{180}Ta. The light elements, hydrogen, carbon, nitrogen and oxygen to mention a few, are therefore especially susceptible to natural isotopic fractionation, while much less physical differences are observed for the heavier elements. The reason that the heavy elements strontium and lead have large and easily measurable differences among their isotopes is principally due to radioactive decay processes (cf. below).

Measuring techniques

Fundamentally, there are two methods to determine the amount of various isotopes in a special material. The first is to directly measure the radioactivity of the isotope in question, by counting particles (of α, β, or γ type) that are produced by a specific decay. This method has been used when applying the Carbon-14 dating technique and for other systems such as U-He and Tritium-^{3}He, and have been described to detail in the literature [18].

Table 1 Isotope systems which have been used in archaeology and cultural heritage

Element	Dating	Provenance	Diet for humans	Migration among humans	Other
H			X		
B		X			
C	XX (C-14)		XX		
N			X		
O		(X)	X	(X)	Paleothermometry
Mg			(X)		
Si		(X)			
S		(X)	X		Ore prospecting, pollution
Cl	(X)				
Ar	X				
Ca			(X)		
Fe		(X)			
Cu		(X)			
Zn		(X)			
Sr		XX		X	
Ag		(X)			
Sn		(X)			
Nd		X			
Hg		(X)			
Pb		XX			
Th	X				
U	X				

The most commonly used systems are marked XX, those often used X, and those recently tested or used (X)

The prevailing way of analyzing isotopes is to make use of some kind of mass spectrometer that is designed to determine the distribution of an element's isotopes. The working principle behind this technique is that different types of atoms or molecules can be separated according to their masses, and the ratios between the isotopes of interest can be subsequently measured. Most mass spectrometers are designed for the analysis of organic compounds. However, several types of mass spectrometers have been developed to determine isotope ratios and the basic features of a few commonly used types are presented here. The first generation of magnetic sector instruments in the 1940:s are often named "Nier spectrometer" after its inventor Alfred Nier [19], cf. Fig. 1. This type is sometimes abbreviated Isotope Ratio Mass Spectrometer (IRMS) and another acronym is Stable Isotope Ratio Analysis (SIRA), often used for analysis of gaseous compounds of light stable elements. During the latest decades, more advanced mass spectrometers have been developed, producing increasingly better precision for sample sizes becoming smaller and smaller (nanogram to picogram levels) [e.g. 20–23]. The amount of sample is therefore rarely a problem, but their purity is of the greatest importance. For solid samples, a Thermal Ionization Mass Spectrometer (TIMS) is often used, e.g.

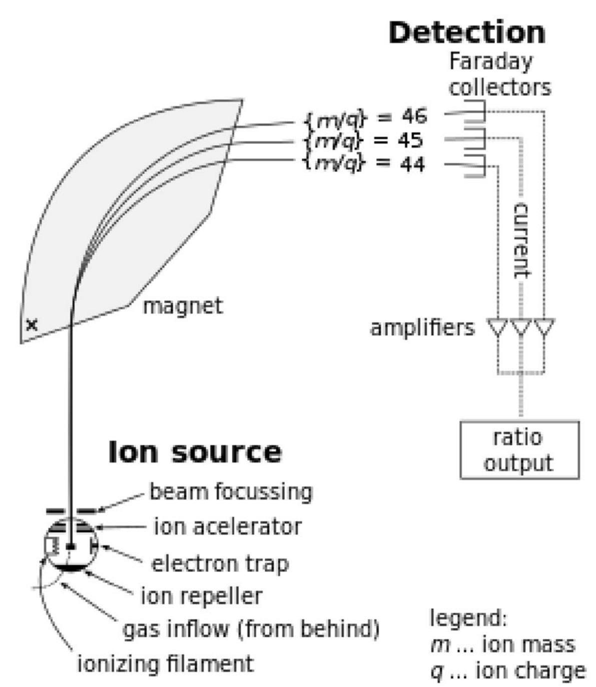

Fig. 1 Schematic picture of a Nier-type isotope ratio mass spectrometer using a gas source analytical medium (in this example carbon dioxide, CO_2). Reproduced after chemical sciences: a manual for CSIR-UGC National Eligibility Test, http://wikibooks.org

