Strontium isotopic signatures of natural mineral waters, the reference to a simple geological map and its potential for authentication of food

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ABSTRACT

This paper presents the investigation of strontium isotope ratios of about 650 different European natural mineral waters as part of the food traceability project "TRACE" funded by the EU. Analysed $^{87}Sr/^{86}Sr$ values in the natural mineral waters range from 0.7035 to 0.7777, which indicates an influence by a great diversity of rocks from young mantle derived basaltic rocks to very old silicic continental crust.

The results of the large scale investigation are used to elaborate a novel spatial prediction for strontium isotope ratios by combining the measured data with a GIS based geological map of Europe.

The resulting map can be used to predict the strontium isotopic composition of groundwater and thus the composition of bio-available strontium, which is available for uptake by plants and subsequently transferred into the food chain. We also show, as an example, that the strontium isotopic composition of honey and wheat from specific sample regions within the TRACE project correlates well with that of the natural mineral water as predicted by our map.

The proof of principle shown in our paper is highly relevant for geographical food authentication as it allows an assessment of the origin of food products without the immediate need for geographically authenticated materials which may not always be available. Our approach provides a cost effective first instance screening tool.

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1. Introduction

To sustain in the globalisation of markets and thus increasing competition many producers have chosen a marketing strategy, which emphasises the uniqueness and/or added quality of their product. In the case of natural mineral waters, the location of a spring in a specific geological environment is often claimed to lend special qualities to the water. Furthermore, the promotion for natural mineral waters sometimes just takes advantage of the natural beauty of certain production regions and associates this with the purity of water. In some cases the natural mineral waters of certain locations with long history are perceived to have beneficial properties.

As soon as it is possible to gain a market advantage by using geographical linked characteristics, there will be an incentive to use possibly cheaper sources and thus it becomes necessary to verify authenticity claims with analytical methods, both in the interest of the consumer and the authentic producer in the case of counterfeit products. Additionally, there is the legal regulation for natural mineral waters to be bottled at source within the EU (Directive 80/777/EEC, Directive 96/70/EG, Commission Directive 2003/40/EC, Council Regulation (EC) No. 692/2003). Therefore, an analytical method for verifying authenticity is an essential requirement to control the product origin claims. For analytical authenticity control and origin assignment of a food commodity, isotope methods combined with traditional chemical analyses have proven their usefulness (e.g. Kelly et al., 2002; Pillonel, Buetikofer, Rossmann, Tabacchi, & Bosset, 2004).

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As part of the EU-funded TRACE project which aims to develop and apply analytical methods for the proof of geographical origin of food the usefulness of strontium isotope ratio investigations was evaluated.

Originally, the use of strontium isotope ratios was restricted to geosciences. However, since Chaudhuri (1978) published a study about the application of $^{87}Sr/^{86}Sr$ to investigate the origin of groundwater, the method has also been widely used in hydrology, although mostly for deep subsurface waters of higher temperature and/or salinity (Chaudhuri & Clauer, 1992; Hofmann & Baumann, 1986; Matter, Peters, & Ramseyer, 1987; Pampura, Plyusnin, & Sandimirova, 1980; Ufrecht & Hoelzl, 2006). Åberg (1995) presented the applicability of the method for several environmental studies.

More recent investigations deal with the application of strontium isotope ratios for human migration studies in archaeology (Bentley, 2006; Hodell, Quinn, Brenner, & Kamenov, 2004; Hoogewerff et al., 2001; Montgomery, Evans, & Wildman, 2006; Price, Knipper, Grupe, & Smrcka, 2004; Åberg, Fosse, & Stray, 1998), for paleodietary studies (Lee-Thorp & Sponheimer, 2003) or for forensic purposes (Beard & Johnson, 2000; Rummel, Hoelzl, & Horn, 2007). In the field of food science the first investigations of origin determination were carried out for wine (Barbaste, Robinson, Guilfoyle, Medina, & Lobinski, 2002; Horn, Hoelzl, Todt, & Matthies, 1998; Horn, Schaaf, Holbach, Hoelzl, & Eschnauer, 1993), milk (Crittenden, Andrew, LeFournour, Young, & Middleton et al., 2007), butter (Rossmann, Haberhauer, Hoelzl, Horn, & Pichlmayer et al., 2000), British mineral waters (Montgomery et al., 2006), rice (Oda, Kawasaki, & Hirata, 2002), and fruit juices (Rummel, Hoelzl, Horn, Rossmann, & Schlicht, 2008).

In order to assign origin to a food sample on the basis of its strontium isotope composition, the isotope ratio of the sample must be compared to data of authentic samples from the region in question. However, because of the usually limited possibilities to compile an adequate database of authentic samples, it cannot be assured that these samples will represent the entire strontium isotope variability of the area. This aspect is especially relevant for products from remote areas where data for authentic reference samples are lacking or unobtainable.

