

HEAVY ELEMENTS' ISOTOPE RATIOS IN ARCHAEOOMETRY

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RESUMO: Nas últimas décadas, os métodos químicos vem ganhando importância na Arqueologia. São usados para a determinação de proveniência *sensu lato*: para a identificação das origens de qualquer material (matérias-primas, artefatos, vestígios humanos e animais), relações comerciais, questões paleoambientais e questões nutricionais. Os elementos químicos, entretanto, tendem frequentemente a fracionar durante o enterramento e a mineralização, de acordo com o seu comportamento geoquímico. Mesmo as medidas de frequência de isótopos de elementos leves (C.N.O.) podem indicar os efeitos de isótopos que também levam a fraccionamentos. Ao contrário destes, as marcas dos elementos pesados dos isótopos (por ex. ^{87}Sr ^{86}Sr , $^{206}, 207, 208\text{Pb}$ / ^{204}Pb , ^{143}Nd / ^{144}Nd) têm um comportamento bastante conservador. Os princípios e as aplicações destes sistemas isotópicos serão apresentados neste artigo, e as limitações serão discutidas em referência à bibliografia sobre o tema.

UNITERMOS: Arqueometria — Isótopos de elementos pesados — Determinação de proveniência

In the last few decades physical and chemical methods have become increasingly more important in archaeological research.

One major application of these methods is in the determination / identification of the geographic origins of raw materials, artefacts and biological remains and, thereby the tracing of trade relations, finding of trophic positions and answering of palaeoenvironmental questions.

The principle of provenance determination lies in identification of at least one remnant feature within a sample, which provides information with regards to its assumed area of origin. The distinguishing feature which is characteristic for a specific location of origin has to fulfill two basic requirements: it has to be location dependent and it must survive secondary physico-chemical pro-

cesses such as burial and any subsequent mineralisation of, say, organic substances.

Chemical composition

The chemical composition of a sample can give hints to its area of origin. The compositional range of most materials varies and the element-abundance of an individual sample is connected to that of the area of origin. This holds true especially for non essential elements, i.e. most trace elements.

In practice however, the actual chemical composition of a sample is determined also by many other factors so that the variance within material of the same provenance often reaches or even exceeds the variance between possible areas of origin. Thus, identifying a link with a specific source area can only be done statistically, if at all and not for a single sample. In addition, the origi-

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nal chemical signatures of archaeological material may be altered significantly during secondary processes. The reason for this is the rather different behaviour of the elements with regard to most physico-chemical processes which results in element fractionation.

Sometimes the selectivity and also the durability of chemical signals can be enhanced by the use of abundance ratios of elements which show similar geochemical behaviour.

The problem of element fractionation is circumvented by the use of isotopic compositions of certain elements as source-signatures, as discussed below.

Isotopes

Isotopes of an element are atoms or nuclides whose nuclei contain the same number of protons, but a different number of neutrons. The term 'isotope' is derived from Greek, and indicates, that isotopes of a given element occupy the same position in the Periodic Table. Most elements are composed of isotopes.

The interesting fact for archaeometry is that the isotopic composition of some elements is variable and depends on the specific sample which is analysed. To judge the suitability of isotope ratios for provenance determination it is important to understand the reasons for isotopic variations.

Light elements' isotopes

Some elements show so-called 'isotope effects'. The difference in mass between the isotopes of these elements causes slight differences in their physico-chemical properties. If these elements then undergo specific physico-chemical reactions such as evaporation, condensation or diffusion, isotope fractionation may occur.

The occurrence and degree of these isotope effects is controlled mainly by the relative mass difference between isotopes (fractionation is proportional to the square root of the quotient of isotope masses) and to a lesser extent by the complexity of the elemental chemistry. 'Naturally' occurring isotope effects, therefore, are restricted to elements with low atomic masses (approximately < 40), where the relative mass difference is large. Isotopes of elements in this range which show variable abun-

dances, which are unrelated to radioactive decay, are called stable isotopes.

