

# Sr isotopic signatures of Portuguese bottled mineral waters and their relationships with the geological setting

## Assinaturas isotópicas de Sr em águas minerais de Portugal e sua relação com o enquadramento geológico

S. Ribeiro<sup>1\*</sup>, M. R. Azevedo<sup>1</sup>, J. F. Santos<sup>1</sup>, J. Medina<sup>1</sup>, A. Costa<sup>2</sup>

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**Abstract:** This work presents the  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope compositions of nine samples of bottled waters from several regions of Portuguese mainland. The Sr isotopic variability displayed by the analysed waters is strongly correlated with the age and mineralogical composition of the aquifer source rocks, suggesting that the  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope signatures of these mineral waters are dominantly controlled by fluid-rock and/or fluid-mineral interaction processes. 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 hosted in carbonate and evaporite formations of Jurassic age have  $^{87}\text{Sr}/^{86}\text{Sr}$  values of 0.70808 and appear to have reached bulk isotopic equilibrium with whole-rock, whereas the waters sourced in Cenozoic siliciclastic sediments tend to exhibit  $^{87}\text{Sr}/^{86}\text{Sr}$  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*, *Carvalhos*, *Fastio* and *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 results obtained also show the relevance of Sr isotopes as geochemical tracers in hydrogeology.

**Keywords:**  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopic ratios, natural mineral waters, water-rock interaction processes.

**Resumo:** Neste trabalho, apresentam-se e discutem-se as razões isotópicas  $^{87}\text{Sr}/^{86}\text{Sr}$  obtidas em nove amostras de águas engarrafadas provenientes de vários pontos do território continental português. A variabilidade isotópica encontrada nas águas analisadas relaciona-se com a idade e com a composição mineralógica das rochas do aquífero de origem, o que sugere que as razões isotópicas de Sr são fortemente controladas por processos de interação água - rocha e/ou água - minerais. Os valores mais baixos de  $^{87}\text{Sr}/^{86}\text{Sr}$  encontram-se nas águas do aquífero de *Monchique* ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.70447$ ), que estão associadas a ocorrências magmáticas alcalinas do Cretácico superior. As águas de *Vimeiro*, captadas em formações carbonatadas e evaporíticas do Mesozoico apresentam valores de  $^{87}\text{Sr}/^{86}\text{Sr}$  de 0,70808, sugerindo que estas águas alcançaram o equilíbrio isotópico com as rochas do aquífero, enquanto as águas associadas a rochas sedimentares siliciclásticas de idade cenozóica possuem razões isotópicas muito próximas dos valores que se encontram na água da chuva (*São Silvestre*;  $^{87}\text{Sr}/^{86}\text{Sr} = 0.71078$ ). Por último, as águas procedentes de rochas graníticas e/ou metamórficas do soco varisco (*Vitalis*, *Luso*, *Carvalhos*, *Fastio* e *Serra da Estrela*) apresentam composições isotópicas de Sr mais radiogénicas ( $^{87}\text{Sr}/^{86}\text{Sr} > 0.7136$ ). Num contexto comercial as diferenças encontradas proporcionam uma ferramenta que poderá ser usada para fins de certificação da proveniência de águas minerais. Os resultados obtidos também mostram a importância dos isótopos de Sr como traçadores geoquímicos em hidrogeologia.

**Palavras-chave:** Razões isotópicas  $^{87}\text{Sr}/^{86}\text{Sr}$ , águas minerais engarrafadas, processos de interação água-rocha.

<sup>1</sup>Geobiotec, Departamento de Geociências da Universidade de Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal.

<sup>2</sup>Geodiscover – Consultores em Hidrogeologia, Lda.. Rua José Cardoso Pires, Lote 32, 2890-119 Alcochete, Portugal.

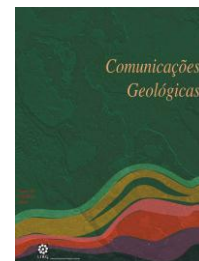
\*Corresponding author / Autor correspondente: [sararibeiro@ua.pt](mailto:sararibeiro@ua.pt)

### 1. Introduction

In the past decades, the European market of bottled mineral waters and spring waters has been steadily growing due to the progressive increase in the water consumption per capita (from 30 L to 108 L per year over the period 1997-2004) (Euzen, 2006; Brach-Papa *et al.*, 2009). As reported by Brach-Papa *et al.* (2009) and references therein, the European legislation on this subject is very strict and contains precise specifications on several parameters such as the maximum concentrations of the major constituents, the type of processes authorized for bottling and the labelling information that should be provided to the consumers by the producers. From the large number of requirements of a “Natural Mineral Water”, the source provenance is one of the most important. Only mineral waters with clear details of provenance are included in the list of “Natural Mineral Waters” recognised by the European Union state members.

Recent studies have demonstrated that Sr isotopes provide a way of fingerprinting different mineral waters and may therefore be applied, in combination with other chemical and isotope data, for source authentication purposes (*e.g.* Négrel *et al.*, 1997; Montgomery *et al.*, 2006; Voerkelius *et al.*, 2010; Marques *et al.*, 2012). 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) (Horn *et al.*, 1993; 1998; Aberg, 1995; Rossmann *et al.*, 2000; Almeida and Vasconcelos, 2001; Barbaste *et al.*, 2002; Crittenden *et al.*, 2007; Rummel *et al.*, 2008).

Strontium is a divalent cation that can easily substitute  $\text{Ca}^{2+}$  in the crystal lattice of Ca-bearing minerals, such as plagioclase feldspar, apatite, titanite, calcite, aragonite and dolomite. It has four naturally occurring isotopes  $^{84}\text{Sr}$ ,  $^{86}\text{Sr}$ ,  $^{87}\text{Sr}$  and  $^{88}\text{Sr}$ .  $^{84}\text{Sr}$ ,  $^{86}\text{Sr}$  and  $^{88}\text{Sr}$  are stable, whereas  $^{87}\text{Sr}$  derives from the radioactive decay of  $^{87}\text{Rb}$  (Faure and Mensing 2005). 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 ( $^{85}\text{Rb}$  and  $^{87}\text{Rb}$ ),  $^{87}\text{Rb}$  is radioactive and decays to radiogenic  $^{87}\text{Sr}$  by  $\beta^-$  emission. 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 sialic 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), whilst Sr-enriched calcareous sediments and limestones are generally characterized by  $^{87}\text{Sr}/^{86}\text{Sr}$  values ranging between 0.706 and 0.709.

