Caderno Lab. Xeolóxico de Laxe
Coruña. 2004. Vol. 29, pp. 119-146

New approach on the hydrogeochemical signatures of Caldas do Moledo thermomineral system (N Portugal): implications for the hydrogeologic conceptual model elaboration

Nova abordagem sobre as assinaturas hidrogeoquímicas do sistema termomineral de Caldas do Moledo (N Portugal): implicações para a elaboração do modelo hidrogeológico conceptual

MARQUES, J. M.[1]; ESPINHA MARQUES, J.[2]; CARREIRA, P. M.[3]; AIRES-BARROS, L.[1], CARVALHO, J. M.[4] e BORGES, F. S.[2]

Resumo

A utilização conjunta de técnicas geoquímicas e isotópicas forneceu informações importantes por forma a encontrar respostas para as questões mais comuns relacionadas com os sistemas de águas termominerais, nomeadamente: i) qual é a origem das águas? ii) onde estão localizadas as áreas de recarga? iii) quais são os principais processos de interacção água-rocha ocorrentes em profundidade? iv) as águas termominerais serão o resultado de processos de mistura no sistema?

As assinaturas isotópicas dos fluidos termominerais, empobrecidos em ^{18}O e ^{2}H relativamente às águas subterrâneas pouco profundas locais, apontam para uma área de recarga localizada em pontos de cota elevada (900 – 1000 m de altitude). A zona de cisalhamento Vigo-Régua parece controlar a recarga e a circulação subterrânea destas águas meteóricas, enquanto que o sistema de falhas NNE-SSW Régua-Verin parece ser o responsável pela criação das condições necessárias para a sua ascensão e descarga. Durante períodos de residência longos (idade aparente pelo método do ^{14}C: 15.66 ± 2.86 ka BP) as águas meteóricas, após infiltração, adquirem mineralização (num ambiente de baixa temperatura) através da interacção água-granito, de acordo com o quimismo HCO_3-Na das águas termominerais. De acordo com os dados geoquímicos e isotópicos, as águas de algumas das nascentes termominerais da área das Caldas do Moledo são o resultado de mistura entre águas termominerais profundas e águas subterrâneas pouco profunda. Contudo, as águas termominerais dos furos de captação não apresentam quaisquer evidências de mistura com águas subterrâneas pouco profundas.

Palavras-chave: sistema termomineral, águas subterrâneas pouco profundas, hidrogeoquímica, processos de mistura, modelo conceptual, Caldas do Moledo, Norte de Portugal.

(1) Departamento de Engenharia de Minas e Georrecursos e Laboratório de Mineralogia e Petrologia (LAMPIST). Instituto Superior Técnico da Universidade Técnica de Lisboa. Av. Rovisco Pais, 1049-001 Lisboa. Portugal. (jmmarques@mail.ist.utl.pt)

(2) Departamento de Geologia da Faculdade de Ciências da Universidade do Porto e Centro de Geologia da Universidade do Porto. Praça de Gomes Teixeira, 4099-002 Porto. Portugal.

(3) Grupo de Química Analítica e Ambiente, Departamento de Química do Instituto Tecnológico e Nuclear (ITN). Estrada Nacional N° 10, 2686-953 Sacavém Codex, Portugal.

(4) Departamento de Geociências da Universidade de Évora. Apartado 94. 7001 Évora, Portugal, e Centro de Geologia da Universidade do Porto.

1. INTRODUCTION

During the last decades hydrogeochemical methods have been applied increasingly to low-temperature thermomineral investigations. Chemical and isotopic analysis of deep thermomineral fluids and shallow cold groundwaters have provided information on i) the sources of groundwater and location of recharge areas, ii) underground flow patterns, iii) age of thermomineral waters, and iv) water-rock interaction processes occurring at depth. Hydrogeochemical investigations are also an important tool to detect minor and/or major changes in the reservoir, regarding temperature and water characteristics. Isotope geochemistry has been widely used as an additional tool to detect mixing between different groundwater bodies. The wide applicability of geochemical methods in all stages of thermomineral exploration is very important due to the relatively low cost involved.

In this paper special emphasis has been put on the role of conventional and isotope hydrogeochemistry to the identification of the regional and local flowpaths of the thermomineral waters associated with Caldas do Moledo Spas (Northern Portugal). In Caldas do Moledo area, mineral waters from boreholes, with discharge temperature from 40 °C to 45 °C, are used in the local spas for diversified treatments. Recently, a study concerning a possible low enthalpy geothermal use, for residential, swimming pool water and domestic water heating, has been carried out. So, the increase of knowledge on the local hydrogeology is extremely important for their sustainable use. Coupled chemical and isotopic data made it possible to improve the hydrogeologic conceptual model of Caldas do Moledo low-temperature thermomineral waters, based on the understanding of the relationships between local shallow groundwaters and deep thermomineral waters.

The study area (Fig. 1) is located in the Central-Iberian Zone of the Iberian Massif (RIBEIRO *et al.*, 1990). Previous studies (e.g. CABRAL, 1995; CARVALHO, 1996a,b; BAPTISTA *et al.*, 1993, 1998; ESPINHA MARQUES *et al.*, 2001a,b) pointed out that the most important tectonic structures in the region are the NNE-SSW Régua-Verin fault lineament and the WNW-ESE to NW-SE Vigo–Régua shear zone, which are included in a major crustal-scale shear zone named the Malpica–Lamego Line (LLANA-FÚNEZ & MARCOS, 2001). The thermomineral springs are located along the Régua–Verin trending fault.

The most abundant lithotype are metasedimentary rocks (Schist-Graywacke Complex, Douro Group) of lower Cambrian age, also including aplite and pegmatite veins (TEIXEIRA *et al.*, 1967; BERNARDO DE SOUSA & SEQUEIRA, 1989). Granitic rocks and aplite-pegmatite veins were newly mapped (ESPINHA MARQUES *et al.*, 2001a,b) in this region (e.g., Cidadelhe granite). The existence of a WNW-ESE major tectonic structure in this section of Douro valley has been pointed out, and the higher spatial concentration of aplite-pegmatite veins in the vicinity of Caldas do Moledo suggests the existence of an underlying granitic mass (e.g. SEIFERT, 1967; ESPINHA MARQUES *et al.*, 2001a).

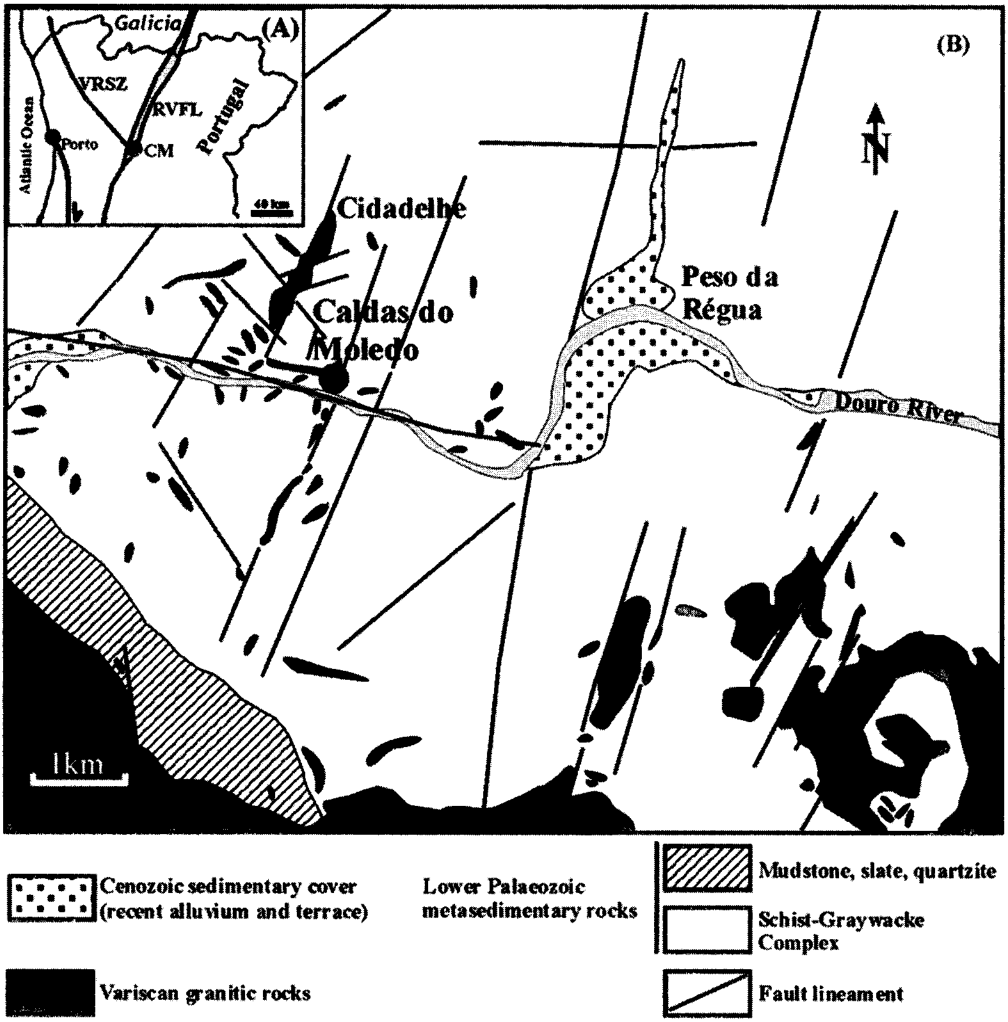

Fig. 1. Regional geotectonic setting of the Caldas do Moledo, Peso da Régua (Northern Portugal). A: Location of the research area and the main tectonic structures of Northern Portugal (VRSZ: Vigo-Régua shear zone; RVFL: Régua-Verín fault lineament); B: Regional geology of Caldas do Moledo (CM) area (adapted from ESPINHA MARQUES *et al.*, 2001a).

2. FIELD AND LABORATORY METHODS

Water samples for chemical (major elements) and isotopic ($\delta^{18}O$, $\delta^{2}H$, ^{3}H, $\delta^{13}C$ and ^{14}C) analyses from the thermomineral system and the shallow aquifers were collected in springs and boreholes. In order to identify a possible mixture between the thermomineral waters and Douro River waters, samples were also collected from the river. Temperature, pH and electrical conductivity were measured *in situ*. Sulphide was precipitated *in situ* as CdS. Total alkalinity was measured a few hours after collection. Filtered water samples for chemical analyses were stored in two polyethylene bottles. One of them was acidified through addition of concentrated HCl for analysis of major cations. The second one was kept unacidified for Cl, SO_4, NO_3 and alkalinity determinations. Chemical analyses were performed at the Laboratório de Mineralogia e Petrologia of Instituto Superior Técnico (LAMPIST)/Portugal, using the following methods: atomic absorption spectrometry for Ca and Mg; emission spectrometry for Na, K and Li; colorimetric methods for F and SiO_2; ion chromatography for SO_4, NO_3 and Cl; potentiometric titration for alkalinity; CdS was titrated (by potentiometry) with sodium thiosulfate.

$\delta^{18}O$ and $\delta^{2}H$ measurements were performed by mass spectrometry (SIRA 10 – VG ISOGAS) by the Grupo de Química Analitica e Ambiente - Instituto Tecnológico e Nuclear (ITN)/Portugal following the analytical methods of EPSTEIN & MAYEDA (1953) and FRIEDMAN (1953). The deuterium and oxygen-18 were measured with an accuracy of 1 °/$_{oo}$ for $\delta^{2}H$ and 0.1 °/$_{oo}$ for $\delta^{18}O$. The values are reported in °/$_{oo}$ to VSMOW. Tritium activity was determined in all the water samples using electrolytic enrichment and the liquid scintillation counting method (detection limit: 0.5 TU). For the tritium analysis, the standard deviation varies between ± 0.9 and ± 1.3, depending on tritium activity of the water samples. The ^{3}H water content is reported in Tritium Unit (TU). The radiocarbon and $\delta^{13}C$ were measured on the TDIC (Total Dissolved Inorganic Carbon) of groundwater precipitated in the field as $BaCO_3$ at a pH environment higher than 9.0. In the laboratory the CO_2 derived from the precipitated carbonate was transformed into benzene and measured by a liquid scintillation counting (^{14}C counting rates). The radiocarbon concentrations are reported in pmc (percentage of modern carbon) the error associated to these measurements is related to the amount of carbon in each sample. During this process a CO_2 gas sample is collected and measured by mass spectrometry in order to obtain the isotopic composition ($\delta^{13}C$). The values are reported in °/$_{oo}$ to VPDB with an accuracy of ± 0.1 °/$_{oo}$.

Physico-chemical and isotopic data of thermomineral and shallow groundwaters from Caldas do Moledo area is presented in Table 1.

3. GEOCHEMISTRY OF THE WATERS

3.1 Geochemical signatures

In the investigation of a thermomineral field, hydrogeochemical signatures of thermomineral fluids can provide valuable information on: i) composition and

Table 1. Representative physico-chemical and isotopic composition of thermomineral and shallow groundwaters from Caldas do Moledo area. (data from MARQUES *et al.*, 2003).

Ref.	Type	Date	T	pH	Cond	Na	K	Ca	Mg	Li	HCO_3	SO_4	NO_3	Cl	F	HS	SiO_2	$\delta^{18}O$	δ^2H	^3H
Nova	(tsp)	4/90	28.2	7.5	400	57.1	2.6	13.6	2.9	0.18	81.1	n.a.	n.a.	24.3	n.a.	n.d.	55.6	-6.39	-35.9	4.90
AC1	(tw)	4/90	46.0	9.1	400	61.5	1.0	3.0	n.d.	0.20	86.0	n.a.	n.a.	23.5	n.a.	1.89	43.9	-6.73	-38.7	n.d.
Nova	(tsp)	7/91	28.1	8.6	350	67.8	1.6	8.6	1.6	0.07	190.2	15.4	n.a.	16.5	n.a.	n.a.	43.4	-6.53	-39.4	2.93
AC1	(tw)	7/91	43.5	9.2	370	78.1	0.9	3.0	n.d.	0.07	129.4	7.0	n.a.	16.1	n.a.	n.a.	41.0	-6.75	-42.3	0.43
AC1	(tw)	11/97	40.0	8.9	339	67.0	1.3	2.7	0.1	0.20	70.4	15.0	0.3	18.7	13.9	n.a.	50.1	-6.48	-35.8	0.63
Valcovo	(sp)	11/97	15.6	6.5	201	18.5	1.3	11.2	5.0	n.d.	26.8	20.6	6.1	28.9	n.d.	n.a.	21.7	-5.64	-37.1	3.04
Ág. Mortas	(sp)	11/97	13.6	7.0	43	5.4	1.7	1.4	0.4	n.d.	12.3	1.1	3.8	5.3	n.d.	n.a.	21.1	-6.02	-37.5	21.6
Gavião	(sp)	11/97	12.7	5.8	40	3.9	0.7	0.8	1.4	n.d.	10.8	1.8	3.8	7.9	n.d.	n.a.	9.9	-6.14	-32.2	3.48
AC1	(tw)	6/98	37.0	9.1	352	91.0	1.2	0.8	n.d.	0.20	84.5	15.8	n.d.	22.8	12.6	n.a.	45.3	-6.64	-41.3	1.00
Valcovo	(sp)	6/98	16.5	7.3	326	23.5	2.3	25.2	10.0	0.06	73.0	35.8	10.2	24.4	n.d.	n.a.	27.1	-6.01	-40.4	5.20
Ág. Mortas	(sp)	6/98	19.2	7.2	46	5.9	1.6	1.7	0.5	n.d.	12.8	0.6	3.9	4.0	n.d.	n.a.	19.1	-6.17	-39.0	1.40
Gavião	(sp)	6/98	13.8	6.0	40	3.9	0.8	1.1	1.5	n.d.	11.7	0.8	0.7	4.4	n.d.	n.a.	11.4	-6.43	-37.1	6.90
Donsumil	(sp)	6/98	14.8	6.2	48	1.3	0.9	2.1	1.1	n.d.	15.3	1.0	0.5	5.1	n.d.	n.a.	16.2	-6.53	-40.8	4.20
Douro	(r)	6/98	21.0	8.1	334	10.8	2.8	46.5	9.3	0.02	112.4	39.0	6.7	11.9	n.d.	n.a.	5.7	-8.20	-55.1	8.00
Douro	(r)	4/99	14.3	7.9	497	19.8	5.3	62.3	12.0	0.02	144.9	77.9	10.3	27.7	n.d.	n.a.	1.5	-8.38	-60.8	4.90
Bica Parque	(sp)	4/99	19.1	7.4	391	49.0	2.6	20.2	3.5	0.20	108.1	43.0	0.4	21.0	7.9	n.d.	43.4	-6.41	-41.4	3.00
Lameira 30	(tsp)	4/99	41.2	9.0	345	75.0	1.0	2.4	n.d.	0.20	75.0	16.4	n.d.	18.4	18.7	1.48	49.0	-6.95	-42.7	0.60
Fresca	(tsp)	4/99	27.6	8.0	451	70.0	2.3	19.0	4.4	0.37	86.0	69.5	0.3	20.8	15.0	n.d.	47.1	-6.81	-42.7	0.90
Outeiro	(sp)	4/99	16.4	7.7	365	31.0	2.9	34.4	0.5	0.06	82.8	63.9	5.2	27.1	4.0	n.a.	30.4	-6.26	-38.2	11.70
Poço Quente	(tsp) *	4/99	22.9	6.7	341	43.0	2.7	19.8	3.5	0.14	68.5	45.1	8.1	24.4	4.7	n.d.	42.2	-5.67	-36.9	4.40
AC1	(tw)	4/99	46.0	9.17	339	75.0	1.0	2.4	n.d.	0.20	76.8	10.8	n.d.	19.0	19.5	n.a.	47.9	-7.00	-40.9	0.10
AC2	(tw)	4/99	42.3	9.01	330	73.0	1.1	2.6	n.d.	0.22	79.9	9.4	n.d.	19.8	18.3	n.a.	50.9	-6.98	-42.7	n.d.

Notes - Concentrations are in mg/l. $\delta^{18}O$ and δ^2H in ‰ *vs* V-SMOW. ^3H in TU. T is the output temperature of the waters (°C). pH and electrical conductivity (Cond in μS/cm) values are from field measurements. n.d. stands for not detected (below detection limit); n.a. stands for not analysed; (sp) shallow spring waters; (tw) thermomineral drilled well waters; (tsp) thermomineral spring waters; (r) river waters. (*)thermomineral spring with distinctive geochemical and isotopic signatures.

homogeneity of the thermomineral fluids, ii) reservoir fluid temperatures (chemical geothermometry, see section 3.2), iii) type of system present (hot water vs steam based), iv) type of subsurface rocks percolated by the thermomineral fluids, v) mineral deposition potential of the fluid, vi) fluids constituents which could have economic value. Chemical analyses of waters collected from hot and cold water bodies can also give important information on the evaluation of mixing processes (see section 3.3), allowing the hydrogeologist to draw some considerations about the conditions occurring at shallow levels. The degree of water-rock interaction will depend on the nature of the rocks, concentration of some dissolved compounds (e.g. pH is controlled by CO_2, affecting the reactivity of the water), temperature and time of water-rock contact (mean residence time of water).

At Caldas do Moledo area, several spring and borehole thermomineral waters emerge with different temperatures (between 27°C and 45°C). Their chemical signatures are quite similar in all major elements (Table 1), being characterised by the following main features:

I) relatively high pH values (between 8.0 and 9.0).

II) TDS values usually in the range of 200 to 350 mg/l.

III) HCO_3 is the dominant anion.

IV) Na is the dominant cation.

V) the presence of reduced species of sulphur ($HS^- \cong 2.5$ mg/l).

VI) high silica values, usually representing more than 15% of total mineralization.

VII) high fluoride concentrations (up to 10 mg/l).

Solutes commonly present in groundwaters could be derived from two main sources: i) inputs from the atmospheric precipitation, derived from marine salts and continental dust, and ii) the result of water-rock interaction. Cations such Na, K and Ca, and bicarbonate ions are the result of hydrolysis reactions promoted by the action of CO_2 mostly produced within the soil zone.

As indicated by the chemical composition of the Caldas do Moledo thermomineral waters, the reservoir rock should be mainly the granite. The following reaction

$$2CO_2 + 2NaAlSi_3O_8 + 11H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 2Na^+ + 2HCO_3^- + 4H_4SiO_4$$

can be used to explain the HCO_3–Na *facies* of Caldas do Moledo thermomineral waters. Furthermore, the high F concentrations found in these thermomineral waters seems to corroborate the extent of water-granite interaction.

An important aspect of hydrogeochemistry is to find a correlation between the different types of waters within a same thermomineral area. Conservative elements such as chlorine are the most important hydrogeochemical tracers used (e.g. GARCIA, 1986; MARINI & SUSANGKYONO, 1999). By preparing scatter diagrams with concentrations of Cl *vs* different species (e.g. Na-Cl, Li-Cl) one can assess different types of geohydrological systems, within a given thermomineral area. In the Na *vs* Cl and Li *vs* Cl diagrams of Figure 2, the data from boreholes AC1 and AC2 hot (≈ 45°C) waters from Caldas do Moledo form a cluster, which is a good indication of the existence of a common reservoir for these waters. On the contrary, the Fresca (≈ 27.6°C) and Poço Quente (≈ 22.5°C) thermomineral spring waters have different chemical tracers

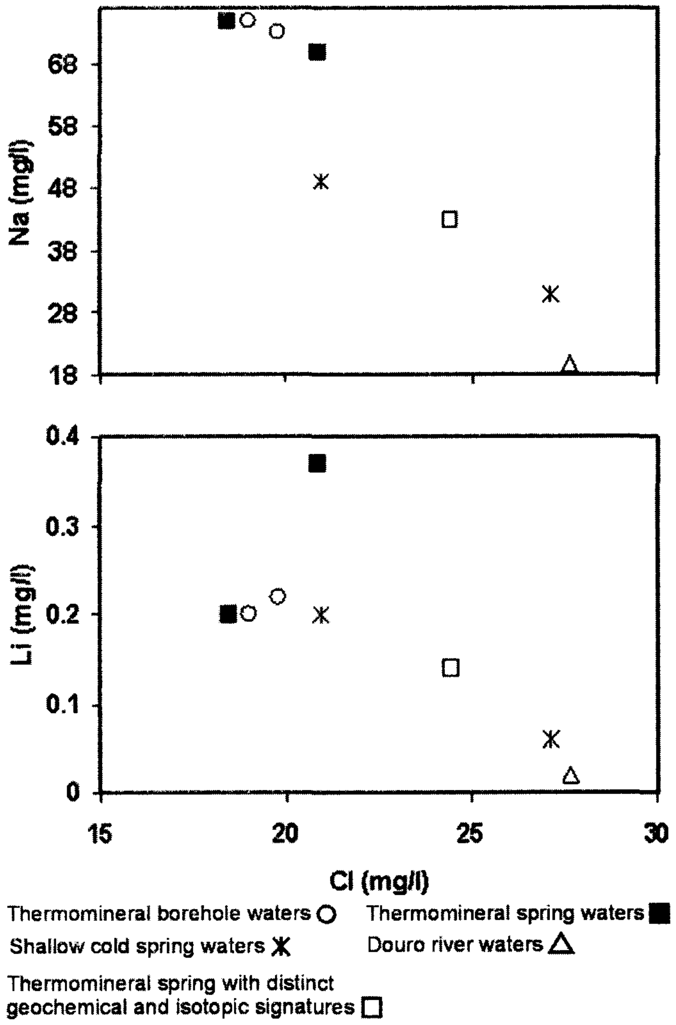

Fig. 2. Na *vