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Sr-ISOTOPE RATIOS OF A SOIL PROFILE (BADLANDS) NEAR RADICOFANI (SOUTHERN TUSCANY)

LES ISOTOPES DU Sr APPLIQUÉS A UN PROFIL DE SOL (CALANQUES) PRÈS DE RADICOFANI (TOSCANE MÉRIDIONALE)

APPLICAZIONE DEGLI ISOTOPI DELLO Sr A UN PROFILO DI SUOLO (CALANCHI) PRESSO RADICOFANI (TOSCANA MERIDIONALE)

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Abstract

The Sr/Ca ratios and Sr-isotope ratios of bulk samples and acetate extracts from a soil profile developed on Pliocene marine clays near Radicofani, in southern Tuscany, were determined. The uniform Sr/Ca ratios in the soil indicated a uniform distribution of the two elements throughout the profile. In contrast, the lower Sr/Ca ratios of acetate extracts from the upper horizons of the soil suggest preferential removal of Sr relative to Ca, perhaps by the plants. These latter seem to accumulate more Sr than Ca during their lifetime. The δ^{87}Sr of acetate extracts suggests that bulk Sr is provided by the calcite of the Mesozoic-Cenozoic sedimentary formations of southern Tuscany. A minor source of Sr, although subordinate, is represented by clastic albite. A grass sample growing on the soil contained the Sr uptaken from both sources.
Key words: *Sr isotopes; Sr/Ca ratios; soil; acetate extraits; Radicofani*

Résumé

Les rapports Sr/Ca et les isotopes du Sr ont été déterminés dans des échantillons de sol et les fractions extraites avec l'acétate d'ammonium, d'un profil développé sur les argiles marines du Pliocène près de Radicofani, dans la Toscane méridionale. Les rapports uniformes Sr/Ca du sol indiquent une distribution uniforme des deux éléments le long du profil. Par contre, les rapports plus faibles des fractions acétate mesurés dans les horizons supérieurs du sol suggèrent un retrait préférentiel éloignement du Sr, probablement par la végétation. Il semble que les herbes accumulent plus Sr que de Ca pendant leur vie. Les valeurs de δ^{87}Sr des fractions acétate suggèrent que la plupart du Sr est fournie par la calcite dérivée des formations sédimentaires mésozoïques et cénozoïques de la région. Une source mineure de Sr est représentée par l'albite clastique. Un échantillon d'herbe ayant poussé sur le sol contenait du Sr dérivé de ces deux minéraux.
Mots-clés: *isotopes du Sr; rapports Sr/Ca; sol; extraits d'acétate; Radicofani*

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Riassunto

Sono stati determinati i rapporti Sr/Ca e i rapporti isotopici dello Sr in campioni di suolo e negli estratti d'acetato di un profilo sviluppato sulle argille marine plioceniche presso Radicofani, nella Toscana meridionale. I rapporti uniformi Sr/Ca del suolo indicano una distribuzione uniforme dei due elementi nel profilo. Al contrario, i rapporti più bassi misurati nelle frazioni d'acetato degli orizzonti superiori del suolo suggeriscono l'allontanamento preferenziale dello Sr, probabilmente ad opera della vegetazione. Sembra che le erbe accumulino più Sr di Ca durante la loro vita. I valori di δ^{87}Sr degli estratti d'acetato suggeriscono che la maggior parte dello Sr deriva dalla calcite delle formazioni sedimentarie meso-cenozoiche della regione. Una sorgente minore è costituita dall'albite clastica. Un campione di erba che cresce sul suolo contiene Sr derivato da ambedue i minerali.

