

**COMPARISON OF Sr ISOTOPIC RATIOS
FROM TWO SOILS NEAR RAVENNA (ITALY) USING
AQUA REGIA AND TWO-STEP SEQUENTIAL EXTRACTS**

**COMPARAISON DES RAPPORTS ISOTOPIQUES DU Sr
DE DEUX SOLS PRÈS DE RAVENNE (ITALIE) EN UTILISANT
L'AQUA REGIA ET L'EXTRACTION SÉQUENTIELLE**

**PARAGONE DEI RAPPORTI ISOTOPICI DELLO Sr
DI DUE SUOLI PRESSO RAVENNA (ITALIA) UTILIZZANDO
AQUA REGIA E L'ESTRAZIONE SEQUENZIALE**

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Abstract

The Sr-isotope ratios of several samples from a natural and an agricultural soil from Ravenna were determined using aqua regia and the two-step sequential extraction. Results indicate that the two-step extraction can provide the researcher with wider and more precise information on Sr sources, thus being a more suitable methodology for achieving scientific goals than the aqua regia extraction. Lastly, the extracts of hydrochloric acid and aqua regia display similar ranges of $\delta^{87}\text{Sr}$, indicating that the two procedures provide comparable information on Sr sources.

Key words: *Sr isotopes; soils; Ravenna; aqua regia; two-step sequential extraction*

Résumé

Les rapports isotopiques du Sr ont été déterminés dans les échantillons d'un sol naturel et d'un autre agricole de la zone de Ravenne en utilisant l'aqua regia et l'extraction séquentielle. Les résultats indiquent que l'extraction séquentielle peut fournir une information plus large et plus détaillée sur les sources du Sr. Elle représente donc une méthodologie plus adaptée aux buts scientifiques que l'extraction avec aqua regia. Enfin, les extraits avec aqua regia et acide chlorhydrique fournissent des valeurs comparables de $\delta^{87}\text{Sr}$, indiquant que les deux procédures donnent des informations analogues sur les sources de Sr.

Mots-clés: *isotopes du Sr; sols; Ravenne; aqua regia; extraction séquentielle*

Riassunto

Sono stati determinati i rapporti isotopici dello Sr di parecchi campioni di un suolo naturale e uno agricolo della zona di Ravenna usando aqua regia e l'estrazione

sequenziale. I risultati indicano che l'estrazione sequenziale può fornire una più ampia e puntuale informazione sulle sorgenti dello Sr, essendo quindi una metodica più adatta a conseguire gli scopi scientifici di quanto non sia l'estrazione con acqua regia. Infine gli estratti in acqua regia e acido cloridrico forniscono valori simili di $\delta^{87}\text{Sr}$, indicando che le due procedure danno informazioni analoghe sulle sorgenti dello Sr.

Parole chiave: isotopi dello Sr; suoli; Ravenna; acqua regia; estrazione sequenziale

Introduction

This paper illustrates the results of a study carried out on several samples from two soils located north of Ravenna (for soil locations see Fig. 1 in Buscaroli et al., 2009, Castorina et al., 2010). Soil samples were analyzed using both the aqua regia extraction and two-step sequential chemical analysis. The comparison has been carried out to understand the differences in the yields and sources of Sr using the two procedures. The aqua regia extraction is the analytical procedure required by Italian law to provide bulk information on leachable metals, and thus Sr, from soils. Therefore, the aqua regia extraction satisfies the necessity of knowing about the possible geochemical risk derived from the release of toxic (and non-toxic as Sr) metals from the soils destined to residential use.

However, such procedure provides no information to distinguish among the different metal sources; this fact is important not only as an academic goal, but also to understand thoroughly the potential geochemical risk. In contrast, the sequential analysis is particularly suitable to distinguish between the contributions from the soil fraction leachable with ammonia acetate and that leachable with hydrochloric acid (Steinmann and Stille, 1997; Drouet et al., 2005). In this context, the fraction soluble in acetate supplies the Sr contained in calcite/aragonite and/or the Sr weakly adsorbed onto the various soil matrices (e.g. clay minerals, organic matter, etc), while the fraction soluble in hydrochloric acid contains the Sr adsorbed more strongly and the Sr released from the other carbonates (mainly dolomite), gypsum, phosphates and Fe-Mn oxides. Moreover, the sequential analysis appears to be more suitable for studying the bioavailable fraction of Sr to plants, as the used acids are similar to the acids secreted by plant roots.

