A strontium isoscape of Italy for provenance studies

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Abstract

We present a novel database of environmental and geological $^{87}Sr/^{86}Sr$ values (n = 1920) from Italy, using literature data and newly analysed samples, for provenance purposes. We collected both bioavailable and non-bioavailable (i.e. rocks and bulk soils) data to attain a broader view of the Sr isotope variability of the Italian peninsula. These data were used to build isotope variability maps, namely isoscapes, through Kriging interpolations. We employed two different Kriging models, namely Ordinary Kriging and Universal Kriging, with a geolithological map of Italy categorized in isotope classes as external predictor. Model performances were evaluated through a 10-fold cross validation, yielding accurate $^{87}Sr/^{86}Sr$ predictions with root mean squared errors (RMSE) ranging between 0.0020 and 0.0024, dependent on the Kriging model and the sample class. Overall, the produced maps highlight a heterogeneous distribution of the $^{87}Sr/^{86}Sr$ across Italy, with the highest radiogenic values (>0.71) mainly localized in three areas, namely the Alps (Northern Italy), the Tuscany/Latium (Central Italy) and Calabria/Sicily (Southern Italy) magmatic/metamorphic terrains. The rest of the peninsula is characterized by values ranging between 0.707 and 0.710, mostly linked to sedimentary geological units of mixed nature. Finally, we took advantage of the case study of Fratta Polesine, to underscore the importance of choosing appropriate samples when building the local isoscape and of exploring different end-members when interpreting the local Sr isotope variability in mobility and provenance studies. Our user-friendly maps and database are freely accessible through the Geonode platform and will be updated over time to offer a state-of-the-art reference in mobility and provenance studies across the Italian landscape.

Keywords: $^{87}Sr/^{86}Sr$ ratio; Kriging; isotope map; spatial modelling; traceability.

1. Introduction

Geology is biological destiny: Whatever minerals land or are deposited in a place determine what or who can make a living there millions of years later.

(Dennis Overby 2021, New York Times)

The provenance of foods, artifacts, animals and individuals is a central topic in archaeology, ecology, forensic science and even in social sciences and humanities. A broad range of methods from genetics to inorganic chemistry can be used to disentangle the geographical origin or the movement of goods/people across the landscape, depending on the nature of the material itself (see e.g. Gregoricka, 2021; Tommasini et al., 2018). Isotope fingerprinting is applied to a variety of samples (e.g. biological tissues, artifacts, rocks, waters) using various isotope systematics of elements such as oxygen (e.g. Pellegrini et al., 2016; Pederzani and Britton, 2019), hydrogen (e.g. Soto et al., 2013), lead (e.g. Vautour et al., 2015; Smith et al., 2019; Killick et al., 2020), strontium (e.g. Bentley, 2006), and sulphur (e.g. Bataille et al., 2021) targeting the different materials depending on the element abundance in the sample and the geobiological process under investigation. In this sense, the radiogenic strontium ratio ($^{87}Sr/^{86}Sr$) is an excellent tracer of low temperature terrestrial processes for the abundance of elemental Sr and its mobility between the bio-, geo-, and hydro-spheres. While ^{87}Sr is the radiogenic-daughter of ^{87}Rb, ^{86}Sr is stable. Since both strontium and rubidium are ubiquitously present as trace elements within the Earth's crust, crustal rocks will thus acquire different $^{87}Sr/^{86}Sr$ ratios in relation to their age and to their initial Sr and Rb contents (Faure and Mensing, 2005). Ultimately, this results in a high-variability of the $^{87}Sr/^{86}Sr$ across the landscape (see e.g. Voerkelius et al., 2010). From the bedrock, Sr is transferred to soil, where it mixes with different local pools as surface waters, groundwaters and atmospheric depositions (Bentley, 2006). This is also why 'bioavailable' Sr (i.e. biologically available) might be isotopically different from the bedrock reservoir. In addition, the contribution of different minerals to the soil pool is variable due to i.e. differential weathering, Sr/Rb content and solubility (Sillen et al., 1998). For example, the contribution of Sr-rich carbonates to the local bioavailable reservoir is much larger than e.g. a more resistant to weathering Sr-rich silicate.

Sr ions exchanges at the Earth surface carry the isotopic fingerprint shaped over time by the radioactive decay of ^{87}Rb and transfer certain isotopes proportions from rocks to soils and waters. From the soil and water, Sr ions enter the ecosystem reaching plants, through root uptake, and animals, through food and drinking water (Capo et al., 1998). In vertebrates, Sr is then mainly fixed in the hydroxyapatite of tooth and bone tissues substituting calcium (Pors Nielsen, 2004). Across this pathway, mass-dependent Sr isotopic fractionation, as shown by e.g. the relative depletion of the stable $^{88}Sr/^{86}Sr$ ratio along the food chain, is likely to occur (Knudson et al., 2010). However, the fractionation of the $^{87}Sr/^{86}Sr$ ratio is deemed to be negligible and, anyhow, corrected during mass spectrometry analyses as constant normalization to an internationally accepted ratio (Ehrlich et al., 2001).

Sr isotope data from biological samples of interest can be then compared with the local bioavailable Sr isotope ratio in order to understand whether the tissue formed locally or in a geologically different place, tracking the movements of people and goods through space and time (Ericson, 1985; Slovak and Paytan, 2012). Therefore, the subsequent step is to pin-point (more or less precisely) the specific geographic origin of the sample. In this sense, comparison with (inter)national geological maps can help to track the provenance of tissues formed on substrate whose isotopic ratio can be somehow predicted or expected, as for example in old metamorphic crystalline basements (i.e. highly radiogenic Sr isotope values) or depleted mantle-derived magmatic areas (low radiogenic Sr isotope values). Yet, a step-forward in isotope fingerprinting is the building of comparative isotopic maps that show the spatial distribution of the isotope signature (Bowen, 2010).

Using patchily-distributed measures of environmental samples, it is possible to build spatial models able to predict the local bioavailable $^{87}Sr/^{86}Sr$ ratio of a specific area. These data are then modelled through geostatistic tools in order to predict at best the $^{87}Sr/^{86}Sr$ ratio of areas with no available data. The resulting prediction maps are known as isoscapes. The utility of such implements has been demonstrated in several fields and they are today largely employed in provenance studies, as baselines for tracking the provenance of unknown specimens (e.g. Hobson et al., 2010; Muhlfeld et al., 2013; Song et al., 2014; Chesson et al., 2018; Colleter et al., 2021; Lazzerini et al., 2021). So far, national isoscapes have been produced for several European and extra-European countries, employing and testing several different methods for the spatial interpolation, including machine learning (Montgomery et al., 2006; Evans et al., 2010; Frei and Frei, 2011; Bataille and Bowen, 2012; Pestle et al., 2013; Hartman and Richards, 2014; Copeland et al., 2016; Kookter et al., 2016; Laffoon et al., 2017; Bataille et al., 2018; Hedman et al., 2018; Willmes et al., 2018; Adams et al., 2019; Ladegaard-Pedersen et al., 2020; Scaffidi and Knudson, 2020; Snoeck et al., 2020; Wang et al., 2020; Frank et al., 2021; Funck et al., 2021; Washburnet al., 2021; Zieliński et al., 2021). Although a large amount of 'bioavailable' Sr data was produced in the past, mostly linked to food provenance and archaeological studies, a national isoscape for Italy is still lacking. A first attempt has been done by Emery et al.

(2018), where an inverse distance weighting (IDW) interpolation was tested using some literature data to produce a preliminary Italian isoscape.

Here, we extended the database presented by Emery et al. (2018), using both novel and published data, and we performed a robust geospatial modelling, employing Ordinary Kriging and Universal Kriging (Willmes et al., 2018). Kriging is a widely used regression method in geostatistics and is based on the principle of 'spatial autocorrelation' (Krige, 1951). This consists in best-fitting a mathematical function (i.e. variogram) to a predetermined number of points with the aim of determining the output value for unknown locations and thus generating a continuous surface map (Oliver and Webster, 1990). We produced maps of Italy exploiting the Kriging methods and using an extensive dataset, which includes both 'bioavailable' and 'non-bioavailable' Sr isotope values (available at geochem.unimore.it/sr-isoscape-of-italy). The latter integrates bulk rock values from magmatic and metamorphic rocks. We acknowledge that to understand the provenance of biological samples, the best approach is to compare their isotopic fingerprint to bioavailable Sr isotope data. However, the inclusion of sparse rock values allowed us to understand the 'weight' of the bedrock influence on the local Sr isotope composition in specific areas of Italy. For this reason, we ultimately generated two maps, one with exclusively bioavailable data and one that includes all the values from the dataset. Maps are freely accessible at geochem.unimore.it/sr-isoscape-of-italy, through the GeoNode platform (geonode.org).