Parole chiave: *isotopi dello Sr; rapporti Sr/Ca; suolo; estratti d'acetato; Radicofani*

Introduction

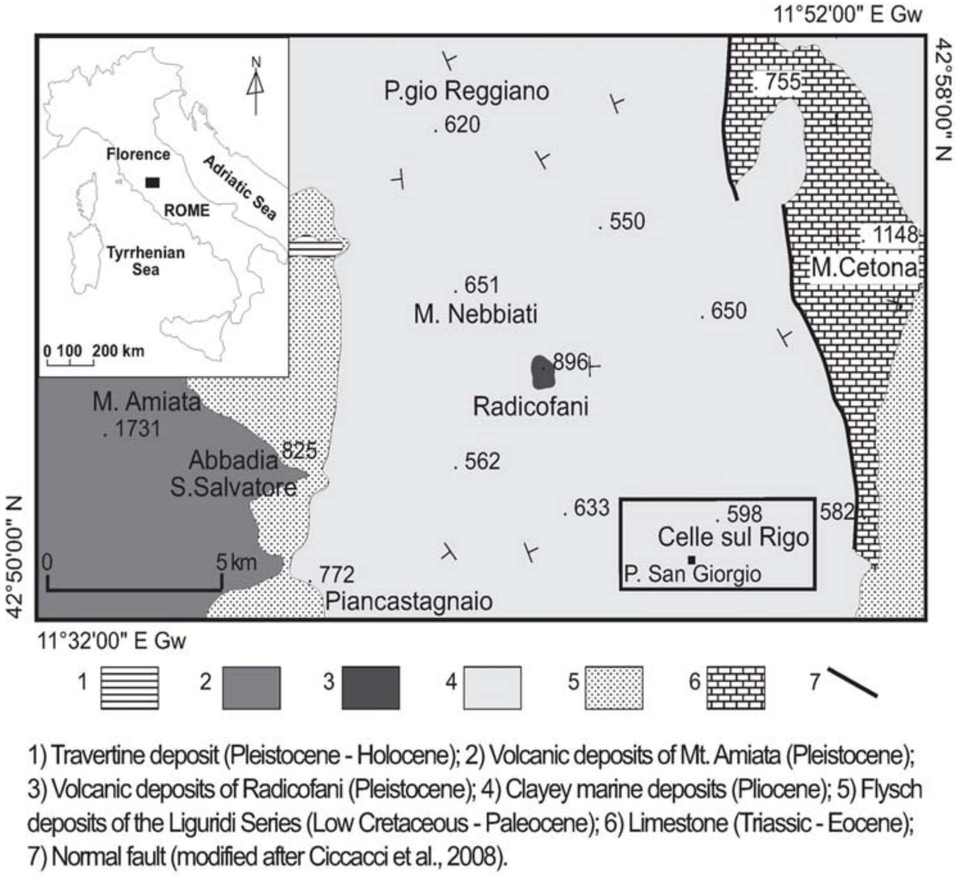
This paper presents an application of the Sr-isotope systematics to the study of a soil profile developed on *calanchi* landforms (badlands) at the village of Celle sul Rigo near Radicofani, in southern Tuscany (Fig.1).
The aim is to trace the pedogenic processes taking place in a natural soil, unaffected by anthropic pollution because of its location far away from towns, highways, industries and unexploited by agriculture. Therefore, the study of this soil yields the Sr-isotope composition of a "blank", to be used as a reference in the studies of other soils of similar characteristics from central Italy. The results have been compared with those of a natural soil from san Vitale Pinewood, north of Ravenna (Castorina and Masi, 2009). The very little number of Sr isotopic studies on Italian soils (Castorina and Masi, 2007, 2008, 2009) has us pushed to make the comparison, despite of the different environmental conditions of the two areas. Nevertheless, the comparison has yielded interesting conclusions. Lastly, as Sr is a proxy to Ca due to the close chemical and geochemical characteristics of the two elements, the study of the behavior and sources of Sr in soils can also help to trace the behavior and sources of Ca, thus widening the interest of the research.

The soil profile and sampling

The soil occurs near the village of Celle sul Rigo at Radicofani, in southern Tuscany (Fig.1). Geologically, this area belongs to the Radicofani basin, i.e. the southernmost part of the Siena basin. After a relatively long period of stable continental land, this area has become subjected to subsidence and, thus, was invaded by the sea in the Lower Pliocene, with the deposition of a thick sequence of sediments. Starting from the Middle Pliocene, the area rose up progressively till the Quaternary and, nowadays, appears as a gently hilly landscape, reaching about

635 m a.s.l. in the study area. The uplift was likely connected with the coeval emplacement of the small volcano of Radicofani, characterized by basic lava flows.

