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Input of $^{87}Sr/^{86}Sr$ ratios and Sr geochemical signatures to update knowledge on thermal and mineral waters flow paths in fractured rocks (N-Portugal)

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ABSTRACT

Strontium isotopes and other geochemical signatures are used to determine the relationships between CO_2-rich thermal (Chaves: 76 °C) and mineral (Vilarelho da Raia, Vidago and Pedras Salgadas: 17 °C) waters discharging along one of the major NNE–SSW trending faults in the northern part of mainland Portugal. The regional geology consists of Hercynian granites (syn-tectonic-310 Ma and post-tectonic-290 Ma) intruding Silurian metasediments (quartzites, phyllites and carbonaceous slates). Thermal and mineral waters have $^{87}Sr/^{86}Sr$ isotopic ratios between 0.716713 and 0.728035. $^{87}Sr/^{86}Sr$ vs. 1/Sr define three end-members (Vilarelho da Raia/Chaves, Vidago and Pedras Salgadas thermal and mineral waters) trending from rainfall composition towards that of the CO_2-rich thermal and mineral waters, indicating different underground flow paths. Local granitic rocks have $^{87}Sr/^{86}Sr$ ratios of 0.735697–0.789683. There is no indication that equilibrium was reached between the CO_2-rich thermal and mineral waters and the granitic rocks. The mean $^{87}Sr/^{86}Sr$ ratio of the thermal and mineral waters (0.722419) is similar to the Sr isotopic ratios of the plagioclases of the granitic rocks (0.71261–0.72087). The spatial distribution of Sr isotope and geochemical signatures of waters and the host rocks suggests that the thermal and mineral waters circulate in similar but not the same hydrogeological system. Results from this study could be used to evaluate the applicability of this isotope approach in other hydrogeologic investigations.

1. Introduction

Recently, integrated advances for describing, modelling and predicting physical, economic, social and political processes related to the hydrogeologic cycle, in particular with regard to Global Climate Change, have attracted worldwide attention both with governmental authorities and the research community. An understanding of the processes related to the hydrogeologic cycle and the possible influence of human activities upon this is crucial for developing methods for sustainable groundwater management. As simple scientific approaches are unable to understand the complex interaction between nature, groundwaters and man, multidisciplinary studies are required to provide understanding for sustainable groundwater resources management. Increasing intensity of groundwater use and possible groundwater-related conflicts between stakeholders (e.g. society, governments, industry and nature) puts increasing pressure on the natural groundwater environment. For decision-making purposes (e.g. exploitation rates, avoiding overexploitation), indicators such as those presented in this paper should be accepted as driving forces to simplify complex information (such as the interrelationship between several hydrogeological systems).

The hydrogeology of the Vilarelho da Raia–Pedras Salgadas region (Fig. 1) has been extensively studied during the last 20 a (e.g. Aires-Barros et al., 1995, 1998; Marques et al., 1998, 2000, 2006, 2010b). In these papers, geochemical and isotopic ($\delta^{18}O$, $\delta^{2}H$, ^{3}H, $\delta^{13}C$ and ^{14}C) data have been presented and discussed. Aires-Barros et al. (1995, 1998) updated the hydrogeologic characterization of the Chaves geothermal area, based on coupled isotopic and geochemical studies carried out on CO_2-rich thermal and mineral waters. Those studies concluded that the ^{3}H content (from 2.0 to 4.5 TU) in the Vidago and Pedras Salgadas mineral waters were mainly related to shallow underground flow paths, rather than mixing between deep mineralized waters and shallow cold dilute groundwaters of meteoric origin. Marques et al. (1998, 2000) studied the origin of CO_2 and the role of CO_2 in the mineralization of the CO_2-rich thermal and mineral water systems. $\delta^{13}C$ values (ranging between −8‰ and −1‰) of CO_2 gas and Total Dissolved Inorganic C (TDIC) indicated that the C in these CO_2-rich thermal and mineral waters is mainly derived from a deep-seated (upper-mantle) source. Furthermore, the low ^{14}C content (from 7.9 to 9.9 pmC) of some of the CO_2-rich mineral waters from the Vidago and Pedras Salgadas areas that contain ^{3}H indicates that

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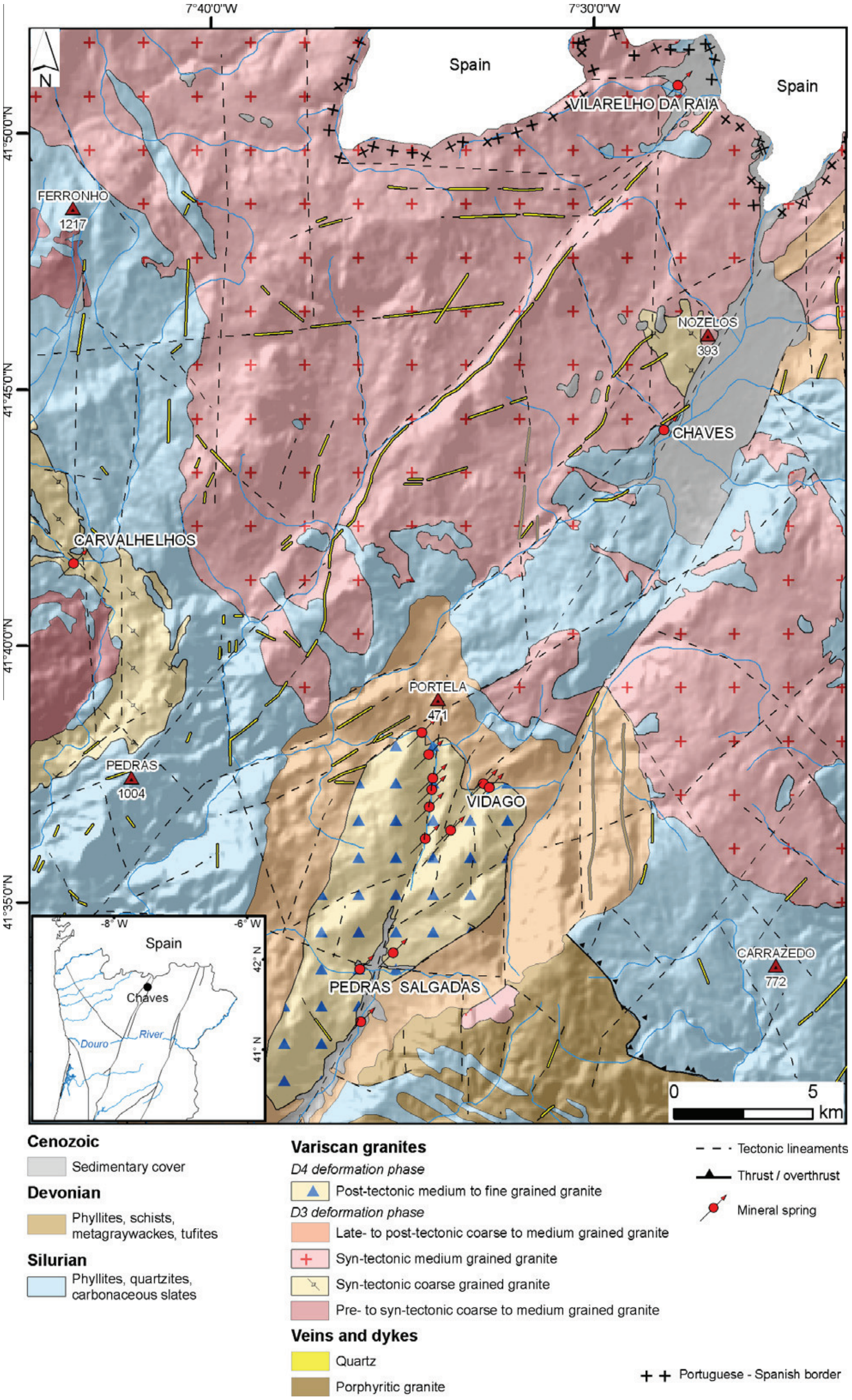

Fig. 1. Regional geological map of the Chaves region (NW Portugal), showing the location of Vilarelho da Raia, Chaves, Vidago and Pedras Salgadas CO_2-rich mineral waters. Adapted and revised from Oliveira et al. (1992) and Pereira et al. (1989). After Marques et al. (2010a).

large quantities of deep-seated (^{14}C-free) CO_2 contributes to the TDIC content. Marques et al. (2006, 2010a) updated knowledge on the relationship between the CO_2-rich thermal (Chaves) and mineral (Vidago and Pedras Salgadas) water systems. They concluded that the reason why some of the most mineralized waters in the region are cold CO_2-rich mineral waters is because water–rock interaction is enhanced at low temperatures, due to the solubility of CO_2 in water increasing with decreasing temperature. Finally, Marques et al. (2010b) discussed the hydrothermal alteration of the Hercynian granites associated with the CO_2-rich thermal and mineral waters, and its significance for the evolution of geothermal systems in granitic rocks. The isotopic ($\delta^{18}O$, δ^2H)

data of the granitic rocks and minerals (e.g. plagioclase, muscovite and chlorite) are consistent with the existence of two separate alteration events (pervasive and vein) caused by hydrothermal waters of different isotopic characteristics.