2. Data and methods

2.1 Sample selection

Strontium isotope data were collected (n = 1831) from the literature (60 manuscripts) and categorized by source in six different clusters (Figure 1), namely '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). For each group, descriptive statistics analyses (i.e. mean, standard deviations and quantiles) were performed using Origin v. 2020 (see Table 1). We incorporated in our dataset both bioavailable and non-bioavailable (namely rocks and bulk soils) Sr isotope data and generated two maps (see below): one including the sole 'bioavailable' data and one including 'all' data ('bioavailable' + 'non-bioavailable'; see Table S1). This allowed us to obtain a broader overview of the Sr isotope distribution across Italy.

Table 1. Descriptive statistics for the different sample categories.

Category	N total	Mean	2 SD	Minimum	Median	Maximum	Interquartile Range (Q3 - Q1)
Plant	72	0.70881	0.00117	0.70778	0.70867	0.71122	0.00069
Water	476	0.71005	0.01013	0.70354	0.70887	0.76384	0.00120
Biomineral	471	0.70872	0.00182	0.70729	0.70866	0.71614	0.00094
Food	296	0.70926	0.00282	0.70679	0.70899	0.72071	0.00071
Soil	273	0.70994	0.00549	0.70528	0.7091	0.72379	0.00131
Rock	332	0.71064	0.01081	0.70319	0.70898	0.753	0.00212
Whole dataset ('all')	1920	0.70964	0.00734	0.70319	0.70888	0.76384	0.00105

Novel data (n = 89) were generated from modern environmental and archaeological samples by solution MC-ICPMS analyses. Samples include modern vegetation, archaeological and modern teeth, snails, waters, rocks and soils. These samples are from areas where archaeological studies are in progress and thus were integrated into the database. Five meteoric water samples collected from pluviometers located in the Emilian Apennine (Montecagno, 44°19'57.76'' N; 10°21'58.57'' E) were also measured for their Sr isotopic composition. These values were not included in the spatial model, but are presented as possible end-members for the Sr cycle in the biosphere, possibly helpful for future studies on Sr mixing (Table 2).

Table 2. Sr isotopes of meteoric waters measured in this study.

Latitude	Longitude	Sampling date	Material	$^{87}Sr/^{86}Sr$	2 SE
44°19'57.76'' N	10°21'58.57'' E	March 2016	Meteoric water	0.70848	0.00001
44°19'57.76'' N	10°21'58.57'' E	June 2016	Meteoric water	0.70873	0.00001
44°19'57.76'' N	10°21'58.57'' E	October 2016	Meteoric water	0.70882	0.00001
44°19'57.76'' N	10°21'58.57'' E	March 2017	Meteoric water	0.70924	0.00001
44°19'57.76'' N	10°21'58.57'' E	July 2017	Meteoric water	0.70897	0.00001

2.2. Solution MC-ICPMS

Samples were processed at the Geochemistry Lab of the Department of Chemical and Geological Sciences (University of Modena and Reggio Emilia) and at Durham University. All the reagents employed were of suprapur grade (Modena) or bidistilled (Durham). Biominerals (i.e. teeth and snail shells) were cleaned with MilliQ water and digested using concentrated HNO_3. The bioavailable Sr fraction from soils instead was extracted using 0.25M acetic acid. Bulk rocks samples were totally digested using a mixture of concentrated HNO_3 and HF. Waters were filtered and acidified with HNO_3 to a concentration of 3M. After drying and re-dissolution by 3M HNO_3, all samples were processed using the Eichrom Sr-spec resin. The $^{87}Sr/^{86}Sr$ ratios were determined by Neptune MC-ICPMS, one housed at the Centro Interdipartimentale Grandi Strumenti of the University of Modena and Reggio

Emilia and one at the Northern Centre for Isotopic and Elemental Tracing at Durham University. Detailed protocols are described in Lugli et al. (2017), Argentino et al. (2021) and Cavazzuti et al. (2019a, b). Repeated measures of NBS987 yielded an $^{87}Sr/^{86}Sr$ value of 0.710237 ± 0.000011 (2 SD; n = 18; Modena) and 0.710267 ± 0.000014 (2 SD; n = 57; Dhuram). All values were reported to an NBS987 accepted value of 0.710248 (McArthur et al., 2001).

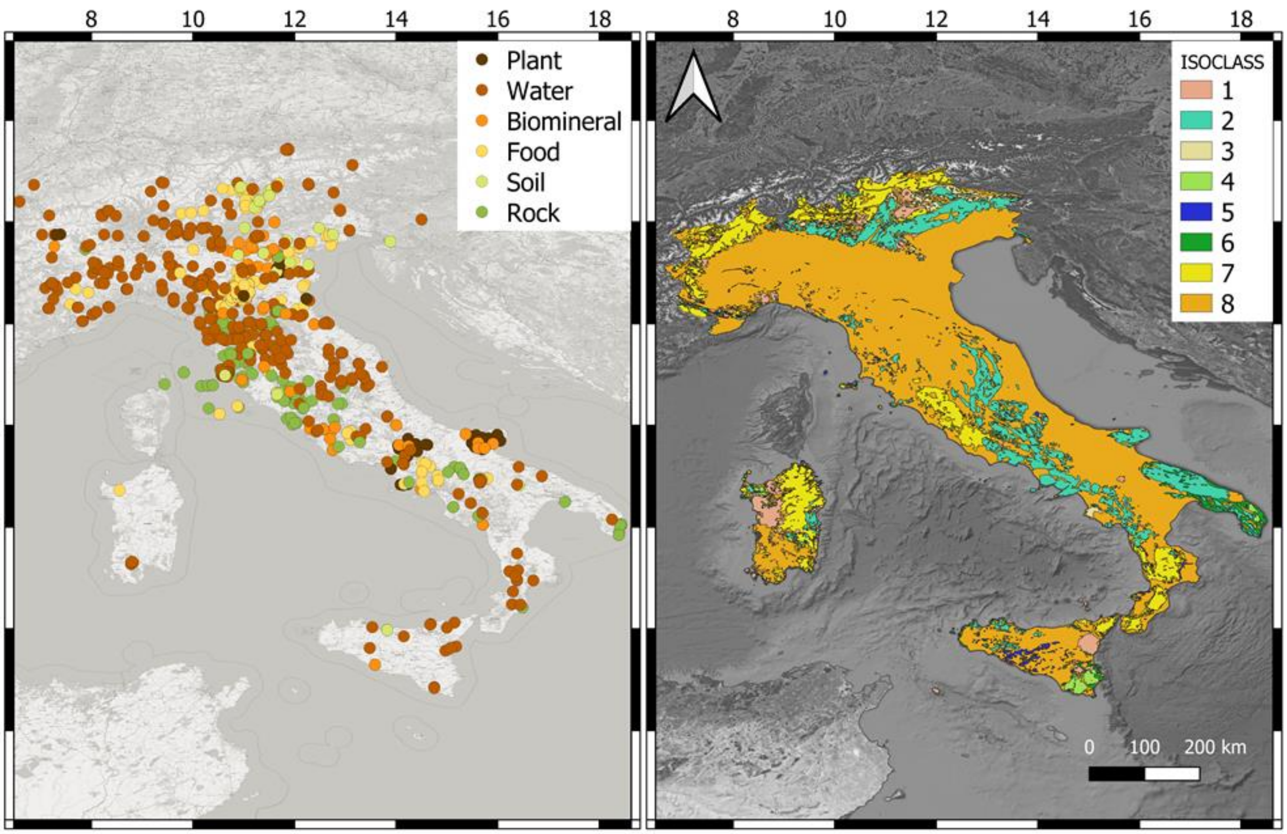

Figure 1. Left panel: locations of the data points considered in this study. Most of the data are from literature, with the addition of novel unpublished environmental/archaeological samples. All the samples in the ‘plant’, ‘water’, ‘biomineral’ and ‘food’ categories are considered ‘bioavailable’, in addition to ‘soil’ leachates. ‘Rock’ and bulk ‘soil’ are considered ‘non-bioavailable’. This map was built in QGIS 3.8, exploiting the OpenStreetMap service. Right panel: Isoclass map of Italy that is a map of the Italian geolithologies classified according to their expected isotope values. This map is based on the geolithological map of Italy available at the Geoportale Nazionale (http://wms.pcn.minambiente.it/ogc?map=/ms_ogc/wfs/Carta_geolitologica.map); the satellite map is provided by Google through the QGIS QuickMapServices plug-in. Isoclass 1: plutonic and volcanic rocks related to MORB mantle magmatism of different ages. Isoclass 2: marine carbonate rock formations of Late Triassic, Cretaceous and Jurassic ages. Isoclass 3: Early and Middle Triassic and Paleogenic marine carbonate rocks. Isoclass 4: Early and Medium Miocene marine carbonate

formations. Isoclass 5: Late Miocene carbonates. Isoclass 6: Pleistocene and Pliocene carbonate formations. Isoclass 7: old metamorphic and magmatic rocks of the crystalline basement and younger volcanics whose magmatism is affected by a radiogenic Sr isotope source. Isoclass 8: all the geolithologies not attributed to an isotope class due to their hybrid nature (i.e. siliciclastic rocks) or to their large Sr isotope variability (i.e., Permian to Devonian carbonates have a very wide range of Sr isotope ratios across several of our defined classes).

