



Sr isotopic signatures of Portuguese bottled mineral waters, their relationships with the geological setting and potential use for product authentication

Sara Ribeiro, Maria do Rosário Azevedo, José Francisco Santos, Jorge Medina
Department of Geociences, Geobiotec, University of Aveiro

Abstract

The Sr isotopic ratios of nine bottled natural mineral waters from Portugal were measured in the Laboratory of Isotope Geology of the University of Aveiro (LGI-UA). The results obtained show that the Sr isotopic variability of these waters is strongly correlated with the age and mineralogical composition of the aquifer source rocks.

The lowest $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are found in water samples from the Monchique aquifer ($^{87}\text{Sr}/^{86}\text{Sr} = 0,70447$), located in Late Cretaceous alkaline magmatic rocks of mantle origin. The *Vimeiro* waters are hosted in carbonate and evaporite formations of Jurassic age and have $^{87}\text{Sr}/^{86}\text{Sr}$ values of 0,70808, whereas the waters sourced in Cenozoic siliciclastic sediments tend to exhibit higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, close to the rainwater value (São Silvestre; $^{87}\text{Sr}/^{86}\text{Sr} = 0,71078$). Finally, the waters coming from granitic and/or metamorphic terrains of the Iberian Variscan basement (Vitalis, Luso, Carvalhelhos, Fastio, Serra da Estrela) display the most radiogenic Sr isotopic signatures ($^{87}\text{Sr}/^{86}\text{Sr} > 0,7136$).

In the modern commercial context, the differences encountered provide a powerful tool for fingerprinting the mineral water origin and may be used for purposes of mineral water authentication. The use of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios may also be extended to studies on the provenance of some foods and beverages, taking into account the influence of the geological / pedological factor on the Sr isotopic composition recorded by the plants.

Rb-Sr isotopes

Strontium is a divalent cation that can easily substitute Ca^{2+} in the crystal lattice of Ca-bearing minerals, such as plagioclase feldspar, apatite, titanite, calcite, aragonite and dolomite. It has four naturally occurring isotopes ^{84}Sr , ^{86}Sr , ^{87}Sr and ^{88}Sr . The ^{84}Sr , ^{86}Sr and ^{88}Sr isotopes are stable, whereas ^{87}Sr derives from the radioactive decay of ^{87}Rb . As a result, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in rocks and minerals tend to increase with time.

Unlike Strontium, Rubidium is incorporated in K-bearing silicate minerals, including K-feldspars, micas and clay minerals. Of the two naturally occurring Rb isotopes (^{85}Rb and ^{87}Rb), ^{87}Rb is radioactive and decays to radiogenic ^{87}Sr by β - emission.

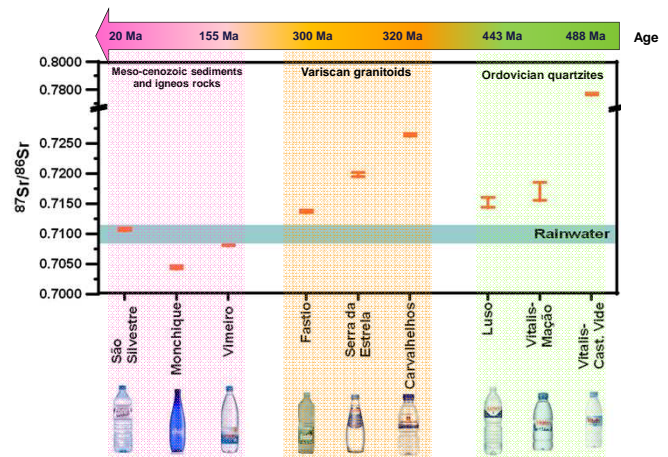


Fig. 3 Average $^{87}\text{Sr}/^{86}\text{Sr}$ isotope compositions of Portuguese bottled mineral waters. The shaded area represents the range of rainwater values in Portugal (data from this study and from bibliography).

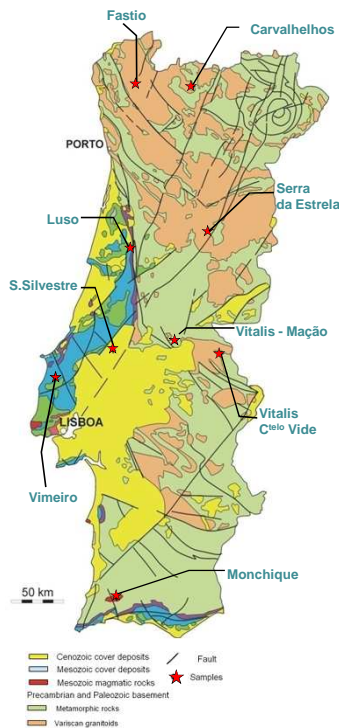


Fig.2 Simplified geological map of Portugal with the geographic distribution of bottled water samples

The Sr released to the water is a function of both the isotope composition and the stability of the aquifer bedrock forming minerals. As the reaction kinetics of mineral dissolution may vary over several orders of magnitude, the Sr isotope signature recorded in the water is dominantly controlled by the most easily weathered minerals and does not always reflect the bulk isotopic composition of the parent rock.