Moving from these considerations, the paper presents a comparative application of the two procedures to a couple of soils, representative of either a natural and an agricultural environment, aimed at verifying the differences in Sr yields and their bearings for scientific research. The results, in turn, allow for giving basic information to the Administrations concerned with the environmental protection.

The studied soils and sampling

They are located north of Ravenna, in san Vitale Pinewood and nearby areas (Buscaroli et al., 2009; Castorina et al., 2010). Pin-9 soil profile, that was dug in the eastern edge of the forest, represents a natural soil of the Po-river delta National

Park, developed in a topographic depression of an old coastal dune. Due to the lack of the vegetation canopy, the soil is potentially exposed to the fallout from chimney emissions of the adjacent industrial zone. In contrast, Pa-4 soil profile occurs in the area west of the forest, where agriculture is developed and, thus, represents a typical farmland. It has developed on a marshland of san Vitale Pinewood, remediated by upfilling with the sediments of the Lamone river. The latter flows down from Romagna's Apennines, composed of flysch and, subordinately, marine clays and sands, all rocks are of Cenozoic age. We collected a sample from each horizon of the two soil profiles, to carry out a detailed study.

Analytical procedure

Each soil sample was first washed with bi-distilled water to remove soluble salts deposited by marine aerosols and/or evaporation of the pore water upwelling during dry summer. Then, each sample was split in two aliquots, one of which was leached with ammonia acetate, and the residue was later leached with hydrochloric acid, while the other aliquot was attacked with aqua regia. Ammonia acetate dissolves calcite/aragonite and allows for releasing the metals weakly adsorbed onto the various matrices.

In contrast, aqua regia as well as hydrochloric acid dissolve carbonates, gypsum, phosphates, and partially both Fe-Mn oxide-hydroxides and organic matter, and allow for releasing metals more strongly adsorbed onto the soil components. Isotopic analyses were carried out at IGAG-CNR c/o Dipartimento di Scienze della Terra, University of Rome "La Sapienza" using a FINNIGAN MAT 262RPQ multicollector mass spectrometer with Re double filaments in static mode. The internal precision (within-run precision) of a single analytical value is given as two standard error of the mean. Repeated analyses of standards gave averages and errors expressed as two standard deviation (2σ) as follows : NBS 987, $^{87}\text{Sr}/^{86}\text{Sr}=0.710241\pm 13$ ($n=20$), $^{86}\text{Sr}/^{88}\text{Sr}$ normalized to 0.1194. Sr-isotope analyses are reported as $\delta^{87}\text{Sr}$, i.e. deviation of the isotopic ratio of the sample from that of seawater standard assumed to be 0 (Richter and De Paolo, 1987).

Analytical results

Table 1 reports the $\delta^{87}\text{Sr}$ values of the three fractions for the studied samples. The acetate extracts of Pin-9 soil encompass a narrow range of $\delta^{87}\text{Sr}$ from -0.80 to -0.41, while the extracts of hydrochloric acid and aqua regia display wider ranges from -0.86 to +0.27, and from -1.04 to +0.37, respectively. All extracts of Pa-4 soil exhibit relatively narrow ranges; in particular, acetate extracts range between -0.34 and +0.09, while hydrochloric acid extracts range from -0.72 to -0.34 and, lastly, aqua regia extracts display rather constant $\delta^{87}\text{Sr}$ between -0.62 and -0.52.

Table1 - $\delta^{87}\text{Sr}$ of the Extracts from the horizons of the studied samples

Soil	Depth (cm)	Horizon	extracts		
			NH ₄ -Ac (1M) $\delta^{87}\text{Sr}$	HCl (1N) $\delta^{87}\text{Sr}$	Aqua regia $\delta^{87}\text{Sr}$
Pa-4	0 - 45	Ap	0.09	-0.72	-0.56
	45 - 60	Bw	0.25	-0.72	-0.57
	60 - 105	C1	-0.32	-0.34	-0.52
	105 - 135	C2	0-73	-0.58	-0.62
Pin-9	0 - 5	A1	-0.41	0.27	0.37
	5 - 10	A2	-0.71	-0.11	-0.21
	10 - 30	Cg1	-0.77	-0.77	-0.47
	30 - 80	Cg2	-0.68	-0.82	-0.67
	80 - 100	Cg3	-0.80	-0.86	-1.03