for strontium and neodymium specimens, and generates very precise results. It utilizes a minute solid sample, previously isolated in a clean laboratory following standard ion exchange procedures. Certain spectrometers, like a MC-ICP-MS spectrometer (Multiple Collector—Inductively Coupled Plasma—Mass Spectrometer; cf. Fig. 2) are equipped with a laser system. Such laser-based systems remove (ablate) particles from the surface of a sample which are led to an analyzer. This technique as well as the ion microprobe (SIMS; secondary ion mass spectrometry) are capable of analyzing samples in situ, which eliminates the need for tedious laboratory treatment. The latter techniques are versatile and can be used for a range of elements, allowing both stable and radioactive isotopes to be analyzed in very small samples; besides, the sample through-put is large compared to e.g. the TIMS technique. The precision obtained with in situ techniques is, however, not as good as for TIMS-analyzed samples. Irrespective of the instrumentation used, samples must be handled with care and thorough analytical protocols need to be followed in order to obtain precise and accurate results. A feature in common for isotopic measurements is the need for standardization, and this is accomplished in different ways and is method-specific. It is common practice to run samples in duplicate to ensure a good reproducibility.

Light stable isotope applications

Stable isotopes of light elements are utilized in many fields. The archaeological applications dominate, for instance to investigate changes in habitat, food, animal herding, dietary tendencies and migration patterns for humans. A commonly used division is between "traditional" stable isotopes of the light elements of primarily H, C, O, N and S, which are further discussed below. Heavier elements such as lead and strontium, as well as "non-traditional" elements (such as Mg, Cl, Fe and Cu) are considered in a subsequent paragraph.

Fig. 2 An MC-ICP-MS spectrometer (Nu Plasma II) at the Department of Geological Sciences, Swedish Museum of Natural History, Stockholm. Photo: Melanie Schmitt

Standards and data for H, C, N, O, S

The lightest of all elements, hydrogen (Z = 1), has two stable isotopes: ^{1}H (major part) and ^{2}H (deuterium; often denoted D), which constitutes only 0.015% of all hydrogen atoms. Carbon (Z = 6) has two stable isotopes, ^{12}C (ca 98.9%) and ^{13}C (ca 1.1%). The ratio $^{13}C/^{12}C$, here denoted R_{13}, varies within a small range in an organism mainly due to consumed food ("you are what you eat"), referring to the stable isotope signature of the body [24]. The value of the sample (*s*) is usually given relative to a standard (*std*) by the expression $\delta^{13}C = [R_{13s}/R_{13std} - 1] \times 1000$. This gives a number (in ‰), easier to handle, which is either positive or negative relative to a standard. The international standard was for many years PDB, a belemnite from the Cretaceous Pee-Dee formation in South Carolina. It is now exhausted, and therefore a V-prefix is used (e.g. V-PDB), following the nomenclature suggested at a conference held in Vienna in 1993 [25].

Nitrogen (Z = 7) exists in nature with two stable isotopes, ^{14}N (ca 99.64%) and ^{15}N (0.36%). The $^{15}N/^{14}N$ isotopic ratio is usually given as $\delta^{15}N$ (in ‰) relative to a standard, commonly nitrogen in the air. Oxygen (Z = 8) exists with three stable isotopes: ^{16}O (99.76%), ^{17}O (0.04%) and ^{18}O (0.20%). Usually the $^{18}O/^{16}O$ ratio is determined, and its value is conventionally given as $\delta^{18}O$ relative to an international standard (V-SMOW or V-PDB). Sulfur (Z = 16) exists in nature with four stable isotopes with mass numbers 32, 33, 34 and 36. Their relative abundances are around 95.0, 0.76, 4.2 and 0.015%, respectively. Usually the $^{34}S/^{32}S$ ratio is determined which is expressed as a $\delta^{34}S$ value versus the Canyon Diablo troilite (CDT), an iron sulfide standard.

Common light elements—archaeology

Among the light elements, carbon has the largest impact of modern archaeological science. Organic carbon is isotopically "light" (i.e. with a comparatively large proportion of ^{12}C) with strongly negative $\delta^{13}C$ values, for pit coal as low as −25‰ and for methane even lower. In archaeology, $\delta^{13}C$ values can usually give information on a human's diet [e.g. 26, 27]. $\delta^{13}C$ changes with the trophic level; lowest for green plants (ca. −27‰), less negative for terrestrial animals (ca. −22‰), and highest for marine animals (ca. −16‰). Even degraded lipids preserved in ancient pottery may be analyzed [28]. Nitrogen isotopes are useful in archaeology to establish a probable diet pattern. An organism can integrate nitrogen from nitrates, ammonium or (rarely) free nitrogen in the air. The $\delta^{15}N$ value of green plants is around 2–4‰, while herbivorous animals have values around 6‰, i.e., a higher trophic level gives a higher value [29]. Marine organisms may have still higher values, and Inuit's whose main food is marine protein can have $\delta^{15}N$ values as high as 18‰ [30].

