

$^{87}\text{Sr}/^{86}\text{Sr}$ Isotope Ratio as a Tool in Archaeological 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 the 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 those 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 soil over time can be very rapid.

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



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1. Introduction

The use of strontium isotopes in archaeological and, more generally, in environmental research, dates back to the 1980s and 1990s of the last century (e.g., [1–3]). Bentley [4] made a very good introduction to and evaluation of the use these isotopes in archaeology. The reader is addressed to this paper for historical information. More recently, several authors critically discussed the application of strontium isotopes to archaeology and the determination and mapping of bioavailable strontium isotopes (e.g., [5–9]), reporting observations which are, in part, summarised in this paper. 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. From experience, we can state that good management of isotopic and chemical data in archaeology and environmental investigation needs basic knowledge not so much on the analytical technique, but rather on the physical meaning of the isotopes of the elements used. This is the reason why basic equations regarding radioactive decay, isotope mixing, and mineral dissolution are introduced in the text. Comprehension of these equations needs mathematical knowledge which constitutes a normal background of any university student.

This paper may be considered as a technical report (in the original significance of the greek τέχνη) where we express our point of view as geochemists and geologists; although, we know that, as stated by Pollard ([10], p. 634), “helpful and constructive critiques . . . outside the fraternity were not always welcomed”. In a very simple and

schematic way, we try to summarize theoretical and practical suggestions, in part separately presented in several papers (e.g., [5–10]), for scientists who have no experience in strontium isotope geochemistry but use it for practical purposes. In particular, hereafter, we want to summarise (i) the basic geochemical concepts necessary for the correct application of strontium isotopes, and (ii) 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. In fact, we believe that in science, a redundancy of bibliographic citations frequently distracts the reader from the topic addressed. Chemical definitions are reported in Appendix A, 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.

2. Strontium and Rubidium Isotopic Abundance, and Decay of ^{87}Rb

The term “isotopic abundance” is frequently used ambiguously in several papers. Thus, we remember that the isotopic abundance of the isotope ^AE of the element E is defined as the ratio $X_{AE} = n_{AE} / n_E$, 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 A). According to the literature, the approximate isotopic abundances of strontium [11] and rubidium [12] 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, the correct application of the isotopes of strontium needs basic knowledge of mineralogy, geology, and geochemistry.

At the low temperatures of the Earth’s 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.

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 is the decay energy (for physical-chemical definition see IUPAC—International Union of Pure and Applied Chemistry. 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,

$$v_{\text{decay}(t)} = -\frac{dn_{87\text{Rb}}}{dt} = \frac{dn_{87\text{Sr}}}{dt} = \lambda n_{87\text{Rb}(t)} \quad (2)$$

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

where dn_{87Rb} and dn_{87Sr} indicate very small variations of n_{87Rb} and n_{87Sr} in a very small time interval dt (approximate mathematical definition), 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 (1), the minus sign in front of dn_{87Rb} is present because, during decay, n_{87Rb} decreases with time, whereas n_{87Sr} increases.

From Equation (2), after simple mathematical manipulation (see Supplementary Material S1), the following general relations are obtained,

$$n_{87Rb(t)} = n_{87Rb(t_0)} e^{-\lambda(t-t_0)} \tag{3}$$

and

$$n_{87Rb(t_0)} = n_{87Rb(t)} e^{\lambda(t-t_0)} \tag{4}$$

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 $n_{87Rb(t)}$ from (4) and remembering that the loss of ^{87}Rb is equal to the gain of ^{87}Sr , we also write:

$$n_{87Sr(t)} - n_{87Sr(t_0)} = n_{87Rb(t_0)} - n_{87Rb(t)} = n_{87Rb(t)} (e^{\lambda(t-t_0)} - 1) \tag{5}$$

where the difference $n_{87Sr(t)} - n_{87Sr(t_0)}$ 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 for a closed system (no matter is changed with the environment) the number of the ^{86}Sr atoms is a constant value, independent on the time, dividing (5) by the constant n_{86Sr} value, we obtain:

$$\frac{n_{87Sr(t)}}{n_{86Sr}} - \frac{n_{87Sr(t_0)}}{n_{86Sr}} = \frac{n_{87Rb(t)}}{n_{86Sr}} (e^{\lambda(t-t_0)} - 1) \tag{6}$$