In order to evaluate the results, a prediction should be carried out on the basis of thorough knowledge of the geological and pedological situation of the region in question (Horn et al., 1993).

The present large scale investigation of $^{87}Sr/^{86}Sr$ in natural mineral waters is used to test if it is possible to identify geologically derived key parameters predominantly responsible for the strontium isotopic signature in the water in order to predict data ranges for samples just by the knowledge of the geographical origin and the use of a common geological map.

First results of $^{87}Sr/^{86}Sr$ analyses in "surface" water samples, ammonium nitrate extracts from soil samples, and honey as well as wheat samples from specific sample regions within the TRACE project, will be used in this study to test the applicability and transferability of predicted data ranges for strontium isotope ratios, gained by the natural mineral water investigation, to other agricultural products and food commodities.

2. Fundamentals

$^{87}Sr/^{86}Sr$ is a parameter reflecting local geochronological and lithological settings by their natural spatial variation.

Strontium isotopic signatures in rocks have evolved over geological time. ^{88}Sr, ^{86}Sr and ^{84}Sr are stable and not radiogenic whereas the abundance of 87Sr increases with radioactive decay of ^{87}Rb (half life: 48.8 x 109 years). Thus, actual $^{87}Sr/^{86}Sr$ is a function of initial $^{87}Sr/^{86}Sr$, initial Rb/Sr and time.

For example, young and rubidium-poor rocks such as Quaternary basalts have low $^{87}Sr/^{86}Sr$ (from 0.702 to around 0.706), whereas older and/or rubidium-rich rocks such as Palaeozoic granites show considerably higher ratios (Faure, 1986).

Any groundwater – in this study bottled groundwater defined as natural mineral water – obtains its characteristic strontium and isotope content from the processes of dissolution and re-precipitation of strontium from minerals. As no significant isotope fractionation occurs the groundwater obtains its isotopic signature from the minerals of the soil and rock strata through which it percolates. Precipitation processes only change the strontium content but do not alter the isotopic signature.

The strontium isotopic composition of groundwater does not reflect the $^{87}Sr/^{86}Sr$ of the bulk soil or rock it comes into contact with, but that of the soluble minerals able to exchange chemically with the water (Horn, 2005; Horn et al., 1998; Åberg, Jacks, & Hamilton, 1989).

When water circulates through the underground ongoing dissolution and precipitation is controlled by the respective recalibrated hydrochemical and hydrophysical properties of the fluid by the surrounding conditions. In the region of Hegau-Schaffhausen at the Switzerland/Germany border detailed hydrogeological investigations, which include comprehensive strontium isotope ratio analyses, appear to indicate that in earth-alkaline waters a first hydrochemical equilibrium status is reached soon after infiltration. The implication is that the specific strontium content and isotopic signature is induced by soil and surface geology within only a couple of years.

If no significant change is enforced on the quasi hydrochemical equilibrium of an earth-alkaline water, the strontium isotopic signature will remain constant for long circulation periods even in more profound and geologically different layers (InterregIIIA-Projektbericht, 2008).

The isotopic composition of groundwater from aquifers in evaporites and marine limestones resembles the isotopic composition of the rocks due to the simple geochemical composition of these rocks and the solubility of the main minerals.

As the strontium concentration and isotope ratio is closely related to the carbonate system, isotope ratios measured in groundwaters from large limestone areas follow roughly the marine curve primarily published by Burke, Denison, Hetherington, Koepnick, & Nelson et al. (1982) and Veizer and Compston (1974), continuously revised e.g. by McArthur (1994) and McArthur, Howarth, and Bailey (2001).

The isotopic composition of groundwater filtered through clastic sediments, metamorphic or magmatic rocks resemble the composition of easily weathering minerals of the corresponding rocks.

3. Sampling

Between 2005 and 2006 participants of the TRACE project collected about 650 different natural mineral water brands predominantly of western Europe. For samples from Hungary, Slovakia, Switzerland, Scandinavian countries, Slovenia, Croatia and for half the samples of Poland private contacts were used. Sampling of bottled natural mineral water was mostly done by simply buying bottles in shops. Producers have voluntarily provided only small selections of waters. The geographical origin was determined by the indicated bottling locality (city) marked on the bottle and/or by the published lists of the EU (Official Journal C59, 09-03-2005; latest update 23-10-2006).

