

Technical Note

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87Sr/86Sr isotope ratio as a tool in archaeological and environmental investigation: limits and risks

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Review

$^{87}\text{Sr}/^{86}\text{Sr}$ Isotope Ratio as a Tool in Archaeological and Environmental Investigation: Limits and Risks

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Abstract: During the last forty years, the use of strontium isotopes in archaeology and biogeochemical research has spread widely. These isotopes, alone or in combination with others, can contribute to trace past and present environmental conditions. However, the interpretation of the isotopic values of strontium is not always simple and requires good knowledge of geochemistry and geology. This short paper on the use of strontium isotopes is aimed at those who use this tool (archaeologists, but not only) but who do not have a thorough knowledge of mineralogy, geology, and geochemistry necessary for a good understanding of natural processes involving these isotopes. We report basic knowledge and suggestions for a correct use of these isotopes. The isotopic characteristics of bio-assimilable strontium depend not so much on the isotopic characteristics of the bulk rock as, rather, on that of its more soluble minerals. Before studying human, animal and plant remains, the state of conservation and any conditions of isotopic pollution should be carefully checked. Samples should be collected according to random sampling rules. The data should be treated by a statistical approach. To make comparisons between different areas, it should be borne in mind that the study of current soils can be misleading since the mineralogical modification of the soil over time can be very rapid.

Keywords: $^{87}\text{Sr}/^{86}\text{Sr}$; archaeology; environment; mineral dissolution; bio-available Sr

1. Introduction

The use of strontium isotopes in archaeological and biogeochemical research dates back to the eighties and nineties of the last century (e.g.: [1–3]). Bentley [4] made a very good introduction and review on the use these isotopes in archaeology. The reader is addressed to these papers for historical information.

Although the use of strontium isotopes is widespread, sometimes in connection with other isotopes, not all archaeologists and biologists can be expected to have a physical-chemical, mineralogical, and geological background to correctly manage strontium isotope data. Hereafter, we express our point of view as geochemists and geologists and, in a very simple and schematic way, we want to give theoretical and practical suggestions to scientists who have no experience in strontium isotope geochemistry. In particular, we want to introduce them to (i) the basic geochemical concepts, necessary for correct application of the strontium isotopes, and (ii) to the limits and the risks of using these isotopes.

In order not to weigh down the text and bore the reader, bibliographic citations in the text are few, but essential. Chemical definitions are reported in the Appendix, whereas accessory calculations, which are necessary for a good understanding of the deep significance of the mathematical relations of the text, are reported in the Supplementary Material. Consequently, the text could be read at two different levels.

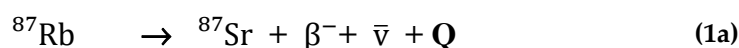
1. Isotopes of strontium and rubidium, and decay of ^{87}Rb

The isotopic abundance for the isotope ^AE of the element E is here defined as the ratio $X_{A_E} = n_{A_E} / n_E$, where n is the number of nuclides ^AE and of the total atoms of the element E present in the system of interest (see Appendix). In general, the value X_{A_E} is variable in the different natural substances; thus, only approximate values of the isotopic abundances in the systems of interest may be given. According to the literature, the approximate isotopic abundances of strontium [5] and rubidium [6] in most terrestrial materials are the following: $X_{84\text{Sr}} \approx 0.55\text{-}0.58\%$, $X_{86\text{Sr}} \approx 9.75\text{-}9.99\%$, $X_{87\text{Sr}} \approx 6.94\text{-}7.14\%$, $X_{88\text{Sr}} \approx 82.29\text{-}82.75\%$; $X_{85\text{Rb}} \approx 72.17\%$, $X_{87\text{Rb}} \approx 27.83\%$ ($X_{85\text{Rb}}/X_{87\text{Rb}} = 2.596$).

The strontium geochemical cycle is very different in respect, for instance, to hydrogen, oxygen, carbon, and nitrogen which scientists frequently use for their research. The distribution of hydrogen, oxygen and carbon isotopes depends mostly on the cycle of these elements in the hydrosphere and atmosphere, whereas the distribution of strontium isotopes depends mostly on the solid earth and its complex surface rock distribution. Therefore, a correct application of the isotopes of strontium needs basic knowledge of mineralogy, geology, and geochemistry.

