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Sr-Nd ISOTOPES IN MOSSES FROM ROMAGNA (ITALY) AND THEIR ENVIRONMENTAL SIGNIFICANCE

LES ISOTOPES DE Sr ET Nd DANS LES MOUSSES DE LA ROMAGNE (ITALIE) ET LEUR SIGNIFICATION ENVIRONNEMENTALE

GLI ISOTOPI DELLO Sr E DEL Nd NEI MUSCHI DELLA ROMAGNA (ITALIA) E IL LORO SIGNIFICATO AMBIENTALE

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Abstract

Sr-Nd isotopes were applied for the first time to the study of several moss samples from a transect stretching through Romagna from the Apennines to the Adriatic sea coast. The isotopic data suggest that the mosses uptake Sr and Nd via atmospheric depositions from both marine carbonates and old siliceous crustal rocks. Anthropic pollution cannot be precisely evaluated because of the lack of univocal isotopic signature of the sources.
Key words: *Sr-Nd isotopes; mosses; Romagna; Sr-Nd sources; pollution*

Résumé

Les isotopes du Sr et Nd ont été appliqués pour la première fois à l'étude des échantillons de mousses pris en Romagne le long d'une section de la côte adriatique aux Apennins. Les données isotopiques suggèrent que les mousses captent Sr et Nd de la poussière atmosphèrique par deux sources, les carbonates marins et les roches de la croûte siliceuse. La pollution anthropique ne peut pas être évaluée certes, car elle n'a pas de signatures isotopiques typiques.
Mots-clés: *isotopes du Sr et Nd; mousses; Romagne; sources de Sr et Nd; pollution*

Riassunto

Gli isotopi dello Sr e del Nd sono stati applicati per la prima volta allo studio di campioni di muschio prelevati da un transetto attraverso la Romagna esteso dal mare adriatico agli Appennini.

I risultati suggeriscono che i muschi prendono Sr e Nd tramite la polvere atmosferica da due sorgenti rappresentate dai carbonati marini e dalle rocce silicatiche crostali. L'inquinamento antropico non può essere valutato con certezza perché non è caratterizzato da parametri isotopici univoci.
Parole chiave: *isotopi dello Sr e del Nd; muschi: Romagna; sorgenti di Sr e Nd; inquinamento*

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Introduction

This paper presents a Sr-Nd isotopic study of moss samples collected from a transect stretching from the Apennines to the coastal plain of Romagna, northern Italy (Fig. 1). Mosses are considered to be reliable bio-monitors of the environment, and particularly of the quality of the air (e.g. Zechmeister et al., 2005), as they uptake nutrients essentially from the atmosphere via humid and dry depositions (e.g. Lan Lee et al., 2005, Vittori Antisari et al., 2009), unlike the uppermost of plants uptaking elements from the soil via roots. So far, there are a very few papers concerning the application of Sr and Nd isotopes to mosses for environmental studies (e.g. Lahd Geagea et al., 2007, 2008a, b), and this is the first one carried out on Italian mosses.

Setting and sampling

The studied mosses belong to the *Hypnum cupressiforme* species, one of the most widespread in Italy. Figure 1 shows the transect from which the samples were collected. It stretches from Muraglione Pass (907 m a.s.l.) in Romagna's Apennines to the coastal plain of Ravenna, encompassing about 90 km. A half of the transect occupies the alluvial plain, while the other half extends through the narrow Apenninian valley of the Montone river. The plain, that is composed of the sediments discharged by Apenninian rivers, ends barred by sand dune ridges, pine tree forests and lagoons/marshes facing the Adriatic sea. Ravenna is the largest town of the area, that hosts an important industrial zone. The fluvial valley stretches from the pede-Apenninian hills south of Forlì up to Muraglione Pass, through formations of the Miocene-Pleistocene ranging from a turbiditic deposit uphill to clays and sands downhill. 18 moss samples were collected from the coastal plain and Ravenna except sample RM-22 collected from the Apenninian valley.

