

Geochemical fingerprints: a critical appraisal

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Abstract: This review provides an overview of geochemical fingerprints currently used in the Earth sciences and discusses their strengths and weaknesses. Special emphasis is given to stable and radiogenic isotopes. Topics to be addressed include various fields of Earth sciences and range from basalts, different water types, biosignatures, bones to anthropogenic fingerprints.

Key-words: isotope geochemistry, trace elements, mantle reservoirs, water types, biosignatures, redox state, anthropogenic fingerprint.

1. Introduction

Fingerprints as defined in the Encyclopaedia Britannica

“...afford an infallible means of personal identification, because the ridge arrangement on every finger of every human being unique and does not alter with growth or age”.

Transferring this definition to the Earth sciences, a “geochemical fingerprint” is a chemical signal that provides information about the origin, the formation and/or the environment of a geological sample. The statement in the above definition “... does not alter with growth or age” is especially important for the Earth sciences. This means a mineral, rock or any other geological material once formed, has to keep its original composition, or in case of small changes during later geological history, must preserve its main geochemical characteristics to an extent that the original chemical signature is still recognizable.

The use of geochemical fingerprints has a long tradition in Earth sciences. Already Goldschmidt (1924) proposed the application of so-called “geochemische Leitelemente” for elucidating genetic relationships among different rock types. A necessary prerequisite for applying geochemical fingerprints is that suitable analytical methods exist which allow the detection of fingerprints. A successful use of geochemical fingerprints, therefore, is much related to the development of analytical techniques for their precise determination. With the introduction of new analytical tools or with improvements in analytical precision and detection limits of older technologies new fingerprints might continue to emerge.

Different kinds of geochemical fingerprints are in use:

- unusual element concentrations (*e.g.*, the Ir anomaly that is produced by large meteorite impacts on the Earth);
- a group of trace elements that form characteristic elemental patterns [*e.g.*, Rare Earth Elements

(REE), Platinum Group Elements (PGE) or normalized multi-element variations plotted in the order of silicate incompatibility/compatibility (so-called spidergrams)];

- characteristic organic molecules (*e.g.*, biomarkers), that denote a specific biosynthesis or a microbial origin;
- different classes of isotopes (*e.g.*, stable, radiogenic, cosmogenic, extinct).

To the class of *stable* isotopes belong most prominently the light elements H, Li, B, C, N, O and S. Typical *radiogenic* isotopes are the daughter products of radioactive elements having a long decay time such as ⁸⁷Sr, ¹⁴³Nd, ¹⁷⁶Hf, ¹⁸⁷Os and the lead isotopes ²⁰⁶Pb, ²⁰⁷Pb and ²⁰⁸Pb. *Cosmogenic* isotopes are products of the interaction of the ambient cosmic radiation that strikes the Earth with molecules in the atmosphere and to a lesser degree on the surface. The most widely used ones for geologic applications are the unstable isotopes ¹⁰Be, ¹⁴C, ²⁶Al and ³⁶Cl and the stable isotopes ³He and ²¹Ne. *Extinct* isotopes are short-lived, now-extinct radioactive isotopes, that only existed in the early solar system. Their existence is documented by anomalously high abundances of stable daughter nuclides. Typical examples are ²⁶Mg, ¹⁰⁷Ag, ¹²⁹Xe and ¹⁸²W.

Geochemical fingerprints are used for the identification of specific geological reservoirs on Earth, which includes the characterization of different environments (marine-freshwater; oxic-anoxic, mantle-crust *etc.*) that play a role in the origin of a rock of interest. In specific, geochemical fingerprints can be applied to:

- differentiate among different mantle reservoirs,
- characterize magmatic rocks from different geotectonic settings,
- distinguish different water types,

- describe changes in the redox state (oxic/anoxic),
- identify biosignatures,
- characterize the evolution of the atmosphere and the ocean,
- elucidate the provenance of clastic sediments,
- document processes that occurred during the very early history of the Earth,
- elucidate impact events,
- demonstrate anthropogenic imprints.

This list is by no means complete. The following sections will discuss examples and model systems to provide an overview of the broad range of geochemical fingerprints and their possible applications.

For all these different types of geochemical fingerprints, it is essential to consider their mobility during secondary processes. Rocks that have been subjected to hydrothermal alteration or metamorphism are likely to be affected by the mobility of elements. For a successful application, it is necessary to demonstrate that elemental or isotope concentrations are undisturbed and, therefore, represent primary features before any geochemical inference can be made. Trace element and isotope mobility is controlled by the mineralogical changes which take place during secondary alteration and by the nature of fluids present in an environment. For trace elements, as a generalization, alkali and earth alkaline elements are considered to be mobile, whereas the High-Field-Strength (HFS) elements are generally regarded as being immobile. This group includes the REE, Sc, Y, Th, Zr, Hf, Ti, Nb and Ta. Although this generalization is valid for most environments, exceptions have been documented. For a proper application as a fingerprint of the source material, it has to be worked out which trace element is indicative of which process. Therefore, great care is necessary, when using trace elements as geochemical fingerprints. On the other hand, isotope ratios are not affected by such secondary processes. The mass difference between any pair of isotopes is too small to be fractionated, except for the light elements where small secondary modifications are possible.

Geochemical fingerprints in the sense of characteristic chemical signatures are observed on all spatial and temporal scales: from very small scales (*e.g.*, chemical zoning within a single crystal at the micrometer scale) to the global scale (*i.e.*, large mantle reservoirs such as the DUPAL radiogenic isotope anomaly in the southern hemisphere; Dupré & Allègre, 1983) and from very short events, *e.g.* impact processes – to very slow longlasting events, *e.g.* the evolution of the atmosphere or the hydrosphere.

Ideally, a geochemical fingerprint is indicative of the origin of a particular sample, excluding any other origin. Examples of this type exist, but many geochemical fingerprints can be interpreted in more than one way and, in these cases, additional information from other sources is needed to support the proposed origin.

In summary, the use of geochemical fingerprints relies on several assumptions, which may or may not be fulfilled. In this review an attempt is made to provide an overview of the different geochemical fingerprints currently in use and

discuss their various strengths and weaknesses. The following case studies by no means represent a complete list, but reflect in a way the author's preferences.