The abundances of these isotopes are given as delta-values with the per mil notation where delta = (isotope ratio sample / isotope ratio standard) / isotope ratio standard x 1000.

An example for an isotope effect and resulting isotope fractionation is the element oxygen which has isotopes with masses of 18, 17, and 16. Water which evaporates from a small puddle is enriched in ¹⁸O as water molecules with lighter ¹⁶O are entering preferably into the vapor phase. Consequently, water in the residue is enriched in heavier ¹⁸O.

Isotope signatures of light elements from source materials are a result of the physico-chemical reactions the material has undergone. They, therefore, vary not only with geological history, but also with other factors such as orographic or climatic condition.

A principal problem of light elements' isotope ratios with regards to provenance determination is the susceptibility for further isotope fractionation during biological processes, or within the burial environment, as well as the falsification of original signals by contamination or material exchange.

Heavy elements' isotopes

Variable isotope abundances also are observed for some heavier elements, which are not susceptible to isotope effects. The reason for variability is in this case a (usually) long lived radioactive decay which results in an isotope of the element considered. Examples for such decay schemes are given in Table 1.

Table 1 — Common decay schemes

mother-isotope		daughter- isotope	half-life
²³⁸ U	→	²⁰⁶ Pb	4.47 x 10 ⁹ y
²³⁵ U	→	²⁰⁷ Pb	7.04 x 10 ⁸ y
²³² Th	→	²⁰⁸ Pb	1.40 x 10 ¹⁰ y
¹⁴⁷ Sm	→	¹⁴³ Nd	1.06 x 10 ¹¹ y
⁸⁷ Rb	→	⁸⁷ Sr	4.88 x 10 ¹⁰ y
¹⁸⁷ Re	→	¹⁸⁷ Os	4.27 x 10 ¹⁰ y

The actual isotopic abundances observed in a specific mineral, rock, soil sample, etc. are dependent on the extent and the time over which the radioactive mother isotope (see Table 1, left column) was present in the past and the radiogenic daughter isotope accumulated as a result.

In geochronometry, a subdiscipline of isotope geochemistry, the time dependent accumulation of radiogenic daughter isotopes is used for dating minerals and rocks. Due to the extreme long half-life of the radioactive mother isotopes these 'clocks' can be used for ages in the range of millions of years, where significant amounts of the daughter isotopes are accumulated. Considering typical concentrations of mother nuclides in natural materials, accumulation of daughter isotopes is low within the last million years such that isotopic ratios remain practically constant.

The abundance of radiogenic isotopes is commonly given relative to a non radiogenic isotope eg. $^{87}\text{Sr}/^{86}\text{Sr}$ which is the ratio of the radiogenic ^{87}Sr relative to stable ^{86}Sr .

Isotopic ratios of heavy elements can be regarded as a long-time memory for the geologic history of a specific region or any material derived from it. Disregarding the inherent geochemical and geochronological information, they can be used in an empirical manner as regional natural tracers which are incorporated into any material. From geologic material the signatures are transferred into any kind of products made from it. In the same way plants, animals, and humans take up these isotopic tracers from the soils via diet and store them in their tissues.

The most important advantage of heavy elements' isotope ratios is their insensitivity to isotope fractionation during all common physical or chemical processes: The isotopic composition of the metal lead, for example, is exactly the same as that of the ore from which it was produced. If this lead is then used as fuel additive, the gaseous lead tetraethyl in the exhaust fumes will show the same lead isotope signature.

Element abundance-ratios and even light elements' isotope ratios would have dramatically changed during these processes.

Of course, the application of heavy elements' isotope ratios has its limitations: although isotope ratios themselves are very stable, original signatures can be overprinted or obscured by mixture with the same element from a different provenance.

In many cases this is not a serious problem, but in certain other cases it may be crucial. In most cases, however, it is possible to overcome these problems. A second disadvantage is the high cost (~ \$ 300/analysis), which is caused by the high analytical effort described as follows.