2.3 Geospatial modelling

All the identified literature data and new data were grouped in an Excel worksheet and imported into SAGA 7.9 for geospatial modelling. We employed two different models to obtain the interpolated $^{87}Sr/^{86}Sr$ maps, namely Ordinary Kriging and Universal Kriging. The latter is drifted using a geological map of Italy as auxiliary predictor, similarly to the Kriging model with external drift of Willmes et al. (2018). However, unlike Willmes et al. (2018), where the isotope groups were defined using clustering techniques on the data itself, we relied on a simplified geological map of Italy (Figure 1), generated *ad hoc* for this project, combining geolithologies and expected isotope values of the rock formations. In particular, we defined eight isotope classes ('isoclass', Figure 1) taking advantage of: 1) the expected Sr isotope range of certain rock formations outcropping in the Italian peninsula as reported in the literature; 2) the categorization of geological units (i.e. metamorphic, magmatic, sedimentary, etc.) of the Italian geolithological map (published by the Geoportale Nazionale, pcn.minambiente.it; see also Figure S1); 3) the Sr isotope seawater curve of McArthur et al (2001), which in Italy finds wide application due to the continuous marine carbonate deposits from the Triassic to the Neogene preserved across the peninsula. Notably a relatively high number of isotope data is available in the literature for metamorphic and magmatic rocks across Italy, which have been measured to understand the geodynamic events that led to the formation of the Alps and Apennines and their emplacement at crustal level. Although most of these data were not included in the database, because no geolocalization was available, their isotope signature was used to define isoclasses as building blocks of the Italian Sr isomap. In addition, several published Sr isotope data were measured on single mineral phases and therefore, being not representative of the bulk rock, could not be used for our purpose.

The range of Sr isotope values of the eight isoclasses is defined as follows: Isoclass 1 (expected $^{87}Sr/^{86}Sr < 0.70682$) includes plutonic and volcanic rocks related to MORB mantle magmatism of different ages. Isoclass 2 ($0.70682 <$ expected $^{87}Sr/^{86}Sr < 0.70783$) includes mainly marine carbonate rock formations of Late Triassic, Cretaceous and Jurassic ages. Isoclass 3 ($0.70783 <$ expected $^{87}Sr/^{86}Sr < 0.70825$) includes Early and Middle Triassic and Paleogenic marine carbonate rocks. Isoclass 4 (0.70825 < expected $^{87}Sr/^{86}Sr$ < 0.70885) includes Early and Medium Miocene marine carbonate formations. Isoclass 5 (0.70885 < expected $^{87}Sr/^{86}Sr$ < 0.70903) includes mainly Late Miocene carbonates. Isoclass 6 (0.70903 < expected $^{87}Sr/^{86}Sr$ < 0.70920) includes Pleistocene and Pliocene carbonate formations. Isoclass 7 (expected $^{87}Sr/^{86}Sr$ > 0.70920) includes old metamorphic and magmatic rocks of the crystalline basement and younger volcanics whose magmatism is affected by a radiogenic Sr isotope source. Isoclass 8 finally includes all the geolithologies that we were not able to attribute to an isotope class due to their hybrid nature (i.e. siliciclastic rocks) or to their wide Sr isotope variability (i.e., Permian to Devonian carbonates have a very wide range of Sr isotope ratios across several of our defined classes).

In attributing the isoclass to a particular geolithology or formation we confronted local rock values from literature and, whenever possible, double checked their consistency with the bioavailable values of our database. When no data were available, we considered the type of rock (i.e. mineralogy) and the age of formation. Initially, we defined several more isoclasses in the Sr isotope range especially in the range between 0.7092 and very radiogenic values (up to 0.75). However, we could attribute with certainty only a few data points from Sardinia to these classes, and therefore we finally grouped all Sr isotope ratios > 0.7092 in a unique class (isoclass 7). We stress that the attribution of an isoclass has not been arbitrary and any attribution is either backed up by isotopic data or consistent with a particular type of magmatism or deposition event (e.i. seawater curve for marine carbonates of McArthur et al., 2001).

For geospatial modelling, the observed variograms were fit through a linear model, with a searching range of ca. 180 km. Similarly to what observed by Hoogewerff et al. (2019), the semivariograms obtained here showed a cyclical-like structure, with a first maximum located at approximately 250 km (Figure S2). The prediction power of the models was evaluated using a 10-fold cross-validation method through SAGA 7.9 (Table 3). The interpolated Kriging models were imported into QGIS 3.18 to generate the final distribution maps (freely available online at geochem.unimore.it/sr-isoscape-of-italy). We note here that Sardinia was excluded from the Ordinary Kriging due to the low number of data from the area.

Table 3. 10-fold cross validation results for Kiriging model performances trough SAGA 7.9.

Model	Dataset	N. data points	RMSE	Normalized RMSE (%)	R^2 (%)
Ordinary Kiring	'bioavailable'	1568	0.0021	3.5	59.5
	'all'	1920	0.0024	3.9	66.0
Universal Kiring	'bioavailable'	1568	0.0020	3.4	59.0
	'all'	1920	0.0022	3.6	69.7

3. Results and discussion

3.1. Data description and distribution

Descriptive statistics for the data considered in this study are reported in Tables 1 and S1 and summarized in Figures 2 and S3. When categorized, the 'rock' group has as expected the larger variance of the whole dataset, with a $^{87}Sr/^{86}Sr$ ranging from 0.70319 to 0.75300 (Figure 2). This group also shows the averagely highest Sr isotope values (0.7106). On the contrary, plants and biominerals are characterized on average by the lowest Sr isotope values (0.7087-0.7088). The most extreme values of the dataset are found within 'rock' (0.70319) and 'water' (0.76384) groups (see Table 1). Bioavailable samples show an average $^{87}Sr/^{86}Sr$ ratio of 0.70941 ± 0.00632 (2 SD), and span between 0.70354 and 0.76384, with a median value of 0.70883. The kernel density distribution of the bioavailable data is strongly asymmetric and leptokurtic (skewness = 8.14; kurtosis = 99.16). Notably, the non-bioavailable samples, including all the rocks and bulk soils, display an average $^{87}Sr/^{86}Sr$ ratio of 0.71069 ± 0.01054 (2 SD), ranging between 0.70319 and 0.75300, with a median value of 0.70900 (Table S1). The distribution of the non-bioavailable dataset is asymmetric but less leptokurtic than the bioavailable (skewness = 3.93; kurtosis = 22.40). Yet, we stress that the number of non-bioavailable data (n = 352) here considered is remarkably lower than the data in the bioavailable dataset (n = 1568), potentially influencing our observations on the data. Similarly, the uneven spatial distribution of 'non-bioavailable' samples across Italy certainly influenced data evaluations and use for this class. $^{87}Sr/^{86}Sr$ ratios of the bioavailable samples were also exploratively plotted against latitude and longitude (Figure 3), searching for potential correlations between these variables. However, no statistically significant trend was observed (both $R^2 < 0.1$). Yet, the two graphs clearly show a preferential distribution of the highest radiogenic Sr values northwards (latitude 44-47° N) and eastwards (longitude 7-12° E). This is expected due to the presence of old metamorphic and magmatic rocks in the Alpine area and magmatic-metamorphic provinces in Central Italy (Tuscany, Latium), and also evident when data are plotted by Italian macroregions (Figure 2).

Five meteoric waters, not included in the previous statistics evaluations (and the interpolated maps) range between 0.70848 and 0.70924, and represent an end-member of the Sr bioavailable cycle. These five waters were sampled from the same pluviometer located in the Emilian Apennine, and they were seasonally collected ca. 3-to-5 months apart from each other. These data highlight a remarkable temporal variability of the local rainwater likely due to the changing contribution of seawater aerosol and crustal dust, with a possible important influence on the local bioavailable Sr (Négrel et al., 2007).