During the last decades, several studies have used Sr isotope ratios to describe the chemical evolution of thermal and mineral waters (e.g. Stettler, 1977; Stettler and Allègre, 1978; Vuataz et al., 1988; Goff et al., 1991; Négrel et al., 1997, 2001; Négrel, 1999; Millot et al., 2007, 2011). In this paper $^{87}Sr/^{86}Sr$ ratios and Sr geochemistry are applied, in both thermal and mineral waters and percolated rocks, to (i) identify the reservoir rocks, (ii) recognize the existence of possible mixing processes, (iii) trace underground flow paths and (iv) better describe the signatures of the water–rock interaction processes at depth. The $^{87}Sr/^{86}Sr$ ratio of a given geological material is dependent on its initial Rb content (Faure, 1986). During the last half century, this methodological approach, initially presented by Gast (1960), Hurley et al. (1962) and Hedge and Walthall (1963), has been applied mainly to the resolution of petrologic problems. Nevertheless, Sr isotopes can be used as an important tool in hydrogeology. The $^{87}Sr/^{86}Sr$ ratios are very good hydrogeochemical tracers because of the high atomic weight of Sr, its isotopes do not fractionate during natural processes. The $^{87}Sr/^{86}Sr$ ratios in waters depend on the Rb/Sr ratios and the age of the rocks with which they interact (Faure, 1986), and differences in $^{87}Sr/^{86}Sr$ ratios can be ascribed to the mixing of Sr derived from different rock sources with different isotopic compositions.

The geochemical behavior of Sr in thermal and mineral waters is dependent on temperature, fluid chemistry, mixing of fluids,

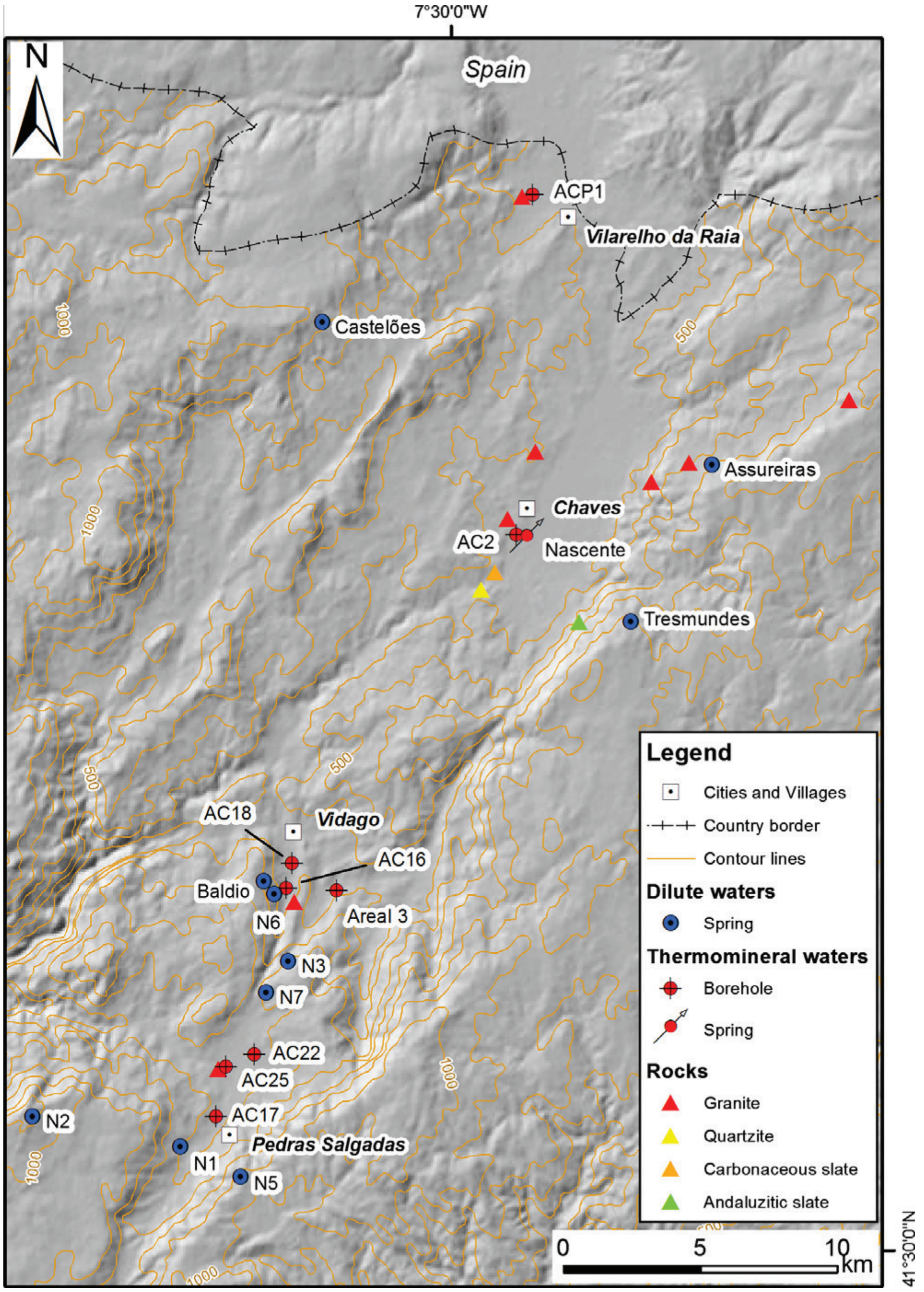

Fig. 2. Location sketch map of water and rock sampling sites. Modified from Andrade (2003).

and Sr concentration and isotopic composition of reservoir rock and vein minerals (e.g. Stettler, 1977; Stettler and Allègre, 1978; Vuataz et al., 1988; Goff et al., 1991; Négrel et al., 1997). For example, Vuataz et al. (1988) reported variations in Sr concentration and ^{87}Sr/^{86}Sr ratios in the hydrothermal outflow plume of the 260–300 °C Valles caldera geothermal system, New Mexico. Dissolved Sr geochemically mimics Ca in the reservoir and Sr concentrations were very low (<0.2 ppm). The ^{87}Sr/^{86}Sr ratios of reservoir fluids ranged from 0.708 to 0.710, similar to ratios in the host volcanic rocks (0.7045–0.7110). Along the outflow plume, mixing occurred between cool carbonate-rich groundwaters and reservoir fluids. Thus, temperature ultimately decreased to 47 °C, Sr became more soluble, and the Sr concentration rose from 0.5 to 1.3 mg/L. Because the host rocks along the outflow path change to Palaeozoic carbonates and shales (^{87}Sr/^{86}Sr ratios from 0.716 to 0.757), hot spring fluids discharging from the outflow plume had ^{87}Sr/^{86}Sr ratios from 0.715 to 0.722. In a geothermal study conducted at Long Valley caldera, California, Goff et al. (1991) compared ^{86}Sr/^{87}Sr ratios in reservoir and hot spring fluids, with ratios in various host rock types and vein calcites. They deduced that reservoir fluids were initially equilibrated at high temperature in a basement complex containing Mesozoic metamorphic rocks. As the fluids migrated, they entered and partially equilibrated with Quaternary volcanic rocks in the caldera. Hydrothermal calcites had ^{87}Sr/^{86}Sr ratios resembling those of the partially re-equilibrated reservoir fluids. In this case, temperature did not drop substantially (from 280 to 200 °C) and Sr solubility did not rise significantly. Consequently, the differences in ^{87}Sr/^{86}Sr ratios among the various samples were not as pronounced as in the Valles case. Nonetheless, the results demonstrated that the vein calcites were probably precipitated from co-existing reservoir fluids. Franklyn et al. (1991) stated that saline deep groundwater has quite constant ^{87}Sr/^{86}Sr ratios, while shallow groundwaters have higher and more irregular ratios, reflecting their derivation from minerals in the overlying soil, of variable thickness and mineralogy. Zuddas et al. (1995) concluded that the Sr concentration in high-temperature environments (e.g. natural geothermal fluids) is mainly controlled by a re-equilibration of neogenic minerals. Regarding the type of reservoir rock, and based on groundwater ^{87}Sr/^{86}Sr ratios in the Eye-Dashwa Lakes pluton (Canada), Franklyn et al. (1991) inferred that in granitic plutons the ^{87}Sr/^{86}Sr ratios of the deep groundwater are mainly the result of interaction with minerals, such as plagioclase.

In a study of granite fluid interaction and Sr availability from different minerals, Zuddas et al. (1995) stated that the dissolved Sr content and the ^{87}Sr/^{86}Sr ratios in groundwaters depend on the dissolution of the minerals from the granite, such as plagioclase, biotite, K-feldspar. Based upon dissolution of feldspars under controlled laboratory conditions Brantley et al. (1998) suggested that interpretation of ^{87}Sr/^{86}Sr ratios of catchments should be carefully analyzed, not only on the basis of whole-rock isotopic composition, but also on the basis of relative dissolution rates of the representative minerals. Those authors also stated that plagioclase dissolves at relatively fast rates and can release significant Sr into solution.

