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## GEOCHEMICAL STUDIES AS SUPPORT OF GEOTHERMICS

#### L. A. AIRES-BARROS<sup>1</sup> & J. M. MARQUES<sup>1</sup>

KEY WORDS: geothermics, geochemistry, isotopes, water/rock interaction.

PALAVRAS-CHAVE: geotermia, geoquímica, isótopos, interacção água-rocha.

#### ABSTRACT

Surface manifestations of underground geothermal fluids circulation are a subject of great scientific and economic interest. Hot and cold mineral waters spurting out in a same area, alteration features detected in drill cores from boreholes and deposition of minerals around springs should be observed and studied in detail providing a lot of information with relatively low costs. This information should be used in the appraisal of the geothermal resources of a potential area for development. This paper reviews some of the geochemical techniques employed in geothermal investigations in order to update local and/or regional geothermal fluids circulation models. For this purpose, some examples of the thermomineral waters issuing at the northern part of Portuguese mainland are presented.

#### RESUMO: Estudos geoquímicos como base da geotermia

As manifestações superficiais da circulação profunda de fluidos geotérmicos são um tema de grande interesse científico e económico. As águas quentes e frias mineralizadas emergindo em determinada área, os fenómenos de alteração detectados em testemunhos de sondagem e as deposições minerais junto às nascentes

<sup>&</sup>lt;sup>1</sup> Instituto Superior Técnico - Laboratório de Mineralogia e Petrologia (LAMPIST). Av. Rovisco Pais, 1049-001 Lisboa, Portugal. Fax: +351 21 8400806; e-mail: airesbarros@popsrv.ist.utl.pt.

devem ser observadas e estudadas pormenorizadamente, conduzindo a uma grande quantidade de informação com custos reduzidos. Esta informação deverá ser utilizada na avaliação dos recursos geotérmicos de uma área potencial para desenvolvimento. Este trabalho faz uma revisão de algumas das técnicas geoquímicas utilizadas nas investigações geotérmicas, tendo em vista aprofundar o conhecimento acerca dos modelos conceptuais de circulação local e/ou regional dos fluidos geotérmicos. Para tal, apresentam-se alguns exemplos associados a águas termominerais do Norte de Portugal.

#### **1. INTRODUCTION**

During the last decades geochemical methods have been applied increasingly to geothermal investigations. Chemical and isotopic analysis of deep geothermal fluids and of the hydrothermal altered rocks have provided information on i) the origin and age of waters, ii) underground flow patterns, and iii) water-rock interaction occurring at depth, in order to help the selection of new drilling sites. During production, geochemical investigations are an important tool to detect minor and/or major changes in the reservoir, regarding temperature and water characteristics. The wide applicability of geochemical methods in all stages of geothermal exploration is very important due to the relatively low cost involved.

#### 2. THE HYDROLOGICAL APPROACH

#### 2.1. GEOCHEMICAL ANALYSIS OF WATERS

In a geothermal area containing many hot springs, a first reconnaissance survey should be carried out in order to plan the sampling sites of springs and to decide upon the number of samples required to get representative sampling, taking into due consideration the distribution of springs, their alignments, and association with geological features ELLIS & MAHON (1977). When the investigation of a geothermal field is at the beginning, chemical analyses of waters collected from hot and cold springs can provide information on the evaluation of mixing processes, allowing the hydrogeologist to draw some considerations about the conditions occurring at shallow levels.

In the initial exploration stages, chemical investigations of geothermal fluids can give information on the: i) composition and homogeneity of the geothermal fluids, ii) reservoir fluid temperatures (chemical geothermometry, see 2.2), iii) type of system present (hot water vs steam based), iv) type of subsurface rocks percolated by the geothermal fluids, v) mineral deposition potential of the fluid, vi) fluids constituents which could have economic value.

An important aspect of geochemistry is to find a correlation between the different types of water within a same geothermal area. Chlorine is one of the most important chemical tracers used. By preparing scatter diagrams with concentrations of Cl vs different species (e.g. HCO<sub>3</sub>-Cl, Na-Cl, Li-Cl, Rb-Cl and Cs-Cl) one can assess different type of geohydrological systems, within a given geothermal area. In the studies performed by AIRES-BARROS et al. (1998) on the CO<sub>2</sub>-rich thermomineral waters issuing at the northern part of Portugal, the major ionic species were plotted against a conservative element such as Cl. In those diagrams, the data from Chaves hot waters form a cluster, which is a good indication of the existence of a common reservoir for these waters (fig. 1). On the contrary, the Vilarelho da Raia, Vidago and Pedras Salgadas cold mineral waters have different chemical tracers content, indicating different underground flowpaths.