It is commonly assumed that Sr isotopes are not significantly affected by mass fractionation during chemical weathering processes (Shand *et al.*, 2009). Therefore, the Sr released to the water is a function of both the composition and the stability of the aquifer bedrock forming minerals (Faure, 1986; Négrel *et al.*, 1993; 2001). 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 (*e.g.* Blum *et al.*, 1993; Aberg, 1995; Jacobson *et al.*, 2002; Bau *et al.*, 2004; Montgomery *et al.*, 2006; Shand *et al.*, 2009). For water reservoirs interacting with silicate lithologies, isotope equilibrium with whole-rock is rarely achieved, because the reactivity rates of their rock-forming minerals are widely variable. In contrast, the waters sourced in carbonate environments often show close to equilibrium Sr isotope compositions due to the high solubilities of carbonate minerals. More complex distribution patterns occur when water systems receive Sr inputs from various sources with contrasting  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (*e.g.* Négrel, 1999; Négrel *et al.*, 2001; Barbieri and Morotti, 2003). The final isotopic characteristics of these waters will be determined by the compositions and the relative contributions of the different end-members involved in the mixture.

Natural waters have short residence times (maximum  $10^3$  years) compared to the half-life of  $^{87}\text{Rb}$  ( $48,8 \times 10^9$  years) and suffer no influence of the  $^{87}\text{Rb}$  radioactive decay. Weathering of carbonate minerals is generally very rapid, but the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in waters from non-carbonate aquifers can be strongly affected by the timescale at which water-rock interaction processes take place. Longer residence times tend to favour the hydrolysis reactions of silicate phases (plagioclase feldspar, followed by K-feldspar and micas), allowing groundwater to approach the equilibrium with the crystalline host rocks (Bullen *et al.*, 1996; Frost e Toner, 2004; Blum e Erel, 2005). According to Frost and Toner (2004), the permeability associated with igneous and metamorphic rocks can also influence the weathering process, with low permeabilities slowing groundwater equilibration rates.

In addition to natural causes, the use of fertilizers (including dolomite, potash, nitrogen and phosphate materials) may produce changes in the rates of release and exchange of Sr in soils and significant variations in the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of shallow groundwaters and streams draining these regions. Groundwater contamination by agricultural activities or other pollutant sources can disturb their original chemical and isotopic characteristics and add further complexities to the investigation of their source provenance (*e.g.* Bohlke e Horan, 2000; Soler *et al.*, 2002; Jiang *et al.*, 2009).

A valid interpretation of water Sr isotope signatures requires therefore a thorough knowledge of the potential hydrogeochemical processes operating along water flow paths, because the Sr isotope composition of natural waters is not

always a conservative property and may be highly influenced by the following factors: (a) reaction kinetics of mineral dissolution and exchange efficiency; (b) thermodynamic equilibrium; (c) water residence time; (d) mixing of waters of distinct provenance and (e) addition of natural or anthropogenic contaminants.

The aim of the present investigation is to determine the Sr isotope composition of natural mineral waters from different geologic environments in Portuguese mainland and assess the extent to which the Sr radiogenic isotopes can be used to trace their origin.

## 2. Geological setting

Portuguese mainland is located in the western and southwestern sector of Iberia, at latitudes between  $42.2^\circ\text{N}$  to  $36.92^\circ\text{N}$  and longitudes between  $9.61^\circ\text{W}$  to  $6.07^\circ\text{W}$  (Fig. 1). In broad terms, it comprises terrains of the Variscan basement, occupying extensive areas in the inner part of the country and a Mesozoic–Cenozoic sedimentary cover, particularly well exposed along its western and southwestern margins (Fig. 1). The Variscan basement, also known as Iberian Massif, is composed of thrust, folded and metamorphosed rocks of Late Proterozoic and Paleozoic age and large granitoid batholiths intruded in the last stages of the Late Paleozoic Variscan oblique continent-continent collision (*e.g.* Ribeiro *et al.*, 1979; Matte, 1986; Quesada, 1991).

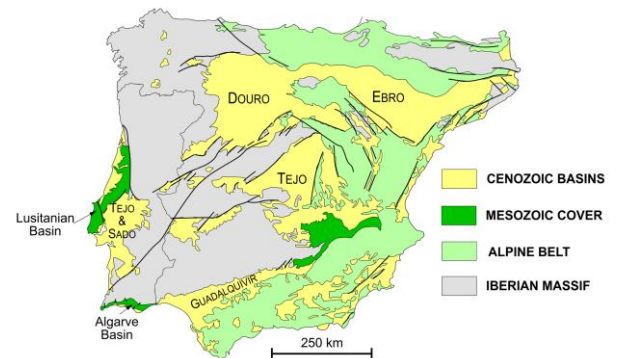


Fig.1. Schematic geological map of Iberia with the main structural units (adapted from Vera *et al.*, 2004).

Fig.1. Mapa simplificado da Península Ibérica com as principais unidades estruturais (adaptado de Vera *et al.*, 2004).

During Mesozoic times, extensional tectonics related to the opening of the North Atlantic Ocean resulted in the development of the Lusitanian and the Algarve rift basins along the western and southwestern borders of Iberia (Ribeiro *et al.*, 1979; Wilson *et al.*, 1989; Rasmussen *et al.*, 1998; Terrinha, 1998). The stratigraphic record preserved in these fault-bounded basins includes Late Triassic red fluvial siliciclastics, Hettangian evaporites and Jurassic to Lower Cretaceous limestones, sandstones and shales, documenting the occurrence of several rifting episodes from early Triassic to early Cretaceous (Wilson *et al.*, 1989; Pinheiro *et al.*, 1996).

Continental breakup was accompanied by three cycles of magmatic activity. The first cycle is represented on-shore by basaltic and dolerite dykes of tholeiitic affinities intruded at around 200 Ma. This episode was followed by the emplacement of Late Jurassic-Early Cretaceous intrusives with transitional characteristics, at approximately 140 Ma (Ferreira e Macedo, 1979; Martins, 1991; Martins *et al.*, 2008; Verati *et al.*, 2007).

