Sr isotopes as mixing and lithological tracers: the Ebro River Basin

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Sr isotopes as mixing and lithological tracers; the Ebro River Basin

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Abstract

The Ebro River, located in North-Eastern Spain, rises near the Atlantic coast in the Cantabrian Mountains and flows into the western Mediterranean Sea through several large cities and agricultural, mining and industrial areas. The river is one of the largest contributors of freshwater in the Mediterranean Sea and ends in the Ebro delta. Through sampling of the Ebro River along its main course and its main tributaries during one field campaign, the behavior of Sr and its isotopes during water/rock interactions at the scale of a large river basin having various lithologies is reported.

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Keywords: Ebro River; Sr isotopes; Water–rock interactions

1. Introduction

This study is part of an ongoing research based mainly on the isotope composition (H, O, Li, B, S and O) together with major and trace elements (SO_4, Ca and Sr) in the dissolved load of 25 river samples collected within the Ebro River Basin in Spain. The Ebro River is one of the largest contributors of freshwater in the Mediterranean Sea and ends in the Ebro delta, one of the most important wetlands in Europe. Bedrocks of the Ebro River Basin are mainly dominated by carbonates and evaporites from the Paleozoic and Mesozoic terrains. This study complements previous investigations using geochemical tracers (major and trace elements, isotopes)[1-3] that revealed evaporate dissolution and input from carbonates as main weathering end-members plus weathering of silicate minerals. The objective is to characterize the processes controlling the Sr isotope signatures of a large river draining predominantly sedimentary bedrocks.

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2. Sample locations and methodology

Representative bedrock samples were also collected along the Ebro river (Fig. 1). Lithologies considered in the sampling strategy include gypsum-anhydrite (4 samples) and carbonate (4 samples). Gypsum samples were collected in Navarra. Sample collected in Ablitas (Fig 1, labelled A) represent the continental deposits of the Miocene while the sample collected in Mafïeru (Fig. 1, labelled B) corresponds to the continental deposits of the Oligocene. One anhydrite sample was collected in the Navarrese Potash Basin located in Navarra (Fig. 1, labelled C) and corresponds to the marine deposits of the Eocene while the second one, collected in Espinagosa (near Barcelona, Fig.1, labelled D) represents the deposits from the Trias (Keuper). Carbonates were collected in several places. The Trias (Muschelkalk) gypsum sample was collected from a core (5.50 m depth) done in Baix (near Tarragona, Fig. 1, labelled E). The continental Miocene was collected in the same place as the gypsum sample in Ablitas (Navarra, Fig. 1, labelled F); the continental Paleocene (Garumnian carbonate facies was collected in Tremp (near Lleida, Fig. 1, labelled G). Finally, the Oligocene carbonate facies was collected in Fraga (near Huesca, Fig. 1, labelled H).

The main Ebro River was sampled upstream and downstream from the confluences of these main tributaries (Fig. 1, numbered 1 to 5) and its main tributaries also sampled (Fig. 1, numbered 7 to 14). Water samples were collected in the middle of each river channel from bridges. The water samples were chemically analyzed by HPLC (Cl, SO_4, NO_3), ICP-AES (Ca, Na, Mg, K) and ICP-MS (Sr). Chemical purification of Sr was performed using an ion exchange column (Sr-Spec) and Sr isotopes were analyzed with a Finnigan MAT 262 thermo ionization multi-collector mass spectrometer.

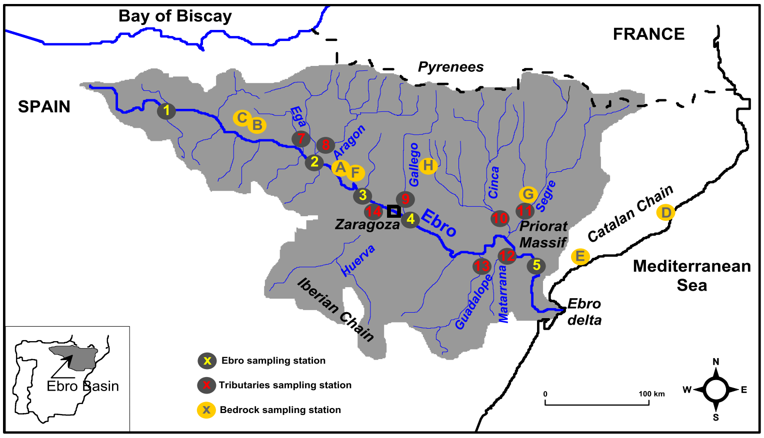

Fig. 1. Location of the Ebro basin in Spain, and of the sampling points , the main river was sampled upstream and downstream from the confluences of the main tributaries (numbers 1 to 5); the tributaries were sampled (numbers 7 to 14); the bedrock samples are referred A to H.