Figure 1 – *Geological sketch map of the Radicofani area showing the location of the studied soil profile at the village of Celle sul Rigo.*



In the area of Celle sul Rigo, where volcanic deposits lack, the marine sediments are constituted by clays and sandy clays of gray-blue or gray-brown color. According to Galiano (2007), these sediments are composed by silt (about 60 %) and subordinate clay (about 30 %). Among non-clayey minerals, quartz and calcite are dominant (38-49 % and 27-41 % respectively) over albite and K-feldspar (10-13 % and 8-15 %, respectively). In particular, average calcite constitutes about 24 wt % of the soil. Among clayey minerals, kaolinite and chlorite are dominant (29-38 % and 22-30 %, respectively) over illite (16-20 %) and interstrate illite-smectite (14-17 %).

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5 samples were collected from the different horizons of the soil and analyzed; a brief description of the main soil characteristics is given in Table 1. A grass sample growing on the topsoil was also collected and analyzed.

Table 1- *Brief description of the main pedological characteristics of the studied soil profile from Celle sul Rigo.*

Depth (cm)	Horizons	Grain size	Characteristics
0-8	A1	silt and subordinate clay	clumpy, skeleton-rich, dark gray color
8-10	A2	silt and subordinate clay	clumpy, skeleton-rich, medium dark gray color
10-45	C	silt and subordinate clay	compact, friabile, angular-block fracture, clay-richer, light gray color
45-55	C/R	more silt and less clay	more compact, carbonate-rich
>55	R	bedrock : silt 60%, clay 27%, sand 13%	more compact, carbonate-rich

Analytical procedure

Ca and Sr contents were determined by ICP-AES at Dipartimento di Scienze della Terra, University of Rome "La Sapienza". Each sample was first washed with bi-distilled water to remove soluble salts. Then, each sample was split in two aliquots, one of which was dissolved completely with $HF+HNO_3$ mixture. The other aliquot was leached out with 1N ammonia acetate to dissolve more soluble carbonates, representing the labile Sr, i.e. that bio-available to plants. Sr for isotopic analyses was separated in a 3 ml AG50 W-X8 resin column. 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 result 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, $^{87}Sr/^{86}Sr=0.710241\pm13$ (n=20), $^{86}Sr/^{88}Sr$ normalized to 0.1194. The results are expressed as $\delta^{87}Sr$ (permil), 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

The Sr/Ca ratios of bulk-soil samples are quite uniform, ranging from 3.78 to 3.81. In contrast, the Sr/Ca ratios of acetate extracts are comparatively less uniform to lower, ranging from 2.51 and 2.95. In particular, lower ratios characterize the upper horizons of the soil. Lastly, the grass sample displays a bulk value of 10.2, and a lower value of 5.7 for the acetate extract. Both values are higher than those of the

corresponding soil samples. The variations of Sr/Ca ratios against depth for all samples are shown in Figure 2.
Acetate extracts display similar values of δ^{87}Sr ranging from -1.34 to -1.44, except the sample from the C/R horizon exhibiting -0.71. In contrast, bulk-soil samples display positive δ^{87}Sr, ranging from 0.76 to 0.96. Lastly, the grass sample exhibits very close δ^{87}Sr in both the acetic extract and bulk sample (-0.71 and -0.60, respectively). These values are close to those of bulk-soil samples. The variations of δ^{87}Sr against depth for all samples are shown in Figure 3.