The last magmatic cycle took place between 100 and 70 Ma and includes the NNW-SSE aligned subvolcanic alkaline complexes of Sintra, Sines and Monchique, the volcanic complex of Lisbon and other minor alkaline intrusions (Miranda *et al.*, 2009).

Finally, the Cenozoic evolution of Iberia was strongly controlled by Alpine compression, involving distinct periods of crustal deformation, fault reactivation, and halokinesis related to multiple episodes of collision between Iberia, Eurasia and Africa (e.g. Mougenot, 1986; Malod and Mauget, 1990; Srivastava *et al.*, 1990; Rosebaum *et al.*, 2002; Alves *et al.*, 2003). These tectonic events are well expressed by a series of unconformity-bounded Cenozoic sequences. Basin infilling resulted from the interplay between alluvial fan, lacustrine, fluvial and shallow marine sedimentation and consists of major siliciclastic facies assemblages associated with minor carbonates (Antunes *et al.*, 1999, Pais *et al.*, 2010).

### 3. Sampling and analytical techniques

The samples analysed in this study were collected from 250 - 1500 mL water bottles from different brands, purchased in grocery stores. Only mineral waters with clear details for provenance, mineral content values and physical parameters were selected for analysis. Their geographical origin was determined through the address labelled on the bottle and further confirmed by direct contact with the technical director of each mineral water company. Many of the waters now exploited on a commercial basis have a long documented history of use and are believed to be endowed with healing properties. Of the nine samples analysed, eight are classified as "Natural Mineral Waters" and one as "Spring Water". In order to assess the effects from mixing of water from several boreholes, filtering and bottling processes and potential seasonal variations of strontium isotope ratios, the characterization of each type of water involved the measurement of two / three replicate samples with different bottling dates and serial numbers. For comparison purposes, samples of rainwater and snow were also collected and analysed. To minimize contamination, snow samples were collected approximately 0.1 - 0.2 m below the snow surface and stored into pre-cleaned containers.

Sample preparation involved previous filtering of rainwater and snow samples through a pre-washed 0.5 µm Millipore filter. All water samples were then acidified to pH 2 with redistilled concentrated HNO<sub>3</sub>. A volume of 250 mL for rainwater and snow samples and 10 - 50 mL for bottled waters was measured into pre-cleaned Teflon beakers and evaporated to dryness. The residue was subsequently acidified with 1mL sub-boiled HF and 0.5 mL sub-boiled HNO<sub>3</sub> and dried. Each sample was then dissolved using 1 mL of sub-boiled 6.2N HCl and evaporated to dryness. Strontium was collected using conventional AG8 50W Bio-Rad resin ion exchange methods and loaded on single tantalum filaments with H<sub>3</sub>PO<sub>4</sub>.

The Sr isotope compositions were determined using a VG Sector 54 multi-collector mass spectrometer in the Laboratory of Isotope Geology of the University of Aveiro. All <sup>87</sup>Sr/<sup>86</sup>Sr ratios were corrected for instrumental mass fractionation and normalized to <sup>86</sup>Sr/<sup>88</sup>Sr = 0.1194. The in-run precision of each analysis lies between 30 to 50 ppm, with two standard deviations from the mean (2σ error) and Sr blanks are less than 250 pg. The international standard SRM-987 gave an average value of 0.710249 ± 6 (n = 18) during this study.

Sr concentrations in the water samples were obtained by inductively coupled plasma mass spectrometry (ICP-MS) in the University of Aveiro.

### 4. Results and discussion

The location of the studied samples is shown in the simplified geological map of Portugal of figure 2. Chemical and Sr isotopic data for rainwater and snow samples are given in table 1. General information for the analysed bottled mineral waters, including source, water type, mineral content values and pH are presented in table 2, whilst their Sr contents and <sup>87</sup>Sr/<sup>86</sup>Sr isotopic ratios are compiled in table 3. Thorough reviews on the main chemical characteristics of Portuguese bottled mineral waters can be found in Lourenço *et al.* (2010).

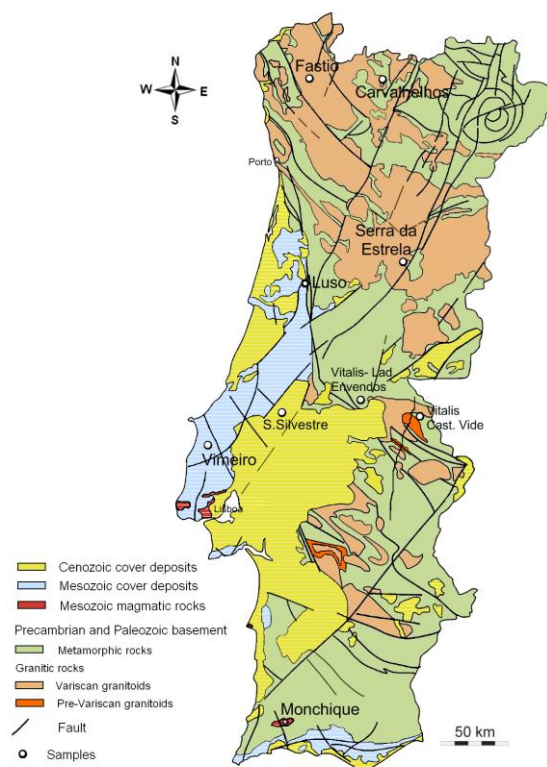


Fig.2. Simplified geological map of Portugal with the geographic distribution of bottled water samples (adapted from geological map of Portugal 1/500 000).

Fig.2. Mapa geológico simplificado de Portugal com a indicação da distribuição geográfica das amostras de águas engarrafadas samples (adaptado da carta geológica de Portugal 1/500 000).

#### 4.1 Rainwater and snow

The Sr isotopic ratios for rainwater (<sup>87</sup>Sr/<sup>86</sup>Sr = 0.709287 - 0.710345) and snow samples (<sup>87</sup>Sr/<sup>86</sup>Sr = 0.708415 - 0.710805) show a considerable degree of overlap (Tab. 1). Despite the small number of samples collected and their scattered spatial and temporal distribution (2005, 2006, 2009 and 2010), the data obtained in this study lie within the range of values published in the literature for rainwater in Portugal and other European countries, such as Spain, France, Germany, Switzerland and Scotland (Fig. 3). The average value (<sup>87</sup>Sr/<sup>86</sup>Sr = 0.70951 ± 0.00033) provides therefore a rough estimate for the isotopic composition of rain in Portugal.