Oxygen is mainly integrated in humans through ingestion of water, the isotopes of which depend on altitude and latitude, and its isotopes may thus be used to verify a hypothetical geographic origin. In humans and animals, sulfur is found in collagen and keratin. These proteins are relatively resistant towards acids and can be retrieved even in prehistoric graves in regions now suffering from acidification [31]. Marine, freshwater and terrestrial ecosystems often display distinctly different sulfur isotope compositions, and accordingly sulfur isotope data in human and faunal tissues can infer the consumption pattern of foods [32–34]. The proportion of deuterium in bone collagen of humans and animals shows a trophic level effect, with increasing values from herbivores to omnivores to humans [35]. A pioneering study of remains of humans, animals and plants from archaeological sites by means of hydrogen isotopes has been published by Yang and Leng [36]. As hydrogen and oxygen are constituents in water, a combined O–H isotope systematics may be useful to trace the origin of water found in e.g. plants and living organisms. Studies involving hydrogen isotopes in hair have been published [37–39].

By combining different isotope systems of light elements, such as carbon, nitrogen, oxygen, sulfur and hydrogen, a detailed understanding can often be reached regarding the origin and diets of e.g. archeological human remains. In particular, sulfur and hydrogen isotope data can be a valuable complement to other stable isotope (C and N) data obtained on human bone. Many studies involving human diets, nutritional ecology, extraction methods and also sheep's wool have been published [40–46], and also a study combining stable isotopes and ancient DNA analyses [47]. Extensive review concerning mammalian proteins has been published by Wilkinson [42]. An interesting multi-isotope study of the remains of King Richard III has been published by Lamb et al. [48]. For instance, there was a significant shift noted in the nitrogen, but not carbon, isotope values towards the end of his life, which may be explained by an increase of luxury food and drink such as game birds, freshwater fish and wine. This is the first suggestion of wine affecting the isotope composition of an individual and thus has wider implications for isotope-based palaeodietary and migration reconstructions.

Common light elements—other applications

The study of light stable elements is also used in many other fields of heritage science. Some of these applications have a geological background. For instance, geologists measure carbon isotopes while prospecting for fossil fuel and to interpret the origin of carbonates. Marble is of great interest in heritage science. It is a metamorphic product of limestone (a carbonate rock), whose dominant mode of formation is from various organisms living in water. Accordingly, its carbon and oxygen isotope compositions have been used to determine the provenance of marble in buildings and monuments in the Mediterranean area. An early study was published in 1972 by Craig & Craig and was later followed by others [49–53].

Oxygen isotopes may also be utilized in studying the origin of e.g. groundwater. For instance, $\delta^{18}O$ for meteorological precipitations shows seasonal variations—those deposited during the summer are less negative than the winter values [54, 55]. Accordingly, $\delta^{18}O$ data can be used for paleo-thermometry [56]. An interesting study has been made by Dansgaard et al. [57]. Cores drilled from Greenland ice were cut into small fractions, which were analyzed for $\delta^{18}O$. In this way, "age rings" similar to tree rings were obtained. The cores could thus be dated, and the age could often be verified from deposits of ashes emitted from known volcanic eruptions. Inversely, earlier unknown eruptions could be identified. Similar applications may as well be used in heritage science where e.g. ash layers are present at excavation sites. Oxygen may also be extracted from silicates, which define the predominant mineral group in nature, by means of a powerful chemical reagent such as bromine pentafluoride [58], and such isotopic compositions can be used to relate an archaeological object to a specific environment, for instance in gemmological applications [59] and potentially to determine the provenience of silica-rich artefacts (e.g. obsidian tools) to a specific rock quarry. Sulfur isotopes have been used in environmental studies of damaged outdoor cultural monuments and buildings [60–65]. In many cases the origin of sulfur in the gaseous oxides was due to the impact of fossil fuels.

Provenancing objects using heavy isotopes (Pb, Sr, Nd)

Numerous examples demonstrate that Pb and Sr (and also e.g. Nd) isotopes may be used to set constraints on the source or provenance of cultural objects. Such applications are based on the long-lived decay series exemplified above for age dating. The difference is that instead of measuring a ratio between parent and daughter isotopes, appropriate isotope ratios including only the daughter element are used for the provenance. For strontium and neodymium, the radioactive decays of interest are ^{87}Rb to ^{87}Sr and ^{147}Sm to ^{143}Nd, and the relevant isotope ratios used are $^{87*}Sr/^{86}Sr$ and $^{143*}Nd/^{144}Nd$ (the asterixis denotes an isotope formed from radiogenic decay). These elements, along with lead, are advantageous because their isotopic variations are comparatively large and easily measured, and their isotope systems are well characterized.