The main objective of this study is to use Sr geochemical and isotopic signatures to improve knowledge on the relationship between CO_2-rich thermal (76 °C) and cooler mineral (17 °C) waters discharging along one of the major NNE–SSW trending faults in northern Portugal. Rain, shallow cold dilute groundwaters and CO_2-rich thermal and mineral waters from Vilarelho da Raia–Pedras Salgadas region were analyzed for ^{87}Sr/^{86}Sr ratios as well as for Sr and major elements. In addition, the ^{87}Sr/^{86}Sr ratios of waters were compared to those of local rock samples. The ^{87}Sr/^{86}Sr ratios of these rocks have been used to understand the relationships between the thermal and mineral waters and the rocks that host the flow systems. Fractured rocks are complex, heterogeneous and anisotropic hydrogeologic environments with irregular distribution of groundwater pathways. Hydrogeologic knowledge and understanding of these intricate environments based on sound interdisciplinary geological, tectonic, hydrogeologic, hydrogeochemical and isotopic studies are indispensable to provide an adequate basis for the development of robust conceptual models and practical applications.

2. Collection procedures and sampling sites

Temperature (°C), pH (using a portable digital WTW pH 325/SET) and electrical conductivity (μS/cm – using a portable digital WTW LF 325/SET) of the waters were determined *in situ*. Total alkalinity was measured a few hours after collection by titration (Andrade, 2003). Chemical and isotopic (δ^2H and $\delta^{18}O$) analysis of the waters were performed following the methods described in Marques et al. (2006, 2010b).

Strontium analyses have been performed on water and rock samples (and mineral separates) located in the middle and in the borders of several grabens (Fig. 2).In order to collect representative water and rock samples for Sr concentrations and ^{87}Sr/^{86}Sr ratios,

Table 1
Sr concentrations and isotope ratios for waters from Vilarelho da Raia/Pedras Salgadas region.

References	Local	Sr (mg/L)	^{87}Sr/^{86}Sr
1st Field work campaign (February, 2000)			
ACP1 (+)	Vilarelho da Raia	0.5827	0.728033
CH1Ch. (*)	Chaves	0.0010	0.710599
Assureiras (X)	Chaves	0.0242	0.729536
Castelões (X)	Chaves	0.0059	0.722967
Campo de futebol (X)	Chaves	0.2942	0.723488
AC2 (+)	Chaves	0.4349	0.727191
Nascente (+)	Chaves	0.4181	0.727154
CH1V. (*)	Vidago	0.0015	0.710804
Baldio (X)	Vidago	0.0254	0.717003
N3 (X)	Vidago	0.0060	0.722858
N6 (X)	Vidago	0.0089	0.719087
N7 (X)	Vidago	0.0104	0.714352
AC16 (+)	Vidago	0.3424	0.723194
AC18 (+)	Vidago	1.3977	0.724280
Areal 3 (+)	Vidago	1.2130	0.720622
CH1 P.S. (*)	Pedras Salgadas	0.0013	0.711326
N1 (X)	Pedras Salgadas	0.0075	0.715094
N2 (X)	Pedras Salgadas	0.0018	0.730712
N5 (X)	Pedras Salgadas	0.0098	0.731135
AC17 (+)	Pedras Salgadas	0.7001	0.716969
AC25 (+)	Pedras Salgadas	0.8195	0.717572
AC22 (+)	Pedras Salgadas	1.3250	0.716754
2nd Field work campaign (July, 2000)			
ACP1 (+)	Vilarelho da Raia	0.5470	0.728035
Assureiras (X)	Chaves	0.0200	0.729496
Castelões (X)	Chaves	0.0050	0.723071
Campo de futebol (X)	Chaves	0.2540	0.723485
AC2 (+)	Chaves	0.3760	0.727181
Nascente (+)	Chaves	0.3730	0.727171
Tresmundes (X)	Chaves	0.0360	0.726818
Baldio (X)	Vidago	0.0230	0.716821
N6 (X)	Vidago	0.0090	0.719034
AC16 (+)	Vidago	0.2920	0.723205
AC18 (+)	Vidago	1.1560	0.724243
Areal 3 (+)	Vidago	0.6050	0.720714
N1 (X)	Pedras Salgadas	0.0070	0.714902
N2 (X)	Pedras Salgadas	0.0020	0.731297
N5 (X)	Pedras Salgadas	0.0080	0.731496
AC17 (+)	Pedras Salgadas	0.6280	0.716936
AC25 (+)	Pedras Salgadas	0.6790	0.717566
AC22 (+)	Pedras Salgadas	1.1560	0.716713

Note: (*) rain waters; (x) shallow cold dilute groundwaters; (+) thermal and mineral waters.

two field campaigns were carried out. In each campaign, approximately 20 water samples were collected and analyzed, including rain, shallow cold dilute groundwaters (spring waters) and thermal and mineral waters from Vilarelho da Raia, Chaves, Vidago and Pedras Salgadas areas (from springs and boreholes). Water samples collected for Sr-isotope analysis were filtered *in situ* using 0.2 μm cellulose acetate filters, and stored in precleaned 250 mL polyethylene bottles. Samples for δ^2H and δ^{18}O analysis were untreated. All water samples were collected after the three field control parameters (temperature, electrical conductivity and pH) remained constant. In addition, several rock samples from different outcrops in the study area were collected and samples of unaltered and hydrothermally altered granitic drill cores were obtained from the Vilarelho da Raia, Vidago and Pedras Salgadas boreholes.

Sample preparation for isotopic analysis of silicate minerals was performed at Centro de Petrologia e Geoquímica of Instituto Superior Técnico – CEPGIST – Lisbon, Portugal. The selected samples (two granitic rocks, one from Vilarelho da Raia – AM1 and one from Vidago – AM2) were crushed and sieved to <0.5 mm. Minerals were separated with a Frantz isodynamic magnetic separator and purified by handpicking under a binocular microscope. The purity and quality of mineral separates were assessed by XRD-analysis at CEPGIST. Occasionally in the rock samples muscovite was visible as clear platy crystals and the selected minerals (microcline, plagioclase, muscovite and biotite) were not strongly intergrown, facilitating mineral separation. Nevertheless, care was taken in the magnetic separation of coarse muscovite, since the magnetic susceptibility of sericitized plagioclase would be expected to lie in between those of pure plagioclase and pure muscovite. Strontium concentrations and ^{87}Sr/^{86}Sr ratios in waters and rocks (Tables 1 and 2) were determined by Geochron Laboratories (a division of Krueger Enterprises, Inc./Cambridge, Massachusetts, USA). Strontium concentrations were determined by isotope mass dilution spectrometry and ^{87}Sr/^{86}Sr ratios by mass spectrometry. Strontium was loaded on single Re filaments and analyzed in dynamic multicollector mode with ^{88}Sr = 3 V. All data (water and rocks) were normalized to ^{86}Sr/^{88}Sr = 0.1194. Long term reproducibility of NBS-987 (a strontium carbonate) was: 0.710247 ± 0.000014 (2 sigma s.d.).

3. Geological, tectonic, geochemical and isotopic background

The geology of Vilarelho da Raia–Pedras Salgadas region (Fig. 1) has been described by Baptista et al. (1993) and Sousa Oliveira and Portugal Ferreira (1995). The geomorphology is dominated by the so-called "Chaves Depression", a graben whose axis is oriented NNE–SSW. It is bound on the east side by the edge of the Padrela Mountain escarpment. The western block is formed by several grabens coming from the Heights of Barroso towards the "Chaves Depression". The study region is located in the Central-Iberian Zone of the Hesperic Massif. The main geological formations are: (i) Hercynian granites (syn-tectonic: 310 Ma and post-tectonic: 290 Ma) and (ii) Silurian metasediments that consist of a sequence of quartzites, phyllites and carbonaceous slates. On the W block of the Chaves graben, the Vilarelho da Raia, Chaves and Outeiro Seco (slightly N of Chaves, see Fig. 2) syn-tectonic granites have a medium- to coarse-grained texture, with abundant biotite and muscovite (approximately 10–15% of the modal composition). Quartz appears strongly tectonized. K-feldspar remains unaltered while Na-plagioclase (An_7–An_8) is sometimes strongly sericitized. Biotite is locally chloritized. On the E block of the Chaves graben, the Faiões (near Assureiras, Fig. 2) post-tectonic granite has a coarse-grained to porphyritic texture, with biotite and muscovite (being biotite predominant). Microcline-perthite and Na-plagioclase (near the limit albite/oligoclase) is also present. Biotite is very

Table 2
Sr concentrations and isotope ratios for rocks and mineral separates from Vilarelho da Raia/Pedras Salgadas region.