As pointed out by Négrel *et al.* (2007), the Sr isotopic signature of rainwater is dominantly controlled by the nature of the atmospheric aerosol sources, including sea salts, crustal dust, volcanic dust, biogenic material and anthropogenic emissions. In the present case, most of the rainwater and snow samples have  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios similar or slightly higher than that of seawater ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.70918 \pm 1$ , Faure and Mensing, 2005) revealing that sea salts are probably the major source of dissolved species for rain and snow falls in Portugal. A significant contribution of continental dusts from silicate terrains of the Variscan basement (e.g. granite, gneiss, metasediments) and/or Cenozoic cover deposits is strongly suggested for the rain and snow samples with more radiogenic compositions ( $^{87}\text{Sr}/^{86}\text{Sr} > 0.709$ ).

Table 1. Strontium contents (ppb) and  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopic ratios for rainwater and snow samples.

Tabela 1. Concentrações de Sr (ppb) e razões  $^{87}\text{Sr}/^{86}\text{Sr}$  em amostras de água da chuva e de neve.

Sampling sites	UTM Coordinates (WGS84)	Sampling date	Sr (ppb)	$^{87}\text{Sr}/^{86}\text{Sr}$
Rain water - NE Portugal (Trás-os-Montes) <sup>(a)</sup>	29T 611600 mE 468400 mN	Nov-05	n.d.	0.710040 ± 82
Rain water - NE Portugal (Trás-os-Montes) <sup>(b)</sup>	29T 611100 mE 4616100 mN	Jan-09	n.d.	0.710008 ± 43
Rain water - NW Portugal (Porto)	29T 580900 mE 4557100 mN	2006	1.62	0.710345 ± 38
Rain water - Central West Portugal (Aveiro)	29T 629100 mE 4497700 mN	2006	4.37	0.709562 ± 62
Rain water - NW Portugal (Porto)	29T 529100 mE 4497700 mN	Jan-09	n.d.	0.708965 ± 31
Snow - Central Portugal (Serra Estrela)	29T 614400 mE 4468800 mN	Mar-06	0.5	0.710805 ± 31
Rain water - Central West Portugal (Aveiro)	29T 624300 mE 4462800 mN	Jan-09	n.d.	0.710177 ± 61
Snow - Central Portugal (W Serra Estrela)	29T 624300 mE 4462800 mN	Jan-09	n.d.	0.708415 ± 34
Snow - Central Portugal (E Serra Estrela)	29T 614400 mE 4468800 mN	Jan-09	n.d.	0.709706 ± 43
Snow - Central Portugal (E Serra Estrela)	29T 617900 mE 4464400 mN	Jan-09	n.d.	0.709349 ± 65
Rain water - SW Portugal (Ajustrel)	29S 673500 mE 4192500 mN	Nov-09	n.d.	0.709460 ± 33
Rain water - Central West Portugal (Aveiro)	29T 529100 mE 4497700 mN	Jan 10	n.d.	0.709356 ± 28
Rain water - Central West Portugal (Aveiro)	29T 529100 mE 4497700 mN	May 10	n.d.	0.709287 ± 30
Snow - Central Portugal (Caramulo)	29T 669500 mE 4489500 mN	Jan 10	n.d.	0.709340 ± 33
Snow - Central Portugal (E Serra Estrela)	29T 614400 mE 4468800 mN	Jan 10	n.d.	0.709292 ± 31
Snow - Central Portugal (E Serra Estrela)	29T 613800 mE 4467900 mN	Jan 10	n.d.	0.709171 ± 41
			<b>Average value</b>	<b>0.70951 ± 33</b>

<sup>(a)</sup> Andrade, (2002); <sup>(b)</sup> Pacheco *et al.* (2009); n.d. – not determined.

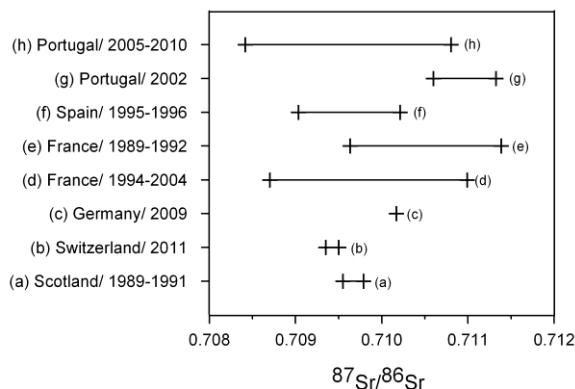


Fig.3. Range of  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopic ratios for rainwater. Legend: <sup>(a)</sup> Bacon and Basin (1995); <sup>(b)</sup> Hindshawa *et al.* (2011) <sup>(c)</sup> Wiegand (2009), <sup>(d)</sup> Négrel *et al.* (2007); <sup>(e)</sup> Probst *et al.* (2000); <sup>(f)</sup> Chiquet *et al.* (1999); <sup>(g)</sup> Andrade (2002); <sup>(h)</sup> This study.

Fig.3. Intervalos de variação da razão isotópica  $^{87}\text{Sr}/^{86}\text{Sr}$  na água da chuva. Legenda: <sup>(a)</sup> Bacon and Basin (1995); <sup>(b)</sup> Hindshawa *et al.* (2011) <sup>(c)</sup> Wiegand (2009), <sup>(d)</sup> Négrel *et al.* (2007); <sup>(e)</sup> Probst *et al.* (2000); <sup>(f)</sup> Chiquet *et al.* (1999); <sup>(g)</sup> Andrade (2002); <sup>(h)</sup> Este trabalho.

#### 4.2 Bottled mineral waters

Sr concentrations and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios for the analysed bottled mineral waters are presented in table 3. The lack of significant differences in the isotopic compositions of replicate samples from the same brand, pumped and bottled at distinct dates, demonstrates that the potential influence of mixing between waters from different boreholes, filtering and bottling processes and/or seasonal variations of strontium isotope ratios can be neglected.

