Radiogenic isotopes and their applications within a range of scientific fields

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Introduction

Isotopic methods have become a very important tool in the study of natural processes, and numerous applications have proved valuable in a diversity of research areas. Most of the early developed methods were devoted to solve problems in bedrock geology and other geological disciplines, and the ability to obtain absolute ages provided a break-through in the understanding of the Earth's history. More recently, novel applications have been tested successfully within e.g. forensics and environmental studies. As a result, a wealth of information has grown over the last few decades through studies involving both stable and radiogenic isotopes. This contribution focuses on the application of radiogenic isotopes, whilst the approach using stable isotopes is further developed by Recio (2008, this volume). To a large extent, the tremendous increase in using isotope geochemical tools in new research areas has been driven by the technical development and introduction of new generations of very sensitive instrumentation. Besides, the chemical separation methods have developed to a point where extremely small samples (down to nanogram levels) can be handled and effects of interferences and contamination can be kept at a minimum.

Contrary to stable isotopes whose abundances are unchanged by radioactive processes, a radioactive/radiogenic isotope is either unstable and decay to another nuclide, or is the result of a decay series. Radiogenic isotopes may be divided into long-lived and short-lived isotopes, and their different half-lifes ($T_{1/2}$; the time during which 50 % of the radiogenic (parent) isotope decay to produce a daughter isotope) have implications for their usage in science. For instance, long-lived isotopes, e.g. ^{238}U (which decays to ^{206}Pb with a half-life of 4468 million years, Ma), are well suited for measuring

time in old geological systems which may have developed billion of years ago. By contrast, a short-lived nuclide, like ^{210}Pb (half-life is around 22 years), may be relevant for dating processes having a duration of a few years.

The aim of the present over-view is to illustrate how radiogenic isotopes can be applied in science, and examples will be presented with relevance for bedrock geology, archeology, forensics, food industry and environmental sciences. The theory of radiogenic isotopes are described in several text-books (see e.g. Faure & Mensing, 2005 for an excellent review), and only a few relevant issues will be recalled here in order to ease further reading.

Some theoretical concepts of radiogenic isotopes

Basically, radiogenic isotopes are applied in two different ways; (1) to provide an absolute age of a sample, and (2) to trace the origin of a component. The decay of ^{87}Rb to ^{87}Sr taken place in biotite can be used to illustrate the age concept. Biotite has a tendency to incorporate a significant amount of rubidium, and to exclude Sr, in its lattice during crystallisation. Rubidium has two naturally occurring isotopes; ^{87}Rb and ^{85}Rb, and the former decays to ^{87}Sr with a half-life of 48.8 billion years. This decay process, following an exponential law, is similar to the principle of an hour-glass; the sand in the upper part (cf. the "parent ^{87}Rb isotope") is passing down to the lower part ("decays to ^{87}Sr ") at a controlled rate described by a linear relationship. The time that has passed since the moment when the hour-glass was over-turned can be approximated by comparing the proportions of the remaining upper sand fraction with that of the lower fraction. Similarly, the ratio between radiogenically formed ^{87}Sr and the remaining ^{87}Rb in the biotite at the time of analyses, a ratio determined by means of mass spectrometry, is proportional to the time elapsed since biotite crystallisation. Using a mathematical notation, the time (t) is defined as follows;

t = $1/\lambda$ ^{x} ln (^{87}Sr /^{87}Rb + 1), where λ is the decay constant for the ^{87}Rb $\rightarrow$ ^{87}Sr decay process.

Thus, the daughter/parent isotope ratio (^{87}Sr/^{87}Rb) becomes bigger with time, which is the same as saying that the age of the biotite is increasing. Similarly, there are other isotopic clocks or geochronometers that can be used, and some of the most widely used

in geochronological applications are the U-Pb, Pb-Pb, K-Ar, Ar-Ar, Sm-Nd, Re-Os and Lu-Hf isotope systems for which some data are given in Table 1.

Method	Decay system	Decay constant	Initial ratio of interest	Common application
U-Pb	^{238}U to ^{206}Pb	1.55125 x 10^{-10}		age dating
Pb-Pb	^{238}U to ^{206}Pb		^{206}Pb/^{204}Pb, etc.	tracer and model age
K-Ar	^{40}K to ^{40}Ar	5.81 x 10^{-11}		age dating
Ar-Ar	^{40}K to ^{40}Ar			cooling ages
Sm-Nd	^{147}Sm to ^{143}Nd	6.54 x 10^{-12}	^{143}Nd/^{144}Nd	age dating, tracer
Re-Os	^{187}Os to ^{187}Re	1.612 x 10^{-11}	^{187}Os/^{188}Os	dating ores, tracer
Lu-Hf	^{176}Lu to ^{176}Hf	1.93 x 10^{-11}	^{176}Hf/^{177}Hf	tracer

TABLE 1. Some relevant parameters for a few selected radioactive isotope system (the half-life is related to the decay constant through the expression; $T_{1/2} = ln\ 2/\ \lambda$

