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Sr ISOTOPIC EVIDENCE FOR STUDYING THE SALINIZATION OF SOILS: AN EXAMPLE FROM THE SAN VITALE PINEWOOD (RAVENNA)

APPLICATION DES ISOTOPES DU Sr A L'ETUDE DE LA SALINISATION DES SOLS: UN EXEMPLE DANS LA PINEDE DE SAN VITALE (RAVENNE)

APPLICAZIONI DEGLI ISOTOPI DELLO Sr ALLO STUDIO DELLA SALINIZZAZIONE DI SUOLI: UN ESEMPIO DALLA PINETA DI SAN VITALE (RAVENNA)

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Abstract

In the frame of a multidisciplinary project of research on the San Vitale Pinewood ecosystem, north of Ravenna, the Sr isotope study of a soil profile developed on an old coastal dune aiming at detecting the effect of salinization is presented. The Sr isotope ratios of the bulk soil samples decreased significantly from upper (0.717) to lower (0.712) horizons because of the abundant marine salts deposited by the brackish water present in the deep soil. While the main source of Sr in the upper horizons is the silicates, especially the feldspaths contained in the old dune sediments; in contrast, Sr in the lower horizons is significantly also of evaporitic origin (0.707-0.709). This latter is dominantly the strontium bio-available to the plants.

Key words: Sr isotopes; soils; salinization; San Vitale Pinewood.

Résumé

Dans le cadre d'un projet multidisciplinaire de recherche sur le processus de salinisation des sols, nous présentons une application des isotopes du Sr à un profil de sol développé sur une ancienne dune côtière dans la Pinède S.Vitale, au nord de Ravenne. La composition isotopique du Sr dans les échantillons du sol tel quel diminue des horizons superficiels (0,717) aux horizons profonds (0,712) par suite de l'abondant dépôt de sels marins par l'eau saumâtre présente dans les horizons inférieurs du profil. Le strontium présent dans les horizons les plus superficiels provient des silicates de l'ancienne dune, en particulier des feldspaths, mais le strontium des horizons inferieurs provient en grade partie aussi du lessivage des évaporites (0,707-0,709). Le strontium biodisponible pour les plantes est surtout dérivé des évaporites.

Mots clés: isotopes du Sr; sols; salinisation; Pinède San Vitale.

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Riassunto

Nel quadro di uno studio multidisciplinare sui processi di salinizzazione che interessano i suoli della Pineta di san Vitale, a nord di Ravenna, viene presentato un esempio di applicazione degli isotopi dello Sr. La sua composizione isotopica nei campioni di suolo tal quale diminuisce significativamente dagli orizzonti superficiali (0,717) a quelli profondi (0,712), a causa della abbondante deposizione di sali marini ad opera dell'acqua salmastra presente nella parte bassa del profilo. Mentre lo Sr presente negli orizzonti superiori del suolo è essenzialmente quello dei silicati dell'antica duna, in particolare dei feldspati, lo Sr degli orizzonti inferiori deriva considerevolmente anche dai sali e minerali evaporitici (0,707-0,709). Lo Sr biodisponibile per le piante è essenzialmente quello derivato dagli evaporiti.

Parole chiave: isotopi dello Sr; suoli; salinizzazione; Pineta di S.Vitale.

Introduction

This paper illustrates a part of a multidisciplinary study of the *Pineta San Vitale* (hereinafter *Pineta*) ecosystem, dealing with the application of Sr isotopes to detect chemical processes occurring in the local soils, affected by salinization hazard. This may contribute to suggest solutions useful to stop or, at least, slow down the decline of the *Pineta* ecosystem.

It is known since the 90's that Sr isotopes may provide interesting information about the sources and the processes involving Sr in soils and groundwaters (e.g. Aberg, 1995; Capo et. al., 1998; Stewart et al., 1998; Négrel et al., 2001). In fact, Sr isotope ratios can allow for detecting the sources of Sr, distinguishing among the contributions from the minerals present in the soil and a variety of anthropogenic and natural sources supplying the element from outside, especially via atmospheric (dry and wet) deposition. These sources are represented by industrial and vehicular emissions, dust from soils, marine aerosol, as well as infiltration of waters from rivers, drainage canals and sea lagoons. All these anthropogenic and natural sources are present in the Ravenna area, that is a typical industrial and farming area near to the Adriatic coastline. Moreover, Sr isotope ratios can allow for determining the main sources of Sr available to the plants, i.e. bio-available Sr. Two papers on the Sr isotopic composition of Sardinian soils have been carried out by Castorina and Masi (2007, 2008); they represent the first contributions concerning Sr isotopes applied to Italian soils.

Geological setting and sampling

Among the soil sites distributed along two transects cutting transversally the *Pineta* area, we have selected Pin-9 site as representative for this paper. This soil profile, the thickness of which encompasses about 1 m, is composed of two main horizons A and C, in turn subdivided in A1 and A2, and C1 and C2 subhorizons, respectively. A level of turf occurs at depth of 30 cm. The soil, that is located at 0.12 m a.s.l., is totally inundated by brackish-saline water at 50 cm of depth.