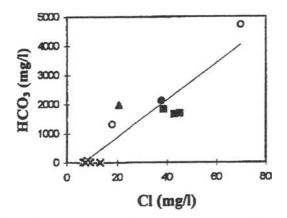


Fig. 1 – Cl vs HCO<sub>3</sub> diagram. (▲) Vilarelho da Raia, (■) Chaves, (○) Vidago, (●) Pedras Salgadas and local shallow waters, (×) local dilute waters. After AIRES-BARROS et al. (1988).

#### 2.2. CHEMICAL GEOTHERMOMETRY AND WATER-ROCK EQUILIBRIUM SIGNATURES

Chemical geothermometry uses the chemistry of hot springs in order to estimate chemical and physical properties of the fluid in the reservoir. This methodology is related with the temperature dependence of the concentrations of certain species, the chemical equilibrium between minerals and water and various chemical reactions.

Many chemical geothermometers have been proposed. Some of the most important include the quartz and chalcedony geothermometers (e.g. ARNÓRSSON, 1975; FOURNIER, 1977), the feldspar (Na-K) geothermometer (TRUESDELL, 1975), the Na-K-Ca and Na-K-Ca-Mg geothermometers (FOURNIER & TRUESDELL, 1973; FOURNIER & POTTER II, 1979) and the Na-Li geothermometer (FOUILLAC & MICHARD, 1981).

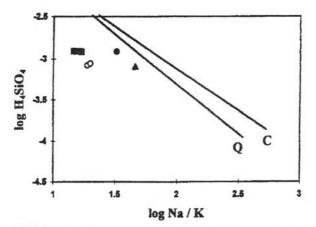


Fig. 2 - log (H4SiO4) vs log (Na/K) diagram (in mol/l). Symbols as in fig. 1. Taken from MARQUES et al. (199).

GIGGENBACH (1986, 1988) developed a methodology to study the equilibrium characteristics of waters using the quick ( $K^2/Mg$ ) and slow (Na/K) re-equilibrating geothermometers. The graphical resolution of this methodology is usually reported in a triangular Na/400 -  $Mg^{1/2}$  - K/10 diagram, in order to distinguish immature waters from those which can be classified as to be partially equilibrated or even full equilibrated.

In the case of the CO<sub>2</sub>-rich Portuguese thermomineral waters, the methodology developed by MICHARD & BEAUCAIRE (1993) was the one adopted to solve the discrepancies related to silica and some of the cation geothermometers (MARQUES *et al.*, 1999). In the diagram log (H<sub>4</sub>SiO<sub>4</sub>) *vs* log (Na/K) of figure 2, 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 (Q). For these waters, the quartz and Na/K temperatures are compatible (MARQUES *et al.*, 1999).

#### **3.** ISOTOPE GEOCHEMISTRY

232

#### 3.1. ISOTOPE GEOCHEMISTRY AND ITS SIGNIFICANCE

Isotope geochemistry has greatly contributed to the present understanding of geothermal systems (IAEA, 1981). The isotopic composition (<sup>18</sup>O, <sup>2</sup>H, <sup>13</sup>C, <sup>3</sup>H and <sup>14</sup>C) of geothermal fluids provide information on their origin, recharge areas and underground flow patterns, and may allow an evaluation of the subsurface temperatures of water-rock interaction. In natural waters, only the relative difference

in the ratio of the heavy isotope to the more abundant light isotope of the sample with respect to a reference usually determined. This difference is designated by the Greek letter  $\delta$  and is defined as follows:

$$\delta = \frac{R_{sample} - R_{reference}}{R_{reference}}$$

where the R's are, in the case of the water, the  ${}^{18}O/{}^{16}O$  or the  ${}^{2}H/{}^{1}H$  isotope concentration ratios. As the differences between samples and references are usually quite small, it is convenient to express the  $\delta$ -values in per mile differences, i.e.:

$$\delta \left( \frac{0}{00} \right) = \delta \times 1000$$

The standard universally adopted as reference for oxygen and hydrogen stableisotope variations in natural waters is the so-called Vienna Standard Mean Ocean Water (V-SMOW).

#### **3.2. ORIGIN AND AGE OF WATERS**

For a long time, no geochemical tools were available to identify the origin of water in geothermal systems. The most proposed hypothesis was that they are of *magmatic* and/or *juvenile* origin. The meteoric origin of geothermal waters was definitely proven by systematic measurements of the hydrogen and oxygen isotopic composition of water and steam from well-known geothermal fields (*e.g.* CRAIG, 1963). The generalised relationship  $\delta^2 H = 8 \delta^{18}O + 10$  describes the interdependence of H and O-isotope ratios in meteoric waters and is described in the literature as the World Meteoric Water Line (WMWL).

Tritium, a radioactive isotope of hydrogen, of half-life 12.5 years, occurs in all meteoric waters through nuclear reactions induced by cosmic-ray bombardment of the stratosphere (IAEA, 1981). The presence of tritium in a water sample is a definitive proof of the presence of some components of recent recharge, because of the high levels of tritium in the atmosphere since the beginning of atmospheric testing of thermonuclear bombs in 1952. The use of carbon 14 (half-life, 5570 years) to the determination of deep-water circulation times is very difficult because we don't know exactly what proportion of the carbon in a geothermal system is derived from the atmosphere or the soil, and from rock carbonates or possibly of magmatic carbon. In addition, in a geothermal system, large proportions of carbon dioxide (and <sup>14</sup>C activity) could be lost through calcite precipitation.

Most high-temperature geothermal systems have the  ${}^{2}H/{}^{1}H$  ratio identical to that of the local groundwaters, indicating their common meteoric origin. However, the  ${}^{18}O/{}^{16}O$  ratio is higher (*oxygen-18 shift*), as the result of isotopic exchange

with the geothermal reservoir rocks. This process takes place only for oxygen, since the hydrogen content in rocks is usually too small to affect the isotopic composition of geothermal waters.

 $\delta^{18}$ O and  $\delta^{2}$ H values of the studied hot and cold CO<sub>2</sub>-rich Portuguese thermomineral waters lie on or close to the WMWL defined by CRAIG (1961), indicating that they are meteoric waters (MARQUES *et al.*, 1998). The isotopic composition of these waters reveals the existence of two groups (V. da Raia/Chaves and Vidago/P. Salgadas) probably exhibiting the influence of the *altitude effect* (see IAEA, 1981).

The altitude dependence of the isotopic composition of the Portuguese CO<sub>2</sub>rich thermomineral waters was reported by AIRES-BARROS *et al.* (1995). The isotopic gradients obtained (-0.26  $^{\circ}/_{oo}$  for <sup>18</sup>O and -1.45  $^{\circ}/_{oo}$  for <sup>2</sup>H per 100 m of altitude) are in good agreement with the values found in Mediterranean regions (IAEA, 1981).

Cold  $CO_2$ -rich mineral waters from Vidago and Pedras Salgadas areas could represent shallow ground- waters (<sup>3</sup>H values up to 8 TU) while the hot  $CO_2$ -rich mineral waters from Chaves could be related to a deep circulation system and, therefore, long residence time (<sup>3</sup>H values between 0 and 2 TU).

The results of studies performed by MARQUES *et al.* (2001c) indicate that Vilarelho da Raia mineral waters should be considered meteoric waters infiltrated mainly on Larouco Mountain, NW of the Vilarelho da Raia area (fig. 4).

Water circulation took place at shallow depths in the upper crust, as indicated by the low outflow temperature (17°C) of these waters. Circulating waters were mineralised by water-gas-granite interactions in a low-temperature environment. The EW fault system that extends from Larouco Mountain towards the Vilarelho da Raia area controls the regional circulation of these waters (as indicated by the low <sup>3</sup>H levels) while local structures create the conditions necessary for their ascent.

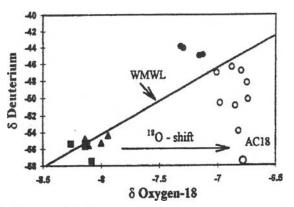


Fig. 3 – δ2H vs δ18O relationship in hot and cold CO<sub>2</sub>-rich thermomineral waters: Symbols as in fig. 1. Taken from MARQUES *et al.* (1998).

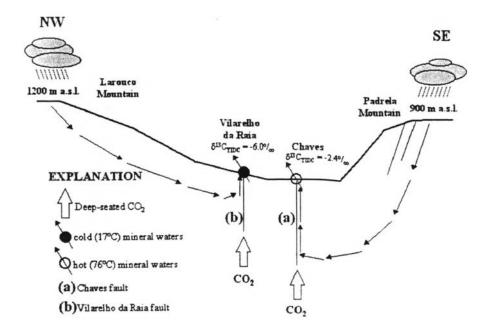


Fig. 4 – Conceptual circulation model of Vilarelho da Raia and Chaves CO<sub>2</sub>-rich mineral waters. Taken from MARQUES *et al.* (2001c).

This conceptual circulation model indicates that Chaves and Vilarelho da Raia CO<sub>2</sub>-rich mineral waters should be considered manifestations of similar but not the same geohydrological system.

Geochemical and isotopic data of shallow and geothermal groundwaters from Caldas do Moledo area (Peso da Régua / N Portugal) have been used to infer the signatures of these systems and to identify the existence of mixing processes (MARQUES *et al.*, 2003).