Figure 4 shows that the nine samples of Portuguese mineral waters are clearly distinguished on the basis of their  $^{87}\text{Sr}/^{86}\text{Sr}$  signatures. The *Monchique* water drawn from Late Cretaceous alkaline magmatic aquifer rocks is the least radiogenic ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.70447$ ) of the analysed mineral waters. The water samples hosted in Jurassic limestones (“*Vimeiro*”) and Miocene sandstones (“*São Silvestre*”) have average  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopic ratios of 0.708086 and 0.71077, respectively, which, in the latter case, are very close to rainwater values. Finally, all the remaining bottled mineral waters come from areas of the Variscan basement and yield very radiogenic isotopic compositions ( $^{87}\text{Sr}/^{86}\text{Sr} > 0.713$ ). As discussed below, the stratigraphic age of the aquifer host rocks and their mineralogical composition appear to be the main factors governing the water Sr isotope signatures.

Table 2. Main characteristics of the samples of Portuguese bottled mineral waters.

Tabela 2. Principais características das amostras de águas minerais engarrafadas Portuguesas.

Commercial Name	Sample location	Water type	Total mineralization (mg/L) <sup>(a)</sup>	pH <sup>(b)</sup>	Temperature (°C) <sup>(b)</sup>
<i>São Silvestre</i>	Pernes, Santarém	Ca-HCO <sub>3</sub>	181	7.13	-
<i>Monchique</i>	Monchique	Na-HCO <sub>3</sub>	294	9.3	27 - 31.5
<i>Vimeiro</i>	Vimeiro	Na-Ca-Cl-HCO <sub>3</sub>	1112	7.34	26
<i>Fastio</i>	Chãoim-Terras do Boura	Na-HCO <sub>3</sub>	25.8	5.8	-
<i>Serra da Estrela</i>	Gouveia	Hypo-saline, silicate	< 52	5.8-6.9	-
<i>Carvalhinhos</i>	Boticas	Na-HCO <sub>3</sub>	229; 255	7.35	22
<i>Luso</i>	Serra do Bucaco	Na-Cl-SiO <sub>2</sub>	47	5.7	27
<i>Vitalis</i>	Ladeira de Emvendos - Mação	Na-Cl-SiO <sub>2</sub>	26	4.8	22
<i>Vitalis</i>	Castelo de Vide	Hypo-saline	45	5.7	-

<sup>(a)</sup> Information from bottle labels;

<sup>(b)</sup> Maximum temperatures from Lourenço and Cruz (2010).

Table 3. Sr contents and  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopic ratios for samples of Portuguese bottled mineral waters and information on aquifer geology.

Tabela 3. Concentrações e razões isotópicas de Sr das amostras de águas minerais engarrafadas e informação geológica do aquífero.

Commercial Name	Sr (µg/L)	$^{87}\text{Sr}/^{86}\text{Sr}$	Acquisition date	Average value <sup>(a)</sup>	Geology of the aquifer and available $^{87}\text{Sr}/^{86}\text{Sr}$ data <sup>(b)</sup>
<i>São Silvestre</i>	64.4	0.710785 ± 30 0.710754 ± 26	May 07 April 11	0.71077 ± 20	Cenozoic detrital complex
<i>Monchique</i>	-	0.704448 ± 30 0.704486 ± 23	Feb. 09 Feb. 09	0.70447 ± 23	Late Cretaceous alkaline intrusives
<i>Vimeiro</i>	618	0.708084 ± 37 0.708087 ± 28	May 07 Jan. 09	0.708086 ± 22	Jurassic limestones and evaporites
<i>Fastio</i>	10.6	0.713631 ± 40 0.713763 ± 29 0.713640 ± 30	May. 07 Jan. 09 Feb. 09	0.71369 ± 19	
<i>Serra da Estrela</i>	9.76	0.719885 ± 30 0.719933 ± 42 0.719688 ± 30	May 07 Set 07 Jan. 09	0.71982 ± 32	Variscan granitoids
<i>Carvalhinhos</i>	38.7	0.726322 ± 61 0.726255 ± 58 0.726415 ± 38 0.726485 ± 35	May 04 Jun 04 Mai. 07 Jan. 09	0.72641 ± 15	Host granite: 0.749238 Silurian formations: 0.760103-0.782684 Plagioclases: 0.716873-0.736393
<i>Luso</i>	2.98	0.715541 ± 30 0.715104 ± 37 0.714939 ± 39	May 07 Jan. 09 Feb. 09	0.71525 ± 80	
<i>Vitalis - Ladeira de Emvendos</i>	-	0.716882 ± 37 0.711733 ± 29	Jan. 09 Feb. 09	0.7170 ± 15	Ordovician quartzites
<i>Vitalis - Castelo de Vide</i>	3.78	0.776543 ± 59 0.77268 ± 40 0.776979 ± 49	May. 07 April 07 Feb. 09	0.77701 ± 71	Portalegre orthogneisses: 0.9573-1.4985

<sup>(a)</sup> Mean value and error presented with a confidence limit of 95%;

<sup>(b)</sup> References in the main text.

#### Cenozoic cover deposits - “*São Silvestre*” water

The *São Silvestre* water is sourced from two similar deep wells (more than 176 m depth) in the Santarém region (Fig. 2). The aquifer (82 - 176 m depth) is located in continental siliciclastic units of Miocene age (Burdigalian - Helvetian), known as the detrital complexes of “*Ota*” and “*Arneiro de Milhariças*”, which are overlain by marls and carbonate sediments from the Sarmatian - Pontian complex. The three sedimentary complexes are part of the infilling deposits of a large basin differentiated at middle Eocene times, as a result of the reactivation of NE-SW fractures - the Lower Tejo Cenozoic basin (Figs. 1 and 2).

In terms of Sr isotopic composition, there are strong similarities between the *São Silvestre* water ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.710754 - 0.710785$ ) and rainwater (Fig. 4). This suggests that the Sr isotopic signature of this water was probably controlled by direct rainfall recharge of the aquifer and has not suffered significant influence of water-rock interaction processes. According to Albino de Medeiros (oral communication), technical director of this water, the admitted short residence time and high velocity flow of water on *São Silvestre* aquifer may therefore have prevented groundwater from equilibrating with the host rocks. The nature of the bedrock (sandstones) can also have contributed to inhibit extensive interaction between groundwater and the surrounding reservoir rocks, because the main mineral constituents in these deposits (quartz  $\pm$  K-feldspar + micas  $\pm$  clay minerals; Manuppella *et al.*, 2006) are not easily dissolved (Bullen *et al.*, 1996; Frost and Toner, 2004; Blum and Erel, 2005).