Analytical procedures

The analysis of heavy elements' isotopes is highly developed in special fields of physics, chemistry and, especially in isotope geochemistry.

The method is destructive, but for one analysis only about 100ng of the respective element is required. Therefore, traces of the elements to be analysed are sufficient. For example, to examine the isotopic composition of Sr in marble, which contains typically 200ppm Sr, only 1/2mg material is required.

Prior to the measurement, the element has to be separated from the matrix of the sample material. This is done by dissolving or leaching the sample in acids and subsequent isolation of the elements with procedures that are specific for every element. The analytical steps have to be performed in special clean-labs with ultraclean reagents and equipment to avoid contamination of the isotopic signal. The measurements are done on solid source Thermion-Massspectrometers (TIMS) (Fig.1). The principal function of the TIMS is relatively simple: ions of an element are accelerated by high voltage in a vacuum. The well focused ion beam passes through a magnetic field and is deflected. The degree of deflection is mass- and charge-dependent, and the heavier ions have the greatest moment of inertia (considered charges to be equal). The intensity of the different ion beams, which corresponds to the isotopic abundances, are registered in Faraday cups or electron multipliers. It is important to note that the very high external precision required is reached only by this type of instrument. The precision of an Inductively Coupled Massspectrometer (ICP-MS) is 2-3 orders of magnitude lower, and thus is not sensitive enough for that kind of isotope abundance measurements under consideration. These type of instruments might be useful, however, in some cases for rapid survey-analysis.

The choice of isotope system to be used in solving a specific problem depends on the question itself and on the material being studied. Pb-isotopes, for example are well suited for the

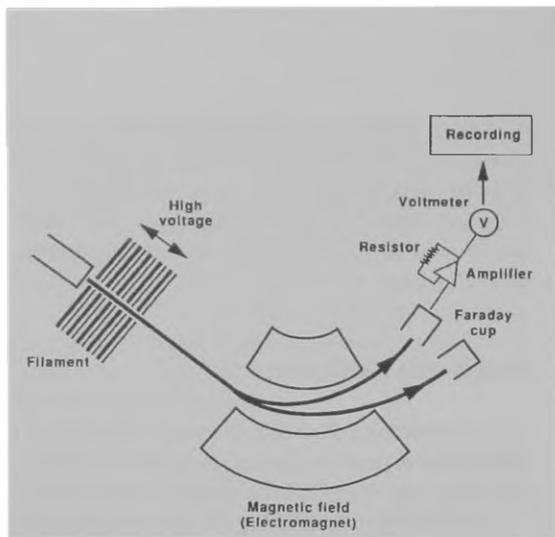


Fig. 1 — Schematic diagram of a mass spectrometer (from Allegre, 1992).

examination of metallic samples and especially palaeoenvironmental questions, whereas Sr-isotopes are well suited for the examination of calcium-bearing samples as carbonatic rock material and calcified tissues, in that calcium is commonly substituted to a certain degree by Strontium.

I will restrict myself here to these two elements and give principles and example(s) for archaeological applications.

Lead

Lead is widely distributed throughout the earth. It forms minerals of its own and is also commonly found as trace element in all kinds of rocks. Lead has four naturally occurring isotopes ^{208}Pb , ^{207}Pb , ^{206}Pb , ^{204}Pb . The isotope 208 is a radiogenic daughter of ^{232}Th , the isotopes ^{207}Pb and ^{206}Pb are radiogenic daughters of the U-isotopes 235 and 238, respectively. It is a peculiarity of lead that it has three radiogenic isotopes that are the decay product of two different elements. The isotopic composition of lead, therefore, varies widely from highly radiogenic lead in old, U- and Th-bearing systems, and young, low radiogenic systems with low Th/Pb and U/Pb ratios.

Lead is toxic and has been linked with several health problems. The wide dispersion of this element by man and lead-poisoning is not only a problem of today but has a history of almost 4500 years.