At the low temperatures of earth surface environment, isotopes of hydrogen, oxygen, carbon, and nitrogen undergo fractionation. On the contrary, at any temperature, the potential fractionation of strontium isotopes, which have high numbers of atomic mass, is very low, if present, and not detected by analytical present-day technology. In other words, whereas the isotope ratios $n_2\text{H}/n_1\text{H}$, $n_{18}\text{O}/n_{16}\text{O}$, $n_{13}\text{C}/n_{12}\text{C}$, and $n_{15}\text{N}/n_{14}\text{N}$ in different substances, coexisting at a given temperature, are generally different, the isotope ratio $n_{87\text{Sr}}/n_{86\text{Sr}}$ is the same (for instance, strontium isotopes are not fractionated by plants or animals when acquired from the environment). In a mineral or total rock considered as closed systems (no matter exchange with the environment occurs), among the strontium isotopes, only the ^{87}Sr may change its number of atoms during the time. This is the main reason for which the isotope ratio $n_{87\text{Sr}}/n_{86\text{Sr}}$ is considered. The same is valid for the isotopes of rubidium ^{87}Rb .

Natural change in the $n_{87\text{Sr}}/n_{86\text{Sr}}$ isotope ratio is due to the unstable atomic nucleus of ^{87}Rb , which decays to ^{87}Sr with emission of a β^- particle:



where $\bar{\nu}$ is an anti-neutrino and Q the decay energy (for physical-chemical definition see IUPAC-International Union of Pure and Applied Chemistry (<https://goldbook.iupac.org/>)). The radioactive decay is a spontaneous nuclear transformation. The speed of this transformation at a generic time t is proportional to the amount of ^{87}Rb which is present in the system at that time. In the mathematical language, for a system which does not exchange elements with the environment, the instantaneous "speed of decay", $v_{\text{decay}(t)}$, at the time t is usually defined by the following relation,

$$v_{\text{decay}(t)} = - \frac{dn_{87\text{Rb}}}{dt} = \frac{dn_{87\text{Sr}}}{dt} = \lambda n_{87\text{Rb}(t)} \quad (1b)$$

$$\lambda = (1.3972 \pm 0.0045) \times 10^{-11} \times a^{-1}$$

where $dn_{87\text{Rb}}$ and $dn_{87\text{Sr}}$ indicates very small variations of $n_{87\text{Rb}}$ and $n_{87\text{Sr}}$ in a very small time interval dt , λ is a constant called "decay constant" (the probability that an atom of ^{87}Rb has to decay in one year), and the letter a indicates the years. In agreement with relation (1a), the sign minus in front of $dn_{87\text{Rb}}$ is present because, during decay, $n_{87\text{Rb}}$ decreases with the time, whereas $n_{87\text{Sr}}$ increases.

From equation (1b), after simple mathematical manipulation (see Supplementary Material S-A), the following general relations are obtained,

$$n_{87\text{Rb}(t)} = n_{87\text{Rb}(t_0)} e^{-\lambda(t-t_0)} \quad (2a)$$

and

$$n_{87\text{Rb}(t_0)} = n_{87\text{Rb}(t)} e^{\lambda(t-t_0)} \quad (2b)$$

where t_0 and t are the time of the beginning of decay computation and the present time, respectively, and e is the Neper's number ($e = 2.71828182 \dots$). Subtracting $n_{87\text{Rb}(t)}$ from (2b) and remembering that the loss of ^{87}Rb is equal to the gain of ^{87}Sr , we also write:

$$n_{87\text{Sr}(t)} - n_{87\text{Sr}(t_0)} = n_{87\text{Rb}(t_0)} - n_{87\text{Rb}(t)} = n_{87\text{Rb}(t)} (e^{\lambda(t-t_0)} - 1) \quad (3a)$$

where the difference $n_{87\text{Sr}(t)} - n_{87\text{Sr}(t_0)}$ is the number of ^{87}Sr nuclides generated by decay in the time interval $t - t_0$.