The principle behind tracing the source for an element, e.g. Sr, can be explained by looking at an event whereby a crustal component separates from the mantle. In this case, the ratio between ^{87}Sr (radiogenically produced isotope) and ^{86}Sr (a stable Sr isotope - not affected by any kind of radioactive process) is of interest and the latter is used as a reference isotope whose abundance remains unchanged with time. Typically, a Rb/Sr fractionation process is related to this kind of event, and the produced crust will have an elevated Rb/Sr ratio compared to that of the residual mantle. As a result of differing Rb/Sr ratios, the post-event accumulation of radiogenic ^{87}Sr in the mantle will be lower than that in the crust, cf. Figure 1. This in turn means that the ^{87}Sr/^{86}Sr ratio will differ between these two geological domains, and the difference will be more pronounced with time and as a consequence the provenance of a sample (mantle- or crustal-derived) can be constrained using its Sr isotopic signature. Similarly, other isotopic systems evolve in an analogous way, and the Sr, Nd and Os isotopic signature for a rock can thus be used to model its origin. Another tracer system of interest in this context is the so called common Pb method which is built on the slow decays of U and Th isotopes to stable Pb isotopes. For instance, in ore geological studies, where the origin of galena often is of interest, the ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb isotope

ratios (^{204}Pb is unradiogenic and is used as a reference isotope) are typically determined. These ratios increase with geological time and with increasing levels of U and Th in a studied system, but in opposite to the behaviour of Sr in the crust/mantle, the obtained Pb isotope ratios of galena (with a U/Pb ratio virtually being zero) do not change with time once Pb has been incorporated into its lattice. Hence, galena-bearing ores formed at different times (and in different geological environments) are characterized by different sets of Pb isotope ratios, and occasionally the Pb isotopic signature of a specific ore is unique providing a direct link between a specimen and a known ore. The way the Pb isotope ratios evolve with time in different environments (e.g. upper crust, lower crust and mantle) has been modelled by different authors, and one of the most widely used model is known as the plumbotectonics model (Doe & Zartman, 1979). Figure 2 displays galena data from the Gangdese copper belt in Tibet (Qu et al., 2004) forming a linear array in consistency with a mixing process involving lead from different environments.
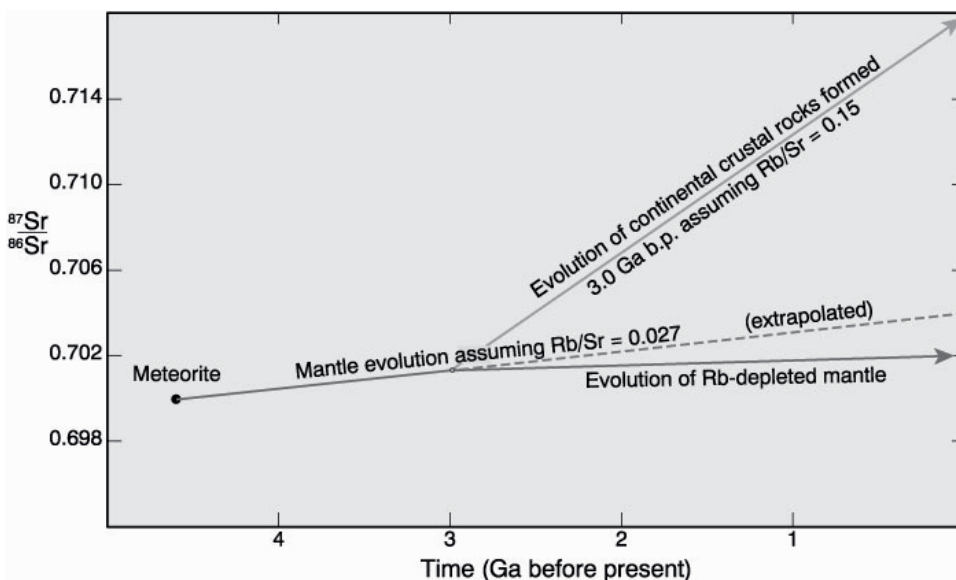

FIGURE 1. *Principal sketch-map showing the differences in Sr isotope ratios that develop once a crustal segment is separated from the mantle at some 3 billion years ago (after Wilson, 1989).*
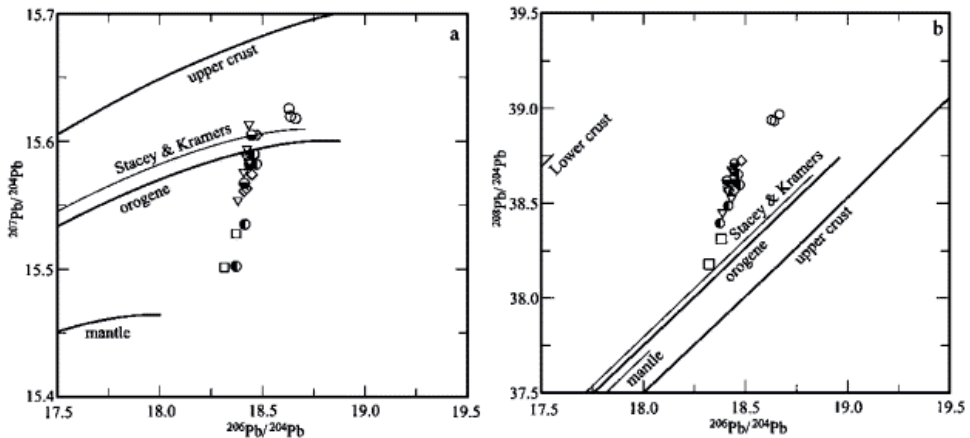
FIGURE 2. Plumbotectonics diagram showing data of galena from the Gangdes copper belt, Tibet along with the evolution curves for the upper crust, lower crust, mantle and orogene (Qu et al., 2004). Also shown is the two-stage model of crustal lead of Stacey and Kramers (1975).

