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Geochemical and isotopic features of hot and cold CO_2-rich mineral waters of northern Portugal: a review and reinterpretation

by * José Marques, Luis Aires-Barros & Rui Graça

Instituto Superior Técnico, Laboratório de Mineralogia *e* Petrologia (LAMPIST),
Av. Rovisco Pais, 1049-001 Lisboa, Portugal. E-mail: pcd2045@alfa.ist.utl.pt

ABSTRACT

During past few years we have been mainly focused on the study of the relation among the hot (76°C) and cold (17°C) CO_2-rich mineral waters discharging, in the **northern** part of Portugal. All mineralised waters belong to the HCO_3/Na/ CO_2-rich type. The results of SiO_2, Na-K-Ca, Na/K and Na/Li geothermometers are not generally compatible. Using the diagrams **log (H_4SiO_4)** *vs* **log** (Na/K) and log (Ca/K^2) *vs* log (Na/K) we have concluded that most of the studied CO_2-rich waters are far from equilibrium. These results are in good agreement with those obtained by the graphical evaluation of water-rock equilibration temperatures using the Na/400, K/10 and $Mg^{1/2}$ concentrations. Vilarelho da Raia cold mineral waters have $\delta^{18}O$ and SD values similar to Chaves hot waters suggesting a common origin for these waters. The heavier $\delta^{18}O$ and SD values found in Vidago and Pedras Salgadas cold mineral waters could be attributed to different recharge altitudes. The high mineralization, low tritium activity and a positive ^{18}O-shift found in Vidago AC18 cold mineral waters could be faced as signatures of a **long** residence time at depth as the result of a regional circulation (as indicated by the lighter SD values).

KEYWORDS

Geochemistry, isotopes, hot and cold CO_2-rich mineral waters, flowpaths, Chaves geothermal area, Portugal

Introduction

In Portuguese mainland, the warmest geothermal waters (*e.g.* Chaves 76°C) are situated in the Northern part of the country occurring along or near major faults (Fig.1). The hot (Chaves) and cold (Vilarelho da Raia, Vidago and Pedras Salgadas) CO_2-rich mineral waters flow from natural springs and drilled wells. During 1990/94 special emphasis has been put on the geohydrologic characterisation of the low-temperature geothermal system of Chaves (AIRES-BARROS *et* al. 1991, 1994, 1995). During 1995/98 two main lines have been considered **for** the evaluation of the local hot and cold mineral water resources: *i)* update **the** conceptual model **of the** underground flow paths associated with the low-temperature geothermal system of Chaves, and *ii)* try to understand whether **the** hot and cold CO_2-rich mineral waters could be faced as surface manifestations of the same geobydrological system (AIRES-BARROS et al. 1998).

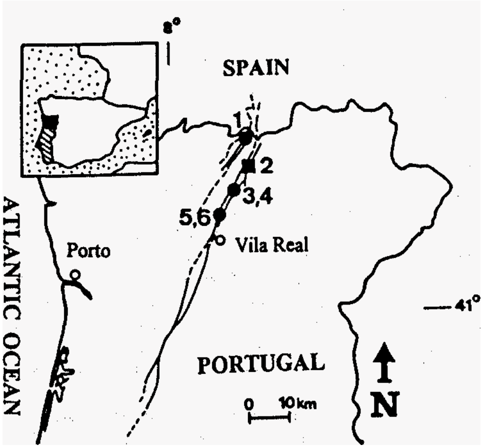

Figure 1: Sketch map of the region, showing the position of main water samples. (1) Vilarelho da Raia area; (2) Chaves thermal area; (3) and (4) Campilho/Vidago area; (5) and (6) Sabroso/Pedras Salgadas area. (■) stands for hot saline waters; (●) stands for cold saline waters.

Geological setting

The geology of Vilarelho da Raia - Pedras Salgadas region has been described by PORTUGAL **FERREIRA** et al. (1992) and BAPTISTA et al. (1993). The region under research **is** situated in the Pre-Mesozoic Hesperic Massif that consists mainly of Hercynian granitic rocks and Paleozoic metasediments. The oldest formations correspond to the Pre-Ordovician schisto-graywacke complex. At Ordovician and Silurian times quartzites and schists were formed. At the end of Palaeozoic these formations have been affected by the Hercynian granites intrusion. The most recent formations are Miocene-Pleistocene sedimentary series. showing their maximum development along the central axis of Chaves graben (3 - 3.5 km wide). The Alpine Orogeny has caused extensive tectonic features responsible for **the** formation of several hydrothermal circuits. At Vilarelho da Raia Chaves, Vidago and Pedras Salgadas areas the ascending hydrothermal circuits are structurally controlled by the **NNE-SSW** megafault, which is hydrothermally active along a belt extending 150 km in Portuguese mainland. The geomorphology is dominated by the Chaves graben whose axis is oriented **NNE-SSW.** It is bounded at the east side by the edge of Padrela Mountain escarpment with a 400m throw. The western block is formed by several grabens coming from the Heights of Barroso towards the Shaves depression. BAPTISTA et al. (1993) presented a tectonic and geomorphologic model for Vidago and Pedras Salgadas region. They propose the existence of a superficial narrow graben (1 to **2** km wide) related with an also superficial reservoir.