For mapping, all geographical coordinates have been determined by the same route planning software (ADAC TourPlaner Europe 2005/2006), which turned out to be the quickest and easiest way to find even the smallest towns. It is assumed that the locality

of the source is within a distance of about 15 km, which is acceptable in this context. It is known that often more than one water source is used for the bottling of one brand, or that the sources tap multiple rock types as there are often sources in complex tectonic fault zones and/or pumped from different geological units. But for our large scale survey these details play a minor role and have therefore been neglected.

The sampling was organised to get a widespread overview of the European market and to obtain a relatively complete geologic and geographic coverage. The availability of some brands was limited or sourcing was too expensive and intricate. As several European countries have quite different drinking cultures and natural mineral water markets, not every country provides the same spatial distribution of natural mineral waters. For example, Germany offers around 800 brands, while Ireland acknowledges only four brands.

Around 700 different (ground) waters – bottled and raw ones – were sampled. Over 90% of the samples were labelled as natural mineral waters. Furthermore, for better coverage of regions with lower amount of bottling plants we included waters labelled as spring – or medical waters, which are also bottled at source. In addition, to evaluate the effect of production processes and different bottling dates on strontium isotope ratios, about 40 raw water samples were measured. These analyses showed that influences from filtering and bottling processes and seasonal variations of strontium isotope ratios can be excluded (Voerkelius & Lorenz, 2009).

The analysed parameters include the analysis of the main ion content, trace element concentration, isotope ratios of S, O, H, Sr and the tritium content (Voerkelius & Lorenz, 2009). In the context of this paper only the tritium content, the total mineral content and the strontium isotope ratio is of relevance.

4. Measurement

The strontium isotope results discussed in this paper were produced in four different laboratories. Instruments used were one Thermal Ionisation Mass Spectrometer (TIMS) and three Multi Collector Inductively Coupled Plasma Mass Spectrometers (MC-ICP-MS). As the participating laboratories already had their established methods for sample preparation, and were equipped accordingly, each followed it's own sample preparation procedures, described below. To allow for comparison of measurement results, the laboratories worked according to the same standard operating procedure (SOP). The SOP included recommendations on Rb/Sr separations, corrections for procedural blanks, the prescription of the $n(^{86}Sr)/n(^{88}Sr)$ and $n(^{87}Rb)/n(^{85}Rb)$ reference values used for discrimination and interfering element corrections (0.1194 ± 0 and 0.38565 ± 0.00030, respectively), and requiring partial internal validation of methods by regularly measuring the NIST SRM® 987 (SOP, 2006).

Depending on the Sr content, from 1 to 50 mL of natural mineral water or soil extracts were evaporated. Honey and wheat (0.3–30 g) were digested by applying microwave digestion, high pressure microwave digestion, or ashing in a muffle furnace. Residues were dissolved in HNO_3 and subsequently Sr was separated from other elements such as Ca, Ba or Rb by ion chromatography on a Sr specific crown ether resin (Sr-spec®).

The TIMS was a MAT 261/262 Thermo Finnigan and measurements were carried out on tungsten single filaments. For quality control and to check for proper operation of the mass spectrometer an international Sr-standard (NIST SRM® 987) was analysed under the same conditions as the samples. One year standard measurements ($n = 100$) yield a precision of 60 ppm for 95% probability limits (0.71025 ± 0.00004). Duplicate analyses on ten samples

showed a reproducibility of <40 ppm, and total blanks are mostly below 100 pg Sr, which is negligible compared to a total Sr content between 100 and 2000 ng in the samples.

The three MC-ICP-MS involved were a Nu Plasma (Nu Instruments), an Axiom (ex-VG Instruments), and an Isoprobe (ex-Micromass). Typically, the instrumentation was equipped with a minicyclonic jacketed cinnabar spay chamber or a porous membrane based desolvation unit, a 0.2 mL min^{-1} microcentric nebuliser and Ni or Pt sampler and skimmer cones.

All four laboratories were involved in five measurement comparisons on natural mineral water test materials. These tests showed for natural mineral water samples a degree of equivalence of about 150–200 ppm between the laboratories.

The results are given as isotope ratios and as δ notation in analogy to the isotopes of the light elements commonly used in the food chemistry sector (Rossmann et al., 2000, Rummel et al., 2008). The δ value is defined as

$$\delta^{87}Sr = (^{87}Sr/^{87}Sr_{analysed}/^{87}Sr/^{86}Sr_{Standard} - 1) \times 1000$$

with $^{87}Sr/^{86}Sr$ Standard = 0.7093 (approximation for baltic sea water) according to Rossmann et al. (2000).

For groundwater dating the analysis of the tritium content of the samples was carried out by Low Level Liquid Scintillation Counting (LSC) after electrolytic 3H enrichment (e.g. Clark & Fritz, 1997). The results are expressed in Tritium Units (TU) with 1 TU = 0.119 Bq/L.