'Greek coins'

A famous example for the use of Pb-isotopes in archaeology is the study of Gale, Gentner and Wagner (1980), with the title: *Mineralogical and Geographical Silver Sources of Archaic Greek Coinage*.

In this study 120 Greek silver coins from the Asyut hoard were analysed for their lead isotopes in order to identify the sites where the silver was mined. The hoard consists of more than 900 silver coins from mainland Greece and Asia Minor. It was accumulated between 450 and 475 B.C., at the beginning of extensive silver coinage in this part of the old world. It is thus highly likely that the coins consist of genuine, rather than recycled silver. Most of the coins were coined in Athens and Aegina. Analysis was carried out on 120 coins, and also on ores from 70 ancient silver mines, which were supposed to be possible sources.

The isotope ratios of all coins from Athens fall into the field of Laurion and Siphnos, two well known silver mining districts. This certified that Laurion, located near Athens, and the Aegean island of Siphnos, were main sources for silver coins of archaic Greece. A third important source with isotopic compositions between those characteristic for Laurion and Siphnos could not be identified, but was considered to be located in Macedonia or Lydia. In combination with Silver and Gold concentrations, also some other minor sources could be identified by their Pb isotopic signature.

Thus, contrary to the previously held belief that Spanish silver was an important source for Greek silver work, only three coins out of 120 have Pb isotope ratios which make it possible that the silver was derived from Lineras or Rio Tinto in Spain.

'Franklin expedition'

The second example with the title: *Source Identification of Lead Found in Tissues of Sailors from the Franklin Arctic Expedition of 1845* by Kowal and cols. (1991) deals with identification of the reason for deadly lead poisoning.

In 1845, the British Arctic Expedition (called the Franklin Expedition after its leader) started with the goal to complete the charting of a north west passage through the North-American Arctic

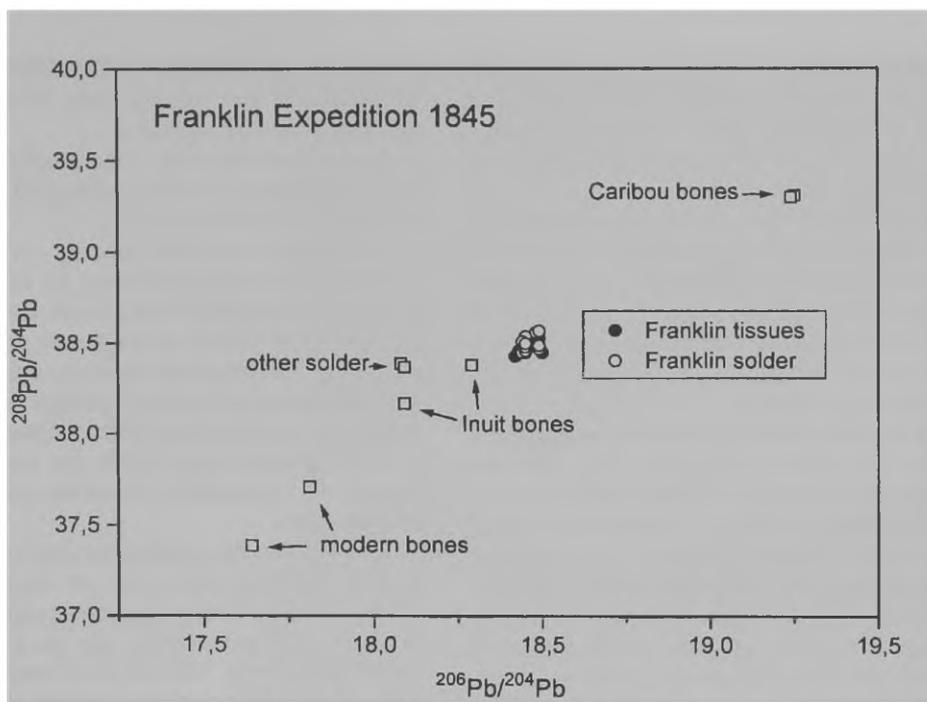


Fig. 2 — $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ of tissues and solder from the Franklin Expedition and reference samples