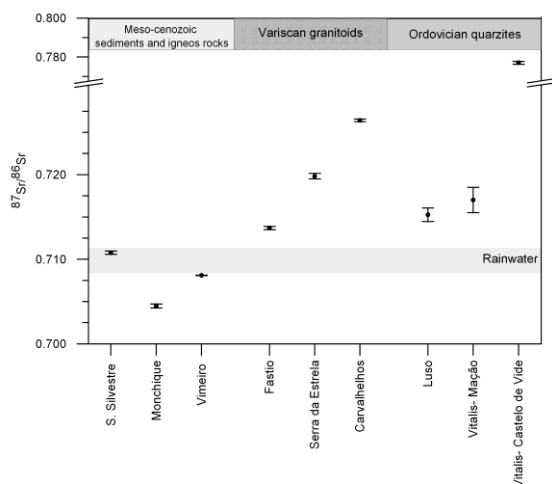


Fig.4. The average  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope composition of bottled waters and respective main geological environments. The shaded area represents the range of rainwater in Portugal from 0.7084 to 0.7114 (data from this study and presented by Andrade, 2002).

Fig.4. Razões isotópicas  $^{87}\text{Sr}/^{86}\text{Sr}$  das águas engarrafadas com indicação do respectivo ambiente geológico. A área sombreada indica o intervalo de variação da água da chuva em Portugal, de 0,7084 a 0,7114 (dados deste estudo e de Andrade, 2002).

However, the relatively high mineralization content and pH value recorded in the *São Silvestre* waters (181 mg/L, pH = 7.13; Tab. 2) and, particularly their elevated Sr concentrations (Sr = 64 ppb, Tab. 2), point to some ion input from the marls and carbonate sediments from the overlying Sarmatian - Pontian formations along their flow path. As, on the other hand, the clastic component of the Cenozoic sediments is mostly derived from weathering of strongly radiogenic Precambrian and Palaeozoic rocks and would therefore have produced waters with relatively high  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopic ratios, an alternative scenario can be proposed. In this model, the isotopic signature of the *São Silvestre* water could have resulted from mixing of distinct Sr sources (meteoric water, carbonates with low  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopic ratios and sandstones with high  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopic ratios).

Irrespective of the model assumed, the available data suggest that the *São Silvestre* mineral aquifer corresponds to a semi-confined aquifer in which water flows on the Miocene detrital formation but also receives water, by leakage, from the overlying carbonates.

### Late Cretaceous alkaline magmatic rocks – “Monchique” water

The Late Cretaceous Monchique alkaline subvolcanic complex crops out in the southwest corner of Portugal (Fig. 2) and consists of two concentric bodies of nepheline syenites and minor occurrences of mafic and ultramafic rocks (Rock, 1978; Miranda *et al.*, 2009). These alkaline magmas of deep mantle origin were intruded into Carboniferous slates and quartzites from the Brejeira Formation, at around 72 Ma (MacIntyre and Berger, 1982; Rock, 1976; Bernard Griffiths *et al.*, 1997; Valadares, 2004).

The *Monchique* water flows through a highly fractured bedrock, taps a deep aquifer (at least several hundred meters deep) and is recovered from drill holes at temperatures of 27° - 31.5 °C (Lourenço and Cruz, 2010; Tab. 2). Its Na-HCO<sub>3</sub> chemical character and high pH values (total mineral contents = 295 mg/L, pH = 9.13; Tab. 2) indicate that groundwater has significantly interacted with the main mineral phases (K-feldspar + albite + nepheline) present in the nepheline syenite host rocks. Progressive dissolution of Na-silicates (albite and nepheline) was probably the major cause for the increase of sodium concentration and alkalinity in the *Monchique* water. However, it is likely that ion exchange reactions between groundwater and Na-rich clays produced by weathering of primary minerals along fracture zones has also contributed to the chemical signature of the *Monchique* water (Venturelli *et al.*, 2003). Also relevant for the geochemical composition of the *Monchique* water is the contribution of other deep-origin components (CO<sub>2</sub>, H<sub>2</sub>S, NaCl and N<sub>2</sub>) (Calado and Vieira da Silva, 2003).

From the group of samples of bottled mineral waters analysed in this study, the *Monchique* water is the least radiogenic ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.704448 - 0.704486$ ; Fig. 4). The  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopic ratios for this sample lie within the range of present-day whole-rock values displayed by the nepheline syenites ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.703674 \pm 52 - 0.705189 \pm 56$ , Valadares, 2004), revealing that groundwater appears to have reached almost complete equilibrium with the aquifer host rocks. Both the bulk chemistry and the Sr isotopic composition of the *Monchique* water may therefore result from long-term fluid-rock interaction mechanisms, at relatively high temperature.

### Mesozoic Limestones – “Vimeiro” water

The *Vimeiro* mineral water comes from a deep-seated confined aquifer ( $\approx 200$  m) of Late Jurassic karstified limestones (Upper Kimmeridgian), located in the southern sector of the Lusitanian Basin (Fig. 1). At the presently exposed level, the limestones occur at the flanks of a NNE-SSW salt anticline structure (Maceira diapir) with a core composed of Late Triassic mudstones, carbonates and evaporites from the “Dagorda Formation” (Hettangian) (Manuppella *et al.*, 1999). The region is famous for its thermal bath resort and highly mineralized springs. The water is heated by circulation down to 1000 m in depth reaching temperatures of 35 °C and discharges in a valley situated on the eastern flank of the diapir zone, with temperatures up to 26°C (Costa, 1982).

The chemical composition (Na-Ca-Cl-HCO<sub>3</sub>) and high total dissolved solids content (1112 mg/L) of the *Vimeiro* bottled mineral water (Tab. 2) can be attributed to intense dissolution of carbonates (calcite/dolomite), sulphates (anhydrite/gypsum) and chloride salts (halite) from the buried Mesozoic carbonate and evaporite formations during deep groundwater flow and mostly during ascending terminal fluxes. Widespread water-rock interaction processes involving highly soluble minerals with typically low Rb/Sr values would have enabled groundwater to equilibrate chemically and isotopically with the aquifer host

rocks, explaining the low  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios found in the sample of the *Vimeiro* water ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.708084 - 0.708087$ , Fig. 4).