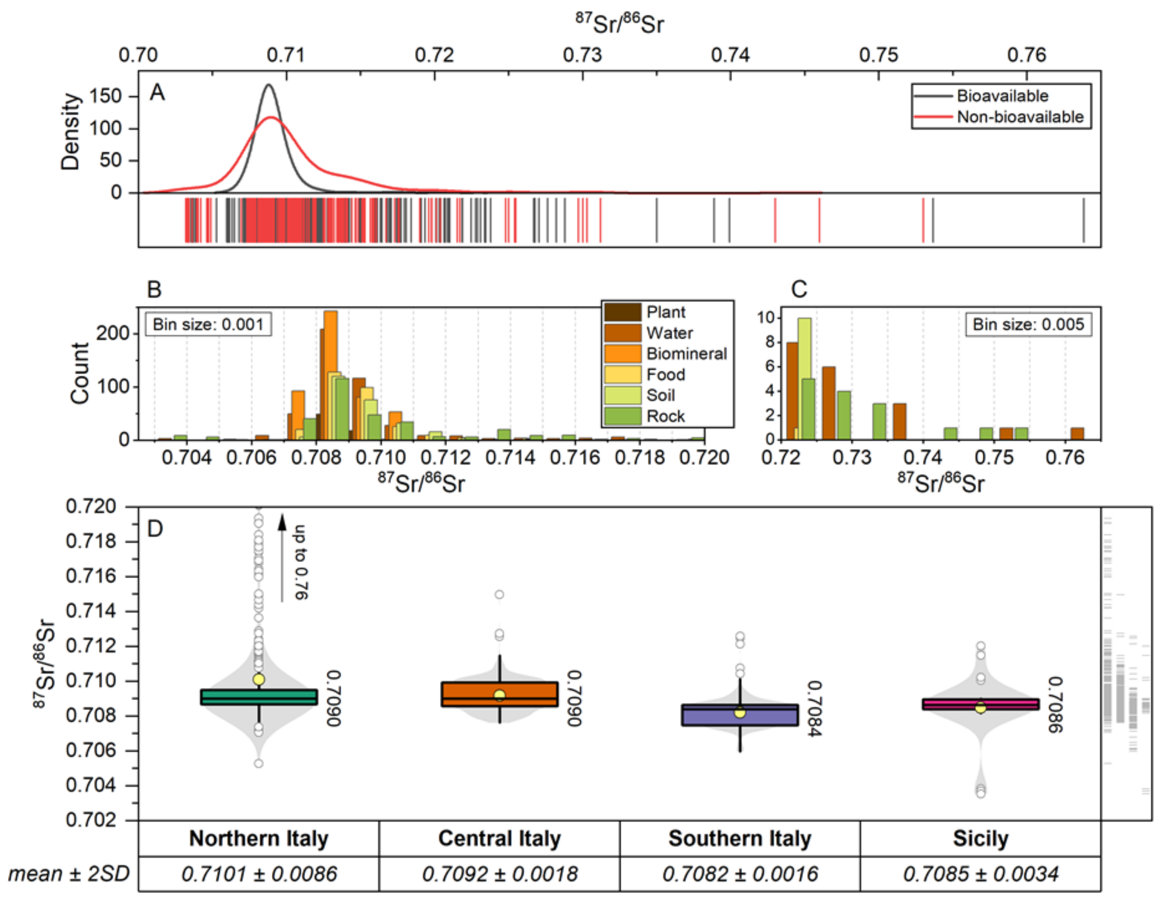

Figure 2. Data exploration. A) Kernel density estimation of bioavailable (n = 1568) vs. non-bioavailable (n = 352) $^{87}Sr/^{86}Sr$ data. B) Superimposed histogram representing the different sample categories between 0.702 and 0.720, with a bin size of 0.001. C) Superimposed histogram of the different sample categories between 0.720 and 0.77, with a bin size of 0.005. Note that the y-scale ranges of the histograms ('count') are different. D) Sr isotope data grouped by geographical areas (macroregions) of Italy, defined according to the National Institute of Statistics (istat.it); median values are labelled close to the box plots; average values ± 2 SD are also reported.

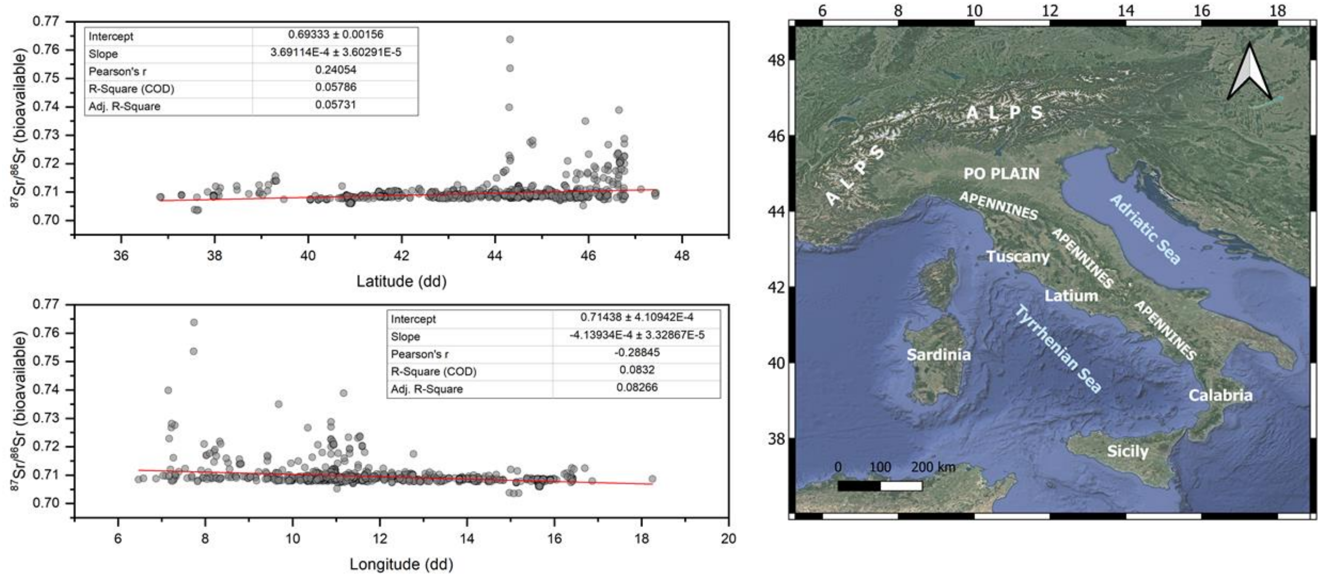

Figure 3. The $^{87}Sr/^{86}Sr$ ratios plotted against latitude and longitude (decimal degrees). No significant linear trend appears; however, most of the radiogenic Sr data are latitudinally distributed northwards and longitudinally eastwards. Graphs and linear trends were produced using Origin v. 2020. Right panel: a geographic map of Italy is reported as reference; main areas cited in the manuscript are labelled.

3.2. Maps

The isoclass map of Italy (Figure 1) allows a first order distinction between the radiogenic Sr isotope provinces, related to the 'old' crustal and radiogenic Sr isotope magmatism units mainly present in the Alps, Calabria, Sardinia and Central Italy, and the unradiogenic provinces related to the depleted mantle magmatism mainly in the Southern Alps and Sicily. Yet, more information can be gathered through the isoscape maps (Figures 4 and 5). These were built modelling the two datasets, namely 'bioavailable' and 'all'. Each figure includes two maps obtained with two distinct Kriging approaches: Ordinary and Universal with external drift. The evaluation of performance of the two models is reported in Table 3. Both methods produced satisfying results, with relatively low normalized root mean squared errors (NRMSE ~3-4%), explaining between ~60 and ~70% of the isoscape variance (R^2). In general, Universal Kriging (with eternal drift) seems to outperform Ordinary Kriging, although the difference is not remarkable (Table 3). The lowest RMSE is observed for the 'bioavailable' Universal Kriging, and is equal to 0.0020; instead, the highest RMSE (0.0024) was obtained for the 'all' Ordinary Kriging model. Altogether, the presence of non-bioavailable (un)radiogenic end-members in the 'all' database seems to limit the prediction power of the Kriging method, both in terms of data over-fitting (higher R^2) and worse variogram modelling (see also Figure S4). To further evaluate the prediction of our modelling we measured the prediction standard errors for the Kriging maps (Figure S4). Both models (i.e. Ordinary and Universal) show similar standard prediction errors, ranging from ca. 5E-7 to 5E-6 for the 'bioavailable' dataset and from 2E-7 to 2E-5 for the 'all' dataset. These errors are low when compared with other spatial interpolation presented in literature for isoscapes (e.g. Willmes et al., 2018; Adams et al., 2019; Wang et al., 2020). Such low values are possibly related to the high number of samples considered in this study (total n = 1920), evenly distributed across Italy (see Figure 1), compared to the available literature studies. Largest errors indeed can be found in Sicily and Sardinia, where the number of samples is significantly lower than in other areas (Figure S4).