2. Extraterrestrial materials

A major difference between terrestrial and extraterrestrial materials is the existence of primordial isotope heterogeneities in the early solar system. Such heterogeneities are not observed on Earth, because they have been obliterated during high temperature processes over geologic time. In primitive meteorites, however, components that acquired their isotopic compositions through interactions with the solar nebula have remained unchanged since that time. The first observation which clearly demonstrated isotopic inhomogeneities in the early solar system was made by Clayton *et al.* (1973). Previously, it has been thought that all physical and chemical processes must produce mass-dependent O-isotope fractionations yielding a straight line with a slope of 0.52 in a plot of $\delta^{17}\text{O}$ vs. $\delta^{18}\text{O}$. This line has been called the "terrestrial fractionation line". When Clayton *et al.* (1973) plotted $\delta^{17}\text{O}$ vs. $\delta^{18}\text{O}$ from minerals of primitive chondrites, their data did not fall on the terrestrial fractionation line, but instead on a line with a slope of 1 (Fig. 1). This relationship can only be explained by mass independent oxygen isotope fractionations indicating an environment that is dominated by an ^{16}O enriched dust component interacting with a ^{16}O depleted gas phase. Different nebular isotopic reservoirs must have existed, since there are distinct differences in bulk meteorite isotope composition. On this basis, Clayton & Mayeda (1978) were able to distinguish different meteorite classes and their different parent bodies. In

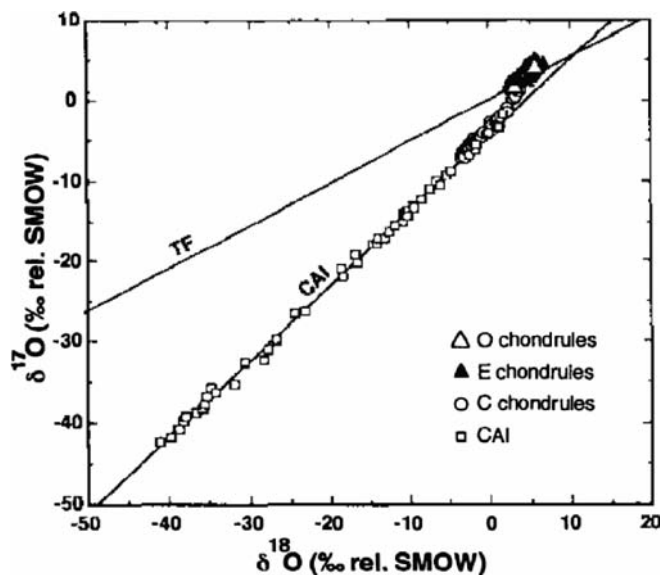


Fig. 1. $\delta^{17}\text{O}$ - vs. $\delta^{18}\text{O}$ -isotope compositions of Ca-Al-rich inclusions (CAI) from various chondrites (Clayton, 1993) (TF: terrestrial fractionation line).

summary, the finding of Clayton and coworkers represents a very prominent fingerprint that has changed the views on the solar system.

3. Mantle reservoirs

The major aim of investigating chemical and isotopic fingerprints in mantle derived rocks (basalt) is to elucidate the structure and evolution of the earth's interior. When a melt from the mantle is transported to the surface, its trace elements and radiogenic elements carry informations about their mantle source.

3.1. Trace elements

Basalts show distinct trace element trends that correlate with a particular tectonic setting, such as mid-ocean ridges, ocean islands, subduction zones *etc.* Pearce & Cann (1971, 1973) were the first using trace elements as geochemical fingerprints to discriminate among older igneous rocks that now occur as greenschist and amphibolites in deformed and metamorphosed terrains, where their source is not easily recognizable. Most commonly, geochemically immobile elements such as Zr, Hf, Ta, Th, Y, and Yb are prime candidates for such a discrimination. (see Fig. 2). The results of this approach, however, may be ambiguous, because trace element abundances not only depend on source composition, but also on several other factors namely the degree and mechanism of melting and melt extraction, the subsequent degree of magmatic fractionation and finally on possible contamination of the magma by crustal material. This altogether makes the application of trace elements as a fingerprint of mantle reservoirs a complex issue. Therefore, this type of approach has lost appeal based upon a closer examination of the reasons why different tectonic environments have variable geochemical signatures.

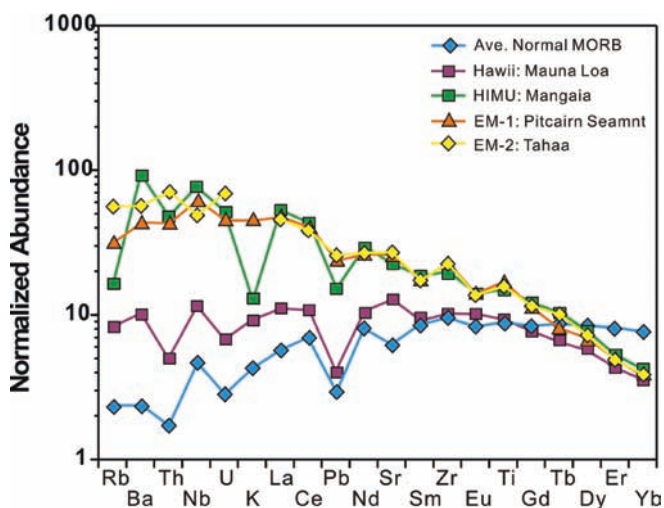


Fig. 2. Primitive-mantle normalized trace element abundance diagrams ("spidergrams") for different types of basalts (average tholeiite, MORB, EM-1, EM-2, HIMU) (after Hofmann, 2003).

Today it is preferred to use particular trace element patterns (spidergrams) or trace element ratios. Spidergrams are plots of the abundances of a set of elements normalized to their element abundances in some standard type material which may represent chondritic meteorites, primitive earth or normal MORB. Spidergrams are ordered in a manner that reflects their relative compatibility in mantle derived melts. What is important is the variation in the pattern of the relative abundances rather than the abundances themselves. Spidergrams have the advantage of representing a large number of trace element abundances of a given sample by a single line. However, they can be confusing because there are no standard rules about the specific sequence in which elements are shown or about the normalizing abundances used. Figure 1 gives examples of a few characteristic basalt samples from different geotectonic settings.

Trace element *ratios* of incompatible trace elements also can serve as tracers of mantle source chemistry. Trace element *ratios* of similarly incompatible pairs, such as Th/U, Nb/U, Nb/La or Sr/Nd can effectively discriminate between different mantle sources. Care should be taken to use ratios of elements with similar bulk partition coefficients during partial melting. Otherwise it may be difficult to separate source effects from melting effects. Some element ratios of mixed incompatibility, such as Zr/Nb or La/Sm which are almost fractionated at the relatively low melt fractions prevailing during mantle melting are less diagnostic of source differences than *e.g.* Th/U, Nb/U, Nb/Ba, Ba/Th, Sr/Nd or Pb/Nd.

3.2. Radiogenic isotopes

Partial melting in the mantle achieves isotope equilibrium between melt and solid residue. This means that the isotope ratio of the melt is identical to that of the source, what makes isotope ratios in mantle-derived volcanic rocks ideal fingerprints of mantle composition.