References	Local	Lithology	Sr (ppm)	^{87}Sr/^{86}Sr
Samples from outcrops				
AM1*	Vilarelho da Raia	Granite	74.0	0.777260
AM60	Chaves	Andaluzitic slate	63.5	0.777421
AM1164	Chaves	Graphitic slate	14.4	0.737563
AM1163	Chaves	Quartzite	16.8	0.726642
AM1149	Chaves	Chaves Granite	87.6	0.753397
AM1150	Chaves	Outeiro Seco Granite	99.5	0.757173
AM1160	Chaves	Faiões Granite	93.1	0.743689
AM1161	Chaves	Faiões Granite	97.5	0.735697
AM2*	Vidago	Vila Pouca de Aguiar Granite	98.0	0.735900
Pflum7	Vila Real	Carbonates	2350	0.709485
Samples from drill cores				
VR13 (53.0 m)	Vilarelho da Raia	Granite	20.1	0.942148
VR18 (70.5 m)	Vilarelho da Raia	Granite	58.8	0.789683
VR70 (195.30 m)	Vilarelho da Raia	Granite	58.7	0.765128
AC21a (14.8 m)	Pedras Salgadas	Vila Pouca de Aguiar Granite	59.9	0.763068
AC21e (106.35 m)	Pedras Salgadas	Vila Pouca de Aguiar Granite	36.0	0.784371
AC26a (25.15 m)	Vidago	Vila Pouca de Aguiar Granite	54.7	0.762890
AC26b (34 m)	Vidago	Vila Pouca de Aguiar Granite	57.6	0.761298
		Mineral		
Minerals				
AM1*	Vilarelho da Raia	Microcline	152	0.76359
AM1*	Vilarelho da Raia	Plagioclase	108	0.72087
AM1*	Vilarelho da Raia	Muscovite	26.0	0.84459
AM1*	Vilarelho da Raia	Biotite	11.0	4.18370
AM2*	Vidago	Microcline	101	0.75644
AM2*	Vidago	Plagioclase	75.0	0.71261
AM2*	Vidago	Muscovite	12.0	2.43938
AM2*	Vidago	Biotite	108	0.70948

Note: (*) Data from Aires-Barros et al. (1998).

chloritized, and is also characterized by several dark pleochroic halos around zircon inclusions. To the S of the Chaves region, the Vila Pouca de Aguiar post-tectonic granite (Vidago–Pedras Salgadas areas) has a medium- to fine-grained texture (sometimes porphyritic). K-feldspar (orthoclase and microcline) quartz, Na-plagioclase and biotite occur as major minerals.

Quartzites are mainly composed of fine-grained quartz with interbedded coarser quartz grains with a strongly indented granoblastic texture. There are also visible thin discrete beds of white mica, spread in the quartz grains. Locally micaceous films (mainly muscovite) are present, giving a schistose texture. This may be evidence of strong tectonization. The phyllites, sometimes andalusitic, show a silky sheen on schistosity surfaces. These rocks have a granoblastic texture, consisting of a banded crystalline mosaic of quartz grains and graphite. Under the petrographic microscope, the quartz grains display undulatory extinction and subparallel disposition. White mica has completely disappeared, being replaced by rare flakes of biotite. The carbonaceous slates are black rocks with well marked foliation and a lepidogranoblastic texture. The graphite (very abundant) occurs either in continuous beds or forming small lenticules, alternating with beds of white mica. The most recent formations are Miocene–Pleistocene graben filling sediments with their maximum development along the central axis of the Chaves graben (Fig. 1).

In the study region the ascending hydrothermal waters are structurally controlled by the NNE–SSW megafault (the Verin–Chaves–Penacova fault), which trends 70–80°E and is hydrothermally active along a belt extending 150 km through mainland Portugal (Fig. 3). The thermal and mineral waters emerge where the following subvertical fracture systems intersect: (1) N–S to NNE–SSW, (2) ENE–WSW, (3) NNW–SSE to NW–SE, and (4) WNW–ESE to W–E (Sousa Oliveira and Portugal Ferreira, 1995). Baptista et al. (1993) stated that the NNE–SSW megalineament reaches great depths (≈30 km) in the study region.

Baptista et al. (1993) and Sousa Oliveira and Portugal Ferreira (1995) noted that Chaves is the only site in the study area where thermal waters issue at high discharge temperature (76 °C) most probably because they emerge within a wide morphotectonic structure (3 km width by 7 km length) with a thickness of graben filling sediments greater than 250 m. In the case of Vidago and Pedras Salgadas areas, the mineral (17 °C) waters issue in places where local structures (small grabens) do not have such large structural features. Therefore, deeper groundwater circulation occurs in the Chaves area because of (i) high relief, (ii) deep fracturing and (iii)

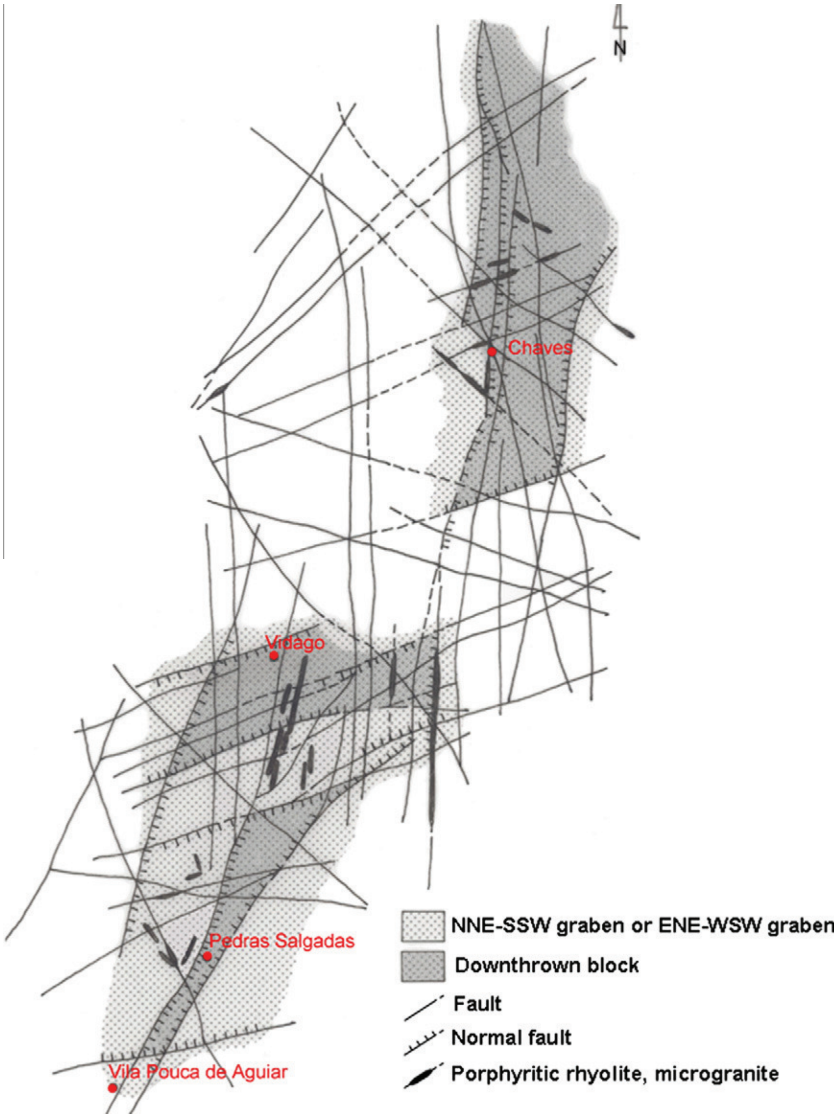

Fig. 3. Structural lineation map showing the subsidence zones in the Chaves, Vidago and Pedras Salgadas basins. Adapted from Sousa Oliveira (2001).

thickness of graben filling sediments (Baptista et al., 1993; Sousa Oliveira and Portugal Ferreira, 1995). Geochemical data from Chaves CO_2-rich thermal waters indicate equilibrium temperatures around 120 °C (Aires-Barros et al., 1995), which are in agreement with the issue temperature of these waters (76 °C). Considering a mean geothermal gradient of 30 °C/km (Duque et al., 1998) and a mean annual air temperature of 15 °C, one can estimate that the Chaves thermal water system reaches a maximum depth of about 3.5 km.

The $\delta^{13}C$ values of TDIC of the CO_2-rich thermal waters are between −8‰ and −1‰ (Marques et al., 1998, 2000), implying a deep-seated (upper mantle) origin for the CO_2. The NNE–SSW megalineament could play an important role in CO_2 extraction and migration from the upper mantle to the surface (e.g. Monteiro Santos, 1994; Marques et al., 1998, 2000; Martins et al., 2009). The deep-seated CO_2 is probably transported from its mantle source to the surface by migration as a separate gas phase incorporated in the infiltrated meteoric waters. This process would occur at considerable depth, in the case of the Chaves CO_2-rich thermal waters, and at shallow levels in the case of Vilarelho da Raia, Vidago and Pedras Salgadas CO_2-rich mineral waters.

Thermal/mineral waters and shallow cold dilute groundwaters of the region can be easily distinguished on site using electrical conductivity measurements. The electrical conductivity of samples classified as dilute waters is <100 μS/cm (Andrade, 2003). Only one sample located near Chaves city has an electrical conductivity of about 500 μS/cm, but high Ca, SO_4 and NO_3 concentrations in this water indicates contamination. The electrical conductivity of samples classified as thermal and mineral waters is >1500 μS/cm.