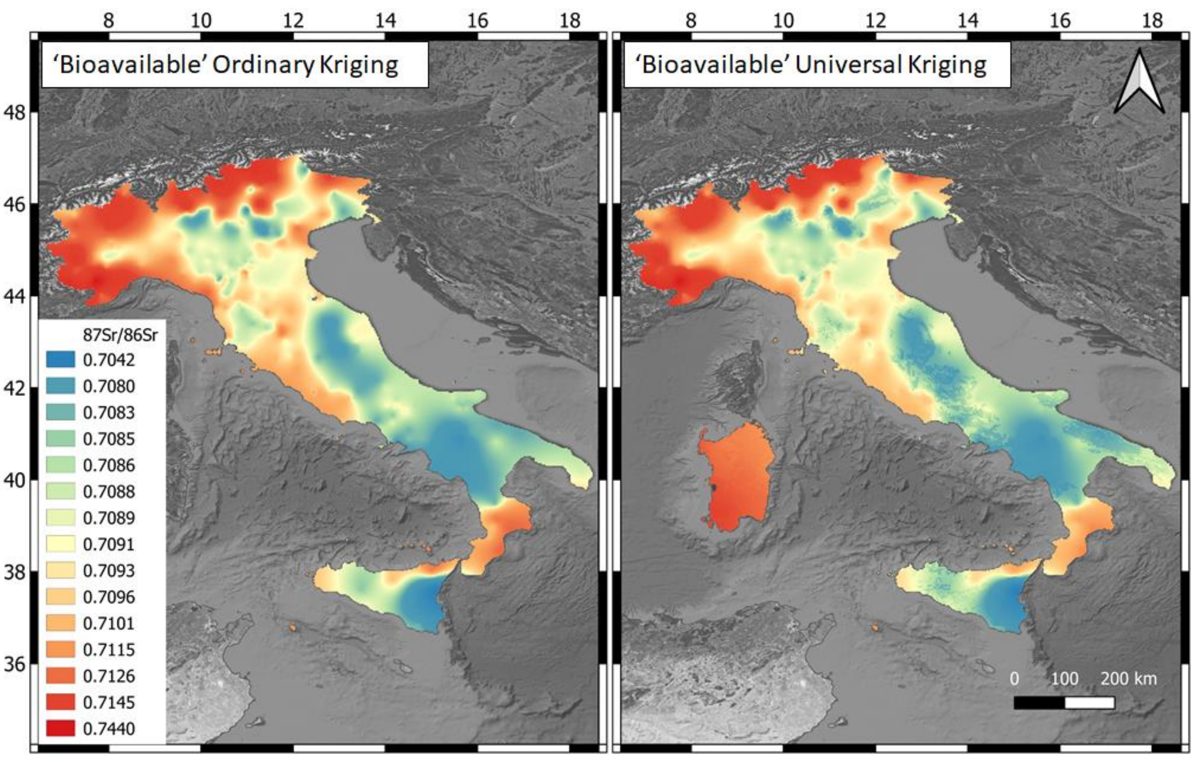

Figure 4. Ordinary and Universal (with external drift) kriging models obtained for the 'bioavailable' $^{87}Sr/^{86}Sr$ dataset. Maps were obtained using SAGA 7.9 and QGIS 3.8.

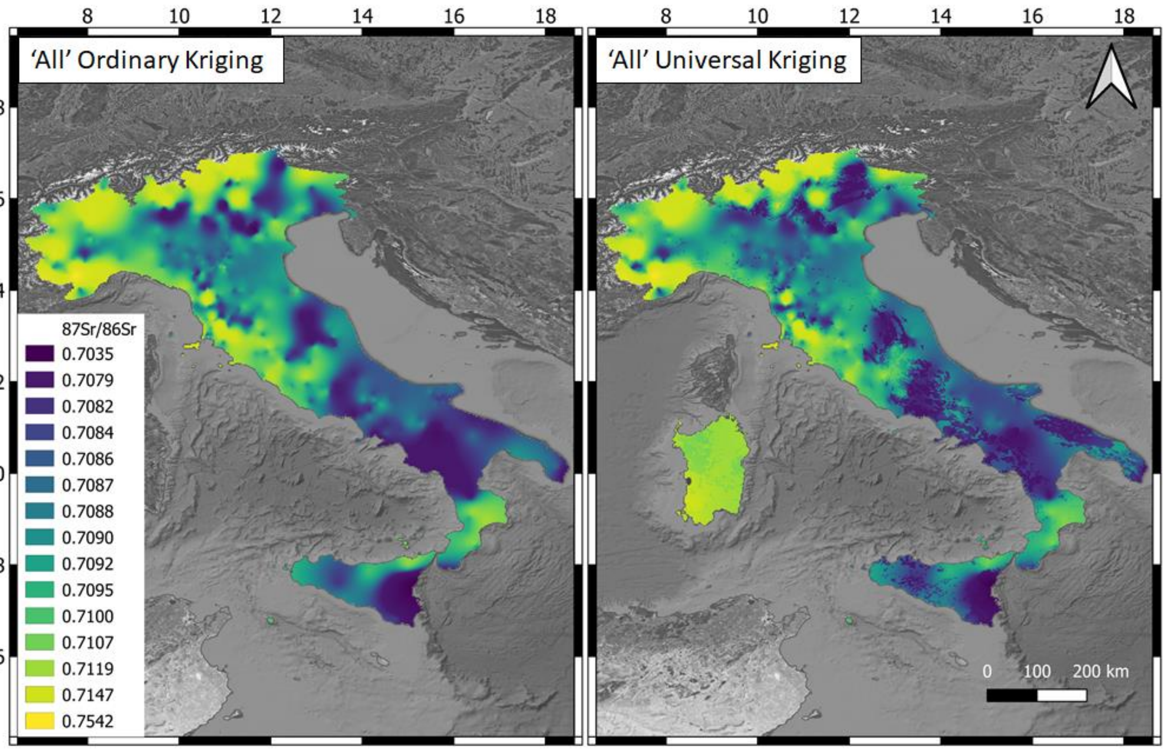

Figure 5. Ordinary and Universal (with external drift) kriging models obtained for the 'all' $^{87}Sr/^{86}Sr$ dataset. Maps were obtained using SAGA 7.9 and QGIS 3.8.

The 'bioavailable' (Figure 4) and the 'all' (Figure 5) maps show similar spatial distribution of the $^{87}Sr/^{86}Sr$ ratios, with the highest radiogenic values clustered in well-defined geological areas of Italy, namely the Alps, the Tuscan Magmatic Province, the Latium volcanic area and the Calabria crystalline basement (Southern Italy). These values are of course related to the radiogenic nature of the natural components from these areas included in our database. Contrariwise, low Sr isotope values are generally present in areas characterized by depleted mantle magmatism such as in Sicily and in Campania and where old carbonates (older than Pliocene) outcrop.

The largest differences in terms of isoscape predicted values among the 'all' and the 'bioavailable' maps arise indeed in these areas (particularly Tuscany and Latium), due to the presence of even higher radiogenic values in local rocks, only partially identified in the bioavailable pool (see Figure S5). The north-western Alpine area also shows significant differences (both in negative and positive) between the two datasets. However, here, only few rock values are present within the 'all' database. This suggests that the observed variations (see e.g. Cuneo area, north-western Italy) are probably linked to model's predictions inaccuracies rather than actual variations of the $^{87}Sr/^{86}Sr$ ratio.

Overall, several small 'hotspots' (both negative and positive) can be recognized when comparing the predictions of the two datasets, particularly in the Alps. We stress that the number of samples in these areas is lower than in other localities; however, another explanation might lie in the complex geometry of the Alps where the bioavailable Sr isotope ratios might differ from those of the exposed rocks because of the geological complexity of the nappes that overthrust each other in the belt and therefore in the differential contributions to the bioavailable Sr possibly from other reservoirs.