To explain the radiogenic isotope systematics observed in basalts of distinct mantle components have been proposed by various authors (*e.g.*, Zindler & Hart, 1986; Hofmann, 1997, 2003). These are the depleted MORB-source mantle (DMM), a component characterized by high Pb-isotope ratios and a subducted slab geochemical signature (HIMU), and two components characterized by different styles and possibly times of incompatible element enrichment (EM-I and EM-II) (see Fig. 3). Additional components have been advocated by some authors, but the evidence for them is not compelling. The spatial and compositional scales of mantle heterogeneities are a matter of debate and cannot easily be constrained by these magma compositions, since any melting event will tend to average out small-scale heterogeneities (Gurenko & Chaussidon, 1995).

3.3. Helium isotopes

The ratio $^3\text{He}/^4\text{He}$ is the ratio of a primordial cosmogenic isotope ^3He to a radiogenic isotope ^4He , being produced

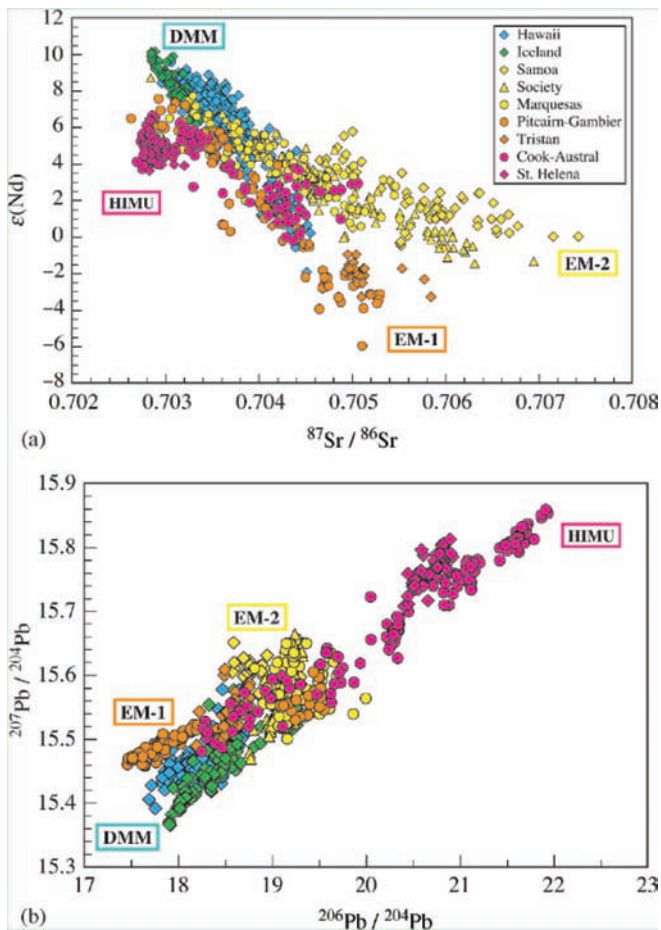


Fig. 3. (a) $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $\epsilon(\text{Nd})$ for ocean island basalts. The selected group of samples represent extreme isotopic compositions in isotope diagrams. They are the “type localities” for HIMU, EM-1, EM-2 and the Depleted Morb Mantle (DMM). (b) $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ for the same ocean island basalts as plotted in 2a (Hofmann, 2003).

by the radiogenic decay of U and Th. The $^3\text{He}/^4\text{He}$ ratio (R) is generally expressed as a multiple of the present day atmospheric ratio R_a . Typical values for R/R_a are <1 for continental rocks, 8 ± 2 for MORB and 5–42 for ocean island basalts (plume source). This difference in $^3\text{He}/^4\text{He}$ ratios between MORB and OIB basalts has led to a model of a depleted, degassed, and homogenized upper mantle and a lower undegassed mantle which contains much more ^3He than the upper mantle (*i.e.*, Farley & Neroda, 1998). $^3\text{He}/^4\text{He}$ ratios in mantle derived rocks have been regarded for many years as one of the best geochemical fingerprints because it has been considered to be the only unambiguous geochemical indicator of a lower mantle and plume component in surface volcanic rocks. Meibom *et al.* (2003) have pointed out that the statistical differences between MORB and OIBs are not as significant as previously thought. By compiling a global data set of $^3\text{He}/^4\text{He}$ ratios of OIBs Class & Goldstein (2005) argued that the differences between MORB and OIBs are due to inefficient degassing of mantle melts rather than due to the existence of a lower mantle plume

source, meaning that an undegassed, primordial mantle reservoir is not required.

4. Different water types

Stable isotopes (H and O) provide the best geochemical fingerprints available for discerning the origin of different water types that move through the exogenic and endogenic water cycle. To avoid confusion some definitions might be helpful.

Meteoric water applies to water that has been part of the meteorological cycle. All continental surface waters fall into this general category. Because meteoric water may seep into the underlying rock strata, it will also be found at various depths within the lithosphere. Although receiving continuously continental run-off of meteoric waters as well as rain – *ocean water* is not regarded as being meteoric in nature, but classified as a specific water type with a characteristic isotope composition. *Juvenile water* originates from degassing of the mantle and has never existed as surface water. The terms “juvenile water” and “magmatic water” have been used synonymously sometimes, but they do not refer to exactly the same thing. *Magmatic water* is a nongenetic term and simply means water that has equilibrated with a magma. It is difficult to prove that juvenile water has ever been sampled. One way to search for juvenile water is by analyzing hydroxyl-bearing minerals of mantle origin (Sheppard & Epstein, 1970). The estimated isotopic composition of juvenile water from such an approach is $\delta\text{D} = -60 \pm 20 \text{‰}$ and $\delta^{18}\text{O} = +6 \pm 1 \text{‰}$.

The principal water types include meteoric water, seawater and juvenile water – all of which have a strictly defined H- and O-isotope composition. All other types of fluids such as formation, metamorphic and magmatic waters, can be considered recycled derivatives or mixtures from one or more of the three reference waters (see Fig. 4).

Maybe the most fundamental contribution of stable isotope geochemistry to the Earth sciences is the observation of a near-linear relationship between δD and $\delta^{18}\text{O}$ values of meteoric waters, generally known as the “Meteoric Water Line (MWL)”. The MWL was first defined by Craig (1961) and represents the basis for the majority of paleoclimatic studies using stable isotopes. Furthermore it represents a characteristic fingerprint of waters of unknown origin in the subsurface. A long-standing geochemical problem is the source of water in hydrothermal systems, with special relevance to hydrothermal ore deposits. One of the principal and unequivocal conclusions drawn from stable isotope studies of fluids in volcanic hydrothermal systems is that most hot spring waters are meteoric waters derived from local precipitation (Craig *et al.*, 1956 and many others). Inasmuch as water is the dominant constituent of ore-forming fluids, knowledge of its origin is fundamental to any theory of ore genesis. Numerous studies of ore deposits have indicated that all water-types may become ore-generating fluids.