A wide range of applications

Applications where radiogenic isotopes are used will here be demonstrated within the fields of bedrock geology, archaeology, forensics, food and beverage industry, and environmental sciences. Given the space limitation, only a few, illustrative case studies can be presented. Essentially, many isotope studies make use of the fact that isotope ratios could act as finger-prints that constrain the origin of the studied object. Sr and Pb isotopes are two isotopic systems which were developed for geological applications, but which are also useful in other disciplines. Compared to many lighter elements which are presently explored (e.g. Si, Sn, Mo, Fe, etc.), Sr and Pb have some advantages. Their isotope systematics is well characterized, their isotopic variations are quite large and easily analyzed, and proven methods for their chemical isolation before analysis exist. In addition, there are several sample types (e.g. carbonates) exhibiting very low Rb/Sr element ratios which make them particularly relevant to analyze. Remembering that carbonates are rich in Ca, and that Sr is geochemically similar to Ca, there will also be substantial amounts of Sr present in carbonates, but basically no Rb. From this follows, that the Sr isotopic ratios in carbonates do not change with time as a result of radioactive decay, and such data have been used to monitor the temporal changes in Sr isotope ratios of the oceans (see e.g. Faure and Mensing, 2005).

Certain samples, like galena and K-feldspar, are characterized by essentially U/Th free systems which suggest that their post-crystallisation Pb isotope ratios stay the same. It deserves mentioning that lead is widely used in many materials, to e.g. improve the quality of glass, and it is found in significant amounts in lead-acid batteries, piping, solder, cable sheathing, radiation shielding, paint and ammunition. Obviously all these categories of objects mimic essentially U/Th free systems that can be fingerprinted by lead isotopes. Considering other heavy elements; such as Nd and Hf, there are only rare Nd or Hf-bearing samples which may be free of the parent elements (Sm and Lu). This means that in applications involving Nd and Hf, sample isotopic ratios actually will evolve slowly with time which is a clear draw-back in tracing sources for old systems often encountered in geological applications. However, in e.g. an archaeological case study where the important question may be to pin-point a nearby source (finger-printing) which delivered Nd/Hf to a young object (man-made in recent time), this limitation may not be serious.

Bedrock geology

Most of the non-geological applications rely on the isotope tracer, or provenance concept, and therefore it seems natural to concentrate on isotope age dating techniques in this section. However, it must be remembered that tracer studies are extremely important in for example petrological work. For instance, both Nd and Hf isotopes are used to provide information about the crustal history of a zircon´s host rock. Examples will be given here with relevance for age dating of ore formation and rock crystallisation.

Dating ores by means of the Rb-Sr and the Re-Os methods

A major task in ore geological research is to date ore formation, but as a rule this is often difficult as minerals suitable for dating typically are not part of the ore assemblage itself. This means that dating normally needs to be accomplished on non-ore minerals whose genetic relationship to the main pulse of ore formation is questionable. There are, however, two relatively recent findings, which form an exception to this rule; Rb-Sr dating using sphalerite and Re-Os dating using molybdenite (and other sulphides) have been demonstrated to give reliable ages.

Successful sphalerite datings have been reported on e.g. Mississippi Valley type (MVT) deposits (see e.g Nakai et al., 1990). This approach requires that a series of sphalerites are analyzed, defining a certain range in Rb/Sr ratios, which makes it possible to fit a line (this line is called an isochron having the feature that its slope is proportional to the age of the system) in a diagram where $^{87}Rb/^{86}Sr$ is plotted versus $^{87}Sr/^{86}Sr$. As sphalerite contains only very minor amounts of Sr and Rb, the crucial step is to avoid the contamination of hypothetically present fluid inclusions. If such inclusions occur, these could carry small amounts of Rb and Sr that may disrupt the isotope systematics related to the proper ore-forming episode. The way to deal with this is to carefully grind the sphalerites using a boron carbide mortar with a very hard surface, thereby removing fluid inclusion waters prior to analysis. The data displayed in Figure 3 represent one of the pioneering studies (Nakai et al., 1990), and in addition to an isochron age it also shows the initial Sr isotope ratio. The latter reflects the type of Sr originally entering sphalerite at the time of ore formation, and the value of ca, 0.7105 is relatively high suggesting a significant input of crustal Sr.
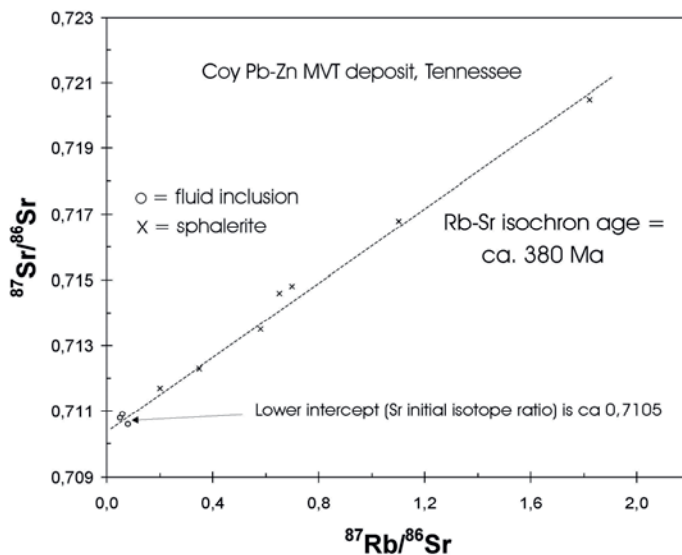

FIGURE 3. A Rb-Sr isochron diagram showing data for sphalerites sampled from the Coy mine in Tennessee (after Nakai et al., 1990).

Molybdenite is a phase, which is not uncommon in ore-forming environments and which has the unique feature of concentrating significant amounts of Re (and to exclude Os) during crystallisation. As a consequence, the amount of radiogenic [187]Os present at the time of analysis (due to the decay of [187]Re to [187]Os) is a monitor of the time elapsed since molybdenite formed, and this time period obviously equals the age of the mineral. A case study from the Harnäs gold deposit in Sweden has also shown promising results when applied to sulphides, like pyrite and arsenopyrite, which are ubiquitous in many ore-forming environments (Stein et al., 2000).

Geochronological dating - U-Pb method on zircon (laser and ion microprobe approaches)

Zircon is an accessory mineral, containing trace levels of uranium but basically negligible amounts of unradiogenic lead that crystallises in small amounts from most intermediate to felsic magmas. It is also a very robust mineral that often withstands alteration and metamorphic processes, and as a result it has been the most commonly U-Pb dated mineral in geochronological applications. In more recent time, the classical way of zircon analysis (by means of thermal ionization mass spectrometric analyses of separate Pb and U aliquots available after wet chemistry separation) has been partly replaced by ion microprobe (SIMS; secondary ion mass spectrometry) and laser ICP-MS (inductively coupled plasma - mass spectrometry) techniques. Two obvious advantages with the latter in-situ techniques are (i) point analyses of individual parts of a zircon crystal could be undertaken, (ii) an ability to derive many point-analyses within a short time. As zircon grains commonly are composite, this means that in-situ techniques can help to unravel a complex, igneous and metamorphic history of a rock. The high-speed of ion microprobe (and laser ICP-MS) analysis has opened up a kind of provenance application, where a large number of zircon grains from sediments are analyzed.

This approach is often used to target potential regions showing age population records that match that of the investigated sample, enabling the reconstruction of the nature of past erosional areas. Imaging techniques using BSE (back-scattered electrons) or CL (cathodoluminescence) are helpful tools guiding the selection of suitable zones for dating (cf. Figure 4).
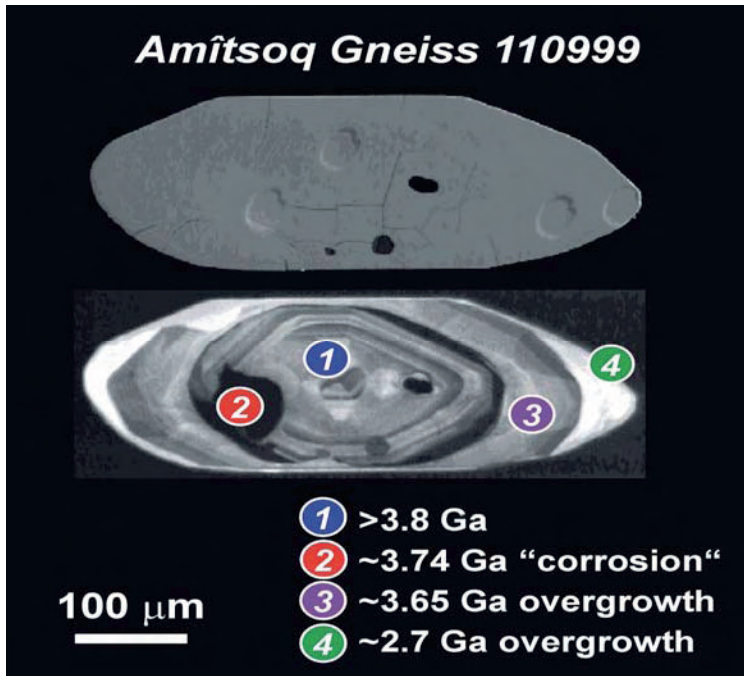
FIGURE 4. Obtained ion microprobe ages (in billion years, Ga) from a zircon of the Amitsoq gneiss, Greenland (upper part shows a SEM image with traces of the craters produced by the incident primary ion beam, whilst the lower is a CL image showing oscillatory zoning and over-growths).

This is obviously important when for instance a zircon contains inclusions (crystallized prior to the main zircon-forming event) that may contain non-negligable amounts of either U or Pb, or secondary over-growths. If such zircons are analyzed in a conventional manner using a small number of crystals, a geologically meaningless, mixed age would result. The quality of ion probe data (ca. ±1 % uncertainty in individual U-Pb ages) is comparable with that of laser results, but the latter is a destructive method creating ablation craters with a depth penetration of some 10-20 micrometers compared to only a few micrometer deep pits induced by the ion microprobe. Lasers produce very short light pulses, with a uniform wavelength, that can be focused onto the surface of a sample (see Kosler & Sylvester, 2003 for applications in geochronology). When the sample is hit, material sputters away (ablates) and can be transported by a carrier gas to a ICP-MS system where small, solid sample particles are ionized and subsequently

analyzed with respect to its isotope ratios. Possibly, laser ICP-MS applications will be even more used in the future as this a versatile tool allowing trace element analyses, Hf and U-Pb analyses to mention a few, and besides this instrumentation is much cheaper than ion microprobes. The presently introduced new generation of femtosecond laser systems appears to yield almost negligible fractionation effects which otherwise may be an obstacle in deriving reliable data. Moreover, this laser type is not heating its immediate neighbourhood, and in medicine such lasers are investigated for the usage of killing individual cancer cells.

Archeology

Provenance studies using stable and radiogenic isotopes have in a way revolutionised the last decades of work in archaeology. In non-geological applications, such as archaeology, it may not be required to interpret the ultimate origin of an object and to constrain the nature of the geological process(es) involved in the formation of the raw material used in the manufacturing process. Instead, the main concern may be to relate an object to a specific environment (e.g. a stone axe to a specific rock quarry, a skeleton to a certain inhabited area). This is to say, that finger-printing is typically of main concern in many archaeological studies, and a limiting factor may occasionally be that appropriate isotope reference data are lacking. Obviously, distinct mineralogical features may also be essential when it comes to constrain the origin of e.g. a stone axe exhibiting some specific banding or intergrown textures. The subjects brought up in the present context include age dating of organic carbon-containing objects, tracing the origin of artifacts, and the migration patterns of animals and humans.

Age dating using the C-14 (radiocarbon) method

^{14}C is produced in the atmosphere by a nuclear reaction where ^{14}N is transformed to ^{14}C (Libby, 1946). Once ^{14}C forms it starts decaying to stable ^{14}N by beta-emission (the half-life is around 5730 years), and its presence in the atmosphere is principally balanced by its production rate and its removal rate through precipitation. When a living plant is growing it absorbs CO_2 from the atmosphere that contains a small proportion of ^{14}C. This small amount is in steady-state equilibrium with ^{14}C in the atmosphere, but when the plant dies the incorporation of CO_2 stops. As a consequence, no further

addition of external ^{14}C to the plant takes place, and the activity of ^{14}C declines at a rate, which is controlled by its half-life. Plants, or organisms which eat plants (including animals and ultimately humans), can be dated by using a beta-counting system. The relatively short half-time and limitations in the detection systems restrict material much older than ca 50.000 years to be dated. Numerous successful ^{14}C dates have been published during the last half-century, and one of the latest was carried out to establish the age of Ötzi, the iceman who died when crossing the Alps some 3330 years B.C. (Fowler, 2000).

Origin of artifacts

The origin of archaeological artifacts has been successfully established at many excavation sites all over the world. The trace amounts of strontium and lead in many archaeological objects have made it possible to apply Sr and Pb isotopes in investigations, giving e.g. insights into past trade routes. A basic foundation for their usefulness in provenance studies, is that these isotopes do not fractionate neither during natural reactions, nor due to treatment by local craftsmen. What may be a serious draw-back, and particularly relevant for Pb, is that isotope populations of known ore districts may overlap considerably. Three examples with relevance to archaeology will be given here.

Batavia, a ship of the Dutch East India Company, was shipwrecked on her maiden voyage in 1628, and made famous by the subsequent mutiny and massacre that took place among the survivors. The remains of this ship is now at a museum in Perth, Australia and some of the items found (copper tacks and nails with traces of lead) have been used in a lead isotope study to provenance their origin (Van Duivenvoorde, 2008). These results demonstrate that the copper metal was derived from more than one source. Lead isotope ratios plotted in Figure 5 prove the existence of a low-radiogenic Pb isotope signature which matches very well the relatively unique signature of ores from the mining district of Bergslagen in southern Sweden. Trading with Sweden at this time is well documented, but it is also clear from the way data plot in the diagram that another, more radiogenic source of lead (exhibiting higher lead isotope ratios), characterize the majority of the samples. This source is more difficult to pin-point as lead from several ore districts in different countries would be consistent with the Batavia

radiogenic signature. On the basis of independent evidence, it is likely that in addition to Swedish Bergslagen copper ore, either ores mined in Japan or Morrocco were transported by Batavia.

The plumbing system in Pompeii during the Roman empire examplifies another case where Pb isotopes were applied (Boni et al., 2000). By analyzing lead pipes belonging to the water supply system, the authors could identify a quite complex data pattern involving three, or more, lead sources. The isotope patterns also suggest that lead in the pipes have been melted and re-circulated to be used in new constructions as part of a major reconstruction programme involving the entire town. The ultimate sources of lead cannot easily be identified, but the suggested end-members include one specific ore at Sardinia. The other sources remain unidentified as the appropriate isotopic compositions can be matched with several ore districts in the Mediterranean region.

At Sagalassos in SW Turkey, archeological excavation works have lately included isotope methods. The main approach has been to use a multi-isotope, and trace element approach in order to constrain the possible sources of raw materials used in manufacturing iron and glass artifacts (Degryse et al., 2006). Three local glass types are known from the area (green glass, blue glass and HIMT = High Iron Manganese Titanium glass), and Sr and Pb data support a theory where the latter two were recycled to produce green glass. On the basis of Sr isotope signatures and absolute Sr contents in the glasses, suggestions have also been put forward with relevance for the ultimate origin of the glass types. Locally found iron artifacts and their origins constitutes another source of discussion at Sagalassos. Limestone-hosted hematite and magnetite ores and hematite placer deposits are known from the area, and their potential association with the iron artefacts is clearly of interest. It turned out that Sr isotope signatures were most useful to provenance the iron-containing objects, whilst Pb data often show a more scattered or overlapping character. Combined with trace element analyses the cited isotope work at Sagalassos provide a good basis for interpreting the origin of raw materials.
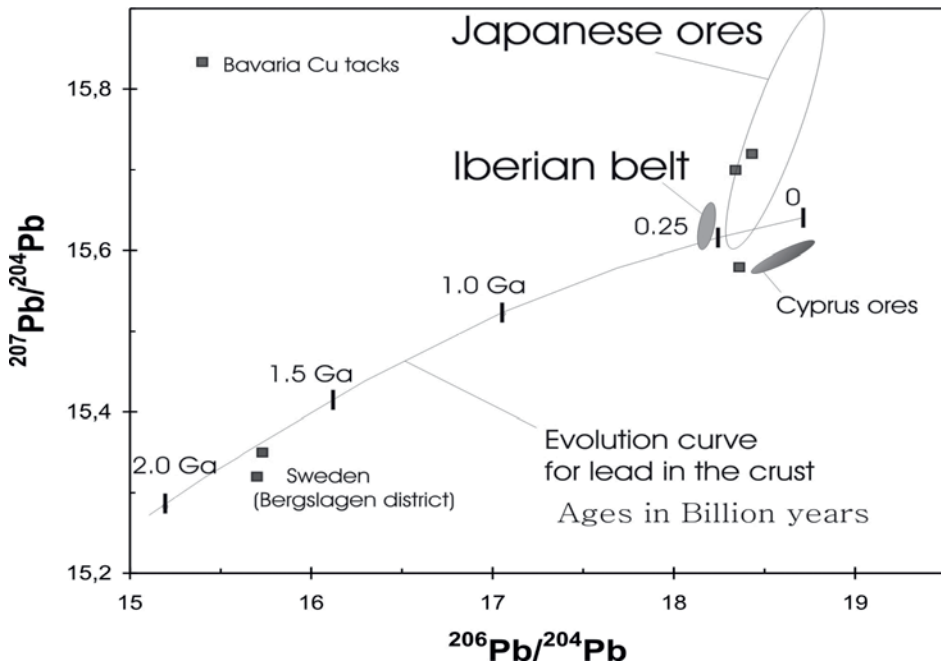
FIGURE 5. Lead isotope data of Cu-tacks from the Bavaria wreckage and some reference fields (after Van Duiwenvoorde, 2008).

Mints and coins form another group of objects which have been successfully provenanced by lead isotopes. Silver coins often carry a substantial amount of lead which follows from the circumstance that argentiferous lead ores often are used for silver production. Laser ablation ICP-MS analyses of Roman silver coins were reported to have been used for assessing the trade and exchange of metals and ores (Pointing et al., 2003).

Tracing the life story of humans (" you are what you eat")

Archaeologists, interested in how people have moved between inhabited regions, may benefit from applying Sr isotopes in their work. The reason is that different regions, characterized by different geology, tend to have quite distinct Sr isotopic signatures or finger-prints. Taken Sr isotopes as an example, there is principally a 1:1 relationship between bedrock, soil, plants and other organisms higher up in the food chain which can be explained as follows. The strontium isotope signature of the bedrock is controlled by geological factors – the soil inherits the isotopic signature of the weathered bedrock – the

plants inherits that of the soil (although added fertilizers may complicate the picture) – animals inherit the signature of the plants, and ultimately this may be reflected in humans which mainly feeds on special animals. An illustrative example of a big isotopic contrast between food, is given by fish from a marine environment (showing a marine, relatively unradiogenic Sr signature) and crops growing on soil derived from an old basement being characterized by a highly radiogenic signature). As the primary isotope signatures are preserved (i.e. not fractionated) as Sr is processed through the food chain, the body skeleton retains a Sr isotope memory of the diet taken in by an individual. As noted before, the usefulness of Sr isotopes is related to the fact that Sr is geochemically similar to Ca which is a major element in the human body. As a result, Sr occurs in amounts (ppm levels) high enough to be analyzed in e.g. teeth and skeleton remains. The Sr isotope systematics in teeth and bones, however, are different. The enamel of teeth becomes mineralized to apatite which hinders teeth-Sr to interact with strontium stored in other parts of the body, and in this way the Sr isotope compositions of teeth reflect a fossil isotope signature that is related to the child-hood. For other parts of the body, there is continuous exchange of Sr between the skeleton and the new Sr ingested through the diet, and it takes like 7-10 years for the isotopic signature of Sr in bone to become fully re-setted once a completely new kind of diet pattern has been in place. Therefore, on the basis of Sr isotope data from teeth and bones, one could in theory identify both the geographical region associated to the child-hood, and the region related to the last ten year period before death (Beard et al., 2000). Beard et al. (2000) used this approach to investigate the migration history of people the remains of which were found in an archaeological site in south-western U.S.

Forensic sciences

An isotope analysis is one of several analytical techniques used in the field of forensics. Here a novel technique will briefly be discussed where short-lived isotopes are used for constraining the time elapsed since the death of a person. Besides, it will be shown how the Pb isotope ratios in bullets and ammunition can be used to discuss their sources(s). It may also be mentioned that smuggling of nuclear materials is posing an increasing threat to society. In the field of nuclear forensics, isotope methods are important in the work of characterizing suspicious material.

Dating post-mortem intervals

A common problem for forensic pathologists is to estimate the post-mortem interval, and several methods involving e.g. growth of insects and application of isotopes (short-lived radionuclides) have been investigated. Diagenetic effects, and related mobilisation of radionuclides, may complicate the interpretation of some results related to certain isotopes, like ^{90}Sr produced by aboveground nuclear weapons testing, not naturally occurring in human bones. Carbon-14 is commonly used in life sciences but its relatively long half-life of 5730 Ma prohibits its use for accurately dating very young objects. Recent investigations have shown a potential of using ^{210}Pb (half-life of 22.3 years) and ^{210}Po (138 days) as a tool for pathologists (Swift et al., 2001). These nuclides, which are intermediate, beta-emitting radioactive members of the ^{238}U decay series, enter the human body either directly through the food, or as an effect of decay of ^{226}Ra which is retained in the body after inhalation. As for C-14 there is a steady-state equilibrium situation, with the levels of ^{210}Pb and ^{210}Po staying approximately constant as long as a human being is alive. These levels are low and require a beta-counting system capable of precise measurements of radioactivity. Although more work is required to explore the full applicability of this approach, the differing half-lifes of the mentioned nuclides suggest that the post-mortem interval, being relevant for forensics (i.e. ranging from days to a few decades), could be constrained with a precision superior to previously used methods.

Bullets and their origin

Ballistic determinations are perhaps the most important method in investigations involving shooting incidents. On the other hand, there are situations where ballistic investigations are inconclusive due to deformation of bullets, and sometimes bullets could not even be found at the crime scene. Bullet residues may remain in the victims body and since bullets typically are made of lead alloys, Pb isotope analyses of such fragments could be a useful tool. A number of studies have been devoted to test the usefulness of Pb isotopes in forensic work (e.g. Ulrich et al., 2004), and considerable differences among Pb isotope signatures of ammunition do indeed exist (Zeichner et al., 2006). One conclusion is that the combination of lead isotope data and trace element analyses usually give the best result. Antimony seems to be a relevant indicator of origin

in some cases as Sb is intentionally added to ammunition to give it desirable properties. It is favourable if reference ammunition could be tested, and ideally a very clear match is found with a bullet used in a crime. In February of 1986 Sweden suffered a national trauma when Olof Palme, the present prime minister, was shot to death. Lead isotope analytical data of bullets form part of the vast investigation material, but sofar no perpetrator has been possible to link to the crime. Certain factors must always be considered when provenancing ammunition. One is that isotopic variations could occur even for the same lot of ammunition if the manufacturer mixes different raw materials representing different sources. Another thing to keep in mind is that Pb isotope data normally only make it possible to either demonstrate a similarity, or lack of similarity, between a bullet and some reference material. That is, one has to be careful not to exclude an alternative interpretation of available isotope data.

Food and beverage industry

In particular, N, C, S and other stable isotopes are nowadays widely used to detect frauds in the food industry. The stable isotopes of the light elements may provide information about altitude/latitude and reflect a climate control, whilst e.g. Sr isotopes may add lithological source information important for an authencity documentation. The usefulness of Sr isotope data is very much dependent on the presence of clear isotopic contrast in a study area which would govern the development of distinct isotopic differences among the samples investigated. For instance, two extreme end-members would be constituted by young basaltic rocks having quite unradiogenic Sr isotope compositions, and old crustal felsic rocks whose elevated Rb/Sr ratios would lead to increasingly radiogenic Sr isotope ratios with time.

Provenancing juice, waters and coffee

Several hundreds of fruit juices have been systematically analyzed from all over the world in a study reported by Rummel et al. (2006). These authors found that Sr isotopes provided useful information pertinent to the origin of juices. This was due to the fact that the geological conditions are quite homogeneous (bringing Sr isotope signatures to be relatively characteristic) in many juice-producing areas within countries such as Spain and countries from Middle and South America. Moreover, occasionally

undeclared additives with a unique isotopic composition could be detected. Montgomery et al. (2006) analyzed mineral waters across Britain and found that their $^{87}Sr/^{86}Sr$ ratios varied systematically as a reflector of the geology of the aquifer rocks (Figure 6). It is implied from their study that the knowledge of the spatial Sr isotope variations in water will be important also for historical and archeological studies. The origin of various food, wine, waters. etc., based on isotopic determinations, have been reviewed by Kelly et al. (2005) who stress the importance of combining as many elemental and isotopic signatures as possible.