Chemistry of the waters

All mineralised waters belong to the HCO_3/Na/CO_2-rich type (with pH ≈ 7). However, from the geochemical point of view, the waters from Vilarelho da Raia/Chaves and Vidago/Pedras Salgadas areas form two separate groups. Chaves hot waters have temperature and TDS values ranging between 48°C - 76°C and 1600 mgll - 1850mg/l, respectively. Free CO_2 is of about 350 mg/l. Vilarelho da Raia cold spring and well waters show chemical composition similar to that of Chaves hot waters but low temperature (≈ 17°C). TDS values are between 1790 mgll - 2260 mg/l and free CO_2 is of about 790 mg/l. Vidago and Pedras Salgadas spring and drilled well waters are distinguished from the previously described mineralised waters in the region by their higher Ca, Mg and free CO_2 content (up to 2500 mgll). Vidago AC18 well waters show considerable higher mineralization (TDS ≈ 4300 mg/l), more than twice the TDS of the other waters of this group. Their output temperatures are of about 17°C.

Geothermometry *vs* water-rock equilibrium

In the case of Vilarelho da Raia, Chaves, Vidago and Pedras Salgadas CO_2-rich mineral waters the results SiO_2 and K^2/Mg geothermometers are in fair agreement (Table 1). The Na/K and Na-K-Ca geothermometers give higher temperatures. The Na/Li geothermometer, indicated by FOUILLAC (1983) as a good thermometric index for CO_2-rich waters of the French Massif Central, seems to give rise to an overestimation of the deep temperatures.

Table 1: Reservoir temperatures (°C) of Vilarelho da Raia, Chaves, Vidago and Pedras Salgadas mineral waters, estimated from chemical geothermometry.

Local	Ref.	Chalc. (1)	Quartz (2)	Na-K-Ca (3)	Na-K-Ca (Mg) (4)	Na/K (5)	Na/Li (6)	K^2/Mg (7)
V.Raia	Facha	70	100	146*	124	101	116	103
Chaves	AC1	90	120	203+	118	188	178	120
Chaves	AC2	91	121	210+	132	204	193	125
Chaves	Spr. 3	92	121	206+	121	191	178	123
Vidago	AC16	72	102	126*	96	176	211	93
Vidago	AC18	74	104	177*	89	171	188	111
P. Salg.	AC17	92	121	106*	92	127	177	80

To solve the discrepancies related to silica and some of the cation geotbermometers we have adopted the methodology developed by MICHARD & BEAUCAIRE **(1993).** In the diagram log **(H_4SiO_4)** *vs* log (Na/K), where the equilibrium quartz/chalcedony - adularia - albite is represented by the straight lines (Q) and (C), respectively. Chaves and Vidago waters lie in the domain of not equilibrated waters. Vilarelho da Raia and Pedras Salgadas waters are close to the equilibrium line (Fig.2): in the case of these waters, the quartz and Na/K temperatures are compatible (Table 1). In the diagram log (Ca/K^2) *vs* log (Na/K) the equilibrium laumontite - adularia - albite - quartz is represented by the straight line **(L).** Waters that lie more or less close to the equilibrium line (Fig. 2) are those where the Na-K-Ca and Na/K geothermometers give similar base temperatures (Vidago AC18 and Chaves AC2). Only Vilarelbo da Raia and Pedras Salgadas waters are more or less close to equilibrium in the two diagrams. This trend is reflected in the fact that most of the geothermometric temperatures are rather compatible.

GIGGENBACH (1986, 1988) developed a methodology to study the equilibrium characteristics of waters using the rapidly (K^2/Mg) and slowly (Na/K) re-equilibrating geothermometers. The graphical resolution of this methodology, for the studied hot and cold CO_2-rich mineral waters, is reported in the $Na/400$-$Mg^{1/2}$-$K/10$ diagram of Figure **3.** Waters from Chaves, Vidago and Pedras Salgadas are immature waters. Waters from Vilarelho da Raia seem to be partially equilibrated. So, it seems that chemical geothermometers should be applied with caution to these CO_2-rich mineral waters and the results of chemical geothermometry should be correlated with the results achieved by other disciplines such as geophysics.