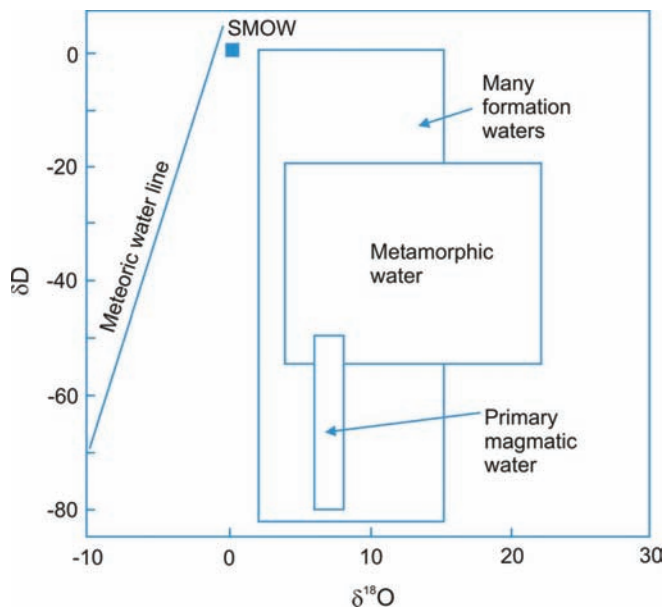


Fig. 4. Deuterium and oxygen isotope compositions of different water types (Hoefs, 2009).

A characteristic feature is that meteoric waters may become dominant in the latest stages of hydrothermal ore formation.

In addition, O- and H-isotopes are a powerful tool in the study of the origin of formation waters. Prior to the use of isotopes, it was generally assumed that most of the formation waters in marine sedimentary rocks were of marine origin. This view was challenged by Clayton *et al.* (1966), who demonstrated that waters from several sedimentary basins were predominantly of meteoric origin. In the view of subsequent studies (Connolly *et al.*, 1990; Stueber & Walter, 1991 and others) basin subsurface waters have very complicated histories and frequently are mixtures of meteoric waters and remnants of original marine pore waters. Very unusual isotopic compositions have been observed in highly saline deep waters from Precambrian crystalline rocks (*e.g.*, Frapè & Fritz, 1987). Their genesis is still unclear and cannot be resolved on the basis of H- and O-isotopes alone. Due to intense, long-lasting water/rock interactions, saline deep waters in crystalline rocks have lost their original signature or in other words their isotope compositions do not indicate any more their primary origin (Fig. 5).

5. The chemical composition of the ocean in the past

The growing concern with respect to “global change” brings with it the obvious need to document and understand the geologic history of sea water. The classic view about the chemical composition of the ocean in the geological past can be described by the principle that the sources are equal to the sinks or, in other words, that the input

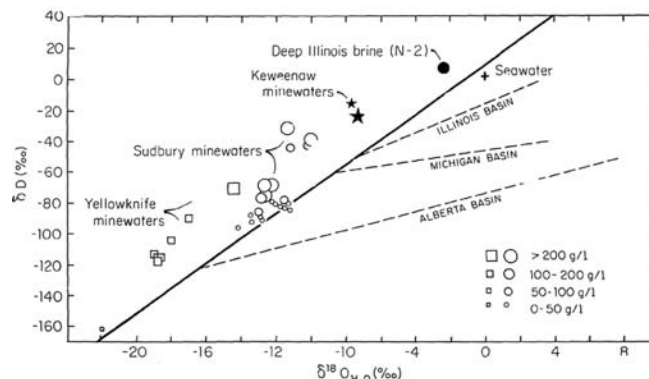


Fig. 5. δD - and $\delta^{18}O$ -values of meteoric and formation waters from North America in comparison to deep crystalline waters from the Canadian Shield (Frapè & Fritz, 1987). Characteristically, the deep very saline waters lie to the right of the Meteoric Water Line (MWL).

mainly through rivers and hydrothermal systems at ridges is balanced by the output, mainly through formation of sediments. This was the general view for many years. Recent studies of fluid inclusions in evaporate minerals, however, have indicated that the concentrations of major cations in ocean water such as Ca, Mg and SO_4 have changed significantly over the Phanerozoic (Horita *et al.*, 2002 and others). It is thus likely that the input fluxes to the oceans and the output fluxes are not always dictated by the residence of ions in the ocean.

In this connection it is important to know which kind of geological samples gives relevant information about the chemical composition of ocean water in the geological past. Only those geological materials are suitable which have not been altered since their time of formation. Samples recording the composition of ancient seawater are chemical precipitates, specifically carbonate secreting organisms – such as foraminifera and brachiopods – and iron and manganese oxides in the form of crusts and nodules. A detailed investigation about possible diagenetic changes has to be carried out before any conclusion about the primary composition can be drawn.

The most sensitive tracers recording the composition of ancient sea water is the isotope composition of chemical sediments precipitated from sea water. The following discussion concentrates on the stable isotope composition of O, C, S and B (Hoefs, 2009) and on the radiogenic isotopes Sr, Os and Nd (Banner, 2004).

5.1. Stable isotopes

Oxygen and carbon isotopes are generally measured in well-preserved fossils precipitated from seawater, such as foraminifera and brachiopods. The $^{18}O/^{16}O$ ratio of fossil shells depends on their temperature of formation and the O-isotope composition of ambient water. If one of these factors is known, the other can be calculated. Thus, oxygen

is the classic fingerprint of past temperatures. Carbon isotope variations in marine carbonates are mainly controlled by biological processes. Production of phytoplankton in the water column removes ^{12}C resulting in an ^{13}C enrichment of the residual dissolved inorganic carbon, whereas the oxidation of organic matter releases ^{12}C -enriched carbon back into the inorganic reservoir. Thus carbon isotope variations record shifts in the amount of carbon being buried (Hayes *et al.*, 1999). Extreme C-isotope variations at the end of the Proterozoic have been interpreted as a collapse of biological productivity due to global glaciations (“snow ball earth”) (Hoffmann *et al.*, 1998). Because of a relationship in C-isotope fractionation between carbonate carbon and organic carbon, a parallel shift in both reservoirs should be observed. Variations in the fractionations between the two reservoirs can, in principle, be interpreted as reflecting variations in the CO_2 -content of the atmosphere (Kump & Arthur, 1999).