Analytical procedure

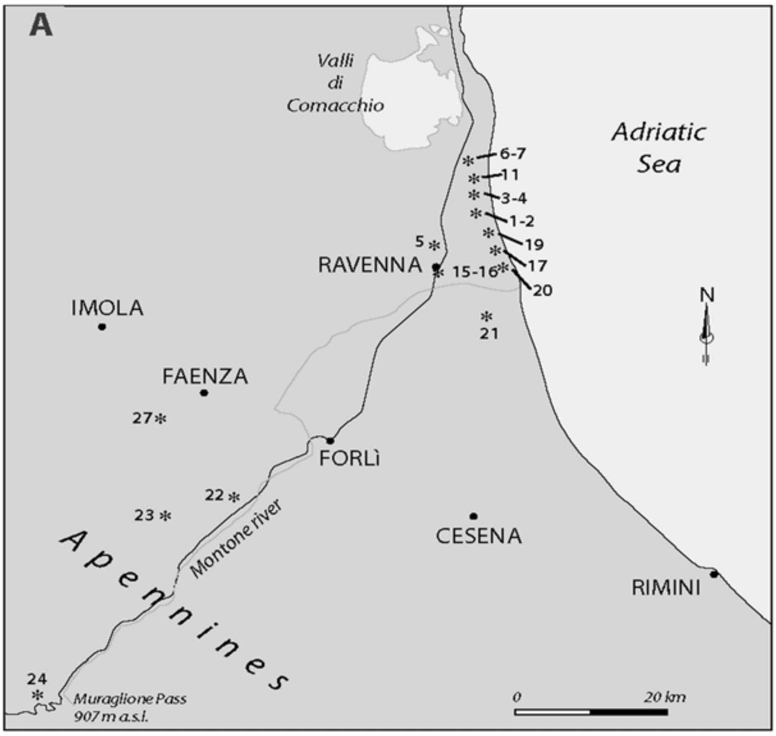
The collection of moss samples and their preparation for the chemical and isotopic analysis is described in detail by Cenci (1999). Therefore, here is given only a brief summary of the procedure. Samples were first washed with bi-distilled water to remove soluble salts, particularly for the mosses collected near the coast. Afterwards, samples were dried in a oven for 12 h at 105°C to drop moisture. Sr and Ca were extracted from 1-3 g splits of each sample, dissolved with a mixture of $HF+HNO_3+HClO_4$; their concentrations were determined using a Varian ICP-AES (Vista MXP Rad). Sr and Nd for isotopic analyses were separated in a 3 ml AG 50 W-X8 resin column.

Nd was separated from the other REE in 2-ml columns filled with hydrogen di-ethylhexylphosphate (HDEHP)-coated Teflon powder, following White and Patchett's (1984) procedure.

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.

Figure 1

Map showing the sampling locations of Romagna’s mosses. The inlet map shows the Romagna location.



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 (2s) as follows : NBS 987 $^{87}Sr/^{86}Sr$ =

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0.710241 ± 13 (n=20), $^{86}Sr/^{88}Sr$ normalized to 0.1194; La Jolla $^{143}Nd/^{144}Nd$= 0.511860±10; and $^{146}Nd/^{144}Nd$ normalized to 0.7219. Total procedural blanks were below 2 ng Sr and below 1 ng Nd for all samples. Sr-isotope ratios are expressed as $\delta^{87}Sr$ values in permil relative to seawater standard assumed to be 0 (Richter and De Paolo, 1987), while Nd-isotope ratios are reported as ε_{Nd} relative to CHUR standard (De Paolo and Wasserburg, 1976).

Analytical results

Table 1 shows the Sr-Nd isotope ratios of samples.

All samples from the Ravenna littoral and most from san Vitale Pinewood exhibit similar $\delta^{87}Sr$, that are generally higher than the value of the Apenninian sample. In particular, samples RM-11 and RM-21 from the innermost parts of san Vitale and Classe Pinewoods display the most negative $\delta^{87}Sr$. These two samples are considered to be the least potentially affected by anthropic pollution due to their secluded locations inside the two Pinewoods. As concerns ε_{Nd}, there is no significant difference among samples apart from mosses RM-11 and RM-22 displaying higher values.

Table1 - Sr and Nd isotope ratios of moss samples from Romagna.

site		sample	$\delta^{87}Sr$	ε_{Nd}
san Vitale Pinewood	south facing lagoon	RM-1	2,3	-9,1
san Vitale Pinewood	south facing lagoon	RM-2	2,6	-8
san Vitale Pinewood	middle facing lagoon	RM-3	3,6	-10,5
san Vitale Pinewood	middle facing lagoon	RM-4	1,2	-10,1
san Vitale Pinewood	middle facing lagoon	RM-5	-0,9	-9,3
san Vitale Pinewood	north next to Romea highway	RM-6	3,3	-10,9
san Vitale Pinewood	north inside the forest	RM-11	-1	-2,8
Downtown Ravenna urban park on a tree		RM-13	0,6	-6,7
Ravenna Littoral (Marina di Ravenna) facing the industrial zone		RM-19	1,9	-7,4
Classe Pinewood inside the forest		RM-21	-1.4	-7,1
Montone river valley site 1		RM-22	-0,2	-7,7

