APPLICATION OF O-H-B-Sr ISOTOPE SYSTEMATICS TO THE EXPLORATION OF SALINIZATION AND FLUSHING IN COASTAL AQUIFERS : PRELIMINARY DATA FROM THE PIALASSA BAIONA ECOSYSTEM (ADRIATIC SEA)

APPLICATION DES SYSTÉMATIQUES ISOTOPIQUES O-H-B-Sr À L'ÉTUDE DES PROCESSUS DE SALINISATION D'AQUIFÈRES CÔTIERS: LA PIALASSA DE LA BAIONA (MER ADRIATIQUE)

APPLICAZIONE DELLE SISTEMATICHE ISOTOPICHE DI O-H-B-Sr ALLO STUDIO DEI PROCESSI DI SALINIZZAZIONE DI ACQUIFERI COSTIERI: LA PIALASSA DELLA BAIONA (MAR ADRIATICO)

Riccardo Petrini [(1)*], **Maddalena Pennini** [(2)], **Alessandra Adorni Braccasi** [(2,1)], **Barbara Stenni** [(3)], **Onelio Flora** [(3)], **Umberto Aviani** [(1)]

[(1)]Dipartimento di Scienze della Terra, Università di Trieste
[(2)]Istituto di Geoscienze e Georisorse, CNR – Pisa
[(3)]Dipartimento di Scienze Geologiche, Ambientali e Marine, Università di Trieste
∗ Corresponding author: e-mail: rpetrini@units.it

Summary

O, H, B and Sr isotopes were identified from surface-waters, ground-waters and waters percolating in soils at the Pialassa Baiona lagoon and nearby inland areas. The preliminary data demonstrate the occurrence of both conservative mixtures between seawater and freshwaters and cation exchange at the salt/fresh water interface during the intrusion. The O and H isotopes indicate that the freshwater component in the binary mixing had the isotopic features of the rainwater from Apennine catchments. Coupled O-H-B isotopes also show that the major contribution of the moving seawater was confined to the deeper aquifers and some of the soil waters. The Sr isotopes highlight the role of cation exchanges when seawater flushes freshwater aquifers, and allow the recognition of the different components of the solute. Deviations from these processes as revealed by B isotopes are interpreted as the evidence of possible anthropogenic inputs.
Key-words: *Stable-isotope geochemistry; saltwater intrusion; coastal aquifers;Pialassa Baiona.*

Résumé

Les isotopes de l'O, H, B et Sr ont été analysés dans les eaux de surface, les eaux souterraines et les eaux de percolation dans les sols dans la lagune de Pialassa Baiona et dans les zones côtières voisines. Ces données préliminaires montrent l'existence de mélanges entre eau de mer et eaux douces et, simultanément, d'échanges cationiques à l'interface eaux douces-eaux salines lors de l'intrusion

marine. Les isotopes stables de l'eau (O, H) indiquent que la composante douce dans le mélange binaire porte la signature isotopique des eaux de pluie des bassins versants de l'Apennin. Le couplage O-H-B montre que l'intrusion de l'eau marine est limitée aux aquifères profonds et à quelques-unes des eaux du sol. Les isotopes du Sr mettent en évidence le rôle des échanges cationiques et permettent de discriminer les différentes composantes de la solution. Des déviations de ce schéma, indiquées par les isotopes du B sont interprétées comme indicatrices de l'activité humaine.

Mots-clés: *Géochimie des isotopes stables; intrusion saline; aquifères côtiers; Pialassa Baiona.*

Riassunto

Sono stati ottenuti dati isotopici di O,H,B e Sr su campioni di acque superficiali, di falda e di percolazione in suoli nell'area lagunare della Pialassa Baiona e zone limitrofe costiere del mare Adriatico settentrionale. I dati sono interpretabili in termini di processi di mescolamento tra acqua di mare e gli acquiferi costieri, con l'aggiunta di fenomeni di scambio ionico associati alla intrusione. In particolare gli isotopi di O-H suggeriscono che la salinazione interesserebbe acque dolci di provenienza appenninica. Gli stessi isotopi, in aggiunta ai dati isotopici di B, indicano che i maggiori effetti della intrusione interessano le acque dei piezometri più profondi ed alcune delle acque dei suoli. Gli isotopi dello Sr identificano gli apporti al soluto da diverse sorgenti e tracciano i fenomeni di scambio che sembrano più efficaci nella porzione settentrionale dell'area. Deviazioni dai processi di mescolamento-scambio ionico sono interpretate come evidenza di apporti antropici.