The isotopic signatures of the Caldas do Moledo geothermal waters, depleted in <sup>18</sup>O and <sup>2</sup>H relative to local shallow groundwaters, points out to a recharge area located at high elevations (850 - 1000 m a.s.l.). During the long residence time (apparent <sup>14</sup>C groundwater age 15.66  $\pm$  2.86 ka BP) the infiltrated waters are mineralised by water-granite interaction (as indicated by the HCO<sub>3</sub>-Na chemistry of the geothermal waters) in a low-temperature environment. The NW Vigo–Régua shear zone seems to control the regional circulation of these waters, while the NNE-SSW Régua–Verin fault lineament seems to be responsible for creating the necessary conditions for their ascent and discharge fig 5.

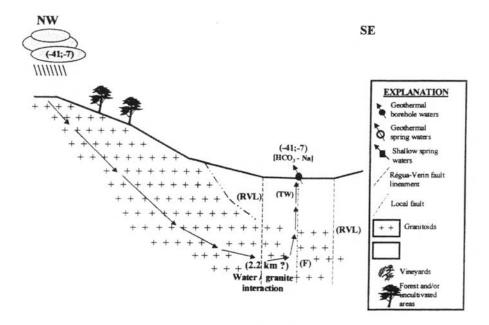


Fig. 5 – Schematic NW-SE cross-section of Caldas do Moledo geothermal water circulation from recharge to discharge. (-41; -7) stands for (δ<sup>2</sup>H; δ<sup>18</sup>O) values; [HCO<sub>3</sub>-Na] stands for water geochemical facies; (RVL) Régua–Verin lineament; (F) fault; (TW) geothermal borehole waters. Taken from MARQUES *et al.* (2003).

The problems arising from the utilisation of low-temperature geothermal waters are different from those of utilising high-temperature geothermal resources. Environmental problems such as subsidence, noise and visual impacts are negligible. On the other hand, the maintenance of the chemical quality of the water is more important than in high-temperature geothermal exploitations. Spas are very dependent on both temperature and water chemistry. Thus, special emphasis has been put on the update of our knowledge on the existence of mixing between geothermal and local shallow groundwaters, mainly based on chemical and isotopic signatures (MARQUES *et al.*, 2003). As shown by means of chemical and isotopic data, some of the geothermal spring waters of Caldas do Moledo area (e.g., Nova spring) should be faced as the result of mixing between shallow and geothermal groundwaters (fig. 6).

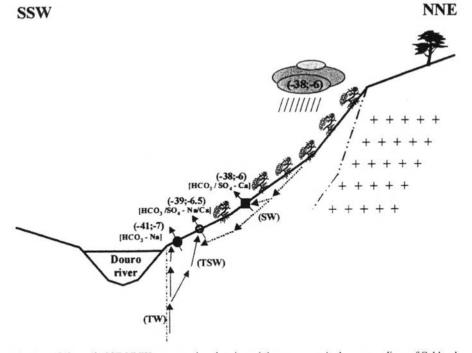


Fig. 6 – Schematic SSE-NNW cross-section showing mixing processes in the surroundings of Caldas do Moledo area. (-41; -7) stands for (δ<sup>2</sup>H; δ<sup>18</sup>O) values; [HCO<sub>3</sub>-Na] stands for water geochemical facies; (TW) geothermal borehole waters; (TSW) geothermal spring waters; (SW) shallow spring waters. Taken from MAROUES *et al.* (2003).

#### 3.3. ORIGIN OF WATER RESPONSIBLE FOR HYDROTHERMAL ALTERATION

The fractionation of an isotope between two phases A and B can be defined by the fractionation factor  $\alpha$ :

$$\alpha_{A-B} = (ratio in A) / (ratio in B)$$

For example, in the reaction in which <sup>18</sup>O and <sup>16</sup>O are exchanged between plagioclase and water, the fractionation of  ${}^{18}O/{}^{16}O$  is expressed as:

 $\alpha_{plagioclase-water} = ({}^{18}O/{}^{16}O \text{ in } plagioclase}) / ({}^{18}O/{}^{16}O \text{ in } water})$ 

237

Experimental studies (HOEFS, 1997; ROLLINSON, 1997) have shown that 1000 ln a is often a linear function of  $1/T^2$  for mineral-mineral and mineral-fluid pairs. This gives rise to the general relationship for the fractionation factor:

1000 ln  $\alpha_{mineral - water} = A + B (10^6/T^2)$ 

where A and B are constants determined experimentally and temperature (T) is in kelvin (Tables I and II).

Table I – Constants for the fractionation of oxygen isotopes between minerals and water according to the equation 1000 ln  $\alpha_{mineral - water} = A + B (10^6/T^2)$ .