Consider now that, in a system containing rubidium, only the numbers of ^{87}Sr and ^{87}Rb atoms change during the time. Thus, since the number of the ^{86}Sr atoms is a constant value independent on the time, dividing (3a) by the constant $n_{86\text{Sr}}$ value, we obtain:

$$\frac{n_{87\text{Sr}(t)}}{n_{86\text{Sr}}} - \frac{n_{87\text{Sr}(t_0)}}{n_{86\text{Sr}}} = \frac{n_{87\text{Rb}(t)}}{n_{86\text{Sr}}} (e^{\lambda(t-t_0)} - 1) \quad (3b)$$

Relation (3b) is usually written in terms of isotopic abundances as follows:

$$\left(\frac{X_{87\text{Sr}}}{X_{86\text{Sr}}} \right)_t - \left(\frac{X_{87\text{Sr}}}{X_{86\text{Sr}}} \right)_{t_0} = \left(\frac{X_{87\text{Rb}}}{X_{86\text{Sr}}} \right)_t (e^{\lambda(t-t_0)} - 1)$$

or, more simply,

$$\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_t - \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_{t_0} = \left(\frac{^{87}\text{Rb}}{^{86}\text{Sr}} \right)_t (e^{\lambda(t-t_0)} - 1)$$

2. The strontium and rubidium in minerals

2.1. General

In the common minerals, strontium and rubidium are mostly enveloped ("coordinated") by oxygen and their bond with oxygen is prevalently ionic (electrostatic forces). Thus, strontium and rubidium may be regarded as Sr^{2+} and Rb^+ ions that are linked to oxygen, O^{2-} . The oxygen atoms are distributed around Sr^{2+} and Rb^+ and placed at the apex of regular or distorted polyhedrons which define, in this way, the shape of Sr^{2+} and Rb^+ lattice sites. Sr^{2+} replaces calcium, Ca^{2+} , and, in minor amount, Na^+ and K^+ in several minerals. For instance, this substitution occurs in common calcium sulphates (gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and anhydrite, CaSO_4), carbonates (e.g. calcite and aragonite, CaCO_3 , and dolomite, $\text{CaMg}(\text{CO}_3)_2$), plagioclase ($\text{Na}_{1-x}\text{Ca}_x\text{Al}_{1+x}\text{Si}_{3-x}\text{O}_8$), K-feldspar (KAlSi_3O_8), and apatite (simplified formula: $\text{Ca}_3(\text{PO}_4)_3(\text{F}, \text{Cl}, \text{OH})$), a mineral that in the form of carbonate hydroxyl apatite is the inorganic component of bones. The ionic radii of Sr^{2+} may change a little bit in relation to the number of the enveloping oxygen atoms. For instance, in aragonite, Ca^{2+} is present in ninefold coordination allowing aragonite to accept easily larger cations such as Sr^{2+} ; in this coordination, Ca^{2+} has ionic radius of about 1.18 Å (1 Å = 10⁻¹⁰ m) [7]. On the contrary, in calcite, Ca^{2+} and Sr^{2+} exists in sixfold coordination having ionic radius of about 1.00 Å and 1.18 Å, respectively.

Rubidium Rb^+ mostly replaces K^+ in trioctahedral micas, including illite. The number of effective coordination ranges from eleven to seven [8], the ionic radii for K^+ and Rb^+ being about 1.46 Å to 1.58 Å and 1.56 Å to 1.70 Å, respectively. In K-feldspar, K^+ and Rb^+ are sevenfold coordinated [9] with ionic radii of about 1.46 Å and 1.56 Å.

Concluding: the crystal lattice features reported above, are relevant for strontium and rubidium distribution in different minerals; in particular, the ionic radius is very important for element substitution; elements with similar ionic radii may substitute each other in the crystal lattice.

The order of magnitude of strontium and rubidium concentration in some common rock-forming minerals is reported in Table 1.

Table 1. Order of magnitude of Sr and Rb concentration in some main rock-forming minerals.

Minerals	Chemical formula	Sr (ppm wt)	Rb (ppm wt)
Gypsum	$\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$	>1000	≈ 0
Anhydrite	CaSO_4	>1000	≈ 0
Plagioclase	$\text{Na}_{1-x}\text{Ca}_x\text{Al}_{1+x}\text{Si}_{3-x}\text{O}_8$	200-1000 ⁽¹⁾	5-40 ⁽¹⁾
K-felspar	KAlSi_3O_8	50-800 ⁽¹⁾	200-800 ⁽¹⁾
Calcite	CaCO_3	100-700	≈ 0
Aragonite	CaCO_3	100-1000	≈ 0
Dolomite	$\text{CaMg}(\text{CO}_3)_2$	100-500	≈ 0
Phyllosilicates ^(*)	Largely variable	<100 ⁽¹⁾	100-2000 ⁽¹⁾

ppmw = part per million in weight; ⁽¹⁾ [10]; ^(*) Clay minerals (in particular, montmorillonite) may adsorb Sr^{2+} on the surface of their crystals; thus, the concentration of Sr^{2+} may be higher than about 100 ppmw.