3. Results and discussion

The eight collected tributaries of the Ebro River show $^{87}Sr/^{86}Sr$ ratio ranging from 0.70786 for the Rio Guadalope with the maximum of Sr content (5090 µg l^{-1}) up to 0.70897 for the Rio Segre with a Sr content around 1840 µg l^{-1}. The lowest Sr content is 970 µg l^{-1} for the Rio Aragon with an intermediate $^{87}Sr/^{86}Sr$ ratio of 0.70814.

Along the Ebro main stream, the samples were collected from 100km up to 450km downstream the river source. The Sr content of samples collected in April along the Ebro main stream increases from 104 µg l^{-1} in the most upstream point up to 1850 µg l^{-1} around 350 km downstream and then decreases to 1270 µg l^{-1}. The $^{87}Sr/^{86}Sr$ ratio first decreases down to 250km downstream, between 0.70864 in location 1 and 0.70837 in location 3 and then increase up to 0.70849 in location 5. As for the Sr content, the variation of the $^{87}Sr/^{86}Sr$ ratio along the main stream fully agrees with the junction with the tributaries.

Fig. 2a shows the variation of the $^{87}Sr/^{86}Sr$ versus the Sr content for the bedrocks without any evidence of relationship. Data are scattered along the $^{87}Sr/^{86}Sr$ axis for the carbonate bedrocks with a ratio ranging from 0.70779 to 0.70918 and a Sr content ranging from 120 up to 1035 µg g^{-1} while the evaporite bedrocks display a $^{87}Sr/^{86}Sr$ ratio from 0.70766 to 0.70830 and a Sr content varying between 2380 and 4590 µg g^{-1}. Fig 2b illustrates the geology of the Ebro Basin.

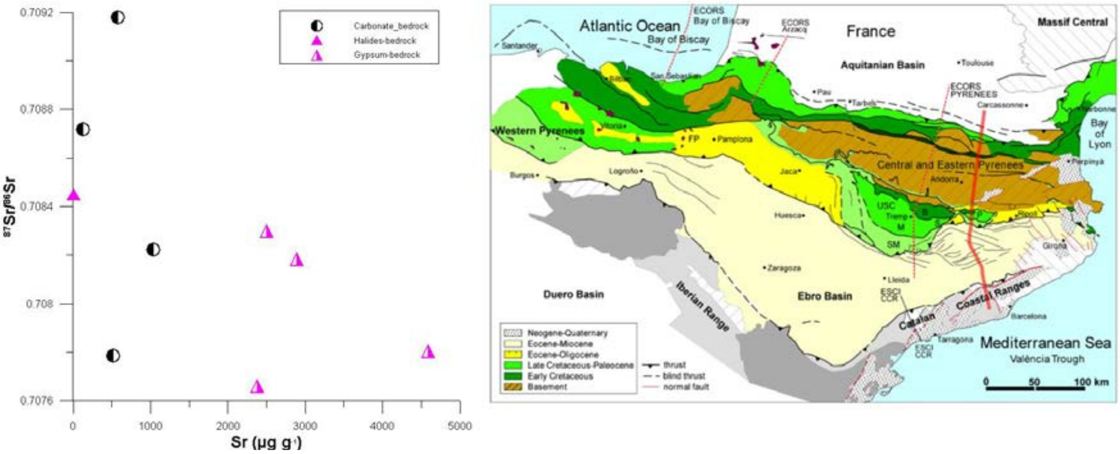

Fig. 2. (a) Plot of the $^{87}Sr/^{86}Sr$ versus the Sr content for the bedrocks, gypsum-bedrock includes gypsum and anhydrite; (b) Simplified geological map of the Pyrenees, including the Ebro River Basin (source: www-personal.umich.edu).

The Sr isotopic composition of surface waters from various tributaries of the Ebro River can be compared to constrain the lithologies/surface water systems. This is based on the fact that $^{87}Sr/^{86}Sr$ ratios vary with Rb/Sr ratios, the age of the material and, since natural processes do not fractionate Sr isotopes, the measured differences in $^{87}Sr/^{86}Sr$ ratios are the result of mixing of Sr from different sources with different isotopic compositions. The sources of Sr that might control the $^{87}Sr/^{86}Sr$ ratio can be constrained by the relationships between the Sr isotopic composition and concentration ratios. Fig 3a illustrates the relationship in a $^{87}Sr/^{86}Sr$ versus 1/Sr graph for the tributaries, the Ebro main stream and the bedrocks. The tributaries are scattered into two groups with the Guadalope, Matarrana, Aragon and Ega having the lowest $^{87}Sr/^{86}Sr$ ratios which decrease as the Sr concentration increases (from Aragon to Guadalope) and the Huerva, Gallego, Cinca, Segre having the highest $^{87}Sr/^{86}Sr$ ratios whereas the concentration does not vary significantly between the samples. The first set of samples is more related to the signature of the bedrocks C-D-G (Eocene marine anhydrite, Trias anhydrite and continental Paleocene carbonate) while the second are more related to the bedrocks E-H (Trias gypsum and Oligocene carbonate). For the Ebro main stream, the initial Sr signature of the river rapidly evolves when the distance increase, the $^{87}Sr/^{86}Sr$ ratio decreases and the Sr content increases from 100 to 250km from the river source. Then the Ebro signature moves towards slightly higher $^{87}Sr/^{86}Sr$ and 1/Sr ratios (350km) and ends at 450km with an increase of the $^{87}Sr/^{86}Sr$ ratio and a decrease of the 1/Sr ratio. Two of the end-members mixing can be identified as rock sources in this figure, mainly for the tributaries. The evolution of the $^{87}Sr/^{86}Sr$ and 1/Sr ratios in the Ebro main stream started with Sr signature representing the third end-member with the lowest Sr concentration, corresponding to an intermediate value of the Sr isotope signature of the bedrocks.

