

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

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Supplementary material, S

S1

Integrating equation

$$V_{\text{decay}}(t) = - \frac{dn_{^{87}\text{Rb}}}{dt} = \frac{dn_{^{87}\text{Sr}}}{dt} = \lambda n_{^{87}\text{Rb}}(t)$$

with initial condition at the time t_0 , we obtain:

$$\ln \frac{n_{^{87}\text{Rb}}(t)}{n_{^{87}\text{Rb}}(t_0)} = - \lambda (t - t_0)$$

and

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

where \ln indicates the natural logarithm, t is the time of interest, t_0 is the initial time when the number of ^{87}Rb atoms is $n_{^{87}\text{Rb}}(t_0)$, and e is the Neper's number ($e = 2.71828 \dots$).

S2

For the mineral phases 1, 2, ..., ϕ , we have:

$$n_{^{87}\text{Sr}}^{\text{tot}} = \sum_{i=1}^{\phi} n_{^{87}\text{Sr}}^i$$

Dividing $n_{^{87}\text{Sr}}^{\text{tot}}$ and the generic value $n_{^{87}\text{Sr}}^i$ by $n_{^{86}\text{Sr}}^{\text{tot}}$ and multiplying by $n_{^{86}\text{Sr}}^i$, and considering the isotopic abundances X , we obtain:

$$\frac{X_{^{87}\text{Sr}}^{\text{tot}}}{X_{^{86}\text{Sr}}^{\text{tot}}} = \sum_{i=1}^{\phi} \left(\frac{n_{^{86}\text{Sr}}^i}{n_{^{86}\text{Sr}}^{\text{tot}}} \frac{n_{^{87}\text{Sr}}^i/n_{^{86}\text{Sr}}^i}{n_{^{86}\text{Sr}}^i/n_{^{86}\text{Sr}}^{\text{tot}}} \right) = \sum_{i=1}^{\phi} \left(\frac{n_{^{86}\text{Sr}}^i}{n_{^{86}\text{Sr}}^{\text{tot}}} \frac{X_{^{87}\text{Sr}}^i}{X_{^{86}\text{Sr}}^i} \right) \quad (1)$$

The ratios $n_{^{86}\text{Sr}}^i/n_{^{86}\text{Sr}}^{\text{tot}}$ for each mineral 1, 2, ..., ϕ is a mathematical weight which evaluates the role of the different phases in defining the isotopic features of the total rock, tot, formed by the minerals 1, 2, ..., ϕ .

The ratio $n_{86\text{Sr}}^i/n_{86\text{Sr}}^{\text{tot}}$ is frequently substitutes by the $n_{\text{Sr}}^i/n_{\text{Sr}}^{\text{tot}}$ ratio, where n_{Sr}^i and $n_{\text{Sr}}^{\text{tot}}$ are the number of strontium atoms in the mineral i and in the total rock, tot, respectively. Thus:

$$\frac{x_{87\text{Sr}}^{\text{tot}}}{x_{86\text{Sr}}^{\text{tot}}} \cong \sum_{i=1}^{\varphi} \left(\frac{n_{\text{Sr}}^i}{n_{\text{Sr}}^{\text{tot}}} \frac{x_{87\text{Sr}}^i}{x_{86\text{Sr}}^i} \right) \quad (2)$$

Multiplying and dividing (2B) by the atomic weight, AW_{Sr} , of strontium, we obtain

$$\frac{n_{87\text{Sr}}^{\text{tot}}}{n_{86\text{Sr}}^{\text{tot}}} \cong \sum_{i=1}^{\varphi} \left(\frac{AW_{\text{Sr}} n_{\text{Sr}}^i}{AW_{\text{Sr}} n_{\text{Sr}}^{\text{tot}}} \frac{x_{87\text{Sr}}^i}{x_{86\text{Sr}}^i} \right) = \sum_{i=1}^{\varphi} \left(\frac{Q_{\text{Sr}}^i}{Q_{\text{Sr}}^{\text{tot}}} \frac{x_{87\text{Sr}}^i}{x_{86\text{Sr}}^i} \right) \quad (3)$$

where Q represents the different masses. Multiplying and dividing for the mass of the minerals 1, 2, ..., φ and of the total rock, tot, is

$$\begin{aligned} \frac{x_{87\text{Sr}}^{\text{tot}}}{x_{86\text{Sr}}^{\text{tot}}} &= \frac{Q_{\text{Sr}}^1/Q_1}{Q_{\text{Sr}}^{\text{tot}}/Q_{\text{tot}}} \frac{Q_1}{Q_{\text{tot}}} \frac{x_{87\text{Sr}}^1}{x_{86\text{Sr}}^1} + \frac{Q_{\text{Sr}}^2/Q_2}{Q_{\text{Sr}}^{\text{tot}}/Q_{\text{tot}}} \frac{Q_2}{Q_{\text{tot}}} \frac{x_{87\text{Sr}}^2}{x_{86\text{Sr}}^2} + \dots + \frac{Q_{\text{Sr}}^{\varphi}/Q_{\varphi}}{Q_{\text{Sr}}^{\text{tot}}/Q_{\text{tot}}} \frac{Q_{\varphi}}{Q_{\text{tot}}} \frac{x_{87\text{Sr}}^{\varphi}}{x_{86\text{Sr}}^{\varphi}} = \\ &= \frac{C_{\text{Sr}}^1}{C_{\text{Sr}}^{\text{tot}}} W_1 \frac{x_{87\text{Sr}}^1}{x_{86\text{Sr}}^1} + \frac{C_{\text{Sr}}^2}{C_{\text{Sr}}^{\text{tot}}} W_2 \frac{x_{87\text{Sr}}^2}{x_{86\text{Sr}}^2} + \dots + \frac{C_{\text{Sr}}^{\varphi}}{C_{\text{Sr}}^{\text{tot}}} W_{\varphi} \frac{x_{87\text{Sr}}^{\varphi}}{x_{86\text{Sr}}^{\varphi}} = \\ &= \sum_{i=1}^{\varphi} \left(\frac{C_{\text{Sr}}^i}{C_{\text{Sr}}^{\text{tot}}} W_i \frac{x_{87\text{Sr}}^i}{x_{86\text{Sr}}^i} \right) \end{aligned} \quad (4)$$

where $C_{\text{Sr}}^1, C_{\text{Sr}}^2, \dots, C_{\text{Sr}}^{\varphi}$ and $C_{\text{Sr}}^{\text{tot}}$ are the weight concentrations of strontium in the minerals 1, 2, ..., φ and in the total rock, tot, and $W_1=Q_1/Q_{\text{tot}}$, $W_2=Q_2/Q_{\text{tot}}$, ..., $W_{\varphi}=Q_{\varphi}/Q_{\text{tot}}$, the relative weight abundance of the different minerals in the total rock. It is noteworthy that (2) -and thus (3)- are rigorously correct only in case the ratio $n_{86\text{Sr}}/n_{\text{Sr}}$ is the same for all the minerals, as demonstrated below.

Consider the number of atoms $n_{86\text{Sr}}^i$ and the number of atoms of total strontium n_{Sr}^i in the generic mineral i and $n_{86\text{Sr}}^{\text{tot}}$ and $n_{\text{Sr}}^{\text{tot}}$ in the total rock, tot. In any mineral i as well as in the total rock, tot, the number of moles $n_{86\text{Sr}}$ will be related to total strontium, n_{Sr} , present in the single phase i or in the total rock, tot. Thus, for any phases and for the total rock we may write the isotope abundance:

$$\frac{n_{86\text{Sr}}^i}{n_{\text{Sr}}^i} = x_{86\text{Sr}}^i \quad (5)$$

$$\frac{n_{86\text{Sr}}^{\text{tot}}}{n_{\text{Sr}}^{\text{tot}}} = X_{86\text{Sr}}^{\text{tot}} \quad (6)$$

Dividing (5) by (6) and rearranging, we write:

$$\frac{n_{86\text{Sr}}^i}{n_{86\text{Sr}}^{\text{tot}}} = \frac{X_{86\text{Sr}}^i}{X_{86\text{Sr}}^{\text{tot}}} \frac{n_{\text{Sr}}^i}{n_{\text{Sr}}^{\text{tot}}} \quad (7)$$

From equation (7), it is evident that equation (2) and (3) may be used in place of (1) only in case for all the different minerals 1, 2, ..., ϕ and, thus, for the total rock,

tot, the $X_{86\text{Sr}}$ values are the same, i.e., $\frac{X_{86\text{Sr}}^i}{X_{86\text{Sr}}^{\text{tot}}} = 1$

S3

Consider equation (3B) referred to the aqueous solution, aq:

$$\frac{X_{87\text{Sr}}^{\text{aq}}}{X_{86\text{Sr}}^{\text{aq}}} \cong \sum_{i=1}^{\phi} \left(\frac{Q_{\text{Sr}}^{\text{aq}(i)}}{Q_{\text{Sr}}^{\text{aq}}} \frac{X_{87\text{Sr}}^i}{X_{86\text{Sr}}^i} \right) = \sum_{i=1}^{\phi} \left(W_{\text{Sr}}^{\text{aq}(i)} \frac{X_{87\text{Sr}}^i}{X_{86\text{Sr}}^i} \right) \quad (1)$$

where aq refers to the total number of the strontium nuclides transferred in solution from the minerals and aq(i) to the number of nuclides transferred to the aqueous solution by the dissolution of the mineral i, and $W_{\text{Sr}}^{\text{aq}(i)}$ indicates the relative contribution of the mineral i to the total strontium transferred into solution.

In conditions far from the solution saturation in calcite and muscovite, in agreement with the kinetic values reported in the text, for calcite and muscovite dissolution in water, aq, we write:

$$\frac{n_{\text{Cc}}^{\text{aq}}}{n_{\text{Mu}}^{\text{aq}}} \cong 10^5 \quad (2)$$

Given the formula weight equal to $GF_{\text{Cc}} = 100.09$ g/mole for calcite and $GF_{\text{Mu}} = 316.32$ g/mole for muscovite and considering the relation (2), for the mass $Q_{\text{Cc}}^{\text{aq}}$ of calcite and the mass $Q_{\text{Mu}}^{\text{aq}}$ of muscovite transferred into solution, the following relation holds:

$$\frac{Q_{\text{Cc}}^{\text{aq}}}{Q_{\text{Mu}}^{\text{aq}}} = \frac{GF_{\text{Cc}} n_{\text{Cc}}^{\text{aq}}}{GF_{\text{Mu}} n_{\text{Mu}}^{\text{aq}}} = 10^5 \frac{GF_{\text{Cc}}}{GF_{\text{Mu}}} \rightarrow Q_{\text{Cc}}^{\text{aq}} = 0.32 \times 10^5 Q_{\text{Mu}}^{\text{aq}}$$

Consider now a rock with muscovite and calcite. In the example of Table S3; we have:

$$Q_{Cc}^{aq} = 0.32 \times 10^5 Q_{Mu}^{aq}$$

$$Q_{Cc}^{aq} + Q_{Mu}^{aq} = Q_{tot}^{aq}$$

Combining the two equations, we obtain:

$$Q_{Mu}^{aq} = \frac{Q_{tot}^{aq}}{1 + 0.32 \times 10^5} = 3.1249_{02} \times 10^{-5} Q_{tot}^{aq}$$

$$Q_{Cc}^{aq} = (1 - 3.1249_{02}) Q_{tot}^{aq} = 0.99996_{88} Q_{tot}^{aq}$$

where small digits have not physical significance but are reported only to make calculation more evident. Thus, the mass of strontium transferred from the minerals to the solution is calculated as follows:

$$Q_{Sr}^{aq(Cc)} = C_{Sr}^{Cc} \times Q_{Cc}^{aq} = 0.080 \times 0.99996_{88} Q_{tot}^{aq} = 0.079997_{50} Q_{tot}^{aq}$$

$$Q_{Sr}^{aq(Mu)} = C_{Sr}^{Mu} \times Q_{Mu}^{aq} = 0.007 \times 3.1249_{02} \times 10^{-5} = 0.021874_{31} \times 10^{-5} Q_{tot}^{aq}$$

Strontium transferred from calcite is very high in comparison to that from muscovite. We omit other calculations, which are evident in Table S3.

Table S3. Example of strontium isotope calculation for a water which dissolves calcite (Cc) and muscovite (Mu)