Assuming that the Sr isotopic composition of the *Vimeiro* groundwater is inherited from the evaporite/marine carbonate rock system with which it interacts, its isotope ratio should encompass the  $^{87}\text{Sr}/^{86}\text{Sr}$  seawater curve for Late Triassic and/or Late Jurassic times. However, the average Sr isotopic ratio obtained in the sample of the *Vimeiro* natural mineral water is slightly higher than the values reported in the literature for Hettangian and Upper Kimmeridgian seawater ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.7077$  and  $0.7069$  respectively; Jones and Jenkyns, 2001). As such, it is possible that the observed increase reflects changes in the Sr isotopic signatures of the reservoir rocks induced by post-depositional diagenetic processes or derive from mixing with more radiogenic non-marine waters. Irrespective of the factors controlling this subtle shift towards more elevated  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios, the Sr isotopic composition of the *Vimeiro* groundwater is entirely consistent with the published data for aquifers associated with Mesozoic marine carbonates ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.7070 - 0.7090$ ; Voerkelius *et al.*, 2010).

#### Variscan granitoids – “Carvalhelhos”, “Fastio”, “Serra da Estrela” mineral waters

The water samples included in this group are all hosted in granitoid intrusions from Northern/Central Portugal (Fig. 2). Most of these plutons were emplaced into metasediments of Late Proterozoic to Paleozoic age, during or slightly after the last Variscan deformation event (D<sub>3</sub>). Based on their structural, petrographical and geochemical characteristics, the Portuguese Variscan granitoids have been classified into four main suites: a) early, syn-D<sub>3</sub> granodiorites and biotite monzogranites; b) strongly peraluminous syn-D<sub>3</sub> leucogranites and two-mica granites; c) late-post-D<sub>3</sub> calc-alkaline granodiorites and biotite monzogranites and (d) late-post-D<sub>3</sub>, slightly peraluminous, biotite-muscovite granites (Azevedo and Valle Aguado, 2013 and references therein). It is generally accepted that the synkinematic leucogranites and two-mica granites have S-type signatures ( $^{87}\text{Sr}/^{86}\text{Sr}_i > 0.708$ ) and should therefore have derived from partial melting of middle crustal metasedimentary sources (Azevedo and Valle Aguado, 2013 and references therein). In contrast, a major contribution from metaigneous lower crust materials and/or interaction with mantle derived magmas appears to be required to produce the least radiogenic I- and H-type syn-D<sub>3</sub> and late-post-D<sub>3</sub> granodiorite-monzogranite suites ( $^{87}\text{Sr}/^{86}\text{Sr}_i < 0.708$ ) (Azevedo and Valle Aguado, 2013 and references therein).

The *Carvalhelhos* water has very peculiar characteristics. It comes from a large hydrologic province of hot and cold CO<sub>2</sub>-rich thermal and mineral springs, located in the Galicia-Trás-os-Montes para-autochthonous terrains of NE Portugal. Many of these CO<sub>2</sub>-rich waters are issued from granitic aquifers, at the intersection of major fault systems, reactivated during Alpine compression (*e.g.* Marques *et al.*, 2006; Marques *et al.*, 2010; Lourenço, 2010). According to several authors, their high CO<sub>2</sub> contents result from fluids of deep-seated (upper-mantle) origin, carrying a CO<sub>2</sub>-rich gaseous phase, that have migrated towards the surface through the regional fault network (*e.g.* Marques *et al.*, 2006; Carreira *et al.*, 2008; Marques *et al.*, 2010).

In the *Carvalhelhos* area, the spring emergences occur close to the contact between the Barroso syn-D<sub>3</sub> two-mica granite and the Silurian metasedimentary sequences, with a temperature of 22°C, a total mineralization of 230 mg/L and a pH of 7.3. The relatively low outflow temperatures suggest that these Na-HCO<sub>3</sub>-CO<sub>2</sub> cold waters represent infiltrating meteoric waters with deep circulation paths (at least 200 m deep), mineralized by water-

gas-rock interaction processes. According to Vieira da Silva (oral communication), technical director of this water, the absence of tritium in samples of the *Carvalhelhos* water collected in 1996, means that infiltration of meteoric water occurred more than 44 years before that date. Carbon isotopes analysis were inconclusive concerning dating of this water, since it is suspected that there is a deep mantle CO<sub>2</sub> contribution to its final composition.

The Sr isotopic ratios for the *Carvalhelhos* water ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.726255 - 0.726485$ ), though more radiogenic than rainwater (Fig. 4), do not lie within the range of present-day values reported by Saraiva *et al.* (2007) for samples of the host granite ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.749238$ ) and the Silurian formations ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.760103 - 0.782684$ ) (Tab. 3), indicating that the bulk equilibrium between rocks and fluids was not attained. In granitic and metamorphic environments, the isotopic exchange between rocks and fluids is highly dependent on the relative leaching stabilities of the different silicate phases (plagioclase feldspar dissolves first than biotite, K-feldspar or muscovite), which may therefore lead to some decoupling of their Sr isotopic compositions (Stettler and Allégre, 1978; Lasaga, 1984, Marques *et al.*, 2006). As, on the other hand, the most easily weathered silicate mineral is plagioclase feldspar, which is Sr-enriched and far less radiogenic than K-feldspar or micas (Tab. 3), it is likely that the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the *Carvalhelhos* mineral waters have been essentially controlled by the dissolution of Na-feldspar, as proposed by Saraiva (2006) and Saraiva *et al.* (2007). The high degree of overlap between the Sr isotopic ratios of the *Carvalhelhos* water and the results obtained by Brough (1990) in plagioclases from similar granitoids ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.716873 - 0.736393$ ) supports this assumption.