All the thermal and mineral waters issuing in the study region are of Na-HCO_3-type and are usually accompanied by CO_2 gas discharges (e.g. Aires-Barros et al., 1995; Marques et al., 2000, 2006, 2010a,b). Chaves spring and borehole waters are hot waters with temperatures between 48 and 76 °C, dry residuum (DR) between 1600 and 1850 mg/L, and free CO_2 between 350 and 1100 mg/L. The associated gas phase is nearly pure CO_2 (≈99.5% volume). Vilarelho da Raia cold spring and borehole waters have comparable chemical compositions, but a low temperature (≈17 °C) compared to Chaves hot waters. Vidago and Pedras Salgadas spring and borehole waters are distinguished from the previously described mineralized waters by higher Ca, Mg and free CO_2 content (up to 2500 mg/L).

The $\delta^{18}O$ and $\delta^{2}H$ values of the Chaves and Vilarelho da Raia CO_2-rich thermal and mineral waters lie on or close to the Global Meteoric Water Line (Craig, 1961), indicating that they are meteoric waters which have directly infiltrated into the bedrock (e.g. Aires-Barros et al., 1995; Marques et al., 2006). The stable isotopic composition of Vidago and Pedras Salgadas waters are also close to the GMWL (Fig. 4). However, the higher $\delta^{2}H$ and $\delta^{18}O$ values of these systems indicate different recharge altitudes and different subsurface flow paths (e.g. Marques et al., 2006).

4. Results and discussion

4.1. Sr source identification

As discussed above, Sr isotopes may be used to determine the origins of Sr in waters and to study water–rock interaction.

4.1.1. Sr geochemical and isotopic signatures of studied waters

Strontium concentrations in rain sampled in the Chaves, Vidago and Pedras Salgadas areas ranged between 1.0 μg/L and 1.5 μg/L. Waters classified as shallow cold dilute groundwaters have Sr contents ranging from 1.8 μg/L to 36.0 μg/L. Strontium contents of thermal and mineral waters ranged between 0.29 mg/L and 1.40 mg/L. The $^{87}Sr/^{86}Sr$ ratios of all waters collected during the two campaigns ranged between 0.714352 and 0.731496. Rain has $^{87}Sr/^{86}Sr$ ratios ranging between 0.710599 and 0.711326. Shallow cold dilute groundwaters have $^{87}Sr/^{86}Sr$ ratios between 0.714352 and 0.731496, while the thermal and mineral waters have $^{87}Sr/^{86}Sr$ ratios between 0.716713 and 0.728035. The $^{87}Sr/^{86}Sr$ ratios and Sr concentrations in the shallow cold dilute and thermal and mineral water samples, collected twice at the same location (winter and summer campaigns) are closely similar, and the Sr isotopic ratios and Sr concentrations of the studied waters can be considered to be representative (Figs. 5 and 6).

Strontium concentrations in rain, dilute and thermal and mineral waters are well correlated with major-element concentrations (Andrade, 2003). Correlation coefficients (*R*) are >0.90 for most of the major ions. The highest correlation coefficients are observed for relationships between Sr and Na, Ca, Mg, Al, HCO_3, Cl and Dry Residuum (DR). According to Andrade (2003), from the observation of the Sr vs. Cl (mg/L) diagram (with a correlation coefficient of 0.94) one can recognize Sr and Cl enrichment from the rain waters in the mineralized waters. However, the cold CO_2-rich mineral waters from Vidago and Pedras Salgadas are those that in general have higher Sr concentrations, contrasting with the hot CO_2-rich mineral waters from Chaves that have relatively lower Sr concentrations. As described by Aires-Barros et al. (1998) and Marques et al. (1999) the higher mineralization of the studied thermal and mineral waters is ascribed to the cold CO_2-rich mineral waters of

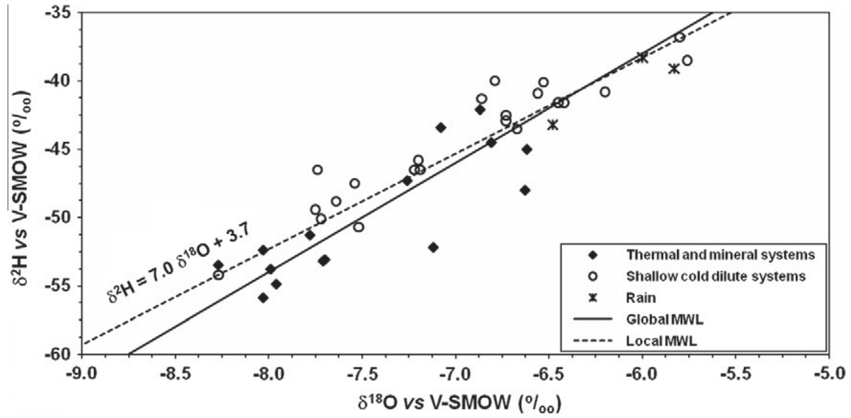

Fig. 4. Plot of $\delta^{18}O$ vs. $\delta^{2}H$ (‰ vs. V-SMOW) for the hot and cold CO_2-rich mineral waters. As reference, the local meteoric water line (LMWL) derived from the isotopic composition of shallow cold dilute groundwater samples collected from springs located at different altitude sites in the region has been plotted. Modified from Andrade (2003).

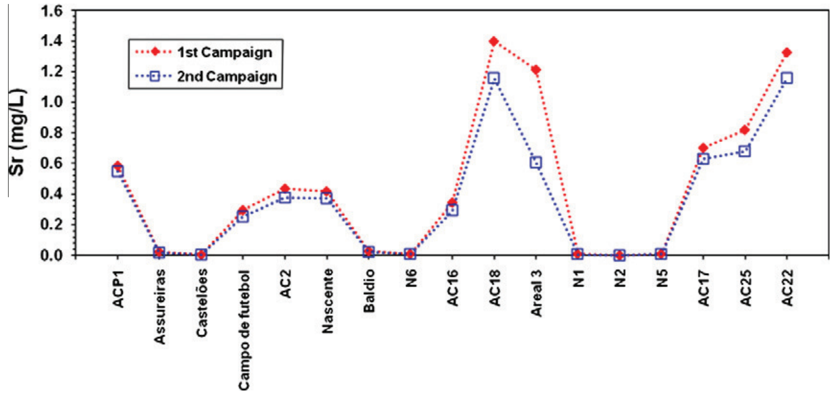

Fig. 5. Sr concentration in dilute and mineral waters; (♦) winter and (■) summer fieldwork campaigns. Modified from Andrade (2003).

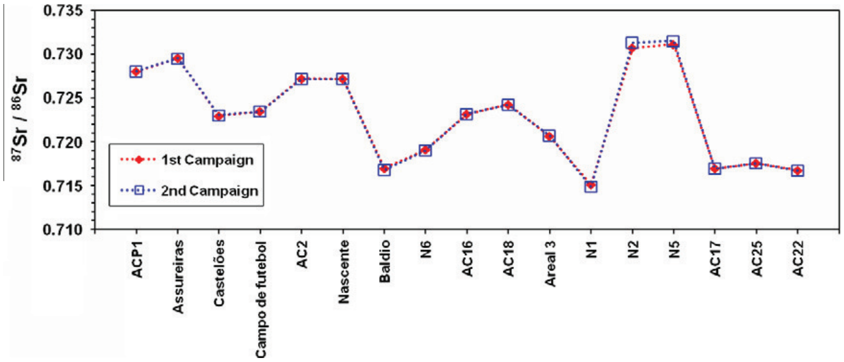

Fig. 6. $^{87}Sr/^{86}Sr$ ratios in dilute and mineral waters; (♦) winter and (■) summer fieldwork campaigns. Modified from Andrade (2003).

Vidago and Pedras Salgadas. As stated by Goff et al. (1991), although the concentrations of the conservative species increase during flashing or boiling, the Sr concentration may decrease due to loss of CO_2 during flashing by the reaction:

$$Sr^{2+}_{(aq)} + 2HCO^{-}_{3\,(aq)} \leftrightarrows SrCO_{3(s)} + CO_{2(g)} + H_2O \qquad (1)$$

Hence, the relatively low Sr and HCO_3 concentrations found in the Chaves thermal waters may be caused by subsurface boiling, whereas the relatively high Sr and HCO_3 in Vidago and Pedras Salgadas mineral waters strongly demonstrates the increasing solubility of divalent ions (Sr, Ca and Mg) with decreasing temperature (Andrade, 2003). In contrast, there are weak correlations ($R < 0.4$) between major ion concentrations (e.g. Na, K, Ca, Mg, Li, Al, HCO_3, F and Sr) and $^{87}Sr/^{86}Sr$ ratios (Andrade, 2003).