Mineral	Α	В	Reference
Quartz	-3.40	3.38	CLAYTON et al. (1972)
Feldspar	-3.53	2.68	TAYLOR (1978)
Muscovite	-3.89	2.38	O'NEIL & TAYLOR (1967)
Biotite	-4.35	1.35	TURPIN et al. (1990)
Chlorite	-5.30	0.70	TURPIN et al. (1990)

Table II – Constants for the fractionation of hydrogen isotopes between minerals and water according to the equation 1000 ln  $\alpha_{mineral-water} = A + B (10^6/T^2)$ .

Mineral	Α	В	Reference
Muscovite (1)	19.1	-22.1	SUZOUKI & EPSTEIN (1976)
Muscovite (2)	19.36	-4.53	LAMBERT & EPSTEIN (1980)
Biotite	-2.8	-21.3	SUZOUKI & EPSTEIN (1976)
Chlorite	0.954 - 0.987		MARUMO et al. (1980)

Notes: (1) for temperatures > 230 °C; (2) for temperatures <230 °C.

According to ROLLINSON (1997), in the case of oxygen isotopic exchange between plagioclase and water,

$$\Delta_{plagioclase-water} = \delta_{plagioclase} - \delta_{water} \approx 1000 \ln \alpha_{plagioclase-water}$$

Using the isotopic ( $\delta^{18}$ O,  $\delta^{2}$ H) composition of a given mineral, and assuming equilibrium conditions, the isotopic composition of water in equilibrium with that mineral can be estimated. Water-rock equilibrium temperatures could be estimated by fluid inclusion studies or by the stability field of alteration minerals. Plotting the  $\delta^{18}$ O and  $\delta^{2}$ H pairs related to waters in equilibrium with a given mineral in a  $\delta^{2}$ H vs  $\delta^{18}$ O diagram the origin (meteoric, metamorphic, magmatic, etc.) of water responsible for hydrothermal alteration can be estimated.

The characterisation of mineropetrographic and isotopic changes in granitic cores, from an exploration borehole (AC2) located in the surroundings of Vilarelho da Raia CO<sub>2</sub>-rich mineral water springs, improved knowledge on water-rock interaction processes occurring at depth.

238

Mineropetrographic observations indicate a pervasive alteration stage which has affected the whole drilled massif. Transformation of biotite and plagioclase have given way to chlorite and sericite, respectively. Microcline rarely includes any secondary minerals. A vein alteration stage was also observed along major fracture zones where the granite is altered into a quartz and white mica (mainly muscovite  $2M_1$ ) mineral paragenesis (foto 1). Regarding pervasive alteration, waters in equi- librium with hydrous minerals muscovite and chlorite at 350°C (fig. 7) show  $\delta^{18}$ O and  $\delta^{2}$ H values which indicate that waters responsible for pervasive alteration could be interpreted as to have a dominated metamorphic origin (Marques *et al.*, 2001a).

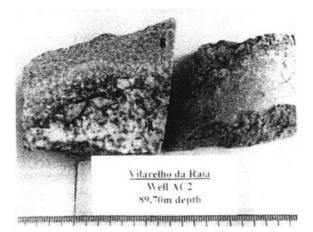


Foto 1 – A drill core from Vilarelho da Raia AC2 borehole. (A) pervasive and (B) vein alteration characteristics.

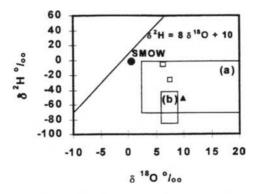


Fig. 7 – Pervasive alteration. δ18O-δ2H diagram for calculated waters in equilibrium with muscovite (▲) and chlorite (□) at 350°C. Water fields from SHEPPARD (1986): (a) metamorphic, (b) magmatic. Taken from MARQUES *et al.* (2001a).

As reported by MARQUES *et al.* (2001a), in the case of vein alteration, waters in equilibrium with muscovites (at 150°C) show  $\delta^2$ H values similar to those  $\delta^2$ H values of present-day meteoric waters of the region. Then, waters responsible for vein alteration have been interpreted as meteoric waters (MARQUES *et al.* 2001a).

### 239

#### **3.4. WATER/ROCK RATIOS**

For a closed system, from which none of the water is lost, the water/rock (W/R) ratio is defined as (TAYLOR, 1974; 1977):

$$W/R_{closed} = \frac{\delta^{18}O_{rock}^{final} - \delta^{18}O_{rock}^{initial}}{\delta^{18}O_{fluid}^{initial} - \delta^{18}O_{fluid}^{final}}$$

The equation for an open system, through which the water makes only a single pass, is given by (TAYLOR, 1977):

$$W/R_{open} = \ln (W/R_{closed} + 1)$$

According to TAYLOR (1977) and ROLLINSON (1993) the original  $\delta^{18}$ O values of rocks that have been hydrothermally altered can be estimated by analysing the same formations outside the hydrothermally altered area. The initial  $\delta^{18}$ O value of the water can be estimated from <sup>2</sup>H/<sup>1</sup>H analyses of the alteration mineral assemblages and the meteoric water equation.