archipelago. The expedition ended with a mass disaster as none of the 129 crewmen and officers survived the expedition. The cause of the disaster has become one of the greatest mysteries of Arctic exploration. Reconstructions of the events leading up to the ruin of the expedition have for a long time relied exclusively on searchers reports and inquiries. Since the establishment of the 'Franklin Forensic Project' in 1981 at the University of Alberta, human remains have been recovered and analysed.

In 1985 spectroscopic analysis accidentally yielded a lead-level of 125ppm in a crew member's bone, which is extremely high, compared to a normal level of 5ppm in bones from Inuits of the same time. This unexpectedly high value was the reason for subsequent analyses of bone and hair samples which showed similarly high values and confirmed that the expedition members were suffering from some degree of lead poisoning. Since very few items of the expedition remained, it was questionable at that time, whether or not it would be possible to identify the source of the lead. In 1986, however, corroded remnants of 125 empty food cans were found at the site of Franklin's winter camp 1845/

46. The large amount of lead-tin solder which was used in fabricating and sealing the cans was striking. Analyses revealed that the isotopic composition of the solder on the food cans and that of the lead found in the tissues of the expedition members was essentially identical (Fig. 2). The isotopic composition of small amounts of lead in the control samples from Inuit indian and caribou bone from King William Island however was distinctly different.

It was concluded that the devastating health effects of the high lead levels in the lead-solder contaminated foods was the major factor which led to the death of the members of that expedition.

Strontium

Strontium is chemically very similar to calcium and partly replaces this element in a wide range of materials. This is well known in Europe since the disaster of Chernobyl, 10 years ago, when radioactive ^{89}Sr and ^{90}Sr was widely distributed in the environment and subsequently incorporated into human tissues.

Strontium has 4 naturally occurring isotopes ^{88}Sr , ^{87}Sr , ^{86}Sr , ^{84}Sr , which are primordial and stable. One of them, ^{87}Sr is, in addition also radioactive and is the decay product of the long lived beta decay of ^{87}Rb (see Table 1).

Observed $^{87}\text{Sr}/^{86}\text{Sr}$ -ratios in common rocks have a spread of only about 2%, which would seem to be a rather small range. However considering the high precision of around 20ppm for the analysis of $^{87}\text{Sr}/^{86}\text{Sr}$, a typical ratio of 0.71000 can be determined to the 5th digit after the decimal point, 2% is a quite large variation.

As mentioned earlier, plants and animals take up the site-specific Sr from their diet and incorporate it into their tissue. Under particular conditions the Sr isotopic composition can be preserved in fossil hard tissue for a very long time. The Sr-isotope method therefore can be applied in order to obtain information on the former habitat. A couple of studies and papers have pointed to the potential of this method for specific scientific questions (Refs).

Another interesting aspect is that the oceans have a very homogeneous and very slowly changing $^{87}\text{Sr}/^{86}\text{Sr}$ -ratio worldwide and which is well known from the Mesozoic to the present day. Since this Sr is incorporated by marine animals with their diet it allows, in principle, to recognize whether - and to estimate to what degree - a land inhabitant lived on marine food (Refs).

'Fossil rhino'

As an example, an investigation on bone and tooth material which has been carried out by our working group, is presented. The aim of the study was to identify the former habitat of a fossil rhino whose remains have been found in strata close to the jaw of *Homo erectus heidelbergensis* at Mauer in Germany. The rhino initially was erroneously identified as a stag - but this has no effect on the results. In addition comparable investigations have also been carried out on samples from the coeval hominid finding place at Boxgrove, Sussex, UK.

The intention was to demonstrate the principle of the method. Comparable studies on material from early Hominids are planned.

In our study we were faced with the very favourable situation that the excavation site is situated at the junction of regions with rather different

lithologies and Sr-isotopic ratios so that the potential habitats of then living animals showed rather different Sr isotope signatures.

In the sketch map (Fig. 3) the locality of Mauer is given together with major geological units and their mean $^{87}\text{Sr}/^{86}\text{Sr}$ -ratios.

As pointed out earlier, primary *in vivo* signatures may become falsified by mixture or exchange with Sr of different isotopic composition e.g. from the burial environment upon mineralisation. This holds true especially if the material which carries the isotopic signature is not very stable, as it is often the case with fossil hard tissues. A major problem therefore is the isolation of biologically meaningful Sr and the proof of its primary nature.

To overcome this problem we used a solubility profile technique that relies on the potential difference in solubility between diagenetic and biogenic hydroxyapatite, the main mineral constituent of bone. The idea is to separate these phases by stepwise washing in dilute acetic acid buffered with ammoniumchloride. In this way, it should be possible to obtain original material, if any remains. The crux, however, is the proof of originality of the dissolved material.

Some authors try to solve this problem by measuring elemental ratios (Ca/P, Ca/Sr) of the bone-apatite leachates. Values typical for biogenic apatites are interpreted as proof for the preservation of original *in vivo* conditions.

We do not agree with this view for various reasons: in our opinion the most reliable information lies in the Sr-isotopes themselves. Besides analyses of the fossil hard tissues (whole samples, leachates etc.), it is also important to map the isotopic background in the sediments at the finding place and the wider area. By this means the potential isotopic range of diagenetic Sr in the samples can be obtained and the primary character of the Sr-signal be judged.

In our study we carried out bulk analyses and a treatment of stepwise mechanical and chemical cleaning and etching of bone and tooth enamel which is less susceptible to diagenesis compared to bone.

In Figure 4 the resulting Sr-isotope ratios are plotted vs. cumulative Sr-release upon progressive leaching, resp. increasing stability of the Sr.

The rhino's bone, dentine and an easily leachable fraction from enamel show Sr-isotopic signatures within the range of the sands of Mauer

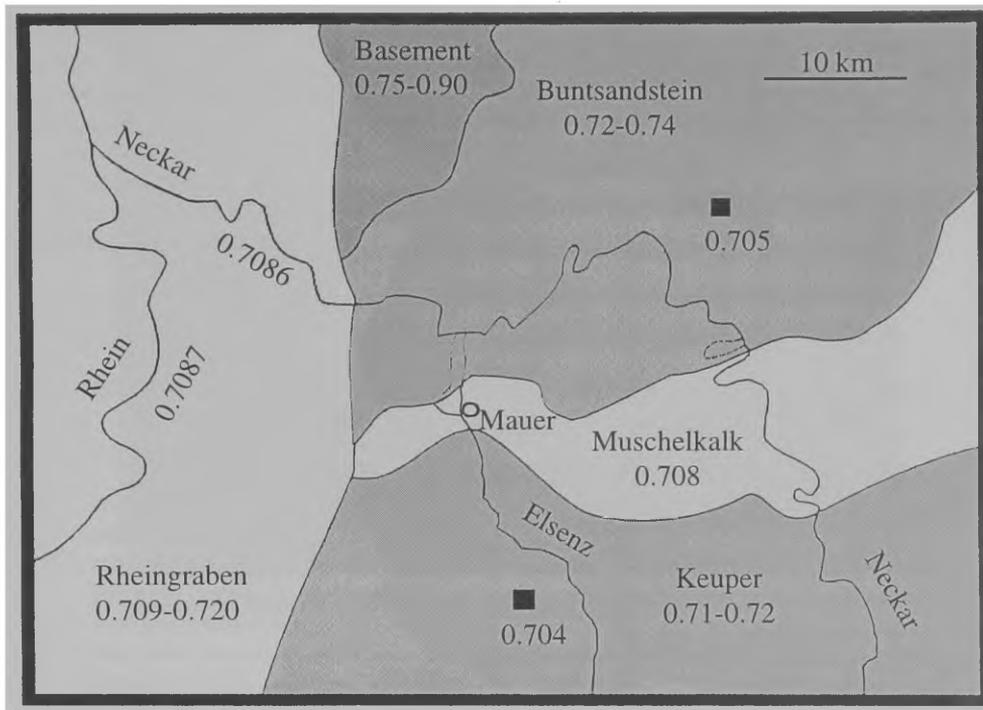


Fig. 3 — Geological sketch map showing locality of Mauer with major geological units and their predominant $^{87}\text{Sr}/^{86}\text{Sr}$.

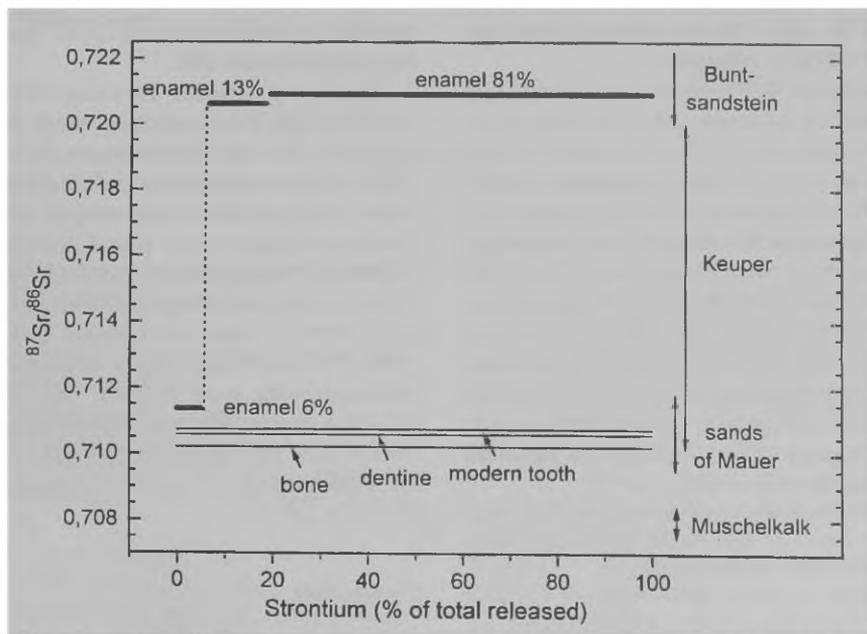


Fig. 4 — $^{87}\text{Sr}/^{86}\text{Sr}$ vs. percentage of strontium released upon differential etching or total dissolution of enamel and dentine from the rhino's tooth and bone compared to the reference material.

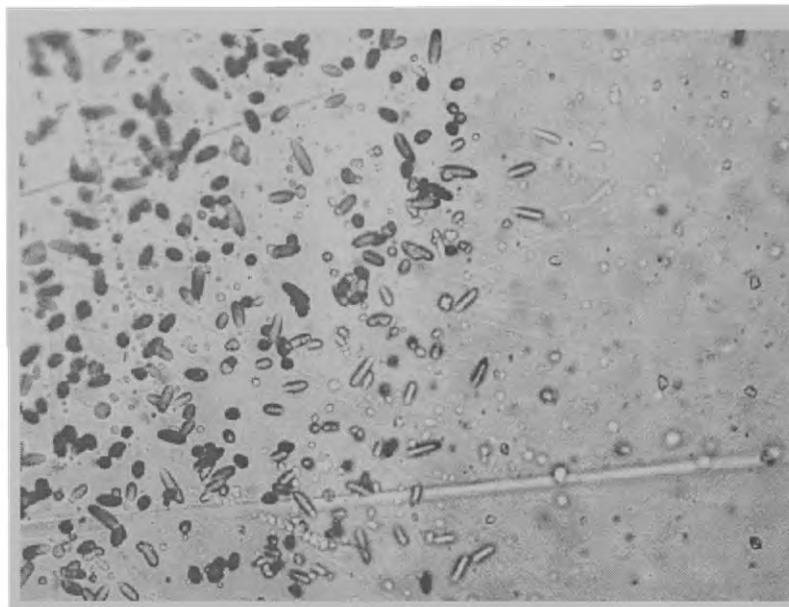


Fig. 5 — U-concentration distribution in dentine and enamel as revealed by neutron-induced ^{235}U fission.