$W_{Cc} = Q_{Cc}/(Q_{Cc} + Q_{Mu})$	0.30	$W_{Mu} = Q_{Mu}/(Q_{Cc} + Q_{Mu})$	0.70
C_{Sr}^{Cc}	0.080	C_{Sr}^{Mu}	0.007
C_{Sr}^{Cc}/C_{Sr}^{tot}	0.919540 ₂₃	C_{Sr}^{Mu}/C_{Sr}^{tot}	0.080459 ₇₃
Q_{Cc}^{aq}	$0.99996_{88} Q_{tot}^{aq}$	Q_{Mu}^{aq}	$3.1249_{02} \times 10^{-5} Q_{tot}^{aq}$
$Q_{Sr}^{aq(Cc)} = C_{Sr}^{Cc} Q_{Cc}^{aq}$	$0.079997_{50} Q_{tot}^{aq}$	$Q_{Sr}^{aq(Mu)} = C_{Sr}^{Mu} Q_{Mu}^{aq}$	$0.021874_{31} \times 10^{-5} Q_{tot}^{aq}$
$W_{Sr}^{aq(Cc)} = \frac{Q_{Sr}^{aq(Cc)}}{Q_{Sr}^{aq(Cc)} + Q_{Sr}^{aq(Mu)}} = \frac{Q_{Sr}^{aq(Cc)}}{Q_{Sr}^{aq}}$	0.99999 ₇₂	$W_{Sr}^{aq(Mu)} = \frac{Q_{Sr}^{aq(Mu)}}{Q_{Sr}^{aq(Cc)} + Q_{Sr}^{aq(Mu)}} = \frac{Q_{Sr}^{aq(Mu)}}{Q_{Sr}^{aq}}$	$0.27372_{99} \times 10^{-5}$
$n_{87Sr}^{Cc}/n_{86Sr}^{Cc}$	0.70700	$n_{87Sr}^{Mu}/n_{86Sr}^{Mu}$	0.8105
$\frac{n_{87Sr}^{aq}}{n_{86Sr}^{aq}} \approx W_{Sr}^{aq(Cc)} \frac{n_{87Sr}^{Cc}}{n_{86Sr}^{Cc}} + W_{Sr}^{aq(Mu)} \frac{n_{87Sr}^{Mu}}{n_{86Sr}^{Mu}} = 0.99999_{72} \times 0.7070 + 0.27372_{99} \times 10^{-5} \times 0.8105 = 0.7070_{00239}$			

W_{Cc} and W_{Mu} , relative weigh amount of Cc and Mu in the total rock. $C_{Sr}^i = Q_{Sr}^i/Q_i$, strontium concentration in the mineral i and $C_{Sr}^{tot} = Q_{Sr}^{tot}/Q_{tot}$, strontium concentration in the total rock. Q_{Cc}^{aq} and Q_{Mu}^{aq} , mass of Cc and Mu transferred from the mineral into solution. $Q_{Sr}^{aq(Cc)}$ and $Q_{Sr}^{aq(Mu)}$, mass of strontium transferred from Cc and Mu into solution. $Q_{Sr}^{aq(Cc)}$ and $Q_{Sr}^{aq(Mu)}$, mass of strontium transferred from Cc and Mu into solution. $W_{Sr}^{aq(Cc)}$ and $W_{Sr}^{aq(Mu)}$, relative weight amount of strontium transferred from Cc and Mu into solution. Digits are reported in excess (small character) for a better comprehension of the calculations.

Assume that, for each investigated archaeological Area 1 and Area 2 we dispose of twenty data of n_{87Sr}/n_{86Sr} obtained on twenty remains collected randomly. We want to verify if the remains *may* be referred to the same group or not. This, of course, depends on the way we use to define the group. In case the distribution of data is statistically “normal” (normality verified, for instance, using the Shapiro-Wilk and Anderson-Darling normality tests), in order of stating that a sample *may* belong to the group of interest, we may use the “contrast” value (“contrast” ≤ 1). On the contrary, if the data distribution is not “normal”, we can use “kernel density”. The “kernel density” estimation is a non-parametric method to estimate the probability density function of a random variable, a method based on *kernel*, which is a smoothing parameter. In the example reported in Table S4-Area 1, the data have “normal” distribution and thus the value of the “contrast” is useful for the attribution of the single sample to the group. In our case, all samples exhibit “contrast” ≤ 1 : thus, we *cannot exclude* that all the samples come from the same group. The data from Area 2, have not “normal” distribution; thus, the parameter “contrast” is not significant. In this case, in our opinion, is better to use the “kernel density” as reported in Fig. S4-Area 2. In this diagram, the distribution simulates bimodal distribution: three samples (0.7086, 0.7089, and 0.7091) are far from the main group. Thus, we state that they may be regarded as not belonging to the group. Note that in case one group merges into the other, for some samples the attribution to one group or to the other could result difficult.

Table S4. Data for two different areas (*exemplum fictum*)

<i>Area 1</i>	<i>Contrast</i>	<i>Area 2</i>
0.7069	0.998	0.7069
0.7076	0.999	0.7076
0.7075	0.999	0.7086
0.7074	0.999	0.7089
0.7071	0.999	0.7091
0.7075	0.999	0.7075
0.7073	0.999	0.7073
0.7074	0.999	0.7074
0.7071	0.999	0.7071

0.7070	0.998	0.7070
0.7072	0.999	0.7072
0.7077	0.999	0.7078
0.7076	0.999	0.7079
0.7073	0.999	0.7073
0.7074	0.999	0.7074
0.7071	0.999	0.7071
0.7072	0.999	0.7072
0.7074	0.999	0.7074
0.7077	0.999	0.7077
0.7078	1.000	0.7079

Normality test, $p(\text{normal})$

Shapiro-Wilk	0.81
Anderson-Darling	0.78
Number of data	20
Average, \bar{x}	0.7073 ₆
Standard deviation, s	0.0002 ₅
Threshold, $\bar{x} + 3s$	0.7081 ₁

Normality test, $p(\text{normal})$

Shapiro-Wilk	0.0057
Anderson-Darling	0.0050
Number of data	20
Average, \bar{x}	0.7076 ₂
Standard deviation, s	0.0006 ₁
Threshold, $\bar{x} + 3s$	0.7094 ₅

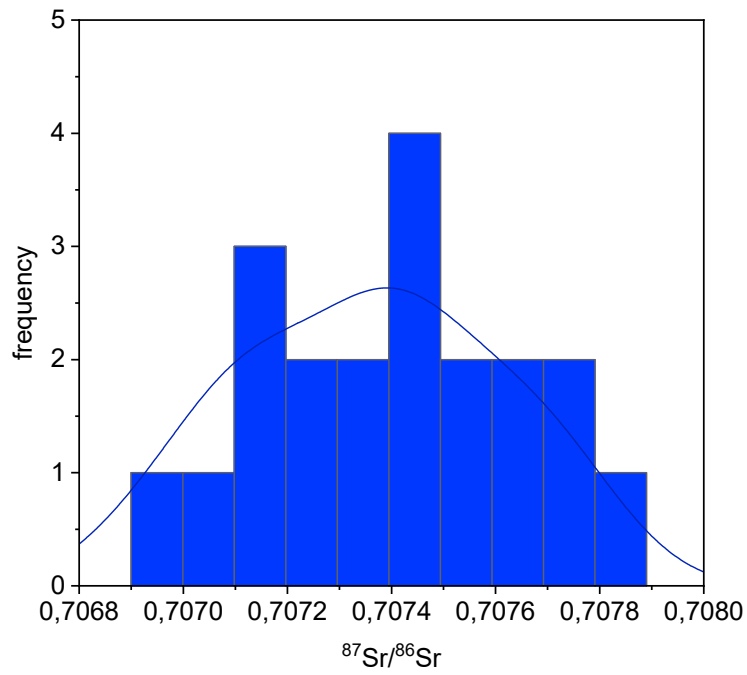


Figure S4-Area 1. “Kernel density” for data of Area 1. Apparently, we could assume that all samples belong to the same group.

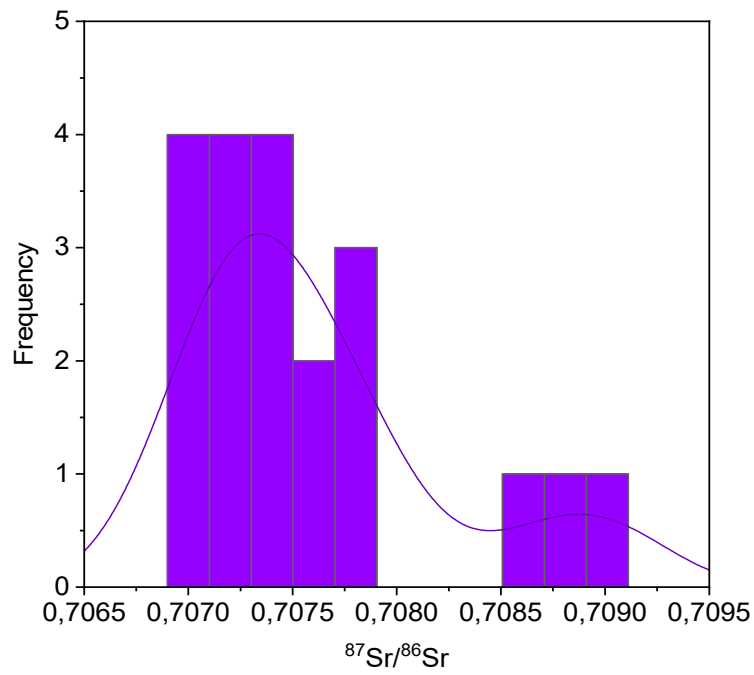


Figure S4-Area 2. “Kernel density” for data of Area 2; the distribution is “bimodal”. Three samples are far from the main group and, thus, we could assume that they belong to a different group.