Environmental sciences

Past climate variations, understanding path-ways of elements in reactions, and anthropogenic contamination are only a few of numerous issues where isotopes have played an important role to clarify the nature of processes.

Dust transport

Continental dust, released from arid regions, are transported over long distances and deposited on the oceans and continents. Obviously, the knowledge of the origin of dust could help in under-standing atmospheric circulation mechanisms (Grousset and Biscaye, 2005). Satelite imaging and air-mass trajectory techniques have been used to trace transport patterns, and also isotope tracer methods (Figure 7).
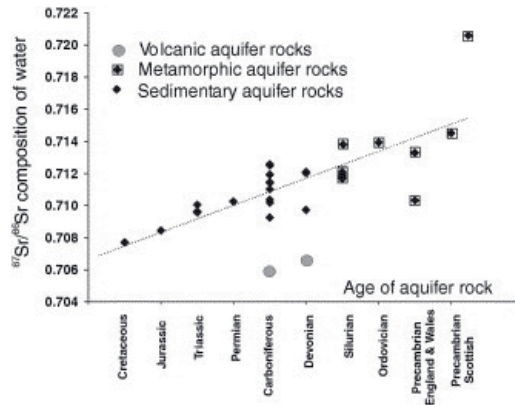

FIGURE 6. *The $^{87}Sr/^{86}Sr$ isotope composition of bottled waters plotted against the geological stratigraphy of the aquifer source rock (after Montgomery et al., 2006).*

Besides, mineralogical and trace element studies may give additional information. The isotope approach has the advantage of providing a direct comparison between collected dust and its potential source area(s).
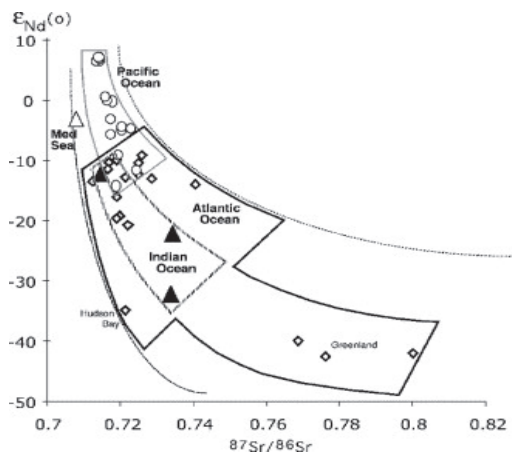

FIGURE 7. Sr-Nd isotopic composition of suspended matter from rivers entering the main world oceans (after Goldstein and Jacobsen, 1988).

This opens up the possibility for modelling dust transport in the past which have important implications for climate reconstructions and historical atmospheric circulation patterns. For example, aeolian dust in the atmosphere can either reflect or absorb solar energy as a function of e.g. mineralogy and grain size. Moreover, continental dust settling in the oceans may affect the marine productivity, and pollutants are also easily carried by dust particles (Grousset and Biscaye, 2005). As for other finger-printing applications, the ability of provenancing dust makes use of the fact that the Nd, Sr and Pb isotope ratios are different in mantle- versus crustal-derived rocks. The example presented here is taken from Greenland´s ice-sheet which was found to have quite variable lead contents. One peak coincided with the period between ca. 150 B.C. and A.D. 50 during the Roman era (Rosman, 1998). The lead isotope composition actually measured in that interval of the ice core demonstrated a good match with lead mined at Rio Tinto in Spain. As this mine is known to have been processed by the Romans it can be concluded that air-borne lead was transported north-wards from Spain and finally

reaching Greenland. Another peak in the lead concentration record, representing about 25-50 times higher Pb concentrations, characterizes the period between ca. 1930 and 1980 and is readily interpreted as a contamination effect of leaded petrol.

Anthropogenic Pb in petroleum and other pollutants

The ALAS model is an important tool for estimating the age of hydrocarbon release (Hurst, 2000). It is based on systematic increases in lead isotope ratios in petrol caused by shifts in sources of lead ores used by the petroleum industry in North America. The ALAS calibration curve relies on isotope measurements of soils and water of known age, affected by petroleum products, and isotope data of the hydrocarbon products themselves. Due to an increasing usage of radiogenic MVT type of ores in leaded petrol, age uncertainties are as low as a few years. An application of this model is to correlate environmental releases of e.g. diesel and motor oil to their sources, and anthropogenic gasoline-derived lead has been mapped for many areas in the U.S.

Numerous studies have been devoted to metal dispersions from mine sites. Pb isotopes is an ideal tool as lead occurs in detectable amounts in most ore-forming environments, whilst the parent elements U and Th typically occur in amounts that is negligible in most provenance studies. Even if the U and Th contents are relatively high in a studied system, the slow decay of these elements to form stable lead isotopes means that for young systems, like those affected by anthropogenic processes, this is not a problem. MacKenzie and Pulford (2002) investigated to what degree former activities at a mine site at Tyndrum, Scotland, could be detected in the environment. Samples of mining wastes, river sediments and peat cores were analyzed. Pb concentrations were high in e.g. river sediments near the mine, but the concentrations decreased markedly downriver from the mining site. Based on obtained Pb isotope data, the main source of lead in the studied samples could be coupled with the mining operations, although a certain influence of local bedrock geology and of leaded petrol could also be detected.

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