Fig. 7 shows a plot of 1/Sr vs. $^{87}Sr/^{86}Sr$ for the CO_2-rich thermal and mineral waters of the studied region. The decreasing $^{87}Sr/^{86}Sr$ ratios from the north to the south (Vilarelho da Raia/Chaves > Vidago > Pedras Salgadas) along the Verin–Chaves–Penacova NNE-trending fault is due to interaction with different granitic rocks that have lower $^{87}Sr/^{86}Sr$ ratios. Effectively, the radioactive decay of the large, monovalent ^{87}Rb atom at a given lattice site causes a replacement by the considerably smaller bivalent ^{87}Sr, which enters more rapidly into solution. As a consequence, the $^{87}Sr/^{86}Sr$ ratios of groundwaters that have interacted with older granitic rocks are typically greater than the $^{87}Sr/^{86}Sr$ ratios of groundwaters that have interacted with younger (post-tectonic) granitic rocks, see Fig. 1 (Stettler, 1977; Stettler and Allègre, 1978; Faure, 1986). The variation of $^{87}Sr/^{86}Sr$ ratios vs. 1/Sr in Fig. 7 can be understood through the existence of three end-members ((a) Vilarelho da Raia/Chaves, (b) Vidago and (c) Pedras Salgadas) of a concentration trend, from rain waters towards the CO_2-rich thermal and mineral waters, suggesting that different underground flow paths host diverse hydrothermal systems. The nonlinear relationship between the several CO_2-rich thermal and mineral waters also suggests that simple mixing does not occur.

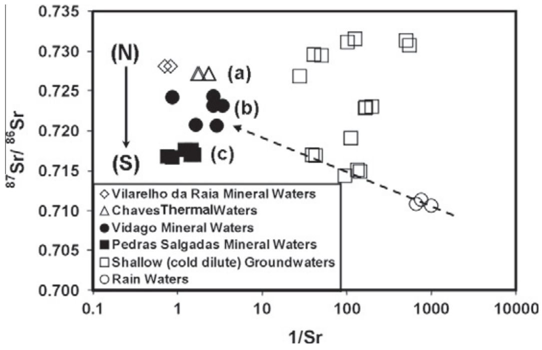

Fig. 7. 1/Sr vs. $^{87}Sr/^{86}Sr$ for the waters from Vilarelho da Raia–Pedras Salgadas region. Sr in mg/L. Modified from Andrade (2003). The dashed straight line is merely indicative of the concentration trend from rain waters towards the CO_2-rich thermal and mineral waters.

The $^{87}Sr/^{86}Sr$ ratios of the CO_2-rich mineral waters increase from south to north along the mega-structure of Verin–Chaves–Régua–Penacova. This trend could be interpreted as the result of groundwater flow from south to north. However, this hypothesis is not feasible since waters with similar $^{87}Sr/^{86}Sr$ ratios have different $\delta^{18}O$ values (Aires-Barros et al., 1995; Marques et al., 1998, 2006, 2010b). One might also expect a general increase in the water mineralization from south to north, which also is not the case (Aires-Barros et al., 1995; Marques et al., 1998, 2006, 2010b). The results obtained indicate that (i) the CO_2-rich thermal and mineral waters, with different recharge altitudes (different $\delta^{18}O$ values: Fig. 4) circulate at depth within granitic environments with different Sr isotopic compositions and (ii) there is no single hydraulically related flow path from Vilarelho da Raia towards Pedras Salgadas, along the Verin–Chaves–Régua–Penacova fault zone.

The $^{87}Sr/^{86}Sr$ vs. (Ca + Mg)/HCO_3 plot (Fig. 8) defines the same end-members; the Vidago and Pedras Salgadas CO_2-rich cold mineral waters are characterized by higher (Ca + Mg)/HCO_3 ratios and lower $^{87}Sr/^{86}Sr$ ratios. This trend could be ascribed to: (i) the fact that, as stated by Greber (1994), in CO_2-rich hydromineral systems low temperatures enhance water–rock interaction particularly increasing Ca and Mg concentrations, and (ii) the fact that in the recharge areas of Vidago and Pedras Salgadas CO_2-rich cold mineral waters, deep circulation involving interaction with another type of rock (e.g. quartzites with lower $^{87}Sr/^{86}Sr$ ratios around 0.726642) must be considered, since diffuse quartzite layers can be found in those areas (see Fig. 1). On the other hand, in Vilarelho da Raia/Chaves the recharge areas are mainly within granitic rocks with much higher $^{87}Sr/^{86}Sr$ ratios (from 0.743689 up to 0.789683). This trend confirms the idea that the three groups of thermal and mineral waters could be the result of similar hydrogeologic systems but not the same system.

4.1.2. Strontium isotopes in rocks

If the $^{87}Sr/^{86}Sr$ ratios of the thermal and mineral waters is considered, they can be compared with their inferred or known reservoir rocks. Geological sampling has provided $^{87}Sr/^{86}Sr$ data from several rock suites in the Vilarelho da Raia–Chaves–Vidago and Pedras Salgadas region. A comparison of $^{87}Sr/^{86}Sr$ variations of the rocks from the study region is shown in Table 2. The Sr isotopic signatures show a clear-cut picture for each type of rock encountered (andalusitic slate, carbonaceous slate, quartzite and granites).

With reference to the presence of carbonate minerals, White et al. (1999) noted that Ca release and CO_2 consumption during chemical weathering of crystalline silicate rocks containing accessory calcite via:

$$CaCO_{3(s)} + CO_{2(g)} + H_2O_{(l)} \rightarrow Ca^{2+}_{(aq)} + 2HCO^{-}_{3\,(aq)} \tag{2}$$

should have important geochemical implications. Although the mass of Ca in granitic rocks resides predominately in plagioclase feldspar (White et al., 1999), in the present research area the granitic rocks contain Na-plagioclase (An_{7-8}). As referred by White et al. (1999), calcite is commonly associated with hydrothermally altered granitic rocks and is generally recognized as an important contributor to Ca fluxes in associated waters (Blum et al., 1998). However, in Vilarelho da Raia–Pedras Salgadas area (this study), microscopic examination of the granitic rocks did not revealed the formation of neogenic calcite. In fact, calcite was not found in hydrothermal alteration assemblages, such as sericite, or along grain boundaries and microfractures of quite unaltered minerals. So, the precipitation of calcite should be ruled out.

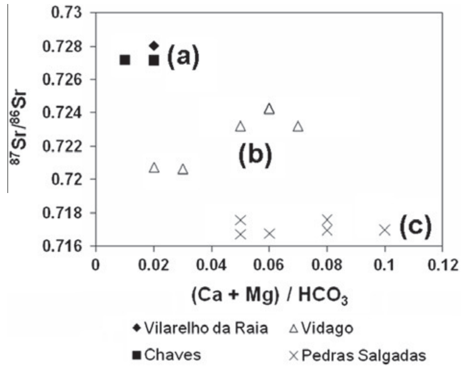

Fig. 8. Plot of $^{87}Sr/^{86}Sr$ vs. (Ca + Mg)/HCO_3 ratios for the thermal and mineral waters of the studied region.

At the Vilarelho da Raia area, the AC2 borehole penetrates 200 m of granitic rocks with different facies and alteration features (Marques et al., 1998). A very large range of $^{87}Sr/^{86}Sr$ ratios is observed. The drill core VR13 has a $^{87}Sr/^{86}Sr$ ratio (0.942148) that is much higher than most of the other granitic rocks of the Vilarelho da Raia–Chaves area, probably due to strong hydrothermal alteration. This rock sample contains strong, quartz veins, several centimeter-thick, with hydrothermal characteristics (Marques et al., 2010b). One of the most striking features of the data is the narrow range of $^{87}Sr/^{86}Sr$ ratios from all types of granitic rocks from Chaves area. The granite of Águas Frias (eastern block of the Chaves graben) has the highest $^{87}Sr/^{86}Sr$ ratios of the granitic rocks and the lowest Sr concentration. This trend of high $^{87}Sr/^{86}Sr$ ratios and low Sr concentrations has also been detected in the granitic drill cores from the Vilarelho da Raia borehole AC2 and could be ascribed to the different degrees of alteration.

When the meteoric groundwaters percolate through the rocks, several hydrogeologic processes may be responsible for the distribution of Sr between the solution and the infiltrated rocks. As stated by Stettler and Allègre (1978), both isotopic exchange and rock dissolution may occur. In the case of granitic rocks, rock dissolution can be understood in terms of congruent dissolution followed by the gradual deposition of newly formed minerals (Garrels, 1967; Garrels and Mackenzie, 1967; Négrel, 1999; Négrel et al., 2001; Millot et al., 2007, 2011). Both mechanisms would keep the $^{87}Sr/^{86}Sr$ ratios in the waters similar to that of the source rock (Stettler and Allègre, 1978). On the other hand, if preferential leaching of a specific rock constituent takes place, the $^{87}Sr/^{86}Sr$ ratios of the water will be constrained by the ratios of the most alterable minerals (Stettler and Allègre, 1978; Négrel, 1999; Négrel et al., 2001; Millot et al., 2007, 2011). For example, McNutt et al. (1990) suggested that Sr in groundwaters within the Canadian Shield is mainly derived from plagioclase dissolution. Fritz et al. (1987) have identified chlorite (as the result of biotite alteration) as the main source of Sr in saline waters. Amongst the minerals typically found in granitic rocks, apatites, feldspars (plagioclase and K-feldspar) and micas (biotite and muscovite) are the minerals that most commonly contain significant amounts of Rb and/or Sr (Négrel et al., 2001). The Rb/Sr ratio increases from plagioclase to biotite and, therefore, the $^{87}Sr/^{86}Sr$ ratios also increases (Négrel et al., 2001). As indicated by Stettler and Allègre (1978), plagioclases and minerals such as biotite, pyroxene, and hornblende provide most of dissolved ions. On the other hand, K-feldspars and quartz are more slowly dissolved. So, as shown by Stettler (1977), it is convenient to restrict the field investigation to a reasonably confined region with a relatively simple geological setting. This is the situation for the present study.