Lead is typically a trace element in bronze, coins and many other metal objects, and a major constituent of crystal glass and lead pigments. This enables lead isotopes to be used to determine the provenance of these objects. Lead exists with four stable isotopes having mass numbers 204, 206, 207 and 208. The three latter isotopes are successively added as a result of decay of U and Th isotopes, and their relative isotopic abundance is often given by the ratios $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$, using ^{204}Pb as a reference isotope [54, 55]. Since these decays are extremely slow, the geological age of a mineral deposit is an important factor for its lead isotopic composition. For Pb-rich ores no significant in situ decay of U and Th takes place after their formation, thus implying that their Pb isotope ratios carry a "fossil record" which represents their time of formation. The isotopic variations in the lithosphere may therefore be considerable, which is favorable when attempting to use Pb isotopes to reveal the provenance of the lead in an object. For example, during the Middle Ages several lead-bearing ore deposits were mined in south Sweden in the so called *Bergslagen* area west and north-west of Lake Mälaren. This region is geologically very old, around 1900-1800 Ma (million years), which gives quite different lead isotope distributions ($^{206}Pb/^{204}Pb$ values cluster around 15.70) as compared with ores from the European continent exhibiting much younger Palaeozoic to Mesozoic (545-65 Ma) terrains, where $^{206}Pb/^{204}Pb$ ore values usually are in the range 17.5–19.0.

When using lead isotopes to provenance an object, it is often customary to display data in $^{206}Pb/^{204}Pb$ *versus* $^{207}Pb/^{206}Pb$ or $^{208}Pb/^{206}Pb$ diagrams, respectively. Numerous reference data from ancient mining districts are reported in this way, and the isotopic compositions of discrete ores or regions may provide characteristic "fingerprints". A disagreement between data for sample and ore deposit, respectively, *definitely* shows that the analyzed lead cannot originate from the deposit in question. An agreement ("isotopic match") indicates that the lead *may* originate from that specific deposit. It must also be remembered that an overlap of isotopic fingerprints may exist between different ore districts, and that lead isotope data are not available for all conceivable mines. However, lead isotope abundances in combination with other observations such as trace elements can often help pinpointing a possible origin of the lead. Efforts to compile an extensive database for lead isotopes have been made by a group in Oxford (the OXALID database) [66], and currently work is in progress for further published data [67]. Strontium, neodymium and oxygen isotopes have been used to provenance ancient glass, for instance in the Mediterranean area [68–74]. Chinese glazes have been examined with strontium isotopes [75]. The results on some of these studies also have relevance for manufacturing techniques.

Lead pigments have also been analyzed for their isotopic composition. In this way ancient Chinese and central Asian pigments have been examined [76]. Fortunato et al. [77] have determined lead isotope abundance ratios in lead white, a common constituent in seventeenth century oil paintings. Works of art by Rubens, van Dyck and other Flemish masters gave very similar lead isotope distributions, which indicates a distinct origin of raw materials. Also Fleming [78] has described how lead pigments in oil paintings by old masters may be used to settle doubts on genuineness. With respect to Swedish material, studies of mediaeval lead pigments from mural paintings, church portals and baptismal stone fonts have been performed with the aim to determine their origin [79–81]. Most lead pigments were found to originate from the Harz and Erzgebirge regions in Germany, but also lead pigments from Russia and Sweden (the *Bergslagen* ore district) were identified.

A large number of archaeological bronze artefacts excavated in Scandinavia have also been analyzed [82, 83]. In these studies, it was definitely shown that the lead in the bronzes did not originate from Swedish ores, but rather from ore regions mainly in Austria, Spain and Sardinia. Ancient silver coins have been studied elsewhere, as well as ancient bronze artefacts, and their origin and authenticity examined with the aid of lead isotopes [78, 84–87]. The ancient plumbing system in Pompeii has been examined for lead isotopes, indicating multiple sources for the lead [88]. The ship *Batavia*, belonging to the Dutch East India Company, was shipwrecked outside Australia in 1628. Some of their copper objects have been analyzed for lead isotopes [89], showing that the metal originated from various sources, among them the Swedish *Bergslagen* region with its very distinct isotopic signature. A final example concerns the murder of the Swedish warrior king Karl XII in 1718. He was shot in Norway with a bullet containing lead to make it heavier. The lead isotope study gave no clear evidence for the lead provenance—however, it was certainly not lead from the Swedish *Bergslagen* region [90].