As is well established, evaporite sulfate closely reflects the sulfur isotope composition of marine sulfate. By analyzing evaporites Nielsen & Rieke (1964) and Thode & Monster (1964) published S-isotope “age curves”. These curves vary from a maximum of $\delta^{34}\text{S}$ of +30 ‰ in early Paleozoic time to a minimum of +10 ‰ in Permian time. High δ -values reflect an increase of bacterial sulfate reduction in shallow basins leading to ^{34}S depleted sulfides and ^{34}S enriched remaining sulfates, whereas low δ -values favour an increase in weathering rates transporting light sulfates from oxidation of sulfides during weathering.

Since evaporates through geologic time contain large gaps and are easy to dissolve, alternative approaches for the reconstruction of sea water $\delta^{34}\text{S}$ values have been the analysis of (i) structurally substituted sulfate in marine carbonates (Kampschulte & Strauss, 2004) and the analysis of marine barites which has advantages because of its resistance to diagenesis (Paytan *et al.*, 2004). Both approaches yield similar curves but with a better age resolution.

Boron isotope in marine carbonates represent a special case, because B-isotope ratios are determined by a large pH-dependent fractionation between boric acid (BO_3H_3) and borate anion (BO_4H_4^-). The pH dependence of B-isotope fractionation offers the possibility of reconstructing past ocean pH-values (Pearson & Palmer, 1999, 2000).

5.2. Radiogenic isotopes

As has been already mentioned, concentrations and isotopic compositions of elements in ocean water are balanced by their annual input and output. The resulting residence times determine the extent of homogenization of elements on a time scale of about 1000 years, the mean residence time of one water molecule in the ocean. Sr and Os with long residence times have therefore a constant isotope composition, whereas Nd, Pb and Hf with short residence times have a regionally variable isotope composition. This makes the latter elements useful tracers for the circulation

pattern of the ocean and for the source identification on the continents and within ocean basins.

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of seawater can be explained by mixing of Sr derived from three different sources (i) young volcanic rocks, (ii) old continental crust and (iii) marine carbonates. The Sr-isotope composition of seawater is, therefore, an indicator of the kinds of rocks that are exposed to chemical weathering on the surfaces of the continents and in the ocean basins at any given geologic time. Since the first investigations by Peterman *et al.* (1970) and Veizer & Compston (1974), many more studies have confirmed systematic Sr-isotope variations of seawater with geologic age (Burke *et al.*, 1982; Veizer *et al.*, 1999 and many others). The time-dependent variations have been successfully used to date marine sediments (“Sr-isotope stratigraphy”, McArthur *et al.*, 2001).

Like Sr, the Os isotopic composition of seawater has changed over geologic time (Peucker-Ehrenbrink *et al.*, 1995). Large fractionation of Re from Os make $^{187}\text{Os}/^{186}\text{Os}$ isotope variations a sensitive tracer of the contribution of crustal ($^{187}\text{Os}/^{186}\text{Os} = 10\text{--}30$) vs. mantle ($^{187}\text{Os}/^{186}\text{Os}$ around 1) sources to the oceans. Os isotope variations in ancient seawater provide therefore an independent parameter with respect to continental vs. mantle fluxes to the ocean. Given the similarities between Re-Os and Rb-Sr isotope systems, one may expect a similar oceanic record for Sr and Os. And indeed, in general, $^{187}\text{Os}/^{188}\text{Os}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ co-vary during Tertiary time, although significant differences exist in detail and during other times that indicate changes in the types of material that provide Sr and Os to the oceans.

The $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of ocean water is a clear tracer of ocean water masses and ocean currents (Piepgras *et al.*, 1979; Piepgras & Wasserburg, 1980). The mean residence time of Sm and Nd in the ocean is only about 300 years, being much shorter than the average mixing time of the ocean, which explains why Nd is not isotopically homogeneous in the various oceanic basins. The $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of seawater varies significantly among the major ocean basins, because the ratio is mainly controlled by inputs from the continents. Because rocks surrounding the Atlantic are generally much older than rocks surrounding the Pacific, the Atlantic has lower Nd-isotope ratios than the Pacific. This, for instance, has been demonstrated by Piepgras & Wasserburg (1982) analyzing water in the Drake Passage at the southern tip of South America. They showed that the water represents dominantly North Atlantic Deep Water which flows around Antarctica from the Pacific side through the Drake Passage. The use of Nd isotopes as a tracer of ocean currents is now in broad use and can be also applied to paleoceanographic studies.

In conclusion, geochemical fingerprints in chemical sediments precipitated from ocean water deduced from radiogenic and stable isotopes reflect very different parameters such as tectonic processes, including weathering and erosion, climatic parameters such as temperature, and atmospheric CO_2 concentrations, pH-value, circulation

patterns *etc.* Their application has great potential, but generally has to be combined with other geochemical data.

6. Provenance studies

A classic application of geochemical fingerprints has been in provenance studies. The term provenance, when applied to detrital minerals refers to the source rocks from which detrital minerals were derived. All clastic sedimentary rocks contain mineral or rock fragments that were derived by weathering and erosion of older rocks. The minerals that survive this process because they resist chemical and mechanical weathering may contain a fingerprint that can characterize the source area and may constrain the tectonic setting. Because secondary effects such as diagenesis and metamorphism might change the original composition of the source rock, a combination of analytical methods is required to have confidence in the provenance indicators.

Determining the source of detrital minerals in sedimentary rocks has undergone tremendous progress in the last years. Advances in SIMS and LA-ICP-MS methods has led to a large increase of studies. Zircon has received the most attention in this respect, because of its resistance against secondary changes and because of its provision of age and source area characteristics (Parrish & Hodges, 1996; Goodge *et al.*, 2002 and others). The age information is used to constrain the maximum depositional age of sedimentary processes. Monazite has similar properties like zircon and thus is another mineral very suitable for provenance studies (*i.e.*, Yang *et al.*, 2006).

Another important provenance fingerprint is provided by the Sm-Nd isotope system that is largely unfractionated by clastic sedimentary processes so that the measured Nd-isotope composition represents an integrated average of the isotopic composition and crust formation age of the source area. The strength of Nd isotopes as a provenance indicator for siliclastic sedimentary rocks lies in the low diagenetic mobility of the REE and in the distinct Sm-Nd characteristics of different crustal source terranes. This approach was pioneered by Miller & O'Nions (1984) who measured model ages of Precambrian and Paleozoic sedimentary rocks of the British Isles. The older sediments generally appear to be derived from source terranes that are Archean in age, whereas the younger sediments appear to be derived from Proterozoic source rocks. This difference was not identifiable by any other method of provenance determination, because the different source terranes are composed of similar rock types. On the North American continent siliclastic Nd isotope variations reveal changes through time of continental shield, Caledonian-Appalachian and Cordilleran source regions (Patchett *et al.*, 1999).

In summary, patterns of ages and trace element geochemistry provide a multifaceted fingerprint of provenance evolution. Such a combined analytical approach

has great potential for ancient sequences that lack unambiguous petrographic provenance indicators and where multiple source terranes have contributed sediment to the basin of interest.