From Fig. 7, it is clear that the fluids collected at the Vilarelho da Raia/Chaves area have the highest $^{87}Sr/^{86}Sr$ ratios. However, $^{87}Sr/^{86}Sr$ ratios of granitic rock samples collected near Vilarelho da Raia and Vidago areas (Table 2 and Fig. 9) are far higher than those of the water samples. This indicates that no equilibrium was reached between these two phases and that the Sr isotope values were obtained from equilibrium being reached between those fluids and particular granitic minerals. The mean $^{87}Sr/^{86}Sr$ ratio of the mineralized waters (0.722419) is similar to that of the plagioclases of the granitic rocks (Vilarelho da Raia: $^{87}Sr/^{86}Sr = 0.72087$ and Vidago: $^{87}Sr/^{86}Sr = 0.71261$; Aires-Barros et al., 1998).

The $^{87}Sr/^{86}Sr$ ratios of the studied CO_2-rich thermal and mineral waters fall in a narrow range of values (see Table 2 and Fig. 9), sim-

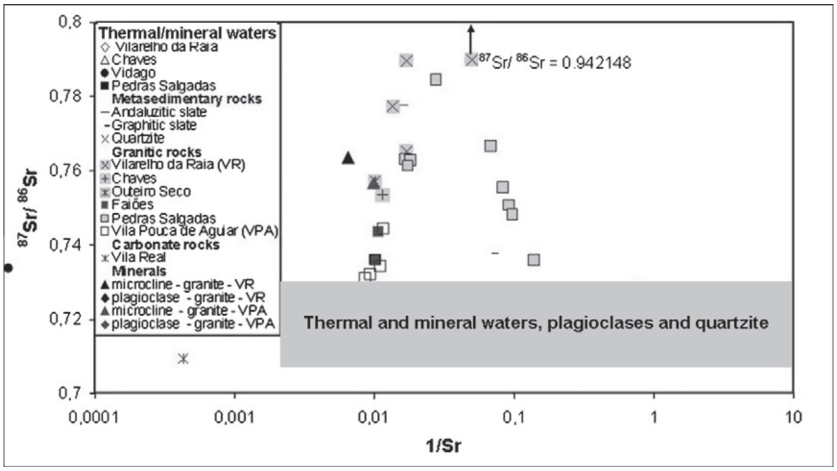

Fig. 9. Plot of 1/Sr vs. $^{87}Sr/^{86}Sr$ for the rocks, minerals and CO_2-rich thermal and mineral waters. Sr in mg/L. Modified from Andrade (2003).

ilar to those of plagioclases but not to that of K-feldspar (microcline), muscovite and biotite, or the whole rock (granites). This suggests that the Sr isotopic composition is the result of plagioclase-water interaction. Franklyn et al. (1991) concluded that the results obtained for saline groundwaters were consistent with thermodynamic and kinetic models (e.g. Lasaga, 1984; Madé and Fritz, 1989) that demonstrate the relatively rapid dissolution of plagioclase with respect to other Sr-bearing rock-forming silicates such as K-feldspar and the micas. Therefore, in open fluid systems (which is the situation in this study) the time for reaction between plagioclase and water will be short and, thus, the Sr isotopic signatures of the fluids will reflect the hydrolysis of plagioclase with low $^{87}Sr/^{86}Sr$ ratios rather than dissolution of the whole rock (Franklyn et al., 1991; McNutt et al., 1987, 1990). However, it is clear that radiogenic Sr from weathering of biotite or feldspars may be effectively removed from various granitic weathered systems (e.g. Blum et al., 1994; Zuddas et al., 1995). Usually K-feldspar and biotite have high Rb contents and hence, high $^{87}Sr/^{86}Sr$ ratios (Faure, 1986). In this case study, if K-feldspar and biotite were strongly involved in the dissolution process, the CO_2-rich thermal and mineral waters that have derived most of their Sr from the hydrolysis of those minerals should have similar $^{87}Sr/^{86}Sr$ ratios, which is not so.

5. Concluding remarks and outlook

This work demonstrates the usefulness of $^{87}Sr/^{86}Sr$ ratios and Sr geochemistry in hydrogeologic studies on a suite of CO_2-rich thermal and mineral waters issuing in the northern Portuguese mainland. It is well accepted that the Sr isotopic composition of groundwaters is a good tracer of the reservoir source, since the Sr isotopic composition of a groundwater is the fingerprint of the isotopic composition of the bedrock with which it has interacted.

The results obtained were used to (i) update knowledge on some of Portugal's most important thermal and mineral waters, (ii) highlight the complexity of CO_2-rich groundwater circulation in fractured rocks, known for their numerous thermal and mineral–water springs, (iii) put forward a new hypothesis on groundwater flow paths; (iv) explore Sr isotopes as a powerful tool to redefine water–rock interaction within the reservoir, and (v) ensure economic use of drinkable CO_2-rich mineral waters, most of them also used for health cures in local spas.

In the case of Vilarelho da Raia–Chaves–Vidago–Pedras Salgadas areas, the essential elements are (*i*) meteoric waters locally recharged, (*ii*) different deep underground flow paths and (*iii*) granitic rocks of different ages. The $^{87}Sr/^{86}Sr$ ratios together with HCO_3, Ca, Mg and Sr concentrations in the thermal and mineral waters were useful to clarify some of the existing uncertainties (e.g. the presence of one or several hydromineral systems). The $^{87}Sr/^{86}Sr$ ratios and Sr concentrations in the thermal and mineral waters do not appear to be independent from the other geochemical parameters (e.g. age of the percolated rocks and temperature dependence of the CO_2 dissolution in water, respectively) and have provided a clear picture on the influence of varying rock types on the thermal and mineral waters derived from the infiltration of local meteoric waters. Enrichment in radiogenic Sr and Sr concentration in waters is observed from the recharge waters (meteoric waters) towards the highly mineralized waters. The Sr-isotope data presented in this study strongly suggest that Vilarelho da Raia, Chaves, Vidago and Pedras Salgadas CO_2-rich thermal and mineral waters can be considered as surface manifestations of different hydromineral systems. Strontium-isotope values of thermal and mineral waters decrease systematically from the north to the south probably due to interaction with younger and isotopically lighter granitic rocks and not because of mixing between the different hydromineral systems. Although this study does not provide a general model of fluid flow within each particular hydrogeologic system, it does give a better idea of the relationship between the several CO_2-rich thermal and mineral waters issuing in the studied region along one of the major NNE–SSW trending faults in northern Portugal.

Knowledge of groundwater circulation and interactions with the surrounding rocks is an important factor to ensure economic use of deep groundwaters in terms of drinkable mineral waters as well as in terms of potential future overexploitation.

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References

Aires-Barros, L., Marques, J.M., Graça, R.C., 1995. Elemental and isotopic geochemistry in the hydrothermal area of Chaves/Vila Pouca de Aguiar (Northern Portugal). Environ. Geol. 25, 232–238.

Aires-Barros, L., Marques, J.M., Graça, R.C., Matias, M.J., Van Der Weijden, C.H., Kreulen, R., Eggenkamp, H.G.M., 1998. Hot and cold CO_2-rich mineral waters in Chaves geothermal area (northern Portugal). Geothermics 27, 89–107.

Andrade, M.P.L., 2003. The isotope geochemistry of thermomineral water. Contribution of the isotopes of Sr ($^{87}Sr/^{86}Sr$) and Cl ($^{37}Cl/^{35}Cl$) in the development of circulation models. The case of some carbon dioxide waters in N Portugal. Unpublished MSc Thesis, Instituto Superior Técnico, Technical Univ. Lisbon, Lisbon (in Portuguese).

Baptista, J., Coke, C., Dias, R., Ribeiro, A., 1993. Tectonics and geomorphology of Pedras Salgadas region and associated mineral springs. In: Chambel, A. (Ed.), Comunicações da XII Reunião de Geologia do Oeste Peninsular, vol. 1. Évora University, pp. 125–139 (in Portuguese).

Blum, J.D., Erel, Y., Brown, K., 1994. $^{87}Sr/^{86}Sr$ ratios of Sierra Nevada stream waters: implications for relative mineral weathering rates. Geochim. Cosmochim. Acta 58, 5019–5025.

Blum, J.D., Grazis, C.A., Jacobson, A.D., Chamberlain, C.P., 1998. Carbonate versus silicate weathering in the Raikhot watershed within the High Himalyan Crystalline series. Geology 164, 411–414.

Brantley, S.L., Chesley, J.T., Stillings, L.L., 1998. Isotopic ratios and release rates of strontium measured from weathering feldspars. Geochim. Cosmochim. Acta 62, 1493–1500.

Craig, H., 1961. Standard for reporting concentrations of deuterium and oxygen-18 in natural waters. Science 133, 1833–1834.

Duque, R., Monteiro Santos, F.A., Mendes-Victor, L.A., 1998. Heat flow and deep temperatures in the Chaves geothermal system, northern Portugal. Geothermics 27, 75–87.

Faure, G., 1986. Principles of Isotope Geology, second ed. John Wiley & Sons, New York.

Franklyn, M.T., McNutt, R.H., Kamineni, D.C., Gascoyne, M., Frape, S.K., 1991. Groundwater $^{87}Sr/^{86}Sr$ values in the Eye-Dashwa Lakes pluton, Canada: evidence for plagioclase-water reaction. Chem. Geol. 86, 111–122.

Fritz, B., Clauer, N., Kam, M., 1987. Strontium isotopic data and geochemical calculations as indicators for the origin of saline waters in crystalline rocks. In: Fritz, B., Frape, S.K. (Eds.), Saline Water and Gases in Crystalline Rocks. Geol. Assoc. Can., Spec. Paper 33, pp. 121–126.

Garrels, R.M., 1967. Genesis of some groundwaters from igneous rocks. In: Abelson, P. (Ed.), Research in Geochemistry. Wiley, New York, pp. 405–420.

Garrels, R.M., Mackenzie, F.T., 1967. Origin of the chemical composition of some springs and lakes. Adv. Chem. Ser. 67, 222–242.

Gast, P.W., 1960. Limitations on the composition of the upper mantle. J. Geophys. Res. 65, 1287–1297.

Goff, F., Wollenberg, H.A., Brookins, D.C., Kristler, R.W., 1991. A Sr-isotopic comparison between thermal waters, rocks, and hydrothermal calcites, Long Valley caldera, California. J. Volcanol. Geotherm. Res. 48, 265–281.

Greber, E., 1994. Deep circulation of CO_2-rich palaeowaters in a seismically active zone (Kuzuluk/Adaparazi, northwestern Turkey). Geothermics 23, 151–174.

Hedge, C.E., Walthall, F.G., 1963. Radiogenic strontium-87 as an index of geologic processes. Science 140, 1214.

Hurley, P.M., Hughes, H., Faure, G., Fairbain, H.W., Pinson, W.H., 1962. Radiogenic strontium-87 model of continent formation. J. Geophys. Res. 67, 5315–5334.

Lasaga, A.C., 1984. Chemical kinetics of water–rock interactions. J. Geophys. Res. 89, 4009–4025.

Madé, B., Fritz, B., 1989. Simulation of granite dissolution at 25, 60 and 100 °C based on thermodynamic potential and kinetic laws. In: Milne D.L. (Ed.), Proc. Water–Rock Interaction Symp, vol. 6. Balkema, Rotterdam, pp. 461–464.

Marques, J.M., Carreira, P.M., Aires-Barros, L., Graça, R.C., 1998. About the origin of CO_2 in some $HCO_3/Na/CO_2$-rich Portuguese mineral waters. Geotherm. Resour. Council Trans. 22, 113–117.

Marques, J.M., Aires-Barros, L., Graça, R.C., 1999. Geochemical and isotopic features of hot and cold CO_2-rich mineral waters of northern Portugal: a review and reinterpretation. Bull. Hydrogéol. 17, 175–183.

Marques, J.M., Carreira, P.M., Aires-Barros, L., Graça, R.C., 2000. Nature and role of CO_2 in some hot and cold $HCO_3/Na/CO_2$-rich Portuguese mineral waters: a review and reinterpretation. Environ. Geol. 40, 53–63.

Marques, J.M., Andrade, M., Carreira, P.M., Eggenkamp, H.G.M., Graça, R.C., Aires-Barros, L., Antunes da Silva, M., 2006. Chemical and isotopic signatures of $HCO_3/Na/CO_2$-rich geofluids, North Portugal. Geofluids 6, 273–287.

Marques, J.M., Carreira, P.M., Espinha, Marques.J., Chaminé, H.I., Fonseca, P.E., Monteiro Santos, F.A., Eggenkamp, H.G.M., Teixeira, J., 2010a. The role of geosciences in the assessment of low-temperature geothermal resources (N-Portugal): a review. Geosci. J. 14, 329–446.

Marques, J.M., Matias, M.J., Basto, M.J., Carreira, P.M., Aires-Barros, L., Goff, F.E., 2010b. Hydrothermal alteration of Hercynian granites, its significance to the evolution of geothermal systems in granitic rocks. Geothermics 39, 152–160.

Martins, H.C.B., Sant'ovaia, H., Noronha, F., 2009. Genesis and emplacement of felsic Variscan plutons within a deep crustal lineation, the Penacova–Régua–Verin fault: an integrated geophysics and geochemical study (NW Iberian Peninsula). Lithos 111, 142–155.

McNutt, R.H., Gascoyne, M., Kamineni, D.C., 1987. $^{87}Sr/^{86}Sr$ values in groundwaters of the East Bull Lake pluton, Superior Province, Ontario, Canada. Appl. Geochem. 2, 93–101.

McNutt, R.H., Frape, S.K., Fritz, P., Jones, M.G., Macdonald, I.M., 1990. The $^{87}Sr/^{86}Sr$ values of Canadian Shield brines and fractures minerals with applications to groundwater mixing, fracture history, and geochronology. Geochim. Cosmochim. Acta 54, 205–215.

Millot, R., Négrel, Ph., Petelet-Giraud, E., 2007. Multi-isotopic (Li, B, Sr, Nd) approach for geothermal reservoir characterization in the Limagne Basin (Massif Central, France). Appl. Geochem. 22, 2307–2325.

Millot, R., Guerrot, C., Innocent, C., Négrel, Ph., Sanjuan, B., 2011. Chemical, multi-isotopic (Li–B–Sr–U–H–O) and thermal characterization of Triassic formation waters from the Paris Basin. Chem. Geol. 283, 226–241.

Monteiro Santos, F.A., 1994. Integrated interpretation of resistivity and magneto-telluric data: application to the study of low enthalpy geothermal reservoirs. Unpublished PhD Thesis, Univ. Lisbon (in Portuguese).

Négrel, Ph., 1999. Geochemical study in a granitic area, the Margeride, France: chemical element behavior and $^{87}Sr/^{86}Sr$ constraints. Aquat. Geochem. 5, 125–165.

Négrel, P., Fouillac, C., Brach, M., 1997. A strontium isotopic study of mineral and surface waters from the Cézallier (Massif Central, France): implications for mixing processes in areas of disseminated emergences of mineral waters. Chem. Geol. 135, 89–101.

Négrel, Ph., Casanova, J., Aranyossy, J.F., 2001. Strontium isotope systematics used to decipher the origin of groundwaters sampled from granitoids: the Vienne case (France). Chem. Geol. 177, 287–308.

Oliveira, J.T., Pereira, E., Ramalho, M., Antunes, M.T., Monteiro, J.H., 1992. Geological Map of Portugal (1:500,000), fifth ed. Portuguese Geological Survey, Lisbon (in Portuguese).

Pereira, E., Ribeiro, A., Marques, F., Munhá, J., Castro, P., Meireles, C., Ribeiro, M.A., Pereira, D., Noronha, F., Ferreira, N., 1989. Geological Map of Portugal (1:200,000), sheet 2. Portuguese Geological Survey, Lisbon (in Portuguese).

Sousa Oliveira, A., 2001. Hydrogeology of the carbon dioxide hydromineral province systems of transmontana: Riverside (Mirandela), Sandim (Vinhais), and Segirei Salgadela(Chaves). Unpublished PhD Thesis, Department of Geology, Trás-os-Montes and Alto Douro Univ (in Portuguese).

Sousa Oliveira, A., Portugal Ferreira, M.R., 1995. Structural control of the hydromineral springs from Pedras Salgadas region (Vila Pouca de Aguiar – Northern Portugal). Memória 4, 485–489.

Stettler, A., 1977. ^{87}Rb–^{87}Sr systematics of a geothermal water–rock association in the Massif Central, France. Earth Planet. Sci. Lett. 34, 432–438.

Stettler, A., Allègre, C.J., 1978. ^{87}Rb–^{87}Sr studies of waters in a geothermal area, the Cantal, France. Earth Planet. Sci. Lett. 38, 364–372.

Vuataz, F.-D., Goff, F., Fouillac, C., Calvez, J.-Y., 1998. A strontium isotope study of the VC-1 core hole and associated hydrothermal fluids and rocks from Valles Caldera, Jemez Mountains, New Mexico. J. Geophys. Res. 93, 6059–6067.

White, A.F., Bullen, T.D., Vivit, D.V., Schulz, M.S., Clow, D.W., 1999. The role of disseminate calcite in the chemical weathering of granitoid rocks. Geochim. Cosmochim. Acta 63, 1939–1953.

Zuddas, P., Seimbille, F., Michard, G., 1995. Granite-fluid interaction at near equilibrium conditions: experimental and theoretical constraints from Sr contents and isotopic ratios. Chem. Geol. 121, 145–154.