Parole chiave: *Geochimica degli isotopi stabili; intrusione salina; acquiferi costieri; Pialassa Baiona.*

Introduction

Coastal aquifers are complex hydrogeological systems characterized by a high lateral and temporal variability in terms of a number of physico-chemical properties (Abbiati, 2003; Michael *et al.*, 2005). In these ecosystems elements undergo transfer through simple mixing between freshwater and seawater and consequent formation of brackish waters, and removal/enrichment processes by ion-exchange processes, absorption between soil and solution, sorption on soil organic matter and the formation of secondary minerals (e.g. Lambrakis, 2006).

The understanding of cation sources and fluxes is hence of primary interest in the study of the environmental changes related to coastal aquifers.

In this context, isotopes offer a valuable contribution which couples with the major and trace element chemistry. In particular, oxygen and hydrogen give indication on the recharge areas and trace the mixing of water bodies with different salinity, while strontium and boron add information on the water-rock (or soil) interaction, as well as on the contribution of anthropogenic sources.

The Pialassa Baiona is an artificial lagoon system created by the water courses regularization from the 18th century. The lagoon maintenance is possible only with continuous interventions of control of the input channels.

In the Pialassa Baiona - San Vitale Pinewood system sandy facies are dominant (Marchesini et al., 2000) and create several permeable horizons separated by sandy-silt or clay levels and with high lateral and vertical variability. This fact causes aquifers differentiation.

Subsurface sediments contain a wide variety of Holocene deposits, with fluvial, deltaic, coastal and shallow-marine facies (Amorosi *et al.*, 1999).

The subsidence natural rate of the study area is about 2.5 mm/year (Gabbianelli et al., 2003), and reached the peak of 110 mm/year after World War II due to the groundwater pumping and gas production (Teatini et al., 2005). The consequence is the marine ingression and the salinization of deep and surface aquifers and the death of the San Vitale Pinewood.

The water circulation is complex and depends on permeability of the different deposits facies and the hydraulic gradient of the water table. Tides cause the seawater inflow through channels and the replacement of the brackish waters.

Materials and methods

Surface waters, precipitations, superficial and deep stratum waters have been sampled.

Surface stratum waters (less than a meter deep) were sampled through soil profiles dug with hand drills. Deep stratum waters were sampled using the piezometers which are placed in the San Vitale Pinewood. Rainwater was sampled through two pluviometers, one placed in the ITAS Department near the study area and the other placed on the Apennine supply basin. Samples for B and Sr isotopic analyses were filtrated in the field at 0.2 and 0.45 microns and stored in poliethylene bottles. Samples for O-H analyses were preserved without any treatment in poliethylene bottles completely filled to avoid any possible isotopic exchange with the atmospheric oxygen.

The boron isotopic composition was determined, after an ion exchange procedure, by positive-thermal ionization mass spectrometry. The boron isotopic composition is expresses as $\delta^{11}B$, i.e. the permil deviation from the certified composition of the NIST-SRM 951 standard.

The oxygen isotopic composition was measured by means of a water-CO_2 equilibration technique at 25°C using a VG Optima mass spectrometer.

The H isotopic analyses were made by water-H_2 equilibration technique at 18°C using a platinum catalizer on a Thermo Finnigan Delta Plus mass spectrometer with an automatic line HDO Device. Sr isotopes were measured by using a VG Micromass 54E mass spectrometer and standard procedures.

Results

The oxygen and hydrogen isotope ratio on rainwater (reported as δ^{18}O- δD values, which represent the ‰ deviations with respect to the standard mean oceanic water SMOW allowed a first construction of a local meteoric water line, given by δD = 7.47*δ^{18}O+9.70. Superficial-water, ground-water and waters in soils have δ^{18}O and δD values in the range -8.53‰ ÷ -0.69‰ and -60.1‰ ÷ -5.8‰, respectively; it has to be noted that waters from the deeper piezometers are characterized by less negative values with respect to the shallower ground-waters. Waters in soils cover a wide range of isotopic compositions. Some of these water samples show an isotopic shift towards the meteoric water line following events of heavy rain, suggesting the direct contribution of precipitation by infiltration. The water channels which supply freshwater are characterized by the most negative isotopic composition with respect to all the remaining samples. The Sr isotopic composition, expressed by the ^{87}Sr/^{86}Sr ratio, is in the relatively narrow range between 0.70872 and 0.70935, with most samples clustering to 0.7091, a value which is close to what measured in seawater at Pialassa Baiona lagoon.

In superficial-water, ground-water and waters in soils δ^{11}B ranges between +5.7‰ and +38.6‰; the higher values approach the composition of Mediterranean seawater and are recorded by the deeper piezometers and some of the soil waters.

Discussion and conclusions

In the δ^{18}O vs. δ D diagram (Fig. 1), the water samples define a straight line which deviates from the local line of precipitations, and is interpreted as the progressive mixing between freshwaters, as defined by the Apennine catchments, and seawater. A first modeling quantifies the seawater contribution as about the 70-90% and 30-60% for the water bodies sampled by the deeper and shallow piezometers, respectively. The contribution of the marine component for most waters from soils would be in the relatively limited range between 40-50%, with the exception of two samples from the northern side of the area, reaching the 75-80%. The δ^{11}B correlates with δ^{18}O (Fig. 2) in ground- and soil- waters. A mixing at different degrees of the recharging fresh, low-B water (Lamone river–type) with seawater could explain the observed δ^{11}B variation. However, in the Northern sector of the *Pineta di San Vitale* boron characteristics in soil water diverge from the main fresh-seawater mixing trend.

More complex processes are needed to explain the isotopic composition of the Pialassa Baiona waters; as also suggested by the observed range in the ^{87}Sr/^{86}Sr ratio (Fig. 3) that indicates the contribution from different sources to the Sr budget. These processes involve cation exchanges with the solid phase triggered by seawater intrusion, the role of organic matter and anthropogenic sources.
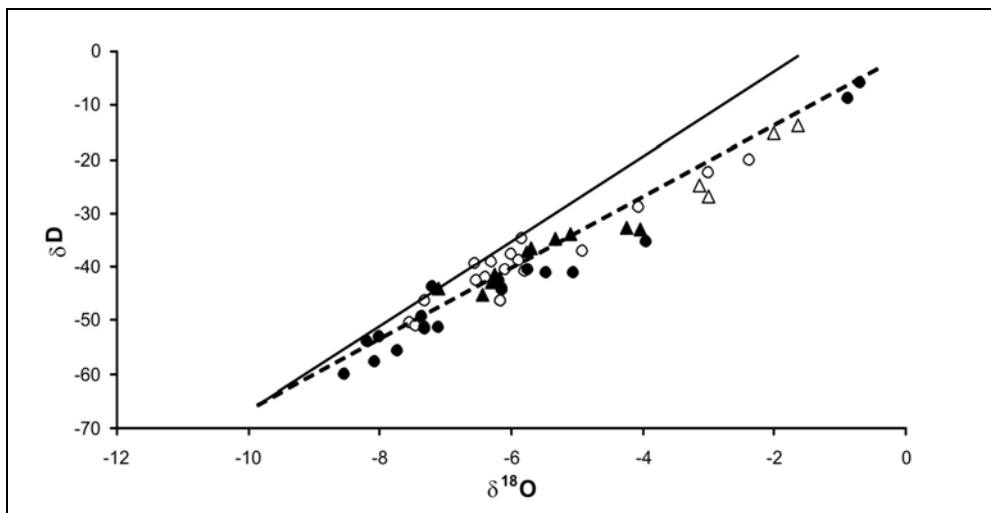
Figure 1 - *δ¹⁸O vs. δD correlation diagram.*
The lines of local precipitation (solid line) and mixing between fresh- and sea-waters (dashed) are also superimposed. Symbols are: open triangle: deep piezometers; solid triangle: superficial piezometers; open circle: water in soils; filled circle: water channels.
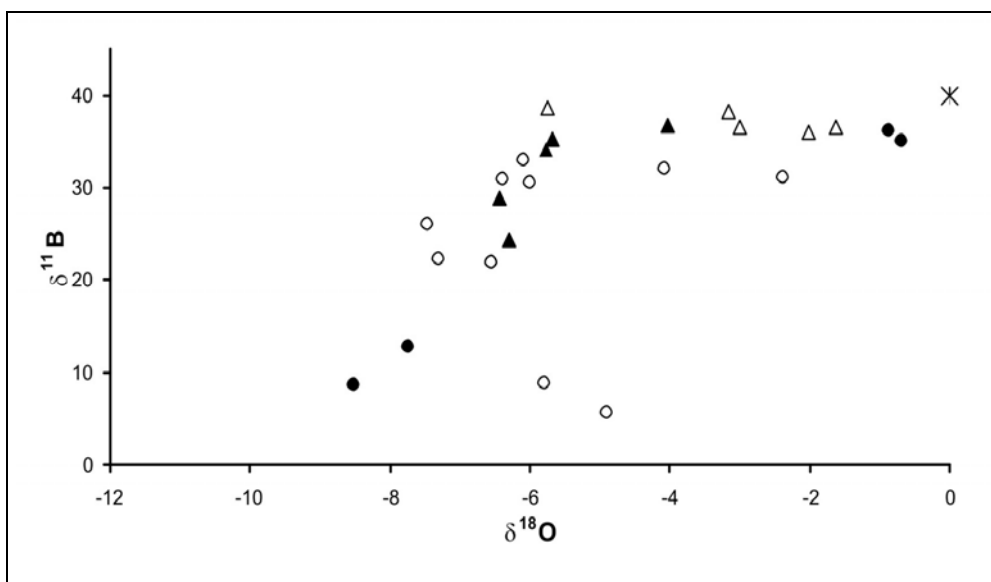

Figure 2 - *δ ¹⁸O vs. δ ¹¹B correlation diagram for the studied samples. Symbols as in the previous figure. The star represents seawater composition.*

Figure 3

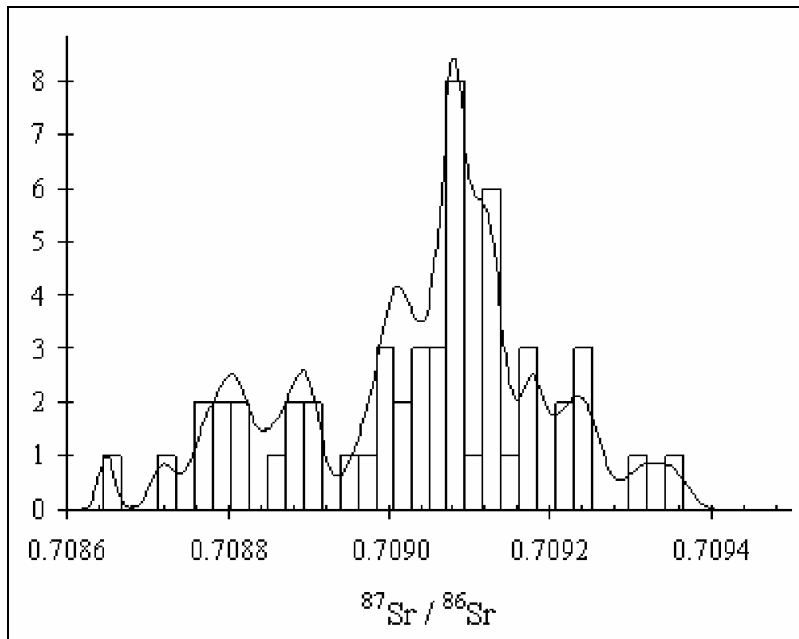*Distribution of the $^{87}Sr/^{86}Sr$ isotopic ratios.*

Possibile sources are:
1) freshwaters;
2) seawater;
3) rainwater;
4) water involved in cation exchanges;
4) fertilizers

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