Sharper details of the isotope zones can be observed in the Universal Kriging map compared to the Ordinary Kriging, due to the definite isoclass boundaries of the guiding map. In general, when looking at specific areas of the map, the Universal Kriging model should be more accurate in terms of spatial prediction, particularly for those areas with few data available. However, the Ordinary Kriging map seems to better mimic the natural averaging of Sr isotope values due to weathering and mixing processes.

3.3. Definition of the local bioavailable Sr baseline for human provenance: a case study

Defining the local bioavailable Sr baseline is currently a hot topic in archaeology and anthropology. Common methods include the measurement of modern environmental samples as waters, plants, snail shells and soil leachates (Bentley, 2006; Maurer et al., 2012; Ladegaard-Pedersen et al., 2020; Toncala et al., 2020), but also through the analysis of local (archaeological) fauna (see e.g. Lugli et al., 2019). Some studies also showed the power of using statistical methods to detect outliers (as Tukey's fences and median absolute deviations) among the human's skeletal isotopic dataset, to constrain local vs. non-local individuals (Lightfoot and O'Connell, 2016; Cavazzuti et al., 2021). Once defined, the local baseline is then used to comprehend the mobility patterns of the investigated human population (i.e. autochthonous vs. allochthonous individuals). However, there is no general consensus on the best practices to employ for determining the local Sr baseline (e.g. Maurer et al., 2012; Britton et al., 2020; Weber et al., 2021). All the methods have indeed intrinsic flaws linked to various sources of error such as anthropogenic contaminations on environmental samples (Thomsen and Andreasen, 2019), temporal changes in the Sr mixing end-members (e.g. Erel and Torrent, 2010; Han et al., 2019) or simply erroneous *a priori* assumptions. For example, were 'local' animals actually 'local'? What is their real home range? Are modern plants, growing on modern soils, isotopically representative of the ancient landscape? All these are open questions that call for further investigations and can lead to data misinterpretation if not considered.

We take advantage of some of the novel data measured for this study to further discuss this issue, focusing on the Bronze Age archaeological site of Fratta Polesine (Cardarelli et al., 2015; Cavazzuti et al., 2019a) in the Po plain (Northern Italy). Locally, the geology is characterized by Holocene alluvial debris, mainly composed of siliciclastic sedimentary deposits related to the erosion of the Alpine belt. We built a bioavailable Sr isoscape excluding the bioavailable data from the site, to compare the Ordinary Kriging interpolated data against the Fratta Polesine measured dataset (Figure 6). The Ordinary Kriging interpolated $^{87}Sr/^{86}Sr$ ratio, in a radius of 10 km from the site, ranges between 0.7091 and 0.7096, with a median value of 0.7094. The measured bioavailable data from Fratta Polesine are averagely less radiogenic (0.7089) but more variable, ranging between 0.7085 (snail) and 0.7094 (modern shallow rooted plant). These specimens plot as three distinct clusters, with plant and soils showing the highest values (0.7092-0.7094), snails the lowest (0.7085-0.7086), and animal enamel falling in the middle (0.7088-0.7089). Such variability in our measured data suggests that different end-members influenced in different ways the environmental specimens. Plants (mostly shallow rooted plants) and soils are indeed likely to be more influenced by atmospheric deposition and anthropogenic contaminants. Yet, the rainwaters from the Apennines show a maximum value of 0.7092 (Table 2), suggesting that other sources (as dust, fertilizers and/or other antropic sources) might have contributed to the plant-soil pool at Fratta Polesine (Thomsen and Andreasen, 2019). Our isoscape agrees with the presence of higher radiogenic values towards the north-east. Hence, we can alternatively hypothesize that underground waters flowing southwards from the Alps into the Po plain might have influenced the local isotope fingerprint of soils and plants from Fratta Polesine.

Snail shells are characterized by the lowest radiogenic $^{87}Sr/^{86}Sr$ ratios among the measured samples. This has been observed before in the literature (Maurer et al., 2012; Britton et al., 2020), and linked to the amount of soil carbonate (up to 40%) incorporated into the diet of land snails (Yanes et al., 2008; Maurer et al., 2012). Animal enamel shows intermediate values, possibly reflecting different sources of drinking water and food (Toncala et al., 2020). For example, the (domesticated?) dog and pig teeth are isotopically compatible with the Po river water, one of the main sources of drinking water close to Fratta Polesine. Human data presented in Cavazzuti et al. (2019a) show a median $^{87}Sr/^{86}Sr$ ratio of 0.7089, with an interquartile range (Q3-Q1) of 0.0006, indicating that most of the individuals are compatible with the baseline of the site and few plot outside the local environmental variability (see Cavazzuti et al., 2019a for more details).

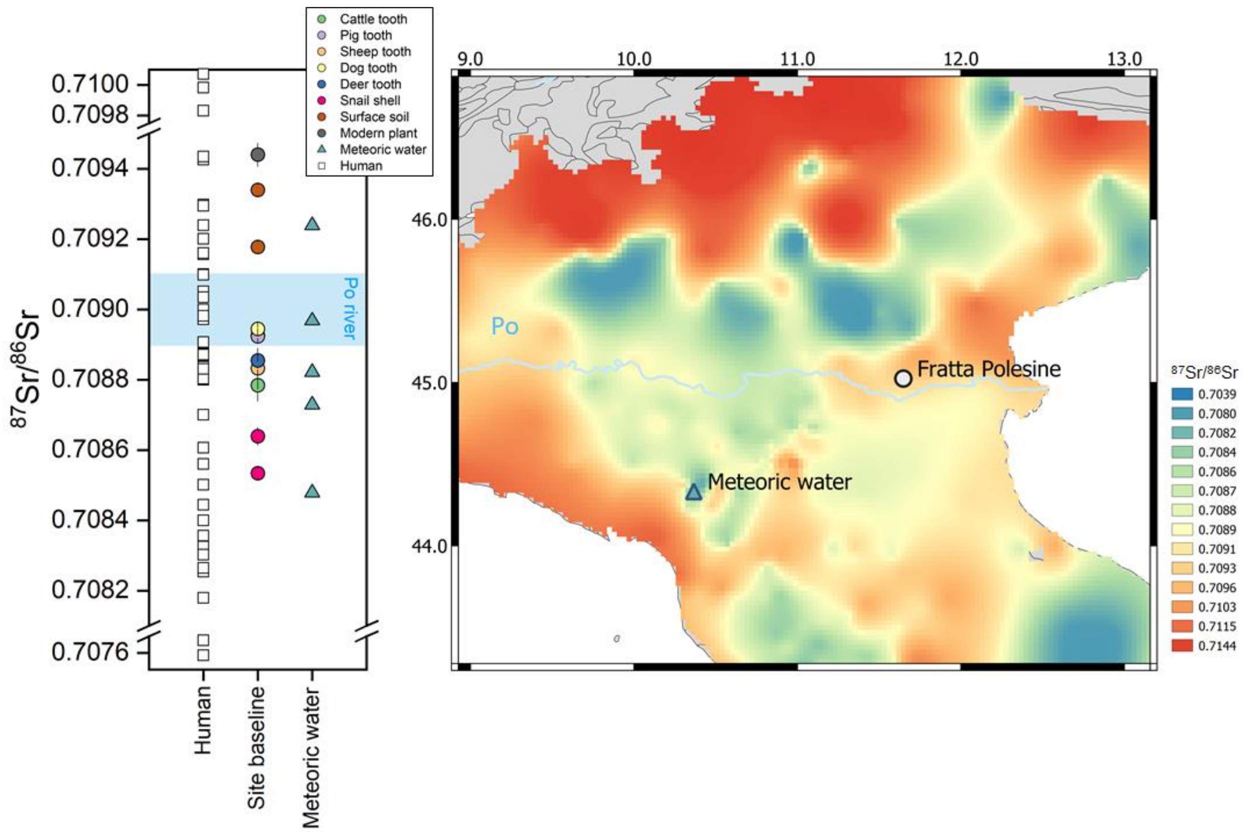

Figure 6. Local baseline at the Bronze Age site of Fratta Polesine (Rovigo, Veneto). Analysed samples include animal tooth enamel, snail shells, surface soil leachates and vegetation. Human data (including both enamel and cremated petrous bone specimens) are from Cavazzuti et al. (2019a). In the graph, meteoric water data from the Apennines (blue triangles) and water data (light blue area) from the Po river (sampling locations close to the site) are reported for comparison. The Sr bioavailable map on the right panel is an Ordinary Kriging interpolation, without the local data from Fratta Polesine. The local (<10 km) predicted $^{87}Sr/^{86}Sr$ range at the site is 0.7091-0.7096 (median 0.7094). The Po river is also shown on the map.