Analytical procedure

Each sample was first washed with bidistilled 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. 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.

Experimental results

Figure 1 depicts the patterns of the vertical distribution of Sr isotopes in the bulk-soil samples and the acetic extracts. The Sr isotopic compositions of the water-soluble salts exhibit no significant variation with depth (0.7091-0.709). In contrast, the Sr isotope ratios of the bulk-soil samples decrease significantly and systematically with depth (0.717-0.712), while the isotopic compositions of the acetic extracts display only slight decrease with depth (0.709 -0.708).

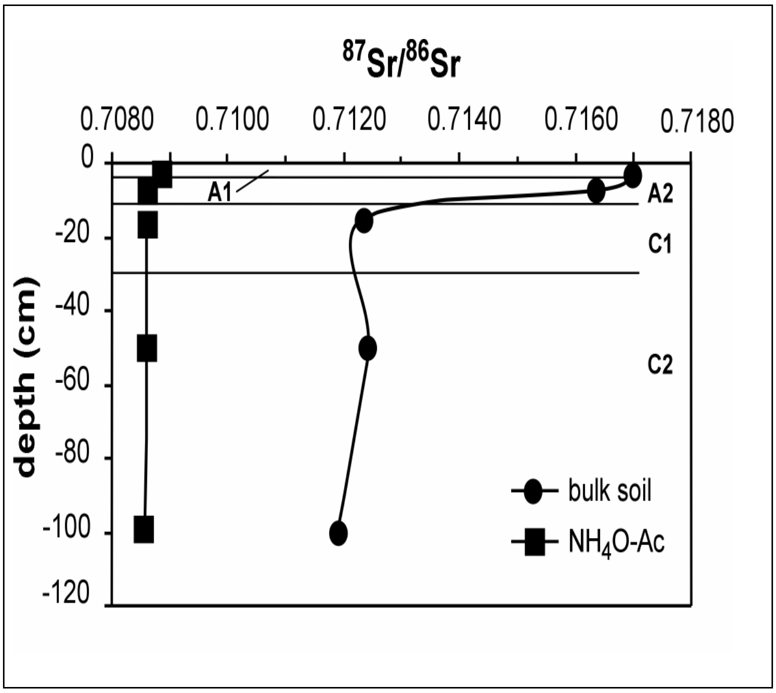

Figure 1

Distribution of the Sr isotopes in the bulk-soil samples and the acetic extracts of PIN-9 soil profile.

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Discussion

As concerns the water extracts, the rather uniform distribution of the Sr-isotope ratios with depth through the profile indicates that the strontium contained in the soluble salts proceeds from a same source. As the latter displays Sr isotopic composition comparable with present-day seawater (Hodell et al., 1990), marine salts represent the source of Sr in the water extracts. Marine salts can be air-borne to the soil as aerosol and/or deposited by the brackish water present in deeper horizons of the soil.

As concerns the bulk-soil samples, their Sr isotopic compositions are always higher than the value of present-day seawater, indicating that bulk Sr derives from a different source. However, as the Sr isotope ratios of the samples from the A horizons are higher than those from the C-horizon samples, there is suggestion of mixing of Sr supplied by two sources. One source is characterized by Sr isotope ratio > 0.717, while the other source displays Sr isotope ratio <0.712. In particular, the higher value suggests a contribution from the silicates, especially from feldspars rather than Rb-rich micas (Conticelli et al., 2002). In contrast, the source characterized by Sr isotope ratio lower than 0.712 may be identified in seawater or marine salts, especially carbonates. They are more abundant in deeper horizons, where they are deposited in the soil pores by brackish water. The significantly variable proportions of the mixing components through the soil profile are clearly evidenced by the sharp decrease of the Sr isotope ratios passing from the A to the C horizon, where the marine component is comparatively more important.

The acetic extracts display Sr isotopic ratios lower than present-day seawater, indicating that the marine carbonates present in soil are not only those derived from present-day seawater but also of older age (0.707-0.709; McArthur et al., 2001).

Lastly, an aliquot of the strontium present in the water and acetic extracts may derive from desorption of the element from colloids and minerals because of the leaching of the samples.

Conclusions

The Sr-isotope ratios of the samples from the different horizons of the soil have brought evidence on the sources of the element and its potential bio-availability to the plants. Two main sources have been recognized: one represented by marine carbonates, the other represented by the silicates, especially the feldspars. Bulk Sr in the soil derives from mixing of the element supplied by the two sources. Moreover, Sr isotopes allow for distinguishing between the carbonates deposited by present-day seawater responsible of the salinization of the soil, and marine carbonates of older age contained in the soil sediments. Bio-available Sr to the plants is only that released mainly from soluble salts and carbonates. Present-day carbonates are deposited by either marine aerosol in the surficial horizons of the soil, and brackish-saline waters at depth.

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