Discussion

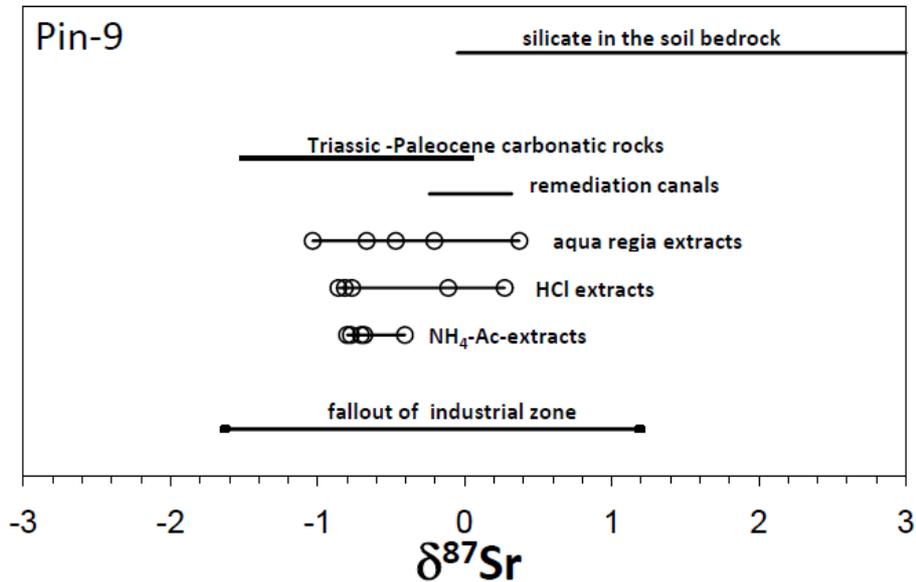
Pin-9 soil

The very narrow range of negative $\delta^{87}\text{Sr}$ from acetate extracts suggests that Sr derives from one source, likely represented by calcite from Cenozoic marine carbonates (McArthur et al., 2001), and/or the Sr desorbed from the various soil matrices.

As concerns the extracts of hydrochloric acid and aqua regia, the comparison shows similar ranges. In particular, as the range is higher for A horizons than the deep soil (displaying values similar to those of acetate extracts), there is evidence of the presence of an additional source of Sr in upper horizons. This source, that is characterized by $\delta^{87}\text{Sr}$ close to 0 and/or positive, can be either natural and/or anthropogenic. As concerns the former, it cannot be represented by gypsum as it displays negative $\delta^{87}\text{Sr}$ (Upper Triassic -1.93, Messinian -0.38; McArthur et al., 2001). The latter might be represented by dolomite and/or phosphates (apatite is the most common one), but these minerals are of very subordinate abundance; thus, their contribution, if any, is negligible. More realistically (e.g. Castorina et al., 2008), the second source may be represented by the Sr leached from Fe-Mn oxides, that adsorb the Sr released from the weathering of the silicates present in the soil bedrock. Due to the $\delta^{87}\text{Sr}$ measured in A horizons, the silicates are likely derived from old crustal rocks. Another potential source can be represented by the Sr carried by the waters of remediation canals, as the Sr adsorbed onto the suspended colloidal fraction displays a range from -0.24 to +0.32 (Petrini et al., 2009). In this context, it is noted that Pin-9 soil is temporarily flooded by the water from the canals during the humid season, because it is located in a topographic depression. Lastly, as concerns potential anthropic sources, they may be represented by the fallout from the chimneys of the industrial zone, facing san Vitale Pinewood. We have no direct measurements of these emissions and, thus, take the range ($\delta^{87}\text{Sr}$ from -1.65 to +1.17) from the literature (Lahd Geagea et al., 2007, 2008a, b). Although this range overlaps the ranges of some natural sources and, thus, is not

characteristic, some contribution from industrial pollution may be possible as the $\delta^{87}\text{Sr}$ measured in the A horizons of the soil fall within the emission range (Fig.1).

Figure 1 - $\delta^{87}\text{Sr}$ ranges for the extracts of Pin-9 sample and reference Sr sources. Open circle represents the isotopic value of each horizon sample.