As regards strontium, the $^{87}Sr/^{86}Sr$ ratio differs for various geological environments, and the local variations can be appreciable. Since strontium is chemically related to calcium, it is partly integrated in teeth and bone in humans and animals. Dental enamel is mainly formed during the childhood and this part does not exchange its strontium subsequent after its formation, while other parts of the body are affected later in life. Strontium and other isotopes can therefore be used to study the migration of humans or animals during their life-time [91–94]. Famous examples are given by various isotopic analyses of the remains of "Ötzi the Ice-man" [95, 96]. There are also examples of multi-isotopic approach in Swedish archaeology, such as "The man from Granhammar", who seems to have travelled a lot before he was finally murdered [97], and there are many further examples [e.g. 98, 99].

Provenancing with less common stable isotope systems

With the advent of new generations of ICP-MS and SIMS instruments, it is today possible to detect and measure natural isotope variations among numerous "non-traditional" elements such as boron, magnesium, silicon, chlorine, iron, nickel, copper, zinc, tin and many others. These have recently attracted a large interest in the scientific community [17, 100, 101]. However, several factors obstruct a general usage in heritage science. Apart from problems with infinitesimal fractionations induced in nature for the heavier elements, as well as uncertainties about the nature of processes leading to measurable fractionations, reference data are still relatively few, and the analytical challenges are large and their common usage in cultural sciences remains to be proven.

Be that as it may, the recent decade has witnessed a steadily increasing interest for isotope studies regarding the above-mentioned elements. Among these boron is the lightest element, with an atomic number $Z=5$, which is advantageous since relatively large isotopic differences may be expected. Boron is a trace element present in natron glass, and a study of Roman glass has recently been published and proven boron to be a provenance indicator for glass [102]. In that paper it could be concluded that the Greco-Roman glasses showed a rather homogeneous isotopic composition, expressed as $\delta^{11}B$.

Magnesium ($Z=12$) has three stable isotopes, and in a recent study Mg isotopes were measured in mammal tooth enamel [103]. It was found that $\delta^{26}Mg$ increases from herbivores to higher-level consumers, discriminating most of the trophic steps. This, combined with values for Ba/Ca, $\delta^{13}C$ and $\delta^{34}Ca$ may prove useful in paleodietary studies. Also, silicon ($Z=14$) isotopes have been studied, usually with a geological focus [104] but has also been used as a proxy for environmental change [105]. Calcium ($Z=20$) is a main constituent of bone. Pilot studies have been undertaken by Reynard et al. [106], using bones from humans and animals from three archaeological sites. There was a significant difference in the $^{44}Ca/^{42}Ca$ isotope ratios between humans and animals, which was attributed to differences in metabolic processes rather than due to dairy consumption among the adult humans. It was also concluded that the bone calcium isotope ratios were not substantially affected by diagenetic changes. Even a preliminary study of selenium ($Z=34$) isotopes in organic Se-bearing species has been published [107].

Some isotope studies of metallic elements will be considered. Isotopes of copper and iron (having two respectively four stable isotopes) have been measured in artefacts [108–114]. A great challenge is that both metals are ubiquitous in the lithosphere, so the task to provenance from their isotopic abundance may be anywhere from difficult to hopeless. A more promising candidate within the isotope field may be zinc with its five stable isotopes. Copper and zinc isotope ratios in human bone and enamel have been examined by Jaouen et al. [115, 116]. Tin, with ten stable isotopes, is interesting being a constituent in many bronze artefacts, but the analysis is indeed complicated. Nevertheless, some interesting studies have been published by Pernicka et al. [e.g. 117–119] and Balliana et al. and others [120, 121]. Mercury (with seven stable isotopes) is also likely to be difficult to use for isotope measurements because of minor fractionation in nature, but it may have a potential as a tracer of organic matter [17]. Analyses of cinnabar pigments (HgS) have actually been undertaken [122], but in this study the provenance was based on the pigments' sulfur isotopes, and fortunately the number of cinnabar sources in Europe is limited. However, this necessitates that the pigment certainly is the *mineral* minimum, and not a synthetic product (called vermilion) made from mercury and sulfur. In the latter case the sulfur may originate from anywhere in Europe. With the aim to trace the provenance of coinage through variations in isotopic abundances, silver, copper, and lead isotopes were measured in 91 coins from the East Mediterranean Antiquity and Roman world, medieval western Europe, sixteenth to eighteenth century Spain, Mexico, and the Andes [123]. The isotope measurements demonstrate that also silver isotopes has a large potential for provenance studies. Pre-1492 European silver can be distinguished from Mexican and Andean metal. European silver dominated Spanish coinage until Philip III, but had, 80 years later after the reign of Philip V, been flushed from the monetary mass and replaced by Mexican silver.