2.2. Strontium isotopes in minerals and whole rock

In this paper the term rock is also used for soil which, from a mineralogical and geochemical point of view, may be mostly regarded as an unconsolidated rock commonly containing organic material. Several papers, which use strontium isotopes for archaeological reconstruction, sometimes address their attention to the isotopic composition of the whole rock or soil. However, it is noteworthy that bulk rock/soil is not important for the acquisition of isotopes by plants and animals. Rather, the different minerals and their solubility in aqueous solutions are relevant. Hereafter, we approach this topic.

2.3. Minerals as constituents of the rock

We may observe a rock from two different point of view: (i) mineralogical composition and (ii) physical state (consolidated and unconsolidated).

(1) Monomineralic consolidated/unconsolidated rock

The rock is formed only by a mineral (e.g., limestone and dolomite rock consisting of calcite or aragonite, and dolomite, respectively) generated at a defined time in an isotopically homogeneous environment (for instance, limestone precipitated from marine water at a defined geological time). In case after deposition the rocks behave as a closed system, the rock is expected to maintain the initial macroscopic isotope homogeneity during the time. Summarising: the isotopic ratio may change during the time, but at a given time it will be the same in all the portions of the rock.

(2) Polymineralic consolidated/unconsolidated rock

(2a) The rock is mineralogically heterogeneous containing several minerals, which, at the time of their generation, had the same isotope ratio. This approximately occurs, for instance, during crystallization of a magmatic silicate magma on the surface or in the interior of the Earth (note that, this is strictly true only in case the different minerals become closed systems at the same temperature; see [11]). In this case, the variation of the isotope ratio of the single mineral from the time of its formation to the time of the measurements depends largely on the original ^{87}Rb content of the single mineral. Summarising: (i) at the time of the rock generation, all the minerals had the same isotope ratio which, however, (ii) change their value with different speed because of their different ^{87}Rb original content. The rock initially was mineralogically heterogeneous and homogeneous for the isotope ratio, whereas at the time of interest, both mineralogically and isotopically heterogeneous.

(2b) At the time of its formation, the rock contains several minerals which already have different isotope ratios. This is typical for clastic rocks, such as soil, moraines and terrigenous sediments, or

clastic consolidated rocks (e.g.: silt, sandstones, conglomerates) which derive by disruption of older rocks. In this case, the variation of the strontium isotope ratio in the different minerals will be due both (i) to the original isotope values of the different rock-forming minerals and, obviously, (ii) to the time which elapsed from the rock generation to the present. Summarising: the rocks, are mineralogically and isotopically heterogeneous both at the time of their formation and at the time of interest.

2.4. Variation of strontium isotopes in different minerals (i) and strontium isotopes in the total rock (tot)

2.4.1. Different decay speed of ^{87}Rb in the different minerals

As reported above, usually the different rock-forming minerals have different initial ^{87}Rb content. Therefore, according to relations (1b) and (2a), the speed of ^{87}Sr generation is dependent on the ^{87}Rb concentration at the time t_0 . Consider the two minerals as, for instance, calcite and muscovite both with the same initial $n_{^{87}\text{Sr}(t_0)}/n_{^{86}\text{Sr}}$ ratio (= 0.7060) but different rubidium content, as reported in Table 2.

Table 2. Data for an example of calculation of strontium isotope ratio for calcite (Cc) and muscovite (Mu)

	W_i	C_{Sr}^i	$n_{^{87}\text{Rb}(t)}/n_{^{86}\text{Sr}}$	$n_{^{87}\text{Sr}(t_0)}/n_{^{86}\text{Sr}}$	$n_{^{87}\text{Sr}(t)}/n_{^{86}\text{Sr}}$
Calcite (Cc)	0.30	0.0800	0.0952	0.7060	<i>0.7061</i>
Muscovite (Mu)	0.70	0.0070	39.11	0.7060	<i>0.7333</i>

$W_i = Q_i / (Q_{\text{Cc}} + Q_{\text{Mu}}) = Q_i / Q_{\text{tot}}$, weight fraction of the rock-forming mineral Cc or Mu generically indicated as i , where Q_i is the mass of the single mineral and Q_{tot} the mass of the total rock consisting of the mineral Cc and Mu. $C_{\text{Sr}}^i = Q_{\text{Sr}}^i / Q_i$, weight concentration of strontium in Cc or Mu, where Q_{Sr}^i is the mass of strontium in the single mineral and Q_i is the mass of the single mineral Cc or Mu. (t), refers to data at the time t of interest; (t_0), refers to data at the initial time. In *italics*, the isotope ratios obtained after $t - t_0 = 50$ Ma (million years). Concentration of strontium in the total rock $C_{\text{Sr}}^{\text{tot}} = W_{\text{Cc}} \times C_{\text{Sr}}^{\text{Cc}} + W_{\text{Mu}} \times C_{\text{Sr}}^{\text{Mu}} = 0.30 \times 0.0800 + 0.70 \times 0.0070 = 0.0289 = 289$ ppm wt (ppm = parts per million).