5. Development of a prediction tool

Although the strontium isotopic signature of a natural mineral water is the result of an individual and often complicated genesis, it is believed that these individual influences will be evened out by the large sample number, so that the results of this large scale investigation can be used for the development of a simplified qualitative prediction tool for the isotopic signature of unknown samples.

As described above, comprehensive investigations in the region of Hegau-Schaffhausen indicate that groundwaters with relatively low mean residence time tend to reflect the strontium isotopic signature of the surface geology (InterregIIIA-Projektbericht, 2008). As a result of these investigations and additionally by knowledge about hydrochemical equilibrium in groundwaters (Hölting, 1989), we assumed that in young natural mineral waters the strontium isotopic signature is governed by that of the soil and surface geology.

In hydrology the analysis of tritium content is used to identify young groundwater. If the tritium content is above detection limit in the natural mineral waters, the groundwater or at least part of the groundwater has a mean residence time of 50 years or less (in the current investigation before 2005 to 2006) – and is classified as young water (Clark & Fritz, 1997). In approximately 85% of all analysed brands tritium exceeds the detection limit of 0.6 TU. Therefore it is justifiable to correlate the strontium isotopic signature of the water samples with surface geology.

In order to verify a correlation between surface geology and strontium isotopic signature of the natural mineral waters, a comparison was made to a geological map. The indicated geology at the production location, as well as information of the whole catchment region including possible geological transition zones, were considered in this comparison.

The European geological map used is GIS based and provided by Pawlewicz, Steinshouer, and Gautier (2003). The map differentiates between geochronology and lithology (intrusives, volcanic rocks, metamorphic rocks and sedimentary rocks).

For improved visualisation of the correlation of the geological units and the strontium isotope values of the natural mineral waters the map was simplified with the aid of geographic information system software (GIS: ESRI ArcMap 9.2) (Fig. 1): According to the prevailing $^{87}Sr/^{86}Sr$ range of the samples located on each geological unit, the natural mineral water samples were grouped correspondingly in six groups. Geological units with similar strontium isotope data ranges to those of the samples located on these units were aggregated in the map and allocated the same colour.

In cases where a limited number of samples were available to represent a geological unit, for example the Paleozoic intrusives, assumptions were made based on fundamental geological knowledge and experience.

In the map in Fig. 1 different geological units are assigned into six distinct groups, which are indicated in the legend in six different colours. The origin locations of the natural mineral water samples are also indicated as spots in Fig. 1. The colours of the individual natural mineral water samples represent the interval into which the measured strontium isotope value was classified. All strontium isotope values were divided into six groups, which correspond to typical values associated with the geological groups indicated on the map. Visual comparison of natural mineral water strontium isotope ratios to strontium isotope ratios of underlying surface geology is now possible. As visually indicated by a difference in the colour of some spots and the underlying geological unit, it is not in all cases possible to predict the strontium isotope value
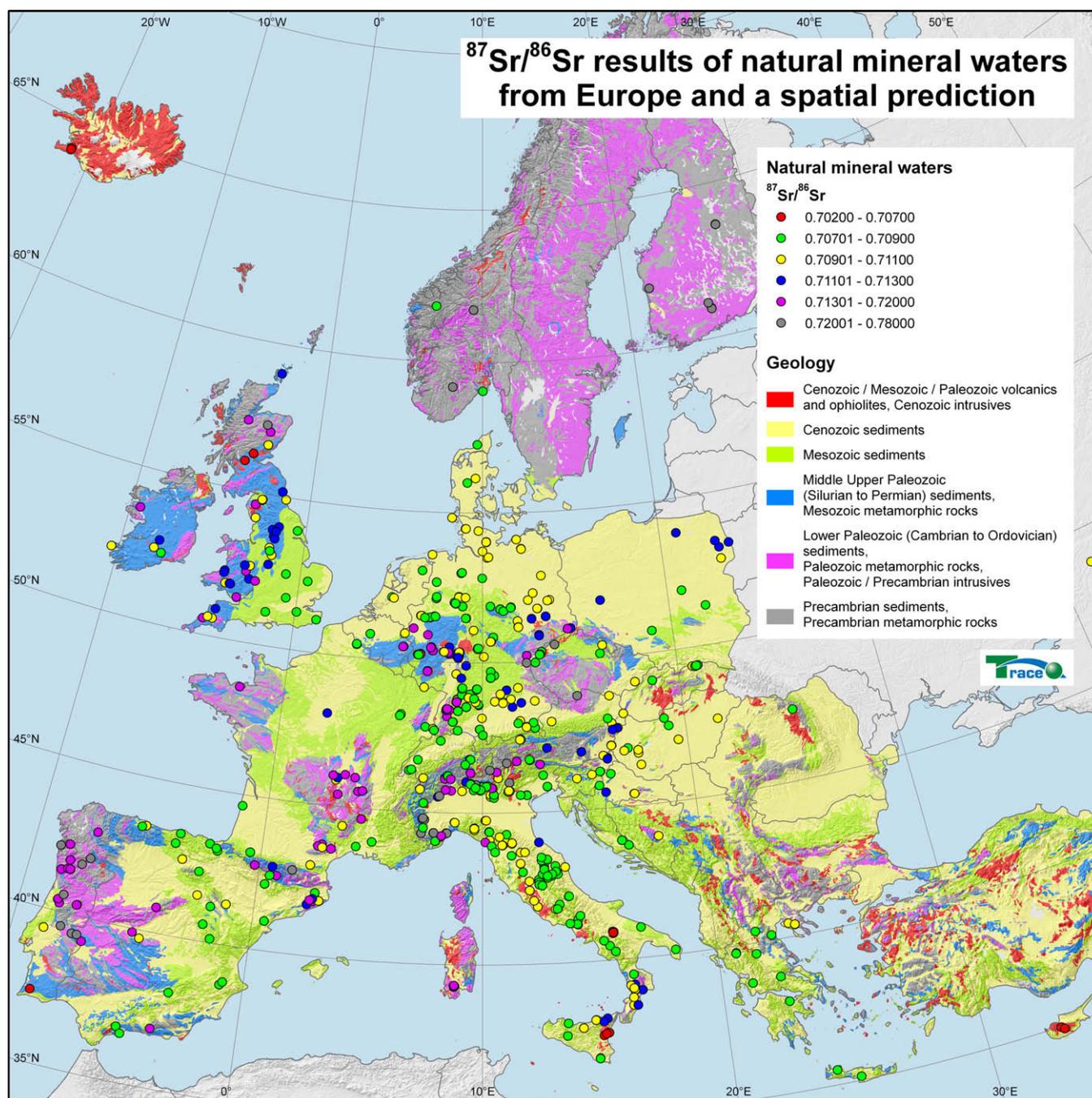