The samples of the *Fastio* and *Serra da Estrela* bottled mineral waters can be clearly distinguished from the *Carvalhelhos* water by their lower concentrations of dissolved solids (< 52 mg/L), pH values (5.8 - 6.9) and average Sr isotopic ratios (*Fastio*: 0.71369, *Serra da Estrela*: 0.71982). Their physico-chemical characteristics and Sr isotopic compositions point to shallower groundwater circulation paths, shorter residence times and less effective fluid-rock (fluid-plagioclase) interaction mechanisms. It should be noted, however, that the aquifer source rocks are in both cases late-post-D<sub>3</sub> Variscan granitoids with younger ages, lower Rb/Sr ratios and less radiogenic Sr isotopic signatures than the S-type granite hosting the *Carvalhelhos* water.

The Gouveia Massif (*Serra da Estrela* water) displays a U-Pb zircon age of  $301 \pm 2.6$  Ma and a Sr isotopic ratio of 0.74421 (Neiva *et al.*, 2009), whereas the Agrelá Massif (*Fastio* water) is  $306 \pm 3.5$  Ma old and shows present-day  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios ranging from 0.720803 to 0.732505 (Dias *et al.*, 1998; 2002). A comparison of water and whole-rock isotope ratios is of little relevance, because full isotope equilibrium with the surrounding country rocks is rarely achieved (Négrell *et al.*, 2001; Shand *et al.*, 2009). Nevertheless, differences in the age and nature of granite reservoirs will have strong effects on the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of their silicate minerals, being therefore possible that the Sr isotopic variability recorded in the three types of granite waters analysed in this study reflects contrasts in the exchange rates and  $^{87}\text{Sr}/^{86}\text{Sr}$  compositions of the plagioclase with which they have interacted, as also demonstrated by Marques *et al.* (2012).

#### Ordovician quartzites – “Luso”, “Ladeira de Envendos”, “Castelo de Vide” mineral waters.

The natural mineral waters of *Luso*, *Ladeira de Envendos* and *Castelo de Vide* are low mineralised water types (Tab. 2), derived from infiltration of meteoric water along a highly fractured

bedrock, consisting mainly of quartzites of Lower Ordovician age (Arenigian). The Ordovician sequences are exposed in the core of a series of NW-SE trending synclines, formed during the first Variscan deformation event (Buçaco, Envendos-Pinhal and Castelo de Vide synclines, respectively).

In a geological environment dominated by quartz-rich lithologies with little or no Sr-bearing minerals, a close match between the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of groundwater and rainfall should be expected. However, the average Sr isotopic compositions of the three mineral water samples (*Luso*: 0.71525; *Ladeira de Envendos*: 0.71700; *Castelo de Vide*: 0.77701) are distinctly more radiogenic than rainwater (Fig. 4), suggesting that the isotopic composition of the recharge waters was substantially modified by the input of easily accessible Sr with high  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios from external sources.

For the *Luso* and *Ladeira de Envendos* hydrologic systems, the increase in the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios relative to rainwater may have resulted from chemical weathering of silicate minerals present either in arkosic / pelitic intercalations within the Arenigian quartzite succession or in the underlying red bed and conglomerate deposits of presumed Tremadocian age (Teixeira, 1981; Oliveira *et al.*, 1992). These low-grade metasedimentary rocks contain, in addition to quartz, variable amounts of feldspar and phyllosilicates (muscovite and chlorite) and may thus have supplied radiogenic Sr to groundwater.

The *Luso* and *Ladeira de Envendos* mineral waters flow through deep-seated fractures (> 100 m) and discharge with moderate temperatures (*Luso*: 27 °C; *Envendos*: 22 °C), pH ranging from 4.8 to 5.7 and very low mineralization contents (Tab. 2). Under these conditions, partial equilibrium between silicic rocks and fluids could have occurred and Sr may have been progressively released to the solution from the primary reacting minerals (feldspar, muscovite, chlorite) and neo-formed clay minerals, promoting the elevation of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in the waters. Their overall chemistry and relatively high silica concentrations are consistent with a chemical evolution primarily controlled by water-rock interaction processes involving acidic weathering of aluminosilicates. In the case of the Serra do Buçaco aquifers (*Luso* region), Vieira da Silva *et al.* (2000) showed that there is a direct correlation between discharge temperature, silica content, maximum depth of circulation and tritium content (residence time).

As first pointed out by Voerkelius *et al.* (2010), the *Castelo de Vide* mineral water exhibits anomalously high  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (0.776543 - 0.777268). The water is sourced from an Ordovician aquifer system (the “Castelo de Vide” syncline) showing the same broad stratigraphic units that the *Luso* and *Ladeira de Envendos* synclines. However, the Ordovician sequences of the Castelo de Vide syncline are in contact with strongly deformed pre-Variscan granitoids (Portalegre orthogneisses), related to an old episode of magmatic activity ( $493 \pm 3.5$  Ma; Solá, 2007). In keeping with their old age and extreme differentiated character, the Portalegre orthogneisses have  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios ranging from 0.9573 - 1.4985 (Solá, 2007). Because the Sr isotope ratios in granite rock forming minerals depend on the age and Rb/Sr ratio of the host, it may be presumed that dissolution of radiogenic plagioclase (and to a lesser extent, K-feldspar and biotite) from the Portalegre orthogneisses could have provided a supplementary source of radiogenic Sr for the *Castelo de Vide* mineral water.

## 5. Conclusions

Based on the results obtained for nine samples of bottled mineral waters from Portuguese mainland, it is possible to draw the following conclusions:

(a) 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;

(b) the Sr isotope ratios of the analysed waters are dominantly controlled by both the nature and stratigraphic age of the aquifer host rocks. The least radiogenic waters are related to Jurassic carbonates / evaporites ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.70808$ ) and Late Cretaceous alkaline igneous sources ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.70447$ ), whereas the Cenozoic siliciclastic sediments host waters with  $^{87}\text{Sr}/^{86}\text{Sr}$  values of 0.71078 and the waters coming from granitic and/or metamorphic terrains of the Iberian Variscan basement display highly radiogenic Sr isotopic compositions ( $^{87}\text{Sr}/^{86}\text{Sr}$  varying between 0.7136 and 0.7770);

(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). 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 (*Carvalhos*, *Fastio*, *Serra da Estrela*, *Castelo de Vide*, *Luso*, *Ladeira de Envendos* waters) and can only be approached by long-term fluid-rock interaction mechanisms at high temperatures (*Monchique* water);

(d) 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.

Finally, 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 paths.

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