Overall, these data suggest that soils (leachates) and plants best reflect the local bioavailable Sr pool, although possibly contaminated by modern and/or antropic end-members. Fauna enamel, if truly local as in the case of domesticated macro-mammals or small home range micro-mammals, mixes various bioavailable Sr sources and more closely mimics the local food and drinking sources. Such evidence clearly highlights the intrinsic limits in using isoscapes, which are commonly composed by a patchwork of literature data from different samples, or modelled on specific samples collected *ad hoc* (as soils or plants). Yet, we stress here that Sr isotopes need to be interpreted following an 'exclusion' principle, and thus employed to *discard* possible areas as point of origin (Holt et al., 2021). This, in turn, suggests that provenancing through isoscapes, and isotope baselines in general, need to be performed with caution. Hence, isoscapes must be considered as 'guides' for data interpretation, rather than an unequivocal provenancing tool, justifying their composite nature to better understand the variability of local Sr pools.

4. Conclusions

We collected a large amount of georeferenced Sr isotope values for Italy. Owing to this database, we were able to produce $^{87}Sr/^{86}Sr$ prediction maps by geostatistical modelling, namely Ordinary Kriging and Universal Kriging. Model performances were evaluated through 10-fold cross validations, resulting in RMSE ranging between 0.0020 and 0.0024.

Bioavailable Sr isotope values across Italy show a remarkable variability, with the Alps and certain metamorphic/magmatic terrains displaying the highest radiogenic values, and are in general well-consistent with the underlying bedrock type.

We took advantage of the produced maps to discuss a local case study and the definition of local baseline in archaeological studies, a currently hot-topic within the field of provenance and mobility studies. In this sense, regional and (extra)national isoscapes are key in understanding the variability of the local Sr pool, broadening our understanding on the mixing of the different end-members to obtain certain isotope signatures in (geo)biological samples.

Distribution maps of Sr isotopes provide a solid interpretative basis for provenance and traceability studies. Our maps and database are freely accessible online and will be updated in the future when new data become available. In this sense, we will continue to collect and analyse new environmental samples from low-density areas (such as Sicily and Sardinia) to improve the prediction power of the models. In addition, we plan to employ novel methods for the spatial modelling of isotope data, using different predictors and machine learning approaches.

Acknowledgments

The Geochemistry Lab at the University of Modena and Reggio Emilia has been funded through a grant of the Programma Giovani Ricercatori Rita Levi Montalcini to AC. This project received funds by the European Research Council (ERC) under the European Union's Horizon 2020 Research and Innovation Programme (grant agreement No 724046 – SUCCESS awarded to SB) and the MIUR FARE programme 2018 (FARE Ricerca in Italia: Framework per l'attrazione e il rafforzamento delle eccellenze - SAPIENS project to SB). Mattia Sisti is thanked for initiating the collection of Sr isotope data and Silvia Cercatillo for water sampling.

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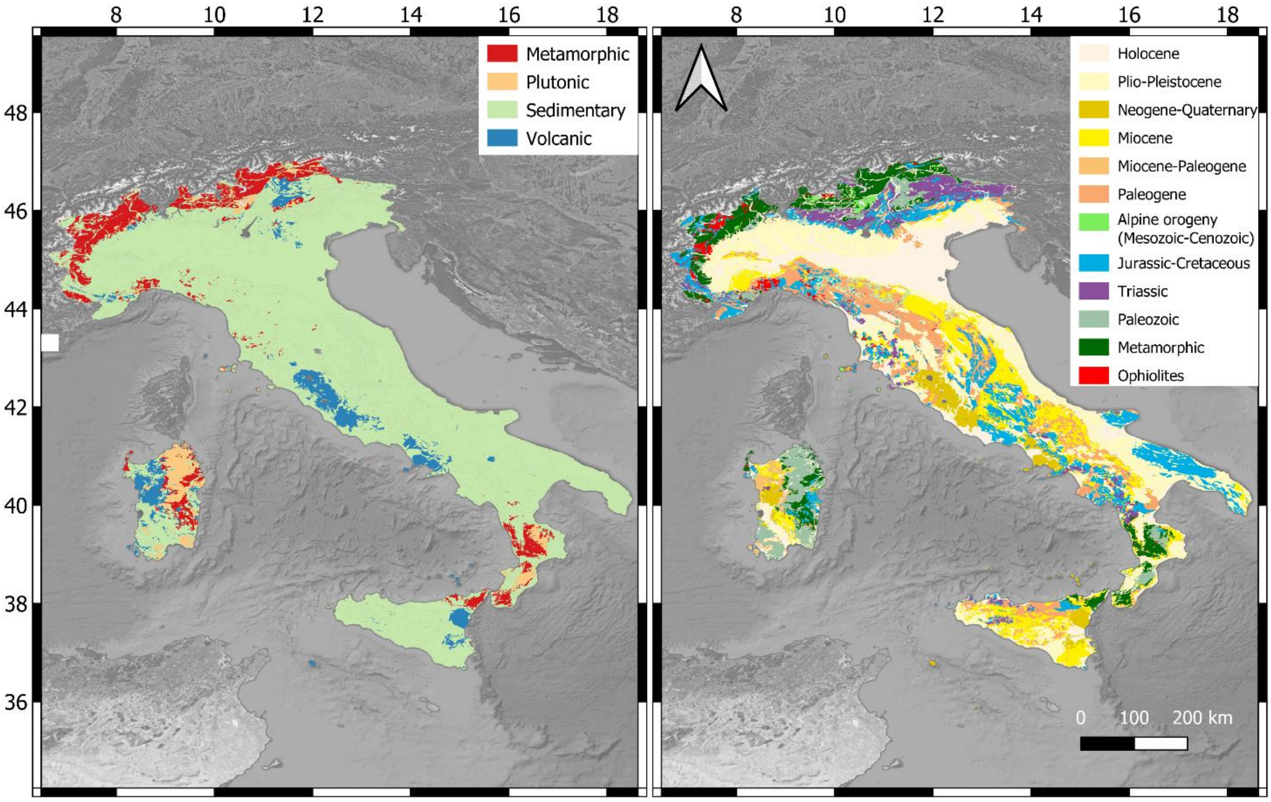

Figure S1. Geological maps of Italy. Left panel: formations are categorized by rock 'family'. Right panel: formations are categorized by age. This map is based on the geolithological map of Italy available at the Geoportale Nazionale (http://wms.pcn.minambiente.it/ogc?map=/ms_ogc/wfs/Carta_geolitologica.map); the satellite map is provided by Google through the QGIS QuickMapServices plug-in.

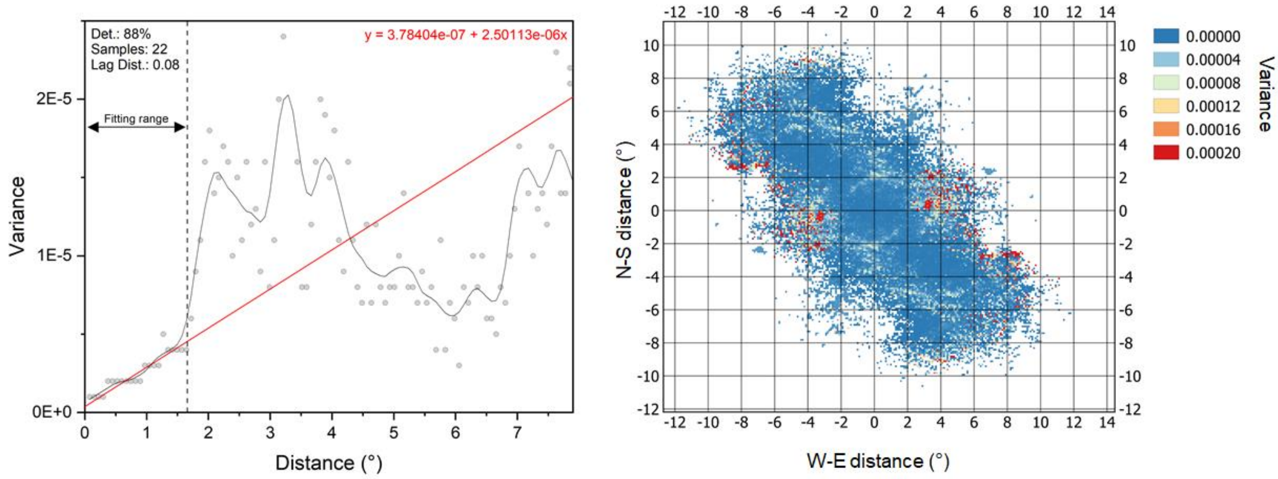

Figure S2. 'Bioavailable' Ordinary Kriging variogram (biplot and surface) obtained through SAGA 7.9.