Fig. 1. Map with $^{87}Sr/^{86}Sr$ results of natural mineral waters from Europe and a spatial prediction (see Supplementary data). The map was drawn by simplifying a GIS based geological map from Pawlewicz et al. (2003).

of a sample based on the geological unit from which it was collected.

In a further iterative procedure, the data ranges were adjusted and allocated to the corresponding geological units. For this process especially natural mineral waters with their catchment area in transition zones of different geological units were checked.

6. Analytical results

656 bottled water samples were analysed and interpreted in this study. An overview of the results of the total mineral and strontium content as well as ranges for $^{87}Sr/^{86}Sr$ is given in Table 1 grouped according to the correlation ranges of surface geology of location and water samples. All results are plotted on the map of Fig. 1. The total mineral content varies from 11 to 12575 mg/L with a relatively low mean value of 797 mg/L. The strontium content ranges from <0.0002 to 22.8 mg/l (Voerkelius & Lorenz, 2009).

Results of $^{87}Sr/^{86}Sr$ of all 656 water samples show a wide range of 0.7035–0.7777 or given in δ notation from −10 ‰ to 96 ‰. This large data range of strontium isotope ratios in our water samples reflects the variation observed in young, mantle derived rocks to old continental crust.

7. Description of analytical results in correlation to the geographical origin and surface geology of production location

Low $^{87}Sr/^{86}Sr$ values of 0.7035 to 0.7070 (−8 to −3 ‰) are encountered in our natural mineral water samples from regions with basaltic volcanic rocks such as the Quaternary and Tertiary volcanic rocks of Europe (Iceland, Etna, Vulture, Alkali basalts of Latin, Eifel, Auvergne). Very low values are also observed in regions of basic Palaeozoic volcanic rocks e.g. in Scotland as also described by Montgomery et al. (2006).

The range from 0.7070 to 0.7090 (−3 to 0 ‰) is observed in water samples from regions with a surface geology of mostly Mesozoic marine sediments displayed in the map (Fig. 1) in green. Almost 40% of the analysed natural mineral waters belong to this group. It includes the natural mineral waters from large limestone areas providing natural mineral water resources of high quality compliable with modern taste.

Mudstones and more clastic sediments with lower carbonate contents but also from Mesozoic geological units, seem to produce waters with higher isotope ratios visible as blue and yellow spots on green ground. However, these rocks are underrepresented in our study and were therefore neglected for our approach.

Due to majority of clastic components in Tertiary and Quaternary sediments of the large plains and basin structures mostly derived from Palaeozoic and even Precambrian rocks, the range of analysed values of the water samples between 0.7090 and 0.7110 (0–2 ‰) is applied to origin regions of surface geology of these sedimentary units.