Relation (6) is usually written in terms of isotopic abundances as follows:

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

or, more simply,

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

3. The Strontium and Rubidium in Minerals

3.1. 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, $CaSO_4 \cdot 2H_2O$, and anhydrite, $CaSO_4$), carbonates (e.g., calcite and aragonite, $CaCO_3$, and dolomite, $CaMg(CO_3)_2$), plagioclase ($Na_{1-x}Ca_xAl_{1+x}Si_{3-x}O_8$), K-feldspar ($KAlSi_3O_8$), and apatite (simplified formula: $Ca_3(PO_4)_3(F, Cl, OH)$), a mineral that in the form of carbonate hydroxyl apatite, is the inorganic component of bones. It is noteworthy that 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 an ionic

radius of about 1.18 ($1 \text{ \AA} = 10^{-10} \text{ m}$) [13]. On the contrary, in calcite, Ca^{2+} and Sr^{2+} exist in sixfold coordination with an ionic radius of about 1.00 and 1.18, respectively.

Rubidium Rb^+ mostly replaces K^+ in trioctahedral micas, including illite. The number of effective coordination ranges from eleven to seven [14], the ionic radii for K^+ and Rb^+ being about 1.56 to 1.70 and 1.46 to 1.58, respectively. In K-feldspar, K^+ and Rb^+ are sevenfold coordinated [15] with ionic radii of about 1.46 and 1.56.

To conclude, 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-feldspar	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⁾

ppm wt = part per million in weight; our evaluation from the abundant literature; ⁽¹⁾ [16]; ^(*) 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 ppm wt.

3.2. Strontium Isotopes in Minerals and Whole Rock

In this paper, the term rock is also used for soil which, from a mineralogical and petrographic point of view, may be mostly regarded as 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.

3.3. Minerals as Constituents of the Rock

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

3.3.1. Monomineralic Consolidated/Unconsolidated Rock

The rock is formed only by a mineral (e.g., limestone and dolomitic rock consisting of the minerals calcite or aragonite, and the mineral 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. To summarise, the isotopic ratio may change over time, but at a given time, it will be the same in all the portions of the rock.

3.3.2. Polymineralic Consolidated/Unconsolidated Rock

(i) 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 [17]). In this case, the variation in the isotope ratio of the single mineral from the time of its formation to the time of the measurements depends largely on the original ⁸⁷Rb content of the single mineral. Summarising: (a) at the time of the rock generation, all the minerals had the same isotope ratio which, however, (b) during the time, change their value with different speed because of their different ⁸⁷Rb original content. The rock initially was mineralogically heterogeneous and homogeneous for the isotope ratio, whereas at the time of interest, it was both mineralogically and isotopically heterogeneous.

(ii) 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 in the strontium isotope ratio in the different minerals will be due both (a) to the original isotope values of the different rock-forming minerals and, obviously, (b) 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.

3.4. Variation in Strontium Isotopes in Different Minerals (i) and Strontium Isotopes in the Total Rock (Tot)

3.4.1. Different Decay Speed of ⁸⁷Rb in the Different Minerals

As reported above, usually, the different rock-forming minerals have different initial ⁸⁷Rb content, and thus, according to relations (2) and (5), the speed of ⁸⁷Sr generation is different for different minerals. Two minerals, calcite (simplified formula: CaCO₃) and muscovite (simplified formula: KAl₂[AlSi₃O₁₀] (OH)₂) both have the same initial $n_{87Sr(t_0)}/n_{86Sr}$ ratio (= 0.7060) but different rubidium content, as reported in Table 2.

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

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

$W_i = Q_i / (Q_{Cc} + Q_{Mu}) = Q_i / Q_{tot}$, 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 minerals Cc and Mu. $C_{Sr}^i = Q_{Sr}^i / Q_i$, 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; (t₀), 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 $C_{Sr}^{tot} = W_{Cc} \times C_{Sr}^{Cc} + W_{Mu} \times C_{Sr}^{Mu} = 0.30 \times 0.0800 + 0.70 \times 0.0070 = 0.0289 = 289$ ppm wt (ppm = parts per million).