Radioactive isotopes used for age dating

Radiocarbon dating

There are separate classes of radioactive decay systems on which different isotopic dating methods are based; *cosmogenic nuclides* (e.g. C-14, tritium and Cl-36), the *uranium/thorium-series disequilibria systems* (e.g. the ^{230}Th-^{232}Th and ^{210}Pb methods), *long-lived systems* (e.g. the U–Pb, K–Ar and Ar–Ar methods), and *radiation damage methods* (e.g. thermoluminescence and fission track methods). The systematics behind these techniques are very different and, with the exception of the carbon-14 method, the reader is referred to text books for more detailed information. The most frequently used archaeological dating technique is the well-known C-14 "radiocarbon" method [4, 6, 18, 124–127]. Successful applications include dating of e.g. human and animal remains, mummies, wood artefacts, parchment, textiles, cereals, charcoal, peat and slag. The method is based on the fact that cosmic neutrons react with atmospheric ^{14}N to form radioactive ^{14}C, which decays by β-emission with a half-life ($T_{1/2}$) of 5730 ± 40 years. (After a half-life, 50% of the radioactive isotopes have decayed). Almost all living matter is constantly exchanging ^{14}C with their environment, mainly by food or atmospheric CO_2. This exchange expires when the organism dies, and the ^{14}C decay can consequently be used as an "archaeological chronometer". The age is determined by measuring the proportion of ^{14}C in relation to ^{12}C and comparing this with corresponding theoretical value for "modern" carbon.

Initially, the organic material to be dated was burned to CO_2 in oxygen, whereupon its radioactivity was determined in a relatively tedious process where the ^{14}C activity was estimated from the measurements of β-particles emitted during decay of ^{14}C to ^{14}N. The procedure also involved a conventional gas mass spectrometer to obtain the $^{13}C/^{12}C$ ratio needed for corrections (cf. below). Accordingly, radiocarbon ages determined some decades ago may suffer from low accuracy. Today the number of ^{14}C atoms in relation to the stable carbon isotopes can be directly measured with an Accelerator Mass Spectrometer (AMS) in samples with as little as 100 µg of carbon, and yet producing precise ages of around ± 40 years for samples being a few 1000 years old. However, there are several sources of error to be considered. For instance, it is imperative to avoid contamination from modern material, which would otherwise give a much too low ("young") age. Likewise, an organism having absorbed carbon dioxide from fossil fuel would cause a much too high age. If trees growing near a high-way would be radiocarbon dated, their "age" would erroneously amount to several million years. Furthermore, a number of corrections are necessary for a reliable result. The $^{14}C/^{12}C$ ratio in the atmosphere has shown small fluctuations with time and locality, and certain calibration curves should therefore be employed. Furthermore, the CO_2 uptake in an organism is affected by isotopic fractionation. It is assumed that in relation to C-12, all organisms discriminate against C-14 about twice as much as against C-13, and this can be accounted for in a procedure involving the determination of the $^{13}C/^{12}C$ ratio. Therefore, many corrections are necessary to the raw radiocarbon age to yield a calendar date [124–128]. Another correction is necessary to compensate for the so-called Suess effect. This is a change in the ratio of the atmospheric concentrations of ^{13}C and ^{14}C by the admixture of fossil-fuel derived carbon dioxide, which is depleted in ^{13}C and contains no ^{14}C. The effect is named after the Austrian chemist Hans Suess, who noted the influence of this effect on the accuracy of radiocarbon dating [129, 130].

Numerous famous and successful C-14 age dating's have been published during the last half-century on materials such as the Dead Sea scrolls, the Shroud of Turin, Egyptian mummies, and Ötzi the Iceman. It must also be remembered that the C-14 technique is only applicable for organic material. However, iron artefacts may be dated because they contain small amounts of the carbon (charcoal) once used for reduction of the iron oxide ore. Bone material can often be dated from its collagen, which is remarkably stable, even in soil suffering from atmospheric acidification [31]. A number of corrections are necessary for a reliable result (cf. below).