Discussion

To understand the significance of isotopic data, the latter have been plotted in the $\delta^{87}Sr$ vs ε_{Nd} diagram of Figure 2. It appears that most samples cluster along a hyperbola, that suggests mixing between two sources. One source is characterized by negative $\delta^{87}Sr$ and higher ε_{Nd}, while the other is represented by positive $\delta^{87}Sr$ and lower $\varepsilon_{Nd.}$ The isotopic characteristics of the former source suggest marine carbonates, while the values of the latter source suggest silicates from old crustal rocks. In other words, mosses would take the Sr and Nd present in the dust derived from the two lithotypes. Figure 2 also shows the reference fields of anthropogenic sources from the literature (Lahd Geagea et al., 2007, 2008a, b).

It appears that only 4 samples fall within the field of industrial pollution. In particular, it is surprising that 2 of these samples, i.e. RM-21 and RM-22 could be polluted, as the former was taken in the core of Classe Pinewood and the latter in the Apenninian valley of the Montone river, both sites being relatively far from sources of industrial contamination.

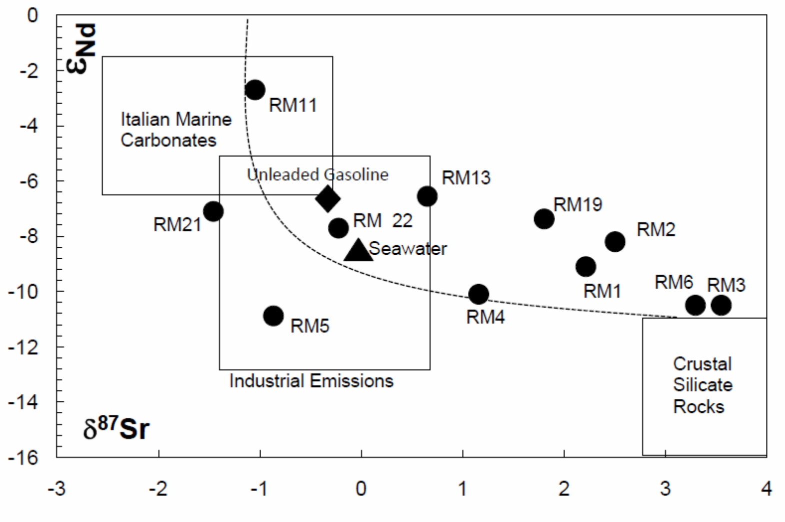

Figure 2

Plot of $\delta^{87}Sr$ vs ε_{Nd} for Romagna's mosses. Fields of natural and anthropic sources of Sr and Nd are also shown.

Of the two other samples, RM-13 was collected from the urban park in downtown Ravenna, and thus, far from the industrial zone; in contrast, its ε_{Nd} may suggest a contribution from traffic pollution, in agreement with the location of the park near to a traffic street. Lastly, sample RM-5 was collected from a farmland, relatively far from the industrial zone, thus, its isotopic signature may derive from dust, reflecting the isotopic composition of alluvium from Romagna's sedimentary Apennines. As a whole, unless to envisage that the isotopic ranges of industrial emissions of the Ravenna area are different from those reported in the literature, the 4 samples plotting in the field of industrial pollution can be reasonably considered exempt from significant contamination. Therefore, the isotopic data of these samples are likely explained by mixing between the two natural sources envisaged for the other moss samples. However, to exclude at all any significant anthropic contribution from industrial sources, it is necessary to extend the study to other samples from Romagna and areas of similar geologic composition but unaffected by major anthropic impact. It may also be useful to carry out the isotopic ratios of Pb on the same samples.

Conclusions

- The first Sr-Nd isotopic study of Italian mosses has been carried out, providing a set of data that join the very scarce data base of the literature on this topic.

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- The comparison of the isotopic signatures of mosses with the values characteristic of natural and anthropic sources of the two elements, does not provide any univocal indication of contributions from the potential anthropic sources. So far, isotopic data suggest a geogenic contribution of Sr and Nd from marine carbonates and old crustal rocks for all samples.
- Although preliminary, this study let us understand the potential information provided by Sr-Nd isotopes on the environmental quality of the air.

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