Using relation (6), after $t - t_0 = 50$ million years from their generation, calcite will assume $n_{87Sr(t)}/n_{86Sr}$ equal to 0.7061 and muscovite equal to 0.7333. The variation for calcite, with a small rubidium amount, is so low because the decay speed of ⁸⁷Rb is very low for this mineral (see relation (3)), whereas for muscovite, the amount of rubidium is high, and thus, the speed of decay is high.

3.4.2. Relation of the Isotope Data for Minerals and for Whole Rock

The minerals 1, 2, . . . , φ indicated generically by the letter i, form 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 S2):

$$\frac{n_{87Sr}^{tot}}{n_{86Sr}^{tot}} \approx \sum_{i=1}^{\varphi} \left(\frac{C_{Sr}^i}{C_{Sr}^{tot}} W_i \frac{n_{87Sr}^i}{n_{86Sr}^i} \right) \quad (7)$$

Relation (4) is a particular expression of a mixing equation which gives a “weighted mean” of the isotope ratio n_{87Sr}/n_{86Sr} for the total rock. The $\frac{C_{Sr}^i}{C_{Sr}^{tot}} W_i$ values are mathematical weights of the different addends, i.e., values which estimate the contribution of the n_{87Sr}/n_{86Sr} 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_{Sr}^{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:

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

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

3.5. 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 and muscovite dissolution in pure water in conditions far from the solution saturation in these minerals. According to the literature (e.g., [18,19], 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 $m^{-2} s^{-1}$, 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 $m^{-2} s^{-1}$ ([20], 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 very high n_{87Sr}/n_{86Sr} 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 this calculation is reported in Supplementary Material S3, where we demonstrated that in a system consisting of calcite and of muscovite with a high n_{87Sr}/n_{86Sr} ratio, the isotope ratio of a water solution which dissolved calcite and muscovite will have an isotope ratio very close to that of calcite, not to that of the whole rock.

Calcite, aragonite, and Ca-sulphates are the most common Sr-rich rock-forming minerals which exhibit the highest solubility. 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 [21], 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 [21] and Petrini et al. [22]: Nardin-Lison, Sant’Anna, Lonigo, Pittarello. For all these localities, strontium for the isotopic determinations was extracted using both $CH_3 COONH_4$ (ammonium acetate) 1 M (pH \approx 7) and HCl 2.5 N (very acidic solution). The reason for using solutions with

different pH values is to consider the different conditions that may be present in the soil in natural conditions: from neutral to acidic (the second is the case when there is a lot of organic substance that decomposes). In practice, in the laboratory, two extreme and opposite conditions of dissolution were considered. For instance, at $\text{pH} \approx 7$, Ca-carbonates and Ca-sulphates are dissolved a moderate to low amount, whereas at a 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, statistically, it cannot be excluded that the average values obtained for solutions at $\text{pH} \approx 7$ and at very low pH values for the same soil sample are the same ($p_{\text{same mean}} = 0.20$, $p_{\text{same median}} = 0.23$). Since in the area there is no evidence of Ca-sulphate occurrence, and the phyllosilicates are, in both cases, poorly dissolved, the data obtained suggest the dominant role of carbonates. It is noteworthy, however, that different extraction methods in general do not give the same values of isotope ratio (see Section 4.2).

Moreover, the analysis of the whole soil after total dissolution gives largely higher strontium isotope values (this is not a realistic condition since, in nature, the dissolution of all the minerals that make up a rock does not occur). This demonstrates that the phyllosilicates present in the soil are only slightly dissolved when treated with neutral (acetate) or acid (HCl) solutions and represent residuals of old rocks with a high strontium isotope ratio. Thus, the total rock isotope data cannot be used for the evaluation of strontium isotopic features of available strontium.

To conclude, 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 animals; rather, the single phases present in the rock are relevant.

3.6. Sorption/Desorption and Minerals

Clay minerals, such as smectite, illite, and kaolinite, as well as 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, [23–25]). 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 the solution only a very small amount of strontium. This, for instance, may sometimes occur when the rocks consist of common rock-forming silicates.

4. Strontium Isoscapes and Their Use in Archaeology

4.1. General

Geochemical prospecting includes any method of mineral exploration based on systematic measurement of one or more chemical properties of a naturally occurring material ([26], 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. [27], is no more than a graphical representation, obtained with the aid of a geographic information system (GIS), of the results of isotope geochemical prospecting.