7. Redox states

The surface of the Earth represents a boundary zone between oxidizing and reducing conditions. While the atmosphere is highly oxidizing, reducing conditions exist in the Earth's interior. Natural waters represent the interface between these two redox states. Redox proxies in the ocean, for instance, can help to pinpoint when redox conditions change for reducing to oxidizing or vice versa. Elements which govern the redox state of natural waters are O, C, N, S, Fe and Mn. Other elements have also variable redox states, but because of their low concentrations trace elements do not control the redox state of a system, but reflect it.

One prominent example is cerium. A relative deficiency of Ce relative to its neighbouring REE is one of the most characteristic features of modern seawater.

Uniquely among the rare earth elements, Ce has two possible oxidation states, Ce³⁺ and Ce⁴⁺. Ce³⁺ has a solution chemistry similar to its trivalent neighbors La and Sm, while its oxidation to Ce⁴⁺ results in the formation of a less soluble form, which is readily removed from the water column either on particle surface coatings or into authigenic minerals. The anomalous behaviour of Ce compared to its neighboring REEs (the Ce anomaly) is quantified by the ratio of the measured abundances of Ce to an expected value Ce* interpolated from the neighboring trivalent:

$$\frac{\text{Ce}}{\text{Ce}^*} = \frac{3(\text{Ce}/\text{Ce}_{\text{shale}})}{2(\text{La}/\text{La}_{\text{shale}})} + 2 \frac{\text{Nd}}{\text{Nd}_{\text{shale}}}$$

A Ce anomaly with a value of 1 means that Ce behaves like a trivalent REE when normalized to shale. Negative anomalies with values less than 1 indicate preferential removal of Ce⁴⁺ and thus oxic conditions. Ocean water exhibits a prominent negative Ce anomaly, which occurs in response to the oxidation of Ce³⁺ to Ce⁴⁺ and the precipitation of Ce⁴⁺ as CeO₂. In anoxic basins, Ce⁴⁺ is reduced to Ce³⁺ and the Ce-anomaly tends to be smaller than is observed in oxygenated waters. The Black Sea, the world's largest stable anoxic basin, provides a good example in which the Ce anomaly changes drastically from 0.1 at the oxic/anoxic boundary to 1.0 (no anomaly) in reducing waters below 200 m (*e.g.*, German *et al.*, 1991).

The Ce anomaly has been proposed as a tracer for large scale anoxia in ancient oceans (Liu *et al.*, 1988; German & Elderfield, 1990). However, the preservation of the seawater redox signal in carbonate and phosphate material is a complex topic, which as summarized by German

& Elderfield (1990) relies on several factors. Unlike the reduction of Ce (IV) to soluble Ce (III), oxidative removal of dissolved Ce (III) occurs at a rate which is slow relative to the mixing time of the ocean. Consequently, the Ce anomaly recorded in a particular sample does not reflect ambient redox condition, but represents an integrated signal related to the redox history of a particular water mass.

8. Biomarkers and biosignatures

Organic matter in the geosphere is a complex mixture of living organisms and detrital remains. This complexity results from the multitude of source organisms, variable biosynthetic pathways and transformations that occur during diagenesis. With respect to specific organic fingerprints a distinction between biomarkers and biosignatures is made.

Biomarkers are organic compounds detected in the geosphere whose basic carbon skeletons suggest an unambiguous link with a known contemporary natural product. They thus provide a link between biological sources of organic matter and organic compounds preserved in sediments. Treibs (1934) demonstration that oils contain porphyrins derived from the tetrapyrrole ring system of chlorophyll pigments was the first application of specific molecules as indicators of biological materials. Today, with more sophisticated analytical techniques many more biomarkers have been introduced that relate particular organic compounds to specific organisms. Biomarkers are, nevertheless, sensitive to diagenetic effects. Often, only a minor structural alteration is sufficient to confuse an initially straightforward biomarker-source relationship.

Biosignatures are commonly reflected in characteristic C-, S-, and N-isotope compositions that provide clues to past or extant biological activity. The idea of using C-isotope compositions in this way dates back to the classic paper of Craig (1953). Already, at that time, there was a discussion in the literature about whether the origin of graphitic carbon in old rocks could be identified as being of biogenic origin (Craig, 1954; Rankama, 1954). This controversy about the evaluation of the meaning of graphite $\delta^{13}\text{C}$ -values from early Archean (3.5–3.8 Ga) rocks has continued till today (e.g., Bolhar *et al.*, 2004). The validity of using carbon isotopes in the search for early life hinges on the assumption that early organic metabolism produced a C-isotope fractionation effect similar to that observed today.

What has to be considered in this connection is the thermal history of these very old metasediments. In early Archean metasedimentary rocks from Greenland, $\delta^{13}\text{C}$ -values range from -22 to -50 ‰ (Mojzsis *et al.*, 1996) that were measured for tiny particles of reduced carbon within apatite grains, which apparently had been shielded from metamorphic alteration. However, a case

also can be made that graphite from Archean rocks may be of abiotic, hydrothermal origin. Early experiments by Lancet & Anders (1970) on organic matter synthesized by a Fischer–Tropsch type reaction resulted in depleted $\delta^{13}\text{C}$ -values as well as recent experiments by Horita & Berndt (1999), Taran *et al.* (2007) and others resulted in abiogenic methane with $\delta^{13}\text{C}$ -values as low as those typically for biogenic methane.

Besides C, S-isotopes have also been used as biosignatures. Large ^{34}S -isotope fractionations are induced during the sulfate reduction process due to the action of sulfate reducing bacteria. This may lead to very ^{34}S -depleted H_2S as observed today in the Black Sea and to very depleted sedimentary pyrite. Concomitant with this process is the production of ^{34}S -enriched residual sulfate. Another characteristic feature of sulfate reduction is significant small-scale spatial variability in S-isotope composition of pyrite. Up to 105 ‰ variations in $^{34}\text{S}/^{32}\text{S}$ ratios within 200 μm was observed in sedimentary pyrites by McKibben & Riciputi (1998). According to these authors, strongly zoned pyrite nodules with ^{34}S -contents increasing from center to edge are a characteristic feature of bacterial sulfate reduction. This zonation arises from progressive precipitation of sulfide from pore water sulfate enriched in ^{34}S providing more ^{34}S enriched sulfide.