Using relation (3b), after $t - t_0 = 50$ million years from their generation, calcite will assume $n_{^{87}\text{Sr}(t)}/n_{^{86}\text{Sr}}$ equal to 0.7061 and muscovite equal to 0.7333. The variation for calcite, with small rubidium amount, is so low because the decay speed of ^{87}Rb is very low for this mineral (see relation 2a), whereas for muscovite, the amount of rubidium is high and, thus, the speed of decay is high.

2.4.2. Relation of the isotope data for minerals and for whole rock

Consider the minerals 1, 2, ..., ϕ indicated generically by the letter i , forming the total rock indicated as tot. If the isotopic features of the different minerals are known, for the different minerals and total rock we may write the following approximate isotope-balance relation (see Supplementary Material S-B):

$$\frac{n_{^{87}\text{Sr}}^{\text{tot}}}{n_{^{86}\text{Sr}}^{\text{tot}}} \cong \sum_{i=1}^{\phi} \left(\frac{C_{\text{Sr}}^i}{C_{\text{Sr}}^{\text{tot}}} W_i \frac{n_{^{87}\text{Sr}}^i}{n_{^{86}\text{Sr}}^i} \right) \quad (4)$$

Relation (4) is a particular expression of a mixing equation which gives a “weighted mean” of the isotope ratio $n_{^{87}\text{Sr}}/n_{^{86}\text{Sr}}$ for the total rock. The $\frac{C_{\text{Sr}}^i}{C_{\text{Sr}}^{\text{tot}}} W_i$ values are mathematical weights of the different addends, i.e., values which estimate the contribution of the $n_{^{87}\text{Sr}}/n_{^{86}\text{Sr}}$ ratio of the different minerals to the isotopic values of the total rock. C_{Sr}^i is the weight concentration of strontium in the generic mineral, i , $C_{\text{Sr}}^{\text{tot}}$ in the total rock, tot, and W_i the weight fraction of the mineral i in the rock (for symbols, see Table 2). As an example, consider a rock formed by calcite and muscovite with the isotopic features reported in Table 2. We write:

$$\begin{aligned} \frac{n_{87\text{Sr}}^{\text{tot}}}{n_{86\text{Sr}}^{\text{tot}}} &\cong \frac{C_{\text{Sr}}^{\text{Cc}}}{C_{\text{Sr}}^{\text{tot}}} W_{\text{Cc}} \frac{n_{87\text{Sr}}^{\text{Cc}}}{n_{86\text{Sr}}^{\text{Cc}}} + \frac{C_{\text{Sr}}^{\text{Mu}}}{C_{\text{Sr}}^{\text{tot}}} W_{\text{Mu}} \frac{n_{87\text{Sr}}^{\text{Mu}}}{n_{86\text{Sr}}^{\text{Mu}}} = \\ &= \frac{0.08}{0.0289} \times 0.30 \times 0.7061 + \frac{0.007}{0.0289} \times 0.70 \times 0.7333 = \mathbf{0.7107} \end{aligned}$$

This value is far both from those of calcite and muscovite.

2.5. Selective mineral dissolution and its important role on the strontium isotopes values in the water solution

Frequently people retain that the bulk-rock isotopic feature is relevant for the isotopic characters of the bioavailable strontium. This, however, is not correct. Hereafter we show that the isotopic features of the single minerals are important.