Water/rock (*W*/*R*) ratios have been estimated using data from drill cores from boreholes associated with Vilarelho da Raia CO<sub>2</sub>-rich mineral waters. The initial  $\delta^{18}$ O values for the rock (+11.41 and +11.47 °/<sub>oo</sub>) were obtained by analysing Vilarelho da Raia granite in two different sites outside the springs area. Final  $\delta^{18}$ O values for the rock (+10.10 to +10.91°/<sub>oo</sub>) are the values measured, on core samples, in bands showing vein alteration characteristics. Assuming the meteoric origin of the water responsible for the vein alteration, the initial water composition was calculated from the <sup>2</sup>H/<sup>1</sup>H ratio of the alteration assemblage (along veins) and the world meteoric water equation ( $\delta^{2}$ H =8 $\delta^{18}$ O+10). The values obtained (from -8.25 to -6.50 °/<sub>oo</sub>) do not seem unrealistic, since they are similar to those of the presentday local meteoric waters. The final water composition was estimated by the O'NEIL & TAYLOR (1967) plagioclase-water isotope fractionation equation:

$$1000 \ln \alpha_{\text{plag-water}} = -3.52 + 2.68 (10^6 / T^2)$$

assuming that  $\delta^{18}O_{plag} \approx \delta^{18}O_{whole-rock}$  (final composition), because plagioclase is an abundant mineral in the rocks and exhibits the greatest rate of <sup>18</sup>O exchange with an external fluid phase. Water-rock interaction temperatures (150 °C < T < 250 °C) were estimated by the stability fields of the alteration minerals along veins. The *W/R* ratios obtained for the open system range between 0.038 and 0.24. These values suggest the presence of a local rock-dominated environment.

240

#### 3.5. SR ISOTOPIC SIGNATURES. FIELDS OF APPLICATION

Strontium isotopes can used as an important tool in hydrogeothermics (STETTLER, 1977). The <sup>87</sup>Sr/<sup>86</sup>Sr ratios are very good hydrogeochemical tracers because the high atomic weight of strontium avoids isotopic fractionation by any natural process. So, the <sup>87</sup>Sr/<sup>86</sup>Sr ratios in waters depend on the Rb/Sr ratios and

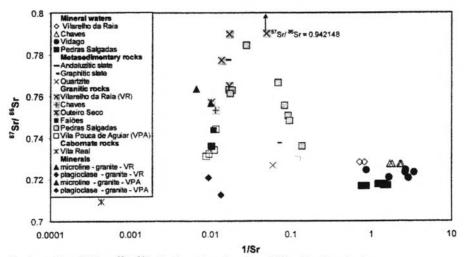


Fig. 8 - Plot of 1/Sr vs 87Sr/86Sr for the rocks, minerals and CO2-rich mineral waters.

the age of the percolated rocks (FAURE, 1986). As stated by STETTLER & ALLÈGRE (1978), if preferential leaching of a specific rock constituent takes place, than the Sr isotopic composition of the water will be constrained by the composition of the most alterable minerals. This geochemical behavior of Sr allows <sup>87</sup>Sr/<sup>86</sup>Sr ratios in waters, associated with a given hydrogeological system, to provide useful information about the sources of Sr and the existence of mixing processes in waters (GOFF *et al.* 1991).

A comparison of <sup>87</sup>Sr/<sup>86</sup>Sr values among the CO<sub>2</sub>-rich thermomineral waters and the rocks/minerals from Vilarelho da Raia – Pedras Salgadas area is shown in figure 8. The Sr isotopic signatures indicate that no equilibrium has been reached between the mineral waters and the whole rocks (MARQUES *et al.* 2001b). On the other hand, the similarity of the <sup>87</sup>Sr/<sup>86</sup>Sr values between the mineral waters and the plagioclases from the granitic rocks corroborates the idea that the plagioclase dissolution is the main water-rock interaction process.

#### 4. APPLICATION TO HDR PROJECTS

The concept of Hot Dry Rock (HDR) systems is rather simple. An injection and a production well have to be drilled in a body of hot rocks and linked together in order to establish an artificial reservoir which as suitable hydraulic and thermal characteristics that will allow the economic extraction of the heat. So, all HDR projects involve the study of the technical and economic feasibility of an artificial

geothermal heat exchanger. In such projects, geological, structural, geophysical, mineralogical, geohydrological and geochemical investigations should be carried out. In these type of Projects, geochemical investigations are mainly related with i) the description of the petrography of the granite (variations of grain size and mineralogical content), ii) the identification of pervasive and vein alteration zones; and iii) the characterisation of secondary (alteration) mineralogy (GENTER, 1990).