It is therefore possible to apply Sr isotopes, in combination with other chemical and isotope data, for source authentication purposes. Since water is completely bio-available to plants and animals and can be transferred to any organic material without significant fractionation of Sr isotopes, the determination of $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios has also been widely used to trace the geographic origin of a large variety of food products (e.g. wine, milk, butter and fruit juices).

Results and discussion

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios obtained in nine bottled mineral waters from Portugal mainland are presented in Fig. 3. The characterization of each brand of water involved the measurement of two / three replicate samples with different bottling dates, during a sampling period of two years. Based on the results obtained, it is possible to draw the following conclusions:

- each of the analysed water samples exhibits a distinctive Sr isotope signature that does not change significantly with time and can therefore be used for purposes of mineral water authentication;
- the Sr isotope ratios of the analysed waters are dominantly controlled by both the nature and stratigraphic age of the aquifer host rocks (Fig. 3). The least radiogenic waters are related to Jurassic carbonates / evaporites ($^{87}\text{Sr}/^{86}\text{Sr} = 0,70808$) and Late Cretaceous alkaline igneous sources ($^{87}\text{Sr}/^{86}\text{Sr} = 0,70447$). The Cenozoic siliciclastic sediments host waters with $^{87}\text{Sr}/^{86}\text{Sr}$ values of 0,71078. The waters coming from old granitic and/or metamorphic terrains of the Iberian Variscan basement display highly radiogenic Sr isotopic compositions ($^{87}\text{Sr}/^{86}\text{Sr} > 0,7136$);

(c) fluid-rock and fluid-mineral interaction processes involving lithologies composed by easily soluble minerals (calcite/dolomite, anhydrite/gypsum and halite) promote bulk isotope equilibrium between groundwater and parent rock (*Vimeiro* water).

(d) for water reservoirs interacting with silicate rocks, isotopic equilibrium with the whole-rock is rarely achieved due to the variable reactivity rates of their mineral constituents (*Carvalhelhos*, *Fastio*, *Serra da Estrela*, *Castelo de Vide*, *Luso*, *Ladeira de Envendos* waters). The bulk isotope equilibrium can only be approached by long-term fluid-rock interaction mechanisms at high temperatures (*Monchique* water).

(e) in non-carbonate environments, the input of radiogenic Sr to the water is a function of the stability, age and Rb/Sr ratios of the aquifer bedrock silicate minerals and appears to be mainly provided by the hydrolysis of plagioclase feldspar and, to a lesser extent, primary phyllosilicates or neo-formed clay minerals.

Conclusions

The presence of significant differences in the Sr isotope composition of the Portuguese bottled mineral waters provides a powerful tool for fingerprinting their origin and to trace the hydrogeochemical processes operating along water flow pathways.

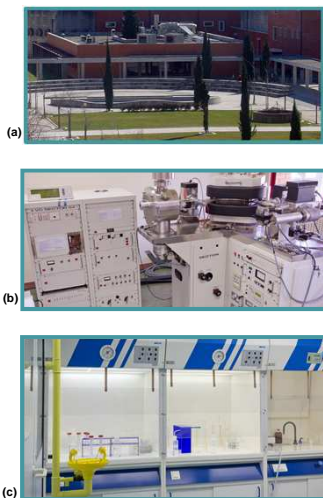


Fig.1 (a) - Overview of the LCA where LGI-UA is installed; (b) Thermal Ionization Mass Spectrometer (TIMS) VG Sector 54; (c) Clean laboratory

Thus, the age and the Rb content of a rock are the major factors controlling its present day $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. Old silicic crustal rocks with high Rb/Sr ratios have the most radiogenic Sr isotopic signatures ($^{87}\text{Sr}/^{86}\text{Sr} > 0,709$). In contrast, geologically young Rb-depleted basaltic rocks typically display the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0,703-0,706). Sr-enriched calcareous sediments and limestones are generally characterized by $^{87}\text{Sr}/^{86}\text{Sr}$ values ranging between 0,706 and 0,709.

Sr isotopes are not significantly affected by mass fractionation during chemical weathering processes.

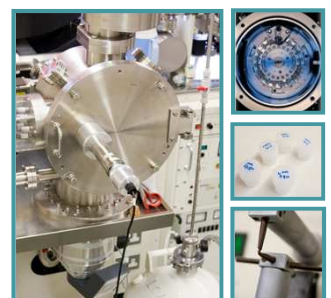


Fig.4 TIMS laboratory.