It is noteworthy that the speed of mineral dissolution (kinetics of dissolution) is different for the different minerals and depends on several factors (e.g.: temperature and pressure, size and morphology of the grains, pH of the aqueous solution, saturation condition of the solution in the mineral phase considered, etc.). For instance, we consider the kinetics of calcite (simplified formula: CaCO_3) and muscovite (simplified formula: $\text{KAl}_2[\text{AlSi}_3\text{O}_{10}](\text{OH})_2$) dissolution in pure water in conditions far from the solution saturation in these minerals. According to the literature (e.g.: [12,13], and references therein), at about 25°C and for pH in the range 5 to 9.5, the dissolution rate of calcite is in the order of magnitude of 10^{-6} mole $\text{m}^{-2} \text{s}^{-1}$, i.e. one meter square of the mineral releases 10^{-6} mole of calcite in a second. In turn, for muscovite at 25°C, the value is about 10^{-11} to 10^{-12} mole $\text{m}^{-2} \text{s}^{-1}$ ([14], and reference therein). Thus, the rate of dissolution of calcite is at least one hundred thousand times the rate of muscovite! Even if muscovite has a very high $n_{87\text{Sr}}/n_{86\text{Sr}}$ values in respect to calcite, the isotopic value of the bioavailable strontium (strontium dissolved in water of the soil) will be very close to the value for calcite. An example of calculation is reported in Supplementary Material S-C, where we demonstrated that in a system consisting of calcite and of muscovite with high $n_{87\text{Sr}}/n_{86\text{Sr}}$ ratio, the isotope ratio of a water solution which dissolved calcite and muscovite will have isotope ratio very close to that of calcite, not to that of the whole rock.

Concluding, we recall again what we stated above: the isotopic features of the whole-rock are not significant in determining the isotope ratio in plants and animal; rather, the single phases present in the rock are relevant.

2.6. Sorption/desorption and minerals

Clay minerals, such as smectite, illite, kaolinite, as well as the organic matter may sorb strontium from circulating water solutions because of the cation exchange capacity of these substances. This process is well known in the scientific literature (see, for instance, [15–17]). Generally, strontium sorption increases as strontium concentration and total salinity of the solution decrease. The $n_{87\text{Sr}}^{\text{sorbed}}/n_{86\text{Sr}}^{\text{sorbed}}$ value of the sorbed strontium is determined by (i) strontium present in the most soluble minerals of the rock and/or (ii) strontium carried by water coming from the environment. The last origin of strontium may be dominant when the minerals present in the rocks are only slightly soluble, thus transferring into solution only very small amount of strontium. This, for instance, may sometimes occur when the rocks consist of silicates.

Calcite, aragonite, and Ca-sulphates are the most common rock-forming minerals which exhibit the highest solubility and are rich in strontium. Thus, these minerals, when present, are expected to mostly affect the isotope ratio of the circulating waters, as demonstrated above for calcite. This is well documented in several places. For instance, in the “Prosecco wine” area in Northern Italy (Aviani 2013), the main Sr-bearing minerals present in the soil are Ca-carbonate, dolomite, phyllosilicates and plagioclase, where some phyllosilicates may assume strontium *via* surface sorption. We considered four places investigated by Aviani [18] and Petrini et al. [19]: Nardin-Lison, Sant’Anna, Lonigo, Pittarello. For all these localities, strontium for the isotopic determinations was extracted using both $\text{CH}_3\text{COONH}_4$ (ammonium acetate) 1 M (pH \approx 7) and HCl 2.5 N (very acid solution). Different extraction

may be made per several different reasons. For instance, at $\text{pH} \approx 7$, Ca-carbonates and Ca-sulphates are dissolved in moderate to low amount, whereas at very low pH, carbonates are strongly dissolved together with Al- and Fe-hydroxides. On the contrary, phyllosilicates are always slightly dissolved. In the “Prosecco wine” area, the values obtained on solutions at pH 7 and at very low pH for the same soil sample are strictly correlated with slope which is not significantly different from the unit ($p_{\text{slope}=1} \approx 0.9$); thus, the values obtained using the different extraction are nearly indistinguishable. Since in the area there is no evidence of Ca-sulphate occurrence, the data obtained suggest the dominant role of carbonates. Moreover, the analysis of the whole soil after total dissolution of the soil gives largely higher strontium isotope values. This demonstrates that, at least in part, the phyllosilicates present in the soil are practically insoluble when treated with neutral (acetate) or acid (HCl) solutions and represent residuals of old rocks with high strontium isotope ratio.

3. Strontium isoscapes and their use in archaeological and biogeochemical sciences

Geochemical prospecting includes any method of mineral exploration based on systematic measurement of one or more chemical properties of a naturally occurring material ([20], and reference therein). It is a very old method to recognize possible geochemical anomalies in a territory and, thus, to identify areas with mineral deposits. Conceptually, isoscape, a term recently used by West et al. [21] is no more than a graphical representation, obtained with the aid of a geographic information system (GIS), of the results of an isotope geochemical prospecting.

The use of strontium isoscapes in archaeological and biogeochemical sciences needs great caution because isoscapes are generally referred to large-scale grid sampling with cells of the order of tens or hundreds of km^2 and, in nature, the variation of the strontium isotope ratio not necessarily merges continuously from a value to another but may be sharp even between neighboring sites when they are located on the boundary between different geological formations. For instance, for Italy covering an area of 302.073 km^2 , Lugli et al. ([22]) used 1920 data of $^{87}\text{Sr}/^{86}\text{Sr}$ ratio: on average, one sampling for 157 km^2 ; for France, Willmes et al. ([23]) used data referred to 840 sites for an area of 551.626 km^2 : one sampling for 657 km^2 ! However, archaeologists and biologists make investigation usually at more little scale. Moreover, frequently the sampling for isoscapes is not random distributed on the area of interest. Thus, at best, the most common isoscapes can only give generic indication for wide areas.

4. Investigating and planning strontium isotope research

We remind the reader that any investigation must be performed keeping in mind what we want to know from strontium isotopes. This is only apparently obvious.

- (1) As general rule, the sampling grid used to perform isoscapes and local investigation should be the same. This of course is practically impossible to obtain because isoscapes are usually made at large scale, as stated above. Thus, for local investigation, scientists should use isoscapes with great caution and integrate them with values obtained from more detailed random sampling. Random sampling is necessary to avoid bias of the data obtained on the samples. Furthermore, the geology and mineralogy of the sampling area should be carefully considered to have an idea of the dominant mineral source of strontium and water circulation.
- (2) Do soil solutions always maintain the isotopic features it had in the past time of interest? This is an important question when we want to use present day soil isotopic values as indicator of past conditions. Sometime, scientists try to define the isotopic background measuring both modern and/or ancient faunal/vegetal samples from the site, a method which may be risky. Indeed, during the time, soil may change rapidly its mineralogical and, thus, isotopic features, that does not allow any comparison with the past conditions. For instance, soil rich in organic material may produce large increase of CO_2 partial pressure in the water solution migrating in the soil, that

increases solubility of calcite. If the leaching proceeds for a sufficiently long time, calcite can disappear completely; in this case, this mineral no longer contributes to the bioavailable strontium. Moreover, in soil free of soluble minerals, the most important role may be played by strontium-bearing water solutions coming from the environment (precipitation or other external sources). Examples of strontium isotope variation due to the environmental water and/or to mineralogical variations of the soil during the time, are reported, for instance, by Åberg [3].

- (3) Are the animals, humans, and plants coming from the same site? The first problem is concerned with the spatial definition of “same site”. It depends, of course, on the aim of the investigation. In other words, we go back to the investigation scale. For instance, Cavazzuti et al ([24]), in studying human settlements located in the Po plain (Northern Italy), assume that the settlements, although far, occur in a very “homogeneous” (do they intend isotopically homogeneous or mineralogically homogeneous or both?) flat area without geographical barriers. They define three different areas around each settlement with radius of 5 km (“site catchment area”), from 5 to 20 km (“immediate hinterland”), and from 20 to 50 km (“broader hinterland”) and they compare the strontium isotope values to the background of these three areal categories.
- (4) What does “same strontium isotope ratio” mean? Modern technology furnishes strontium isotope data with analytical uncertainty on the fifth or even on the sixth decimal digit, whereas, also for small area (up to one km² as an order of magnitude), the isotope data at best may exhibit variation on the fourth decimal digit (see for instance [26]). If it is so, two samples could be considered as having the same value if they do not differ on the fourth digit. Thus, in principle, the identification of exotic samples not belonging to the population of data related to materials coming from a defined area should consider the variability of the isotope data for the area. If possible, this variability should be defined as reported below; i.e., using accurate geochemical parameters measured *on a statistically sufficient number of samples* (indicatively, more than 10; the use of few samples may be misleading!):

$$\text{background} = \text{average of the data, } \frac{\sum x}{n} = \bar{x}$$

where $\sum x$ = sum of the data x obtained on random samples from the area of interest, and n = number of data.

$$s = \text{experimental standard deviation of the data, } \sqrt{\frac{(x-\bar{x})^2}{n-1}},$$

here assumed very similar to the theoretical standard deviation, σ , for the entire population of data.
 threshold = background + $k \times$ standard deviation, $\bar{x} + k s$, where k is the “coverage factor”. Frequently, for practical problems, $k = 3$ is assumed. Theoretically, in place of k , an appropriate value of the “Student’s t ” should be used.