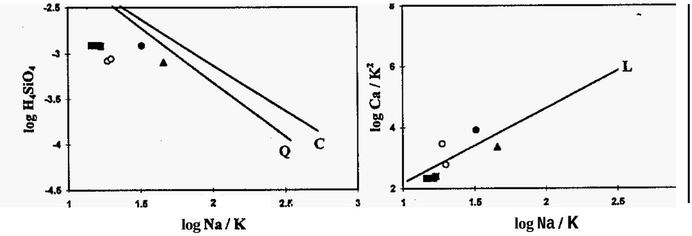

Figure 2: log (H_4SiO_4) vs log (Na/K) and log (Ca/K^2) vs log (Na/K) diagrams (in mol/l) for the studied waters. (▲) Vilarelho da Raia, (■) Chaves, (○) Vidago and (●) Pedras Salgadas waters. After MICHARD & BEAUCAIRE (1993).

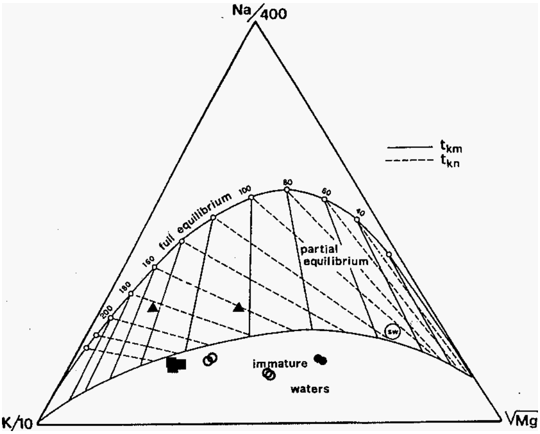

Figure 3: Graphical evaluation of water-rock equilibration temperatures in the studied thermo-mineral waters, using relative Na, K and Mg concentrations (in mg/kg). After GIGGENBACH (1988) and GIGGENBACH & CORRALES (1992). Symbols as in Fig. 2.

Isotopic signatures

$\delta^{18}O$ and δD values of the hot and cold CO_2-rich mineral waters lie on or close to the world meteoric water line (WMWL: **6D = $8\delta^{18}O + 10$**) indicating that they **are** meteoric waters which have been directly infiltrated into the bedrock (Fig. 4). Stable isotopic composition of dilute cold waters of the region (Fig. 4) indicates that the more depleted waters are those related to sampling sites located at higher altitudes, showing $\delta^{18}O$ and δD values close to those of Chaves thermal waters. AIRES-BARROS et al. (1994) presented the isotopic gradients of -0.26°/oo for ^{18}O and -1.45°/oo for D per 100 m of altitude. The lighter composition of Vilarelho da Raia/Chaves waters (Fig. 4) indicates that they **are** mainly recharged from meteoric waters infiltrated at the highest altitude sites (up to 900m a.s.l.) reached at Padrela Mountain / **NE** Chaves. The higher $\delta^{18}O$ and 6D values related to Vidago and Pedras Salgadas waters (Fig. 4) could be attributed to different recharge altitudes or mixing with recent dilute meteoric waters.

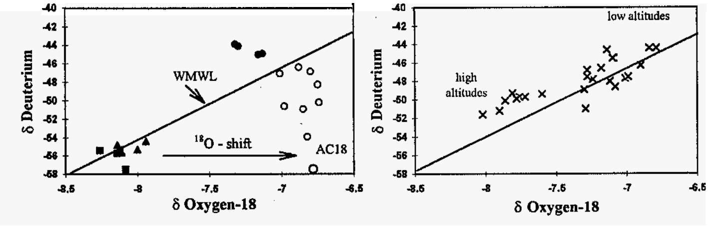

Figure 4: SD** vs **$\delta^{18}O$ (°/oo** vs **V-SMOW) relationship in hot and cold mineralised waters of Vilarelho da Raia/Chaves and Vidago/Pedras Salgadas areas, and in (X) dilute cold waters of the region (river, stream and spring waters). Symbols as in Fig. 2.

The hypothesis of mixing requires that the low mineralised waters diluting Vidago and Pedras Salgadas mineral waters be relatively young, derived from local infiltration at low altitude sites, and have $\delta^{18}O$ values higher than the analysed dilute cold waters of the region which are representative of precipitation falling at midhillside locations. ***So,*** it seems that dilution effects can be ruled out (Fig. 5). We have to admit that waters of Vidago and Pedras Salgadas group derive from precipitation that infiltrates in the local permeable outcrops, and the different ^{3}H and Cl contents seems to be the result of different flowpaths leading to different degrees of water-rock interaction and ^{3}H decay. The mineralization of the cold waters seems to be more controlled by the availability of CO_2 rather than by the residence time in the aquifer. Cold CO_2-rich waters from Vidago and Pedras Salgadas could represent shallow groundwaters and hot CO_2-rich waters from Chaves could be related to a deep circulation system and, therefore, long residence time.

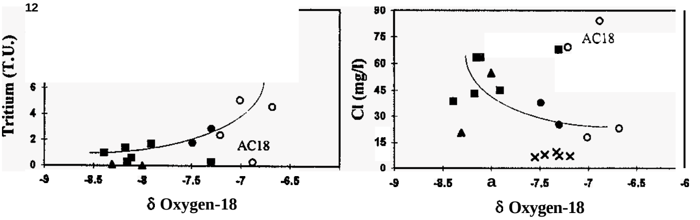

Figure 5: Tritium and Cl values vs *$\delta^{18}O$ data for waters from Vilarelho da Raia - Pedras Salgadas region. $\delta^{18}O$ in ‰ vs V-SMOW. (X) stands for dilute cold waters (spring waters) located at midhillside locations. Symbols as in Fig. 2.*

Storage of the mineral maters at depth

As stated by AIRES-BARROS et al. (1998), the constant ratios of major ionic species (*e.g.* HCO_3, Na, K, Li) plotted against a conservative element such as Cl indicates that the chemistry of these waters seems to be related with the same geological environment, where higher salinities (Vidago AC18 waters) should correspond to larger residence times probably associated with deeper circulations. This trend indicates that most of the Cl in waters could be derived from granitic rocks by leaching. In the HCO_3, Na, K, Li *vs* Cl diagrams presented by **AIRES-BARROS** et al. (1998), the data from Chaves hot waters (wells AC1, AC2, and spring No. 3) form a cluster, which is a good indication of the existence of a common reservoir for these waters. On the contrary, the Vilarelho da Raia, Vidago and Pedras Salgadas cold mineral waters have different chemical tracers content than the Chaves hot waters, indicating different underground flowpaths. It should be refereed that the stable isotope data related with Vidago and Pedras Salgadas waters is also widely scattered.

Water-CO_2 exchange reaction

In the case of Chaves thermal waters, the lack of an ^{18}O-shift could be explained by oxygen isotope exchange between $H_2O_{(l)}$ and $CO_{2(g)}$. ALMEIDA (1982) presented $\delta^{18}O$ values of water and CO_2 related to Chaves thermal waters. $\delta^{18}O$ value of $H_2O_{(l)}$ was -8.04 ‰ vs SMOW and the corresponding value in $CO_{2(g)}$ was +25.62 ‰ vs SMOW. Using this data, we have calculated the additive fractionation factor $\varepsilon_{CO2(g)\ -\ H2O(l)}$. The value obtained (+33.66‰) indicates that equilibrium temperature (FRIEDMAN & ONEIL, 1977) is close to the measured temperature of 76°C at sampling. Concerning oxygen isotopes, it seems that

$H_2O_{(l)}$ and $CO_{2(g)}$ are in equilibrium. ***So,*** the lack of an ^{18}O-shift in Chaves thermal waters should be mainly related with **i)** the inexistence of a high reservoir temperature at depth (as indicated by the geothermal interpretation) and *ii*) relatively small water-rock contact time. Isotopic influence of CO_2 on the $\delta^{18}O$ value of the water should be excluded. Figure **4,** enhance the existence of a peculiar ^{18}O shift for Vidago AC18 cold mineral waters. The high TDS, Cl concentration (considered as a good tracer of water-rock interaction), the low tritium activity and a deuterium content (which indicates a recharge area at the highest topography in the Padrela Mountain), suggest that Vidago AC18 well waters are the result of a regional circulation.

Concluding remarks

The combined chemical and isotopic data suggests that the hot and cold CO_2-rich mineral waters of Vilarelho da Raia - Pedras Salgadas region could be derived from both local and regional groundwater sources. As the result of probable re-equilibration of the CO_2-rich waters during the upflow, no reliable geothermometric estimates can be made. Some differences detected in water characteristics could be the result of water circulation paths varying in length and residence time. The enrichment in ^{18}O and D, and the ^3H activity observed in some Vidago and Pedras Salgadas waters indicate that these cold mineral waters could represent shallow groundwaters infiltrated at low altitude sites. The correlation between high salinity, low tritium activity and a positive ^{18}O shift found in Vidago AC18 cold mineral waters could be an evidence for a longer circulation path through the subsurface rocks.

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