Sedimentary pyrite depleted in ^{34}S by more than 20 ‰ has been observed as far back in geological time as the Precambrian and is generally taken as evidence for the activity of sulfate reducing bacteria. There is ongoing debate about the first onset of bacterial reduction in the geological record: Ohmoto *et al.* (1993), Shen *et al.* (2001) and Shen & Buick (2004) argue for a beginning at around 3.3 and 3.4 Ga. Shen *et al.* (2001) observed sulfides with maximum sulfur isotope fractionations of 21 ‰. Nevertheless, the question is still open whether inorganic processes might also produce fractionations in this range. Recent analytical progress in measuring all four stable isotopes ^{32}S , ^{33}S , ^{34}S and ^{36}S , additional evidence can be gained to decouple hydrothermal vs. biological processes (Ono *et al.*, 2006) even when $\delta^{34}\text{S}$ -values are inconclusive. Using this approach Ueno *et al.* (2008) argued that quadruple sulphur isotopes in barite and pyrite from the 3.5 Ga old Dresser Formation, Australia indicate the existence of microbial sulfate reduction at 3.5 Ga ago.

Another isotope system which has been discussed in the recent literature are Fe isotopes. Virtually all reduction from Fe^{3+} to Fe^{2+} at the Earth's surface is mediated by the metabolism of dissimilatory bacteria. Biological processes therefore may produce measurable Fe-isotopic fractionations because the metabolic processing of Fe involves a number of steps such as transport across membranes that may fractionate Fe isotopes. Experiments with dissimilatory Fe-reducing bacteria of the genus *Shewanella* indicate that iron isotope fractionations are a function of Fe(III) reduction rates: at low rates the produced Fe^{2+} is isotopically depleted by 1.3 ‰, whereas the depletion is up to 3 ‰ at high rates (Johnson *et al.*, 2008).

Iron isotope fractionation has been also observed during bacterial Fe oxidation (Croal *et al.*, 2004). Fe(II) oxidizing

phototrophs may produce under anaerobic conditions a ferrihydrite precipitate that is 1.5 ‰ higher than the aqueous Fe(II) source. Controversy still exists whether the iron isotope variations observed in microbial experiments are primarily controlled by kinetic or non-biological equilibrium factors. Since abiotic iron reduction/oxidation reactions may reveal fractionations similar in direction and magnitude to microbial reactions (Johnson *et al.*, 2002; Skulan *et al.*, 2002), the presence of Fe isotope variations is not in itself conclusive evidence of biotic activity. This complicates the ability to use iron isotopes to identify microbiological processing in the rock record (Balci *et al.*, 2006).

Of special significance in this connection are biosignatures on Mars, because McKay *et al.* (1996) have claimed that Martian meteorite ALH 84001 – found in Antarctica – contains evidence of past Martian life. Various kinds of apparent biosignatures with characteristic isotope compositions have been suggested: organic matter, carbonate minerals, magnetite grains, sulfide minerals. After intensive investigations during the last years, none of these proposed biosignatures have survived as such.

9. Bones and teeth

Geochemists use trace element and isotope signals in fossil bones and teeth to infer the environmental conditions under which animals and humans lived. Bones and teeth are synthesized within the body and the chemical composition of these materials is determined by a combination of environmental parameters and of biological processes. Trace elements and isotopes are incorporated into bone and teeth from both diet and environmental water. In marine animals, the most important source of trace elements is seawater, whereas food sources are more important than drinking water in terrestrial animals. Bone is continually resorbed and re-deposited throughout life, so its trace element composition is an integrated record of trace element exposure. By contrast, teeth, precipitate progressively and are chemically invariant after formation.

Bones are relatively porous materials, which are composed of tiny calcium phosphate crystals intermixed with about 30 % (dry weight) organic matter. Teeth are essentially non-porous and composed of relatively large calcium phosphate crystals that includes only minor amounts (<2 %) of organic matter. These structural differences lead to differences in the susceptibility of bone and teeth to post-mortem alteration. The mineral in bone and teeth is a form of hydroxylapatite $\text{Ca}_{10}(\text{PO}_4, \text{CO}_3)_6(\text{OH})_2$. Apatite is capable of admitting a wide range of cations and anions into the lattice. To use bone and teeth apatite as a geochemical fingerprint, an understanding of the processes occurring during the fossilisation (diagenesis) of bones and teeth is essential. As shown by Kohn *et al.* (1999) and Tütken (2003) the diagenesis of bone is a multistage process which depends both on internal structural and chemical parameters and on external factors of the diagenetic

setting. Geologic age seems to be of minor importance, as most chemical changes take place within a thousand to hundred thousand years during early diagenesis (Tütken, 2003).

During decay of the organic collagen matrix a chemical exchange with the environment takes place due to the loss of collagen and the diagenetic recrystallisation of the microcrystalline bone apatite to carbonate-fluorapatite. A number of elements may become enriched in the diagenetically altered biogenic phosphate. For example, F, Fe, U and REE are sensitive tracers of diagenesis as these elements are enriched by several orders of magnitude in fossil bones.

The scientific scope of stable isotope studies on bones and teeth is very broad. They focus on the best preserved tissues, which are biological apatites – bone, dentin, and enamel. Carbon isotopes closely reflect diet and can be used in a variety of paleoecological studies (the distinction between C₃ and C₄ plants). Histograms of $\delta^{13}\text{C}$ -values of C₃ and C₄ plants and the CO₃ component of mammal tooth enamel clearly indicate that the isotope difference between different classes of plants are passed onto herbivores (see Fig. 6).

Oxygen isotope ratios in bioapatites depend on the isotopic composition of local water, climate (humidity), and diet. In some studies, these dependencies have been clearly demonstrated and climatic signals have been delineated (*e.g.*, Fricke *et al.*, 1998). Nevertheless our knowledge on the factors that determine the oxygen isotope composition

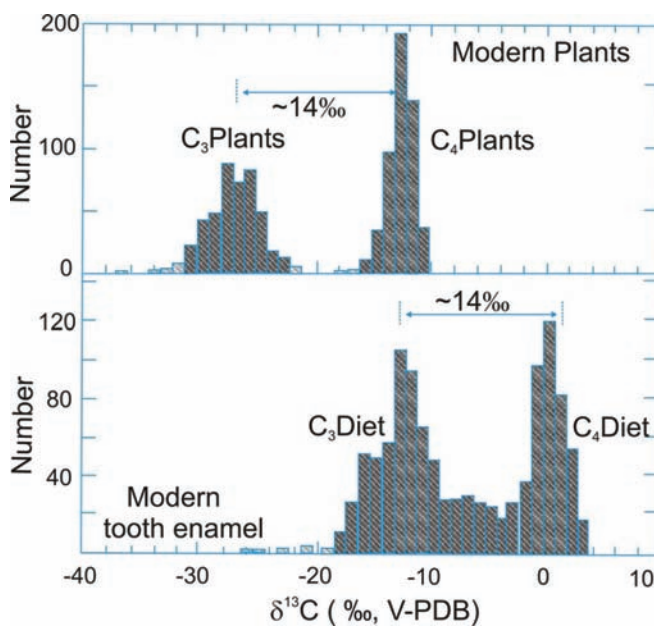


Fig. 6. $\delta^{13}\text{C}$ -values of C₃ and C₄ plants (upper half) and the CO₃ component of mammal tooth enamel (lower half). The isotope difference between C₃ and C₄ plants is passed onto mammals with an ^{13}C enrichment of 14 ‰ that mainly reflects the isotope fractionation between the bulk $\delta^{13}\text{C}$ of an animal and the $\delta^{13}\text{C}$ of the carbonate component in tooth enamel. Isotope compositions of teeth that fall between C₃ and C₄ endmembers reflect mixed feeding (Kohn & Cerling, 2002).

of biopatites is rather rudimentary, which restricts work to comparison of one taxon through time to eliminate physiological effects (Kohn & Cerling, 2002).