Natural mineral waters with $^{87}Sr/^{86}Sr$ values of the data range from 0.7090 to 0.7110, shown in yellow in Fig. 1, represent the second most abundant part of all analysed waters and account for about 30 %.

Surface geology of Palaeozoic low-metamorphic rock cover leads to $^{87}Sr/^{86}Sr$ from 0.7110 to 0.7130 (2–5 ‰) in the natural mineral waters (coloured blue in Fig. 1). The value range draws the line around Ordovician rocks. No clear differences were observed for samples of more clastic or carbonate rocks, respectively.

High ratios exceeding 0.7130 (>5 ‰) in natural mineral water samples are found exclusively (the only exceptions are Rhenish massif and Northern area of Black forest) in areas of Lower Palaeozoic and crystalline rocks of the old Variscian and Caledonian orogens. The clearest signal can be found in the Iberian Meseta of Portugal and Spain which also provided the highest $^{87}Sr/^{86}Sr$ of 0.7777 (96 ‰) analysed in one sample.

Ratios exceeding 0.7200 (>15 ‰) in water samples can even be distinguished from the lower ratios by differentiating between areas of surface geology of Palaeozoic sediments and low grade metamorphic rocks on the one hand, and areas of Precambrian and high-grade metamorphic rocks on the other hand. Although this differentiation could not be verified on every point of location, it was indicated by colouring in grey in contrast to lavender.

This study clearly shows an overall correlation between $^{87}Sr/^{86}Sr$ of the water samples with the surface geology (Fig. 1), which can easily be deduced from the compliance of the analysed values of the natural mineral waters with the postulated data ranges for the corresponding geological unit of the map. Exceptions to this correlation will now be considered:

Deviations are observed especially for samples originating in areas of Quaternary plains (coloured in yellow), which are mainly covered with glacial gravel. Samples from German plains show ratios between 0.7086 and 0.7109 (−1 and 2 ‰), whereas higher ratios even up to 0.7130 (5 ‰) were analysed in samples produced in Poland. The differences in value ranges can be accounted for by the detritus material which covers a wide range of rock ages and lithologies of metamorphic rocks, intrusives and volcanic rocks, and originates from Scandinavia (Henningsen & Katzung, 2006).

Other deviations were identified where Mesozoic sediments are dominated by mudstones instead of limestone as explained above.

Some of the natural mineral waters from areas with middle and upper Paleozoic surface geology in the UK and Ireland show lower ranges as indicated by the colouring of the geological unit of our map, and in contrast some samples from the Rhenish Massif in Germany show even higher ranges.

The groundwaters that are used for natural mineral waters in UK are often very young and pumped from shallow depths in comparison to other countries (Voerkelius and Lorenz; 2009). Therefore we suggest a significant unknown surface influence to account for the isotope deviation, but this point should be further addressed in future studies.

An example of deviations from the overall picture on a smaller scale is found in western Germany. The Eifel area is especially interesting because both Palaeozoic rocks and Quaternary volcanic rocks are exposed. The Volcanic area produces the CO_2 of the most traditional bottled natural mineral waters. "Natural mineral water" was originally established as a food commodity because of the popularity of natural sparkling waters (Green & Green, 1985). While sulphuric and thermal waters were used for medical applications, CO_2-rich waters of the Eifel became famous as table

Table 1
Strontium isotope ratios of 656 water samples in comparison to mineral – and strontium contents.

Number of samples	Number of samples (%)	Total mineral content (mg/L)	Sr (mg/L)	$^{87}Sr/^{86}Sr$	$\delta^{87}Sr$ (‰)
28	4	62–3523	<0.0002–3.69	<0.7070	<−3.24
245	37	29–1257	0.005–22.8	0.7070–0.7090	−3.24 to 0.42
179	27	28–8976	0.006–12.3	0.7090–0.7110	−0.42 to 2.40
66	10	36–3780	0.025–6.35	0.7110–0.7130	2.40–5.22
100	15	17–6631	<0.0005–3.45	0.7130–0.7200	5.22–15.09
38	6	11–7238	<0.0017–0.94	>0.7200	15.09–99.68

waters. Many Eifel natural sparkling waters are pumped from Devonian slate although the lower $^{87}Sr/^{86}Sr$ ratios still show the relation to the Quaternary volcanic rocks (around 0.7057– 0.7087 in contrast to >0.7136). Further detailed studies are required to determine if the observed isotope ratios refer to deep mantle fluids containing strontium or to soils and covers of the recharge, which contain easily accessible strontium from volcanic rocks and dust.