(0.7094-0.7118), the stratum where the specimens were found. These initial steps represent the easily exchangeable phases that are most likely influenced by diagenetic Sr-exchange with the sediment. A comparable Sr ratio was found in a tooth of an inhabitant of the city of Mauer who cultivated most of his food on these sediments.

If the range in $^{87}\text{Sr}/^{86}\text{Sr}$ of the sands from Mauer is considered as reference, only 6% of the Sr in enamel are replaced by Sr from sediment. 13% of the enamel shows much higher isotope ratios and is only slightly contaminated by sedimentary Sr, while the larger fraction (81%) exhibits a (minimum) value for the primary (*in vivo*) isotopic ratio. This ratio, most far from the sedimentary one provides the best inherited isotopic signal. Of course this peak or plateau is not necessarily the true biological value, but at least approximates it. The $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.7208 must be attributed to Buntsandstein (Lower German Triassic) and excludes other potential habitats from the wider area.

In the sedimentary environment we find only much lower ratios, so that such high isotope ratios cannot be attributed to diagenesis.

In addition we tested the stability of the best domain against diagenetic effects independently by U-radiography and electron microprobe analyses, which give distributional information on critical elements. By these methods a closed system

behaviour is verified by the obvious existence of strong differences in the concentration of indicative elements between neighbouring domains.

In Figure 5 the U-concentration distribution in dentine and enamel in the fossil rhino's tooth is revealed by neutron-induced ^{235}U fission-tracks in a plastic detector foil.

The sharp contact between dentine with relatively high U concentration (many tracks, $56.6 \pm 0.9\text{ppm}$) and enamel (few tracks, $226 \pm 37\text{ppb}$) indicates that no significant U-diffusion took place between the dentine and the enamel, and implies, that the enamel was a closed system. Similar information was obtained from microprobe profiles (F, Na) over the dentine-enamel boundary (Th. Fehr, pers. comm.). Thus, the isotopic and chemical results of this study imply negligible cation exchange in the tooth enamel. The $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.7208 in the enamel shows that the rhino lived, at least its early years when its teeth were growing, in the Buntsandstein, at least 5 kilometers north of the finding place.

Conclusion

The heavy elements' isotope methods (Sr, Pb, Nd) can be a strong tool for provenance determination of any material.

Its application, as an addition to other methods, is suitable if other (cheaper) methods alone fail to give unambiguous results and if the following prerequisites are fulfilled:

- the possible areas of origin/habitat show different isotopic signatures
- there are indications that original signatures are preserved — at least in part.

In any case, several independent methods should be applied in order to make the results more reliable.

Acknowledgement

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RESUMO: Within the last decades chemical methods are gaining importance in archaeology. They are used for provenance determinations *sensu lato*: for clearing up origins of any materials (raw material, artefacts, animal and hominid remains...), trade relations, palaeo environmental questions, and trophic positions. Chemical elements, however, frequently tend to fractionate during burial and mineralisation according to their geochemical behaviour. Even isotope abundance ratios of light elements (C.N.O.) may show isotope effects which also lead to fractionation. In contrast to these, heavy element's isotope signatures (e.g. $^{87}\text{Sr}/^{86}\text{Sr}$, $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$, $^{143}\text{Nd}/^{144}\text{Nd}$) behave rather conservatively. Principles and applications of these isotopic systems will be presented and limitations will be discussed by referring to literature on the subject.

UNITERMOS: Archaeometry — Heavy elements' isotopes — Provenance determination

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