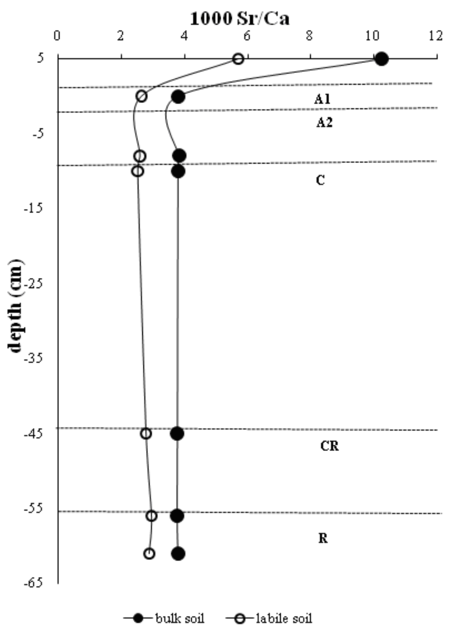

Figure 2 – *Variation plots of Sr/Ca ratios versus depth for the studied soil.*

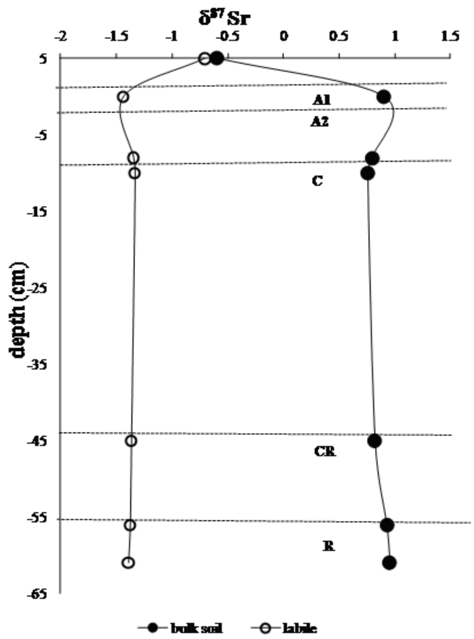

Figure 3 – *Variation plots of δ^{87}Sr versus depth for labile and bulk-soil Sr contents in the studied soil.*

Discussion

The higher Sr/Ca ratios of bulk-soil samples than acetate extracts are explained by the Ca and Sr contributions from the silicates (mainly albite) present in the bedrock beside calcite. The uniform values indicate a constant distribution of these minerals throughout the profile. Moreover, the lower Sr/Ca ratios of acetate extracts from upper horizons relative to the deep soil suggest preferential removal of Sr relative to Ca in the topsoil, probably by plants. Lastly, as concerns the grass, the higher Sr/Ca ratio in the bulk sample than in the acetate extract indicates accumulation of Sr relative to Ca in the plant. In particular, Sr appears concentrated two times more in the bulk plant than in the acetate fraction.

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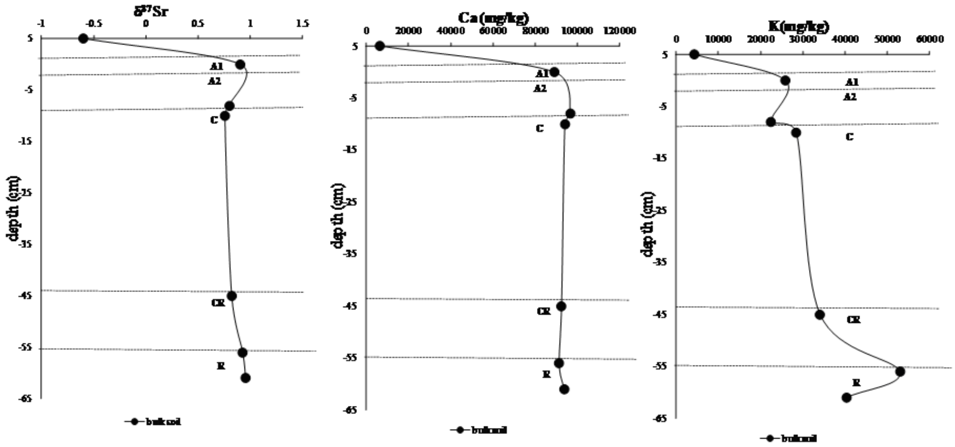
The similar $\delta^{87}Sr$ displayed by bulk-soil samples from the different horizons indicate a common source of Sr. In this context, the very good correlation between Ca and Sr isotopes throughout the profile (Fig. 4) suggests that Sr is basically associated with Ca minerals (mainly calcite and subordinate albite). In contrast, the poor correlation between K and Sr isotopes (Fig. 4) indicates that the Sr associated with K minerals (illite and K-feldspar) is very subordinate, in agreement with the subordinate amount of these minerals in the soil.