Though the highest ratios had been expected for samples coming from Scandinavia (see Fig. 1, also Henningsen & Katzung, 2006), two samples from Norway show surprisingly low values (<0.709). As carbonate sediments are rare in these regions an influence of seawater is discussed for these cases. Horn (2005) already suggested that in regions where the exposed rocks do not provide much strontium by weathering, the input of dust and precipitation will determine the strontium isotopic signature.

Although not many deviations were observed for similar geological units within the investigated Mediterranean and the northern areas of Europe, the transferability particularly for the great cratons (e.g. Africa) with thick weathering zones or arid zones remains to be proven through sampling and analysis.

8. Transferability of the prediction method to other food products

Beard and Johnson (2000) already tried to model the strontium isotope variation in the continental United States in order to use it as a general guide to expected isotopic variation in skeletal elements in a particular region. The model assumed that the $^{87}Sr/^{86}Sr$ varies only as a function of age of the surface geology. In contrast, our map (Fig. 1) is based on analysed natural mineral waters and can therefore be applied as a first estimation of strontium isotope ratios in young groundwater.

As water – and not rocks and sediments or soils – is completely bio-available to plants and animals, it is assumed that the value ranges observed and correlated with surface geology is an improvement over the use of a geological map for the prediction of strontium isotope variation in agricultural products.

The strontium isotopic signatures of water enter the food chain (i.e. plants and animals) and can be transferred to any organic material without significant fractionation (Horn et al., 1998). According to Horn (2005), in this application no significant influence by fertilizer is assumed.

Based on the map of Fig. 1 the $^{87}Sr/^{86}Sr$ value range for each of the sample regions within the TRACE project was predicted (Fig. 2). The sample regions range from 160 to 13500 sqm. The prediction considered not only the geological unit of the site but also that of the surroundings.

Comparison of the results of the mean values of the analysed "surface" water samples used for agriculture (mostly First order streams and springs) with the predicted value ranges show that around 90% of the mean values were within the predicted data range. Exceptions are the sample regions BAR and IRE: The sample region of BAR is geologically inhomogeneous with a special prediction of 0.707–0.720, sample region IRE is probably influenced by sea spray as the site is near to the Atlantic.

Comparison of first results of the samples of ammonium nitrate extracts from soil samples, as well as samples of the food commodities honey and wheat show a generally good correlation to the "surface" water samples. Noteworthy deviations from the value range of "surface" water is observed for honey and wheat samples
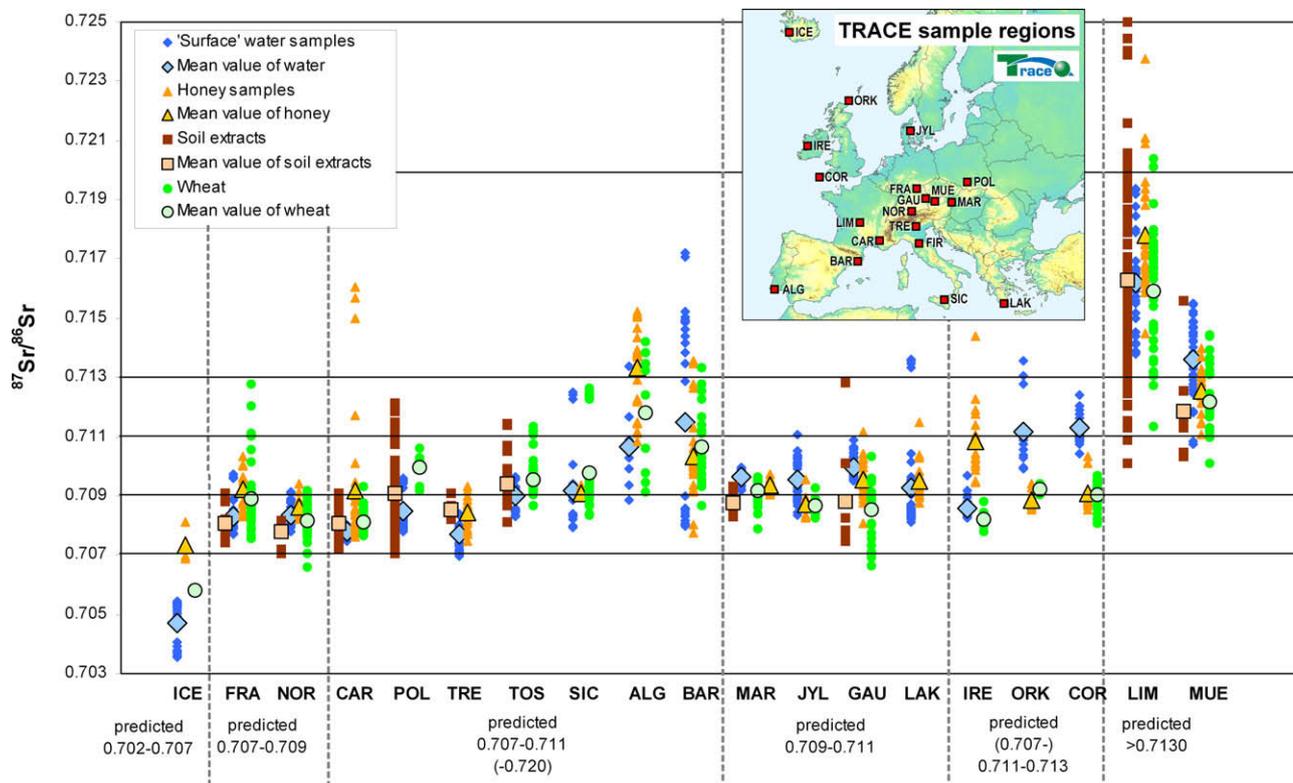
Fig. 2. $^{87}Sr/^{86}Sr$ results from water samples used for agriculture (mostly First order streams and springs), of water extracts from soil samples, of honey and wheat samples from several sample regions in Europe. The prediction of the $^{87}Sr/^{86}Sr$ value range for each of the sample region is based on the geological map of Fig. 1. The abbreviation for the sample regions are: ICE = Iceland, FRA = Germany (Franconia), NOR = Germany (Allgaeu), GAU = Germany (Gaeuboden), CAR = France (Carpentras), LIM = France (Limousin), POL = Poland, TRE = Italy (Trentino), TOS = Italy (Tuscany), SIC = Italy (Sicily), ALG = Portugal (Algarve), BAR = Spain (Barcelona), MAR = Austria (Marchfeld), MUE = Austria (Muehlviertel), JYL = Denmark (Jydland), LAK = Greece (Lakonia), IRE = Ireland, ORK = Orkney Islands and COR = England (Cornwall).