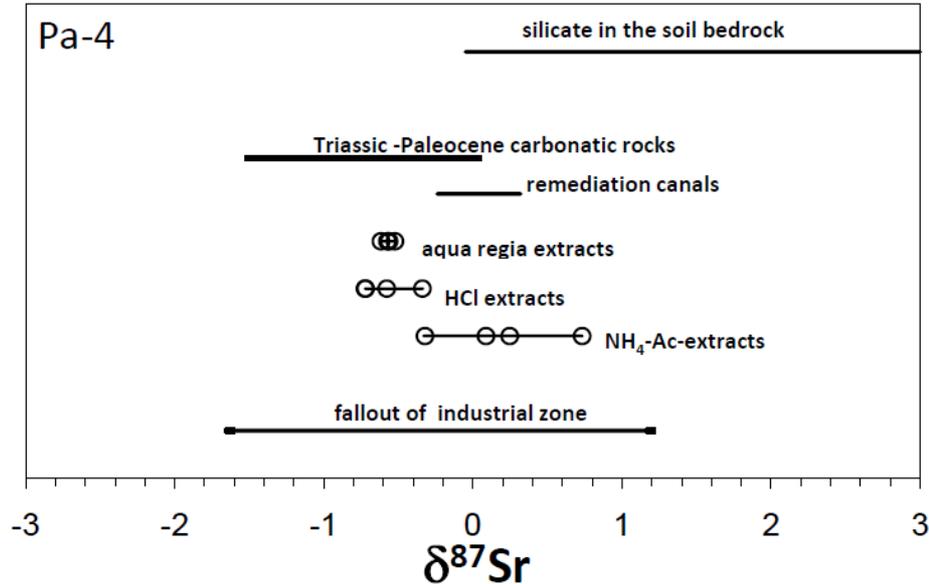
Pa-4 soil

The relatively large range of $\delta^{87}\text{Sr}$ of acetate extracts indicate the presence of two sources of Sr in this soil. One source, that occurs mainly in upper horizons, is characterized by positive $\delta^{87}\text{Sr}$, while the other present in C horizons shows negative $\delta^{87}\text{Sr}$. While the latter source resembles marine carbonates, the former source can be either natural and/or anthropic.

As concerns natural sources, the $\delta^{87}\text{Sr}$ suggest that Sr derives from the weathering of old crustal silicates via desorption from soil matrices, and/or irrigation waters from remediation canals (Petrini et al., 2009). In favor of weathered silicates, there is the fact that weathering is expected to be more effective in the upper horizons of the soil. As concerns anthropic sources, the agricultural use of this soil might suggest that Sr is supplied by some natural fertilizers. Anyway, the low P contents measured in the soil (Vittori Antisari et al., 2010) rule out the possibility the study Sr-bearing fertilizers derived from marine phosphorites are used. In fact, the common fertilizer used in that area is synthetic (N-P-K). Lastly, it might be envisaged some contribution from industrial emissions due to the location of the soil close to the factory zone; however, this hypothesis would imply that the

industrial particulate matter is soluble in ammonia acetate, in contrast with the negative evidence of Pin-9 soil, subjected to the same pollution. The comparison for the extracts of aqua regia and hydrochloric acid shows overlapping $\delta^{87}\text{Sr}$ ranges; therefore, the source of bulk Sr in both groups of extracts is probably the same. Measured $\delta^{87}\text{Sr}$ suggest marine carbonates as a possible source (Fig. 2).

Figure 2 - $\delta^{87}\text{Sr}$ ranges for the extracts of Pa-4 sample and reference Sr sources. Open circle represents the isotopic value of each horizon sample.



Conclusions

There is a significant difference unveiled by the two-step sequential chemical analysis, that is not apparent using the aqua regia attack only. In fact, the $\delta^{87}\text{Sr}$ of acetate extracts from Pa-4 soil point to a significant contribution of Sr from an external source to the soil. This source cannot be represented by fertilizers, despite of the agricultural use of this soil, because the low P contents measured in the soil rule out the use of Sr-bearing natural phosphorites. The likely explanation implies weathered old crustal silicates and/or irrigation waters from remediation canals.

The comparison between the extracts of hydrochloric and aqua regia in either soil shows similar ranges of $\delta^{87}\text{Sr}$, indicating that the bulk Sr extracted following the two procedures derives from the same sources. In this respect, therefore, dissolving soil samples with aqua regia or hydrochloric acid may yield similar results.

For the case study here presented, results suggest that the bulk Sr extracted from the two soils derives from marine carbonates. Moreover, the $\delta^{87}\text{Sr}$ of A horizons suggest an additional source of Sr represented by either weathered bedrock silicates and/or the Sr adsorbed onto the suspended colloidal fraction of remediation waters.

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