10. Anthropogenic fingerprints

An extreme diversity of geochemical fingerprints are present in the geosphere due to human activities. Some of the most widespread anthropogenic pollutants are:

- chlorinated hydrocarbons
- heavy metals and
- artificial radionuclides.

For all three classes of anthropogenic pollutants isotopes are of special importance. The anthropogenic production, release and dispersal of *organochlorine compounds* into natural settings is a matter of worldwide concern, because these compounds tend to persist in the environment and remain available for bioaccumulation in organisms. On the other hand, natural attenuation processes (biodegradation, dispersion, sorption, volatilization) are at work to reduce the concentrations of these contaminants. The use of C and Cl isotopes as tracers of pollution requires the isotope ratios of the polluting product to be significantly different from the natural isotopic abundance. Jendrzewski *et al.* (2001) demonstrated on a set of chlorinated hydrocarbons from various manufacturers that isotopes of both carbon and chlorine had a large compositional range. The range of chlorine is especially significant because it is much larger than that of inorganic Cl and distinctly different from Cl-isotope ratios for inorganic compounds.

A promising means for mitigating contamination is *in situ* bioremediation, in which microbes convert chlorinated hydrocarbons to benign products such as CO₂, chloride and biomass. Substantial carbon and chlorine isotope fractionations during biodegradation may preclude, however, the easy application of such isotope ratios as a tracer of pollution. The extent of degradation is generally calculated from an enrichment of heavy isotopes in the remaining compounds using the Rayleigh equation. Therefore, a precise knowledge of the isotope fractionation processes accompanying transport and biodegradation of organic contaminants is needed to assess the contamination history.

Amongst the *heavy metals*, which have been emitted to the atmosphere by human activities Pb, Hg, Cd, Zn and the PGE group are the most important. Nriagu (1979) presented the first global inventory of anthropogenic emissions of Cd, Cu, Ni, Pb and Zn to the atmosphere for the year 1975. Nriagu & Pacyna (1988) provided an update of the earlier data and extended it to other trace elements. Several archives have been used to analyze anthropogenic pollution: among the most important are ice cores from Greenland and Antarctica (Candelone *et al.*, 1995).

The best example of an anthropogenic fingerprint is lead. Patterson (1965) first drew public attention of increased lead levels in the environment. Ice cores from Greenland indicated that the amount of lead today is much

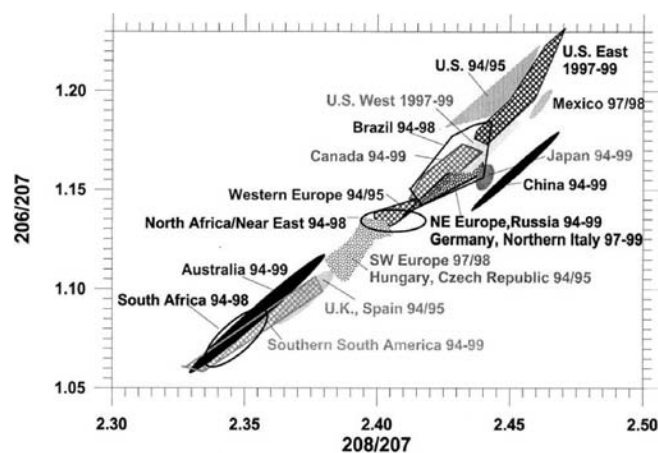


Fig. 7. Global Pb isotope compositions of airborne particles between 1994 and 1999, reflecting the isotopic differences of Pb ores used in the production of alkyllead gasoline (Bollhöfer & Rosman, 2001).

higher than in pre-industrial time. Alkyllead, used as an antiknock agent in combustion engines, was the largest source of atmospheric lead pollution up to 1970s, when action was taken to reduce the ambient air Pb levels. The isotopic composition of alkyllead, and consequently that of lead compounds emitted from burning of leaded gasoline, reflects the composition of the Pb ore used in its production. Provided isotopic compositions of the lead contaminants are known, lead isotopes are a suitable tool to characterize sources and pathways of atmospheric pollution over long distances (Bollhöfer & Rosman, 2000, 2001). By analyzing aerosols from the northern and southern hemisphere these authors found characteristic geographical variations in the Pb isotope composition (Fig. 7).

Artificial radionuclides in the environment result from the atmospheric testing of nuclear weapons and the 1986 Chernobyl nuclear reactor accident. The Chernobyl nuclear reactor accident in the Soviet Union on April 26, 1986 provided a point source and a time marker of massive release of radioactivity into the lower atmosphere which subsequently accumulated on the European landscape. Radionuclides which are most abundant and/or display the greatest activity are ¹³⁴Cs, ¹³⁷Cs, ⁹⁰Sr, ¹⁰³Ru, ¹⁰⁶Ru, ¹⁴¹Ce, ¹⁴⁴Ce, ¹²⁹I, ¹³¹I and ²³⁸Pu, ²³⁹Pu, ²⁴⁰Pu. Despite the most unfortunate consequences of this event, the pulsed input of a suite of short- and long-lived radioisotopes into various ecosystems has offered a unique opportunity to measure time scales of physical, geochemical and biological processes (Santschi *et al.*, 1988, 1990).

11. Concluding remarks

The concept of geochemical fingerprints has a long tradition in Earth sciences. It can be regarded as one of the cornerstones of geochemical research. The purpose of this

review has been to demonstrate how geochemical fingerprints can be used to identify geological processes. Numerous geochemical fingerprints have been proposed, out of which characteristic examples have been presented.

The application of geochemical fingerprints crucially depends on the development of adequate analytical techniques. Further advances of the existing methods and the introduction of new techniques will undoubtedly strengthen the existing fingerprints or will establish new fingerprints. Nevertheless, what is sometimes neglected is the fact that geochemical fingerprints in most cases are not self-evident, but ambiguous and need to be supported by further geological and/or petrological evidence. In this respect, great care is necessary when applying geochemical fingerprints.

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