Dating with other isotope systems

Dating with the C-14 techniques has its limitations when older artefacts are to be dated. After ten half-lives (about 60,000 years) only one per mil of the original amount of ^{14}C atoms remains, which is challenging for a high-quality analysis. In this case, radioactive isotopes with longer half-life's can be considered. For instance, ^{36}Cl with a half-life of 301,000 years may be utilized for very old materials in specific cases [131]. Tritium (^{3}H), decaying to ^{3}He with a half-life of about 12 years, is produced from cosmic-ray neutrons interacting with ^{14}N. Tritium is a minor constituent of water molecules on the surface of the earth due to fall-out from meteoric precipitation. The tritium component in water can be used to determine the age of a water mass (e.g. groundwater). Tritium analyses, based on the measurement of emitted β-particles, combined with analyses of ^{3}He (tritium—^{3}He method) have been applied on problems in archeology [132]. However, because of atmospheric testing of nuclear weapons, the amount of tritium in the atmosphere rose and this may obstruct the interpretation of data. In this context also the ^{90}Sr isotope may be mentioned which originates in a similar manner as tritium. Nuclear accidents like that in Chernobyl (1986) have influenced the concentration of ^{90}Sr in the atmosphere.

The effect of so called uranium/thorium-series disequilibria give rise to a number of dating methods. Briefly, these disequilibria occur when biologic and inorganic reactions break the complex chains which define the decay of U and Th parent isotopes. This, in turn, leads to an interplay between various processes and for instance the application of the $^{238}U/^{234}U—^{230}Th$ series methods enable events up to 500,000 years to be dated. Examples include dating of lake sediments, corals, dropstones and early human species, archeological sites [55; and references therein]. Obviously, this may be applied in studies of anthropology and ancient mining. In geology, where long time scales often are considered, rocks are dated by using decay series like A (parent isotope) → B (daughter isotope), where element A has a very long half-life. The common principle of these systems is that time can be determined by measuring the ratio between newly formed daughters and remaining parent isotopes. For instance, ^{238}U decays to stable ^{206}Pb with a half-life of ca. 4.5 billion years, but despite this slow decay it has been shown that the technique is capable of dating carbonate samples as young as 250,000 years [133, 134]. The age of fossil enamel has been successfully determined with U–Pb dating techniques [135]. Another useful decay series, with applications to archeological finds, is K–Ar (and a variant known as the Ar–Ar method which is based on the same decay of ^{40}K to ^{40}Ar). For instance, the fossil remains of "Lucy" from Awash Valley in Ethiopia could be dated to 3.2 million years by use of K–Ar and Ar–Ar dating of a surrounding layer of volcanic ashes [136]. Another well-known example utilizing the Ar–Ar isotope technique is the dating of the Vesuvius eruption (AD 79). Despite the slow decay of ^{40}K to ^{40}Ar (half-life 1250 million years), which therefore entails large analytical challenges to date young events, Renne et al. [137] were able to obtain an Ar–Ar age indistinguishable from the historical age of the eruption.

Finally, fission track dating and thermoluminescence are two dating methods which have been applied on glass objects and on dating ceramics [138, 139]. The former method relies on counting tracks caused by spontaneous fission of ^{238}U atoms, whereas the latter is based on electromagnetic emission from non-conducting crystalline solids. Dating of fossil bones and teeth has been tested by means of fission tracks [140].

Limitations

This paper has exemplified how certain isotope systems can be used to reveal a human's diet, migration patterns or age. However, there are often limitations which can make the results uncertain. A determined age may be if not erroneous so at least questionable. The problems with the C-14 dating technique has already been discussed. Following the first enthusiasm over this remarkable method, it has been shown that a number of corrections are necessary to get a reliable result, and that older dating's might be questioned. It is of the greatest importance that no trace of "modern" carbon has polluted the sample used for the dating. Uncertainty how to validate other experimental isotope data is discussed below. An example worth considering is the dating of the Turin shroud, discussed by Meacham [141].

Many isotope studies are focused on archaeological examinations of human remains in order to ascertain information on diet or diseases. A body may have rested in the ground for centuries or thousands of years and may have been affected by the surrounding soil. In particular, diagenetic effects on bone and teeth have been studied. The problem is important because bone apatite yields dietary information about various life-stages. Most authors agree that diagenesis is a problem for these materials, and that the conditions at archaeological sites must be evaluated in each case [142–145]. Also a study of modern and ancient buried wood has been published, showing a linear correlation between carbohydrate content and the stable carbon isotope composition, because the carbohydrates are preferentially degraded during early diagenesis [146]. Usually an inorganic compound is more stable than organic and biological material, so the problem of diagenesis is likely to be smaller for metal artefacts, ceramics etc. However, also weathering may potentially alter the original isotopic composition of an object, and it may be essential to compare analytical results from both inner and outer parts of the artefacts. Furthermore, contamination from modern material that accidently got mixed with an object of some kind, and also conservation treatments, may jeopardize a judicial interpretation of the results obtained. Occasionally, it is of outermost importance to avoid the destruction of an object which may imply that a technique like SIMS (in situ technique affecting only a very tiny surficial area) is recommendable.