from the sample regions near the Atlantic ICE, COR, and ORK, indicating that here the influence due to sea spray is of higher significance for the $^{87}Sr/^{86}Sr$ values in the commodities than for the analysed "surface" water samples:

Honey samples from sample region ICE show higher strontium isotope values than the "surface" water samples, whereas honey and wheat samples from sample regions ORK and COR show lower values than the "surface" water samples. The food commodities from these regions seem to approach the $^{87}Sr/^{86}Sr$ value of seawater strontium of about 0.7092 (Capo & DePaolo, 1990).

Pourcelot, Stille, Aubert, Solovitch-Vella, and Gauthier-Lafaye (2008) suggest that dust and input from the atmosphere can have a significant influence on $^{87}Sr/^{86}Sr$ in the upper part of soil.

The overall correlation between the analysed and predicted value ranges (Fig. 2) confirms our assumption that our map can also be used for strontium isotope ratio prediction in other natural products.

9. Conclusion

In contrast to the numerous small scale investigations using strontium isotope ratios, this study presents results of a large scale investigation with a high amount of analysed water samples which clearly illustrate the potential of strontium isotope ratio analysis for authenticity control.

Though most of the natural mineral waters were not pumped from units of the surface geology but from deeper layers, a good or at least feasible correlation of the $^{87}Sr/^{86}Sr$ of the natural mineral water samples with the surface geology was observed.

Furthermore, the study presents an overview of the observed value ranges of this parameter. Combining the measured data with a GIS based geological map it is possible to predict qualitative spatial information of strontium isotope values. The information provided by this map can be used advantageously in authenticity control not only to estimate the isotopic signature of a natural mineral water, but also for other food products.

This is of relevance especially for the validation of the origin of products from remote areas where data for authentic reference samples are lacking or cannot be obtained. A prediction of the values from an area based on the geological map can also be used as a decisive tool to evaluate the potential of strontium isotope ratio analysis in a particular case of authenticity proof for any food product.

The applicability of the elaborated map for prediction of strontium isotope ratios for other agricultural products and food commodities was successfully tested by comparing first results of $^{87}Sr/^{86}Sr$ analyses in "surface" water samples, ammonium nitrate extracts from soil samples, as well as honey and wheat samples from specific sample regions within the TRACE project.

Based on this study it is proposed that strontium isotope ratios can contribute significantly to resolve questions of geographical origin. A prerequisite is, however, the knowledge of the spatial catchment area of an object.

An improvement of our system or provided map would be the construction of a "prediction" map with predicted value ranges for commodities produced at each geological unit. Based on complex statistical and graphical efforts the map may provide overlapping value ranges for the specific units and also consider big scale regional differences such as the observed deviations between the Quaternary plains of northern Germany and Poland (see above).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.foodchem.2009.04.125.

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