A qualitative indication of the probability that the single value is outside the investigated population, is given by the so-called “contrast”:

$$\text{contrast} = \frac{x}{\text{threshold}}$$

In the event the contrast value is higher than one, it is reasonable to conclude that the sample *could not* be part of the group.

- (5) In general, we can only establish if the analyzed individuals *may* belong to the same group, not that they *belong* to the same group. In fact, samples settled on different areas with similar geological formations exhibit the same isotopic values even if the areas are far one from the other. This happens, for example, if the individuals come from areas located on carbonate formations of very similar geological age and with a similar genetic and diagenetic history. This is an important limit for the use of strontium isotopes alone. For example, in the Illasi valley, Lessini mountains, NE of Verona (Italy), plants grew on hydrothermalized carbonatic formations of Late Carnian to Liassic ages have very similar isotopic values even if they are located many kilometers far one from the other (about 0.7083 ± 0.0003 , our unpublished data). On the contrary, samples coming from the same hypothetical locality straddling Cretaceous and Late Carnian-Liassic formations could exhibit significant isotopic differences already on the fourth digit (Cretaceous carbonate, 0.7077 against Late Carnian-Liassic carbonates, 0.7083). Thus, it is very important to investigate in detailed the geology and mineralogy of the area before using strontium isotopes. Frequently, this is not sufficiently considered in the scientific papers.
- (6) Plants are largely used in archaeological prospecting because they are a very good indicator of available elements. It is noteworthy, however, that (i) present day plants may give reliable indication on the past conditions only in case the soil geochemistry and mineralogy did not change during the time (see point 2) and that (ii) in areas with soil profile which exhibit chemical and mineralogical variation with the depth, all the plants used should have their roots down to similar depth (for instance, trees and cereals could give different information).

5. Future directions

We tried to explain how the use of the strontium isotopes may be sometimes problematic in archaeological and biological research.

(ia) We cannot assume that the current geochemical, mineralogical, and geological conditions of the investigated area are the same as in the past because variation of the surface conditions is frequent also during a short time.

(iia) The use of large-scale isoscapes is risky because local investigation is usually performed at smaller scale.

We give the following suggestions for geochemical investigation and related inferences.

(ib) Before studying human, animal and plants remains, an accurate control of their diagenetic condition is essential because pollution of the samples by environmental strontium-bearing material with different isotope ratio is very easy (for instance, diagenesis with dissolution/deposition of carbonate).

(iib) The samples (soil, bones, plants, *et cetera*) should be selected randomly. Usually, this is not considered in the literature.

(iiib) To try reliable scientific conclusion, the investigation of large number of remains and related measurements, is necessary. Without large number of data, comparison between different areas is risky, resulting statistically not significant.

(ivb) For each area, data far from the prevalent distribution values could be identified with some statistical method; for instance, using threshold values ("contrast" > 1) or, in the case the distribution of data is not normal, using non-parametric statistics as, for instance, the "kernel density estimation"

(KDE) (see [25], statistical software PAST). Supplementary material S-D report an example of calculation.

(ivb) If samples fall outside the prevalent distribution interval, we can state that they *do not* belong the same group. The individuals falling in the prevailing distribution interval are *not necessarily* belonging to the same group; we can only state that it is *not excluded* they belong to the same group (see point 5 of the text).

Supplementary Materials: The following supporting information can be downloaded at the website of this paper posted on Preprints.org.

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Appendix A

Nuclide: generic nuclear species with number of protons Z and neutrons N .

Element, (${}_Z\text{E}$): atomic species defined by the number of protons; for example, ${}_{38}\text{Sr}$, generically indicated as **Sr**.

Isotope (${}^A_Z\text{E}$): atom of the same element E with defined N value ($A = Z + N$, Atomic Mass Number); for example, ${}^{86}_{38}\text{Sr}_{48}$ for simplicity indicated as ${}^{86}\text{Sr}$.

Isotopic abundance: $X_{A_E} = n_{A_E} / n_E$, where n_{A_E} and n_E are the number of atoms of the isotope ${}^A\text{E}$ of the element E and the total atoms of the element E in the material of interest, respectively; for example, $n_{{}^{86}\text{Sr}}$ and n_{Sr} .

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