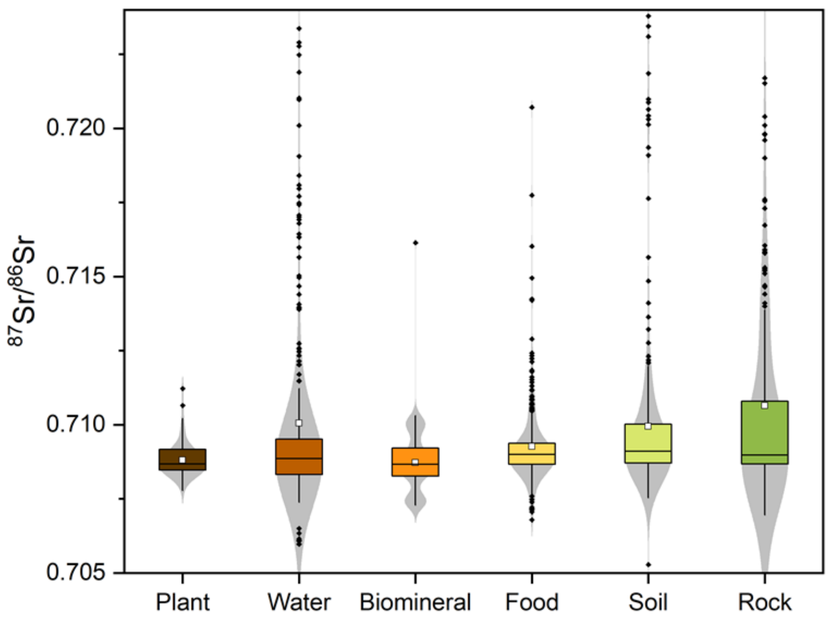

Figure S3. Box plot graph representing the $^{87}Sr/^{86}Sr$ ratios of the different sample categories. The gray shadows are data distributions obtained by kernel density estimations. Note that the graph is cut at 0.724 to improve readability, with some outliers plotting beyond the graph range.

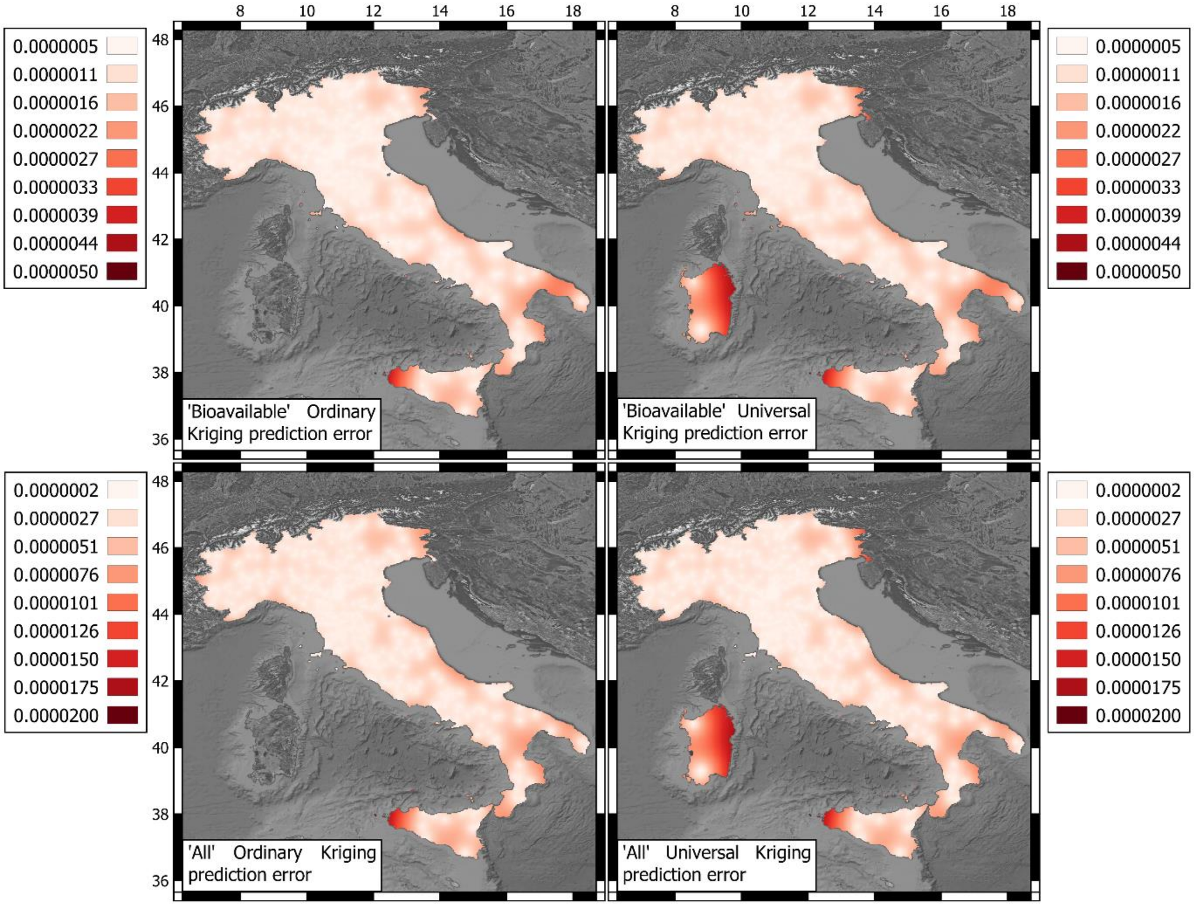

Figure S4. Prediction standard error for the Kriging models. Maps were obtained using SAGA 7.9 and QGIS 3.8.

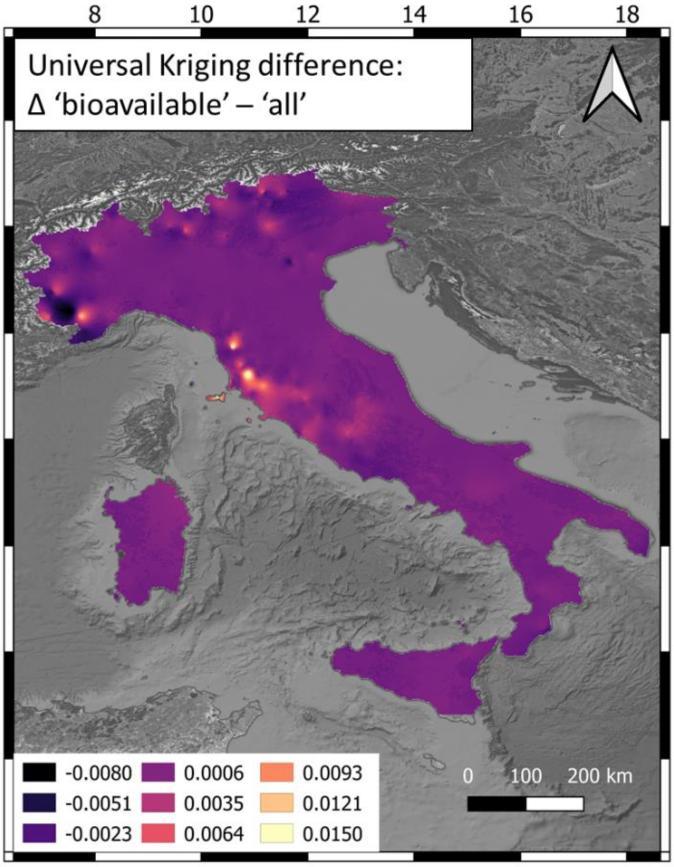

Figure S5. $^{87}Sr/^{86}Sr$ difference between 'all' and 'bioavailable' Universal Kriging models; e.g. a positive value means that Sr isotope data are higher in the 'all' map. Maps were obtained using SAGA 7.9 and QGIS 3.8.

Table S1. Descriptive statistics for the whole dataset and (non-)bioavailable samples. 'Bioavailable' samples are 'plant', 'water', 'biomineral' and 'food' categories, in addition to 'soil' leachates. 'Non-bioavailable' samples are 'rock' and bulk 'soil'.

Category	N total	Mean	2 SD	Minimum	Median	Maximum	Interquartile Range (Q3 - Q1)
'Bioavailable'	1568	0.70941	0.00632	0.70354	0.70883	0.76384	0.00091
'Non-bioavailable'	352	0.71069	0.01054	0.70319	0.709	0.753	0.00223
'All'	1920	0.70964	0.00734	0.70319	0.70888	0.76384	0.00105