The use of strontium isoscapes in archaeological and biogeochemical sciences needs great caution for the following reason:

- (i) Isoscapes generally refer to large-scale grid sampling with cells in the order of tens or hundreds of km^2 , and in nature, variation in the strontium isotope ratio does not necessarily merge continuously from one value to another, but it may be sharp, even between neighboring sites when they are located on the boundary between different geological formations. A good example of this condition is reported by Montgomery et al. [5]. Moreover, frequently, sampling for isoscapes is not randomly distributed in the area of interest. For instance, in Italy, covering an area of

302.073 km², Lugli et al. [28] used 1920 data of the ⁸⁷Sr/⁸⁶Sr ratio: on average, one sample for 157 km²; in France, Willmes et al. [29] used data referring to 840 sites for an area of 551.626 km²: one sampling grid for 657 km²! The criteria for sampling, including the sampled materials, is another important point. In the isoscape of Italy, Lugli et al. [28] include data related to 'plant', 'water', 'biomineral' (i.e., bones, teeth, and bio-calcareous shells), 'food', 'soil' (including both exchangeable soil fractions and bulk soils) and 'rock' (mainly evaporites, metamorphic and magmatic rocks, and a few sedimentary bulk rocks). Thus, at best, the most common isoscapes can only give generic indications for wide areas.

- (ii) As a general rule, the sampling grid used to perform isoscapes and local investigations 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.

4.2. Archaeological Investigation and Present-Day Environmental Condition

For a detailed discussion about problem of material selection for the strontium isotope measurements of archaeological and present-day environmental samples, we address the reader to Holt et al. [7]. In addition to the observations of Holt et al. [7], we remember that the determination of bioavailable strontium in soil in some amount depends on the method used for strontium extraction. For instance, for the same soil sample, we obtained a value of 0.707743 using extraction with water at pH \cong 5.7 (pure water initially in equilibrium with CO₂ of the atmosphere, P_{CO₂} \cong 10^{-3.5} bar) and a value of 0.708139 using extraction with CH₃COONH₄ (ammonium acetate) 1 M. This discrepancy may generate a bias in the data distribution.

In archaeological research, the first important question is: does soil always maintain the isotopic features it had in the past in an area of interest? We need a correct answer to this question when we want to use a present-day isoscape as an indicator of past conditions. In addition to climate modification, geomorphological, and mineralogical changes due to erosion of the soil and/or deposition of allogenic material by water flows, wind, anthropic land management, and chemical processes may generate important geochemical variations. For instance, soil rich in organic material may produce a large increase in CO₂ partial pressure in water solutions migrating in the soil, which increases the 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 environmental water and/or to mineralogical variations in the soil over time, are reported by Åberg [3].

5. 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: in particular, archaeologists need data referring to the past, not to the present; biologists possibly need data referring to the past and/or to the present. This implies different type of sampling and strontium archives.

- (i) Sampling should be random to avoid bias of the data obtained on the statistical population sample. Homogenized sampling, where several samples are collected in a defined small area and then reduced to only one homogenized sample for analysis [7], in our opinion, is not a good method, because in this way, the variance in the data population for the area of interest is reduced. This could make definition of allogenuous samples and comparison with other areas impossible.
- (ii) 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 areas (up to one km² as an order of magnitude), isotope

data, at best, may exhibit variation in the fourth decimal digit (see, for instance, [24]). If that is so, two samples could be considered as having approximately 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 in isotope data for the area of interest.

- (iii) Are the sampled biological remains from the same site? The answer depends on (a) the spatial definition of “same site” and (b) how we define the belonging of biological remains to the area of interest.
- (a) Spatial definition depends, of course, on the aim of the investigation. In other words, we go back to the investigation scale. For instance, Cavazzuti et al. [30], in studying human settlements located in the Po plain (Northern Italy), assume that the settlements, although far, occur in a very “homogeneous” (it is not clear what they mean: isotopically homogeneous, mineralogically homogeneous, or both?) flat area without geographical barriers. They define three different areas around each settlement with a 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.
- (b) The belonging of human or, in general, animal remains to the area of interest depends on how we operationally define this belonging. Operatively, the minimum time of belonging may be evaluated through the mean residence time of calcium or strontium in bones. The mean residence time, however, depends on the bone type and on the age of the individuals. For instance, the turnover for femur is about 25–30 years, whereas for ribs is about 5–10 years. Therefore, using the ribs of an individual from another area, the individual will be found to belong to the area of interest approximately 5–10 years after its arrival. Instead, using the femur, it will appear to belong to that area after 25–30 years. Thus, in a defined area, using contemporaneously data from femur and rib, the variability in the strontium data may increase. This is not sufficiently considered in the scientific papers.
- (iv) Before sampling, the geology and mineralogy of the area should be carefully considered to give an idea of the dominant mineral sources.
- (a) An accurate geological analysis suggests that, reasonably, the soil of the area of interest did not change its mineralogical and geochemical characteristics from the time of the settlement to the present. Under this condition, the isotopic prospecting of the available strontium of the present-day soil and plants is the most elementary way for determining the isotope reference background which the biological remains of the area of interest may be compared to.
- (b) There is evidence or suspect that the mineralogy and geochemistry of the area are not preserved; obviously, present day material cannot be used to define the geochemical background of the area. In this case, different biological remains (teeth, bones, shells, seeds, et cetera) may be used. In the event of an area of interest having no archaeological evidence (different types of burial, funerary objects, behaviour of the different animal species, etc.), suggesting a different provenance of human or animal remains, all the last ones must be considered as *potentially* belonging to the settlement of interest. It is evident that in this way, the variability in the isotope data could be significantly expanded, and some external individuals could be attributed to the settlement.
- (v) If possible, the variability in the data should be defined using a high number of analyses obtained from different individuals (indicatively, more than 15; the use of too few samples may be misleading). For each area, in case the data have normal distribution, data far from the prevalent distribution values could be identified with some statistical method. For instance:

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

here, assumed very similar to the theoretical standard deviation, σ , is 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. Using $k = 3$, there is only a very small probability (less than about 1%) that a sample will be mistakenly excluded from the group to which it belongs. 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 case the distribution of data is not normal, non-parametric statistics may be used, for instance, the “kernel density estimation” (KDE) (see [31], statistical software PAST 4.15). Supplementary Material S4 report an exemplum fictum of calculation.

- (vi) In general, we can only establish if the analyzed individuals *may* belong to the same group, not that they do 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 from one another. This happens, for example, if the individuals come from areas located on carbonate formations of a 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 grown on hydrothermalised carbonate formations from the Late Carnian to Liassic ages have very similar isotopic values (about 0.7083 ± 0.0003 , our unpublished data), even if they are located many kilometers away from one another. On the contrary, samples coming from the same hypothetical locality straddling Cretaceous and Late Carnian–Liassic formations exhibit significant isotopic differences already on the fourth digit (Cretaceous carbonate, 0.7077 against Late Carnian–Liassic carbonates, 0.7083) (see also [5]).

6. Summary

We tried to explain how the use of strontium isotopes may be sometimes problematic in archaeological research. These are the main points to be used as a vade mecum when approaching strontium isotope study in archaeology:

- (i) We cannot assume that the current geochemical, mineralogical, and geological conditions of the investigated area are the same as in the past because variation in the surface conditions is frequent also during a short time.
- (ii) The use of large-scale isoscapes is risky because local investigation is usually performed on a smaller scale.
- (iii) Before studying human, animal, and plant remains, an accurate control of their diagenetic condition is essential because pollution of the samples by environmental strontium-bearing material with different isotope ratios is very easy (for instance, diagenesis with dissolution/deposition of carbonate).
- (iv) The samples (soil, human/animal remains, plants, etc.) should be selected randomly. Usually, this is not considered in the literature.

- (v) To reach a reliable scientific conclusion, the investigation of a large number of remains and related measurements is necessary. Without a large number of data, comparison between different areas is risky (statistically insignificant).
- (vi) If samples fall outside the prevalent distribution interval, we can state that they do not belong to the same group. The individuals falling in the prevailing distribution interval do not necessarily belong to the same group; we can only state that it is not excluded they belong to the same group.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/quat7010006/s1>.

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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 (${}^A_Z\text{E}_N$): 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: $X_{A\text{E}} = n_{A\text{E}} / n_{\text{E}}$, where $n_{A\text{E}}$ 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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