The provenance of an artefact can be determined or at least suggested from the isotope analysis of elements like lead, strontium and neodymium. Many other elements have also been used, like boron, copper, tin etc. The technical developments during the last decades allows extremely small sample volumes to be investigated which, however, make tough demands regarding the analytical protocols used at isotope laboratories. In particular, it is crucial to maintain very low levels of laboratory contamination and consider appropriate standardization procedures to master instrumental isotopic fractionation and use precautions not to alter the isotopic composition during pre-analysis sample treatment. For those heavy elements, for which isotopic differences among samples are notoriously small, optimized laboratory procedures are especially important. It may be difficult to convincingly prove, based on e.g. neodymium isotopes, that certain samples have a different provenance than others, due to the minor isotopic differences that are developed. Yet, it may still be possible to group samples by claiming that one set of samples has an isotopic signature that is distinct from that of another set. Lead isotope provenancing of objects is governed by relative large isotopic differences developed among potential source areas, but a complication is that there might be an isotopic overlap between geographical regions. There is a problem with isotopic overlap also for e.g. Cu and Zn and a further hinder for a successful provenancing when using these systems is that there are typically numerous potential regions sharing a specific type of metal deposit. At the best, some conceivable deposits can be dismissed.

Possible future applications

Isotope measurements are now routinely used in many fields such as geology, medicine, heritage science, archaeology, forensics, environmental studies and in the food and beverage industry. At present about ten elements, or *isotope systems*, are currently used on a routine basis for investigations in the field of heritage science (Table 1). The technical development of spectrometers has now reached a stage where so called compound-specific type of analysis is possible. Data from this approach is normally obtained by using a gas chromatograph (GC) which allows a controlled introduction of a certain molecular species into a MC-ICP-MS system and then e.g. analyzes the isotopic composition of carbon in organic species, or chlorine contained in e.g. pesticides. Another interesting technique utilizing specific isotopic properties is NMR, Nuclear Magnetic Resonance, today commonly used in medicine to study anomalies in human tissues. The method is based on the weak magnetic field of the nuclei of certain isotopes such as ^{1}H and ^{13}C, which in a strong magnetic field may cause resonance with low-frequency radio waves. The technique has also been used to investigate old human remains [147].

In the future, probably many more elements' isotope systems may be used. Hypothetically, for instance elements such as potassium, titanium, chromium, manganese, nickel and the platinum metals group are of interest in the study of cultural objects, preferably as components in multi-isotope studies. Moreover, isotope studies may successfully be combined with analytical data for trace elements. Although not based on isotopes, the hydration method is also worth mentioning in this context. This method allows dating of obsidian, a dense volcanic rock often used for producing stone tools [148]. Dating of microfossils in flint artefacts with the aid of palynological techniques is also possible at many instances. Understanding isotope systematics has also proven useful when investigating the effect of human activities on the environment. Considering the constantly growing field of applications and the fact that each new generation of mass spectrometers induce a much better accuracy, the future use of isotopes in heritage science is certainly likely to grow with time.

Authors' contributions

AN and KB have together written the manuscript. Both authors read and approved the final manuscript.

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Authors' information

Anders G. Nord (born in 1942). At the University of Stockholm he acquired a sound knowledge of chemistry, physics, mathematics, and mineralogy. He graduated in chemistry (1974) and was later associate professor. During employment at the Swedish Museum of Natural History, a system for analysis of light stable elements was built in cooperation with Kjell Billström. Other fields were carbon-14 dating and lead isotope analyses. For 20 years he was finally employed at the National Heritage Board of Sweden as a conservation scientist, with focus on the degradation of archaeological artefacts and museum objects, as well as analysis of medieval murals. Helping colleagues regarding isotope data for provenance and other interpretations was another important task. Anders Nord is still active as a research scientist and has so far published about 200 scientific papers and contributed to eight books.

Kjell Billström (born in 1954) studied geology at the University of Stockholm, where he graduated. Since 1978 he has been employed at the Department of Geosciences at the Swedish Museum of Natural History. He first worked with light stable isotopes, but has later concentrated on ore formation, development of the earth crust, and geological dating using heavy radioactive elements. He has also a wide experience in problems where lead isotopes have been of certain importance, and of testing and running various models of mass spectrometers.

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