Figure 4 – *Variation plots of $\delta^{87}Sr$, Ca and K contents versus depth for bulk samples of the studied soil.*



The almost uniform isotopic $\delta^{87}Sr$ of acetate extracts suggest that there is a common source of labile Sr. This latter is represented by calcite and/or the Sr weakly adsorbed onto soil matrices, and released by acid. As bulk calcite is geogenic in origin, and the clays were deposited in the Lower Pliocene, the $\delta^{87}Sr$ of acetate extracts might reflect the isotopic composition of seawater of that time, assuming calcite was then precipitated. This hypothesis finds no support, as the $\delta^{87}Sr$ of Lower Pliocene seawater (-0.23) is higher than the values measured in acetate extracts (by -1.39). An alternative hypothesis is to consider the calcite present in clays mainly as clastic. In other words, being clays a typical siliciclastic formation, it is assumed that most of the carbonate present is also of clastic origin. In this view, the measured $\delta^{87}Sr$ is likely the average of all carbonates present in the formations bordering the former Siena sea basin in the Lower Pliocene. In this context, as these formations were represented by Mesozoic and Cenozoic sedimentary rocks, carbonate clasts are expected to display $\delta^{87}Sr$ between -2.67 (Jurassic) and -0.28 (Messinian). Mixing of calcites from these rocks in different proportions may yield the value of -1.39.

Lastly, as concerns the grass sample, the similar $\delta^{87}Sr$ of the acetate extract and bulk soil indicate that the whole Sr uptaken by the plant proceeds from both calcite and albite. Therefore, mixing of the Sr released from albite with that released from the carbonate in different proportions, can yield a $\delta^{87}Sr$ close to 0.65.

Difference between the soils from Celle sul Rigo and San Vitale Pinewood

As concerns the $\delta^{87}Sr$ of acetate extracts, the Pinewood soil displays higher (-0.41 A horizons; -0.80 Cg horizons) values than the Celle sul Rigo soil (-1.34 A horizons; -1.44 C horizons). Considering that the carbonate fraction present in the two soils derives from different sources (in particular, the Pinewood soil is composed of sediments from the Po-river basin encompassing a large range of lithotypes of different ages), this fact can explain the different $\delta^{87}Sr$ measured in acetate extracts of the two soils. Likewise, the bulk-soil samples of the Pinewood soil display higher $\delta^{87}Sr$ (11.01 A horizons; 3.88 Cg horizons) than the bulk-soil samples of the Celle sul Rigo soil (0.76 A horizons; 0.96 C horizons). The difference likely reflects the variable abundances of Sr-bearing minerals in the two soils; for instance, Sr-bearing carbonates range between 1 and 10 % in the Pinewood soil, while they are averagely by 24 % in the soil from Celle sul Rigo, and, conversely, the former soil contains more silicates than the latter. The different abundance of Sr-bearing minerals in the two soils, in turn, reflects the different origin of sediments in the two profiles.

As a whole, the comparison between the two groups of soils shows what is the significance of the measured Sr-isotope ratios, allowing for distinguishing between the sources of the element and, indirectly, the environmental characteristics. Moreover, the isotopic data appear to be independent of the pedogenic stage of soils, as the Pinewood soil is comparatively more developed. Therefore, Sr isotopes appear to be a very sensitive geochemical tool to trace the processes taking place in the soil, also in the case of different pedogenic evolution.

Conclusions

The uniform Sr/Ca ratios of bulk-soil samples indicate the uniform distribution of Ca-Sr bearing minerals through the profile. In contrast, the lower Sr/Ca ratios in acetate extracts from the upper horizons of the soil suggest preferential release of Sr relative to Ca, probably by plant uptake. A sample of the grass growing on the soil displays higher Sr/Ca ratio than the relative acetate extract, suggesting preferential Sr accumulation.

The Sr-isotope ratios measured in the soil profile suggest:

-the Sr of acetate extracts mainly derives from calcite and, subordinately, albite, both inherited from the Mesozoic-Cenozoic marine sedimentary rocks bordering the Siena basin in the Lower Pliocene.

-the Sr of bulk-soil samples and the grass growing on the soil derive from both mineral sources.

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Lastly, the comparison of Sr-isotope ratios of the soils from Celle and san Vitale Pinewood shows differences explained mainly by the different chemical and mineralogical compositions of the two soils.

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