Besides these studies, HDR boreholes also provide an excellent opportunity for other types of investigations (isotopic studies), in order to characterise the isotopic features of secondary minerals present in the productive and non-productive zones. The main objective of these studies is to predict the water-rock interaction processes that could occur during the project operation (hydraulic stimulation).

#### 5. CONCLUDING REMARKS

The investigation of geothermal systems takes place in progressive stages, which frequently overlap. These studies embraces many activities, including investigation and exploration, and must be carried out within the framework of a conceptual model of the system, which is improved as more and more information is collected. The key to sustainable management of geothermal water resources is having the knowledge required to make the right decisions. Geochemistry, including isotope geochemistry, is a nuclear tool to trace water circulation within a given geothermal system. Both stable and radioactive isotopes can be used to investigate water sources, how they have been recharged, the water-rock interaction processes occurring at depth, if they are at risk of pollution, and whether geothermal waters can be used in a sustainable way.

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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). *Environmental Geology*, 25 (4), 232-238.
- AIRES-BARROS, L., MARQUES, J. M., GRAÇA, R. C., MATIAS, M. J., WEIJDEN, C. H. VAN DER, KREULEN, R. & EGGENKAMP, H. G. M. (1998) – Hot and cold CO<sub>2</sub>-rich mineral waters in Chaves geothermal area (northern Portugal). *Geothermics*, 27 (1), 89-107.

- ARNÓRSSON, S. (1975) Application of the silica geothermometer in low-temperature hydrothermal areas in Iceland. Am. J. Sci, 275, 763-784.
- CLAYTON, R. N., O'NEILL, J. R. & MAYEDA, T. K. (1972) Oxygen isotope exchange between quartz and water. J. Geophys. Res., 77, 3057-3067.
- CRAIG, H. (1961) Standard for reporting concentrations of deuterium and oxygen-18 in natural waters, *Science*, 133, 1833-1834.
- CRAIG, H. (1963) The isotopic geochemistry of water and carbon in geothermal areas. Nuclear Geology in Geothermal Areas (Tongiorgi, E., Ed.), Consiglio Nazionale delle Ricerche, Laboratorio di Geologia Nucleare, Pisa, 17 pp.
- ELLIS, A. J. & MAHON, W. A. J. (1977) Chemistry and geothermal systems. Energy Science and Engineering: resources, technology, management. An International Series. Academic Press.

FAURE, G. (1986) - Principles of Isotope Geology. 2nd Ed. John Wiley & Sons.

- FOUILLAC, C. & MICHARD, G. (1981) Sodium/lithium ratio in water applied to geothermometry of geothermal reservoirs. *Geothermics*, 10, 55-70.
- FOURNIER, R.O. (1977) Chemical geothermometers and mixing models for geothermal systems. *Geothermics*, 5, 41-50.
- FOURNIER, R.O. & POTTER II, R.W. (1979) Magnesium correction to the Na-K-Ca chemical geothermometer. *Geochim. Cosmochim. Acta*, 43, 1543-1550.
- FOURNIER, R.O. & TRUESDELL, A.H. (1973) An empirical Na-K-Ca geothermometer for natural waters. *Geochim. Cosmochim. Acta*, 37, 1255-1275.
- GENTER, A. (1990) Géothermie roches chaudes sèches: le granite de Soultz-sous-Forêts (Bas-Rhin, France). Fracturation naturelle, altérations hydrothermales et interaction eauroche. *Document du BRGM*, 88, 193 pp.
- GIGGENBACH, W. F. (1986) Graphical techniques for the evaluation of water/rock equilibration conditions by use of Na, K, Mg and Ca contents of discharge waters. *Proc.* 8th New Zealand Geothermal workshop, 37-44.
- GIGGENBACH, W. F. (1988) Geothermal solute equilibria Derivation of Na-K-Ca-Mg geoindicators. Geochim. Cosmochim. Acta, 52, 2749-2765.
- GOFF, F., WOLLENBERG, H. A., BROOKINS, D. C. & KRISTLER, R. W. (1991) A Sr-isotopic comparasion between thermal waters, rocks, and hydrothermal calcites, Long Valley caldera, California. *Jour. Volca. Geoth. Res.*, 48, 265-281.
- HOEFS, J. (1997) Stable Isotope Geochemistry. Completely Revised, Updated and Enlarged Edition. Springer-Verlag.
- IAEA (1981) Stable Isotope Hydrology. Deuterium and Oxygen-18 in the Water Cycle. IAEA, Vienna, *Technical Reports Series*, 210.
- LAMBERT, S. J. & EPSTEIN, S. (1980) Stable isotope investigations of an active geothermal system in Valles Caldera, Jemez Mountains, New Mexico. *Jour. Volc. Geoth. Res.*, 8, 111-129.
- MARQUES, J. M., AIRES-BARROS, L. & GRAÇA, R. C. (1999) Geochemical and isotopic features of hot and cold CO<sub>2</sub>-rich mineral waters of northern Portugal: a review and reinterpretation. *Bulletin d'Hydrogéologie*, 17, 175-183.
- MARQUES, J.M., AIRES-BARROS, L., GRAÇA, R.C., MATIAS, M. J. & BASTO, M. J. (2001a) – Mineral/fluid reactions associated with a low-temperature geothermal system (N-Portugal). *Water-Rock Interaction 2001*, Cidu (ed.), Swets & Zeitlinger, Lisse, ISBN 90 2651 824 2, 1553 – 1556.
- MARQUES, J. M., ANDRADE, M., AIRES-BARROS, L., GRAÇA, R. C., EGGENKAMP, H.G.M. & ANTUNES DA SILVA, M. (2001b) – <sup>87</sup>Sr/<sup>86</sup>Sr and <sup>37</sup>Cl/<sup>35</sup>Cl signatures of CO<sub>2</sub>-rich mineral waters (N-Portugal): preliminary results. New approaches characterizing groundwater flow. Seiler & Wohnlich (eds). A.A. Balkema, 1025-1029.

- MARQUES, J. M., ESPINHA MARQUES, J., CARREIRA, P. M., GRAÇA, R. C., AIRES-BARROS, L., CARVALHO, J. M., CHAMINÉ, H. I., BORGES, F. S. (2003) – Geothermal fluids circulation at Caldas do Moledo area, Northern Portugal: geochemical and isotopic signatures. *Geofluids*, 3, in press.
- MARQUES, J. M., MONTEIRO SANTOS, F. A., GRAÇA, R. C., CASTRO, R., AIRES-BARROS, L., MENDES VICTOR, L. A. (2001c) – A geochemical and geophysical approach to derive a conceptual circulation model of CO<sub>2</sub>-rich mineral waters: a case study of Vilarelho da Raia, northern Portugal. *Hydrogeology Journal*, 9, 584-596.
- MARUMO, K., NAGASAWA, K. & KURODA, Y. (1980) Mineralogy and hydrogen isotope chemistry of clay minerals in the Ohunuma geothermal area, NE Japan. *Earth Planet. Sci. Let.*, 47, 255-262.
- MICHARD, G. & BEAUCAIRE, C. (1993) Les eaux thermales des granites de Galice (Espagne): des eaux carbogazeuzes aux eaux alcalines (Thermal waters from granites of Galicia (Spain): from CO<sub>2</sub>-rich to high -pH waters. *Chem. Geol.*, 110, 345-360.
- O'NEIL, J. R. & TAYLOR, P. JR. (1967) The oxygen isotope and cation exchange chemistry of feldspars. *Am. Mineral.*, 52, 1415-1437.
- ROLLINSON, H. (1993) Using geochemical data: evaluation, presentation, interpretation. Longman Scientific & Technical. John Wiley & Sons, Inc., New York.
- SHEPPARD, S. M. F. (1986) Characterisation and isotopic variations in natural waters. In: J. W. Valley, H. P. Taylor and O'Neill (eds.). Stable isotopes in high temperature geological processes. *Rev. Mineralogy, Miner. Soc. Am.*, 16, 165-183.
- STETTLER, A. (1977) <sup>87</sup>Rb-<sup>87</sup>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) <sup>87</sup>Rb-<sup>87</sup>Sr studies of waters in a geothermal area, the Cantal, France. *Earth Planet. Sci. Lett.*, 38, 364-372.
- SUZOUKI, T. & EPSTEIN, S. (1976) Hydrogen isotope fractionation between OH-bearing minerals and water. *Geochim. Cosmochim. Acta*, 40, 1229-1240.
- TAYLOR, H. P. (1974) The application of oxygen and hydrogen isotope studies to problems of hydrothermal alteration and ore deposition. *Econ. Geol.*, 69, 843-883.
- TAYLOR, H. P. (1977) Water/rock interactions and the origin of H<sub>2</sub>O in granitic batholiths. J. Geol. Soc. London, 133, 509-558.
- TAYLOR, H. P. (1978) Oxygen and hydrogen isotope studies of plutonic granitic rocks. Earth Planet. Sci. Let, 38, 177-210.
- TRUESDELL, A.H. (1975) Geochemical techniques in exploration. Proc. 2<sup>nd</sup> U.N. Symp. Dev. Use Geothermal Resour. San Francisco, 1, 53-79.
- TURPIN, L., LEROY, J. L. AND SHEPPARD, S. M. F. (1990) Isotopic systematics (O, H, C, Sr, Nd) of superimposed barren and U-bearing hydrothermal systems in a Hercynian granite, Massif Central, France. *Chem. Geol.*, 88, 85-98.