The use of a cation ratios rather than absolute concentrations alone avoids variations due to dilution or concentration effects The $^{87}Sr/^{86}Sr$ versus the Ca/Na ratios in Fig 3b suggested the influence of three end-members and it is worth noting that this combination help to better constrain the end-members as the variation in the Sr isotopes between the halides, anhydrites and carbonate end members is significant. The dissolution of silicate cannot be considered in the mixing scheme (low Ca/Na and high $^{87}Sr/^{86}Sr$ ratios). Two mixing lines can be calculated[4] between three end-members as illustrated in Fig. 2b and explaining all of the data. The variability in the tributaries is explained by two calculated mixing lines. The first one rely the halide end-member (lowest >Ca/Na ratio) and a carbonate end-member with the highest $^{87}Sr/^{86}Sr$. This end-member is represented by an Oligocene carbonate facies collected near Huesca on the Cinca basin (Fig. 1, sample labelled H). The second one rely the halide end-member and an anhydrite end-member with the lowest $^{87}Sr/^{86}Sr$. This end-member is represented by a Trias (Keuper). anhydrite sample collected near Barcelona (Fig.1, labelled D).

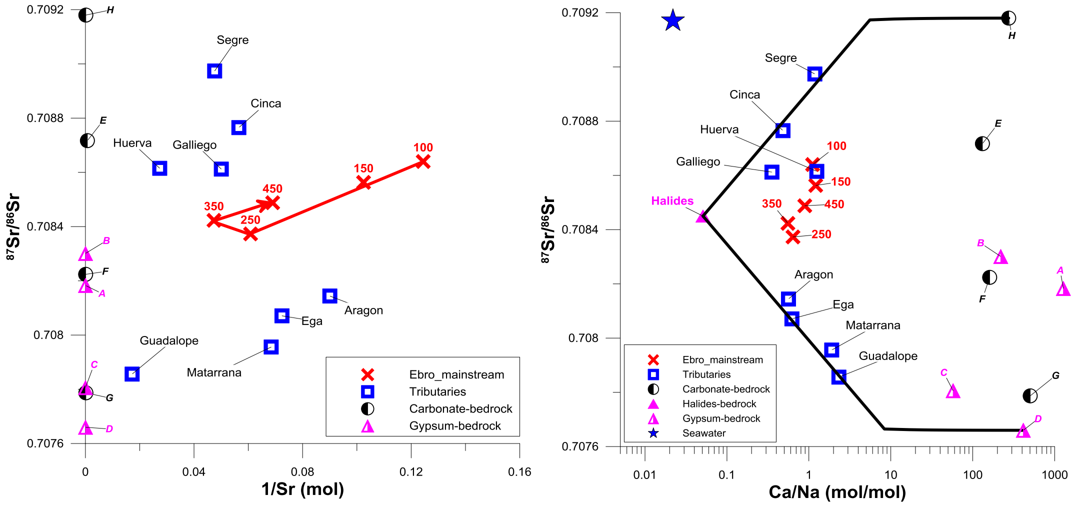

Fig. 3. (a) Plot of the $^{87}Sr/^{86}Sr$ versus the reverse of the Sr content in the main river (red numbers are the distance from the source of the river), the tributaries and the bedrocks; (b) Plot of the $^{87}Sr/^{86}Sr$ versus the Ca/Na ratios in the main river, the tributaries and the bedrocks. Red numbers are the distance from the source of the river for the sampling along the main stream of the Ebro.

4. Conclusion

The behavior of Sr and its isotopes during water/rock interactions was investigated at the scale of the Ebro (Spain), a large river basin. Comparing Sr isotope ratios and Sr contents illustrates the hydrological functioning of the Ebro River. The evolution of the $^{87}Sr/^{86}Sr$ and Sr contents along the main stream of the river fully agree with the junction with the tributaries, confirming that Sr isotopes are an excellent tracer of water mixings at the basin scale in most of the cases. Comparing Sr isotope and Ca/Na ratios evidenced the role of anhydrites/halides weathering for some tributaries (Guadalope, Matarrana, Aragon, Ega), the role of carbonates/halides weathering for the others (Gallego, Cinca, Segre); the Ebro main stream being a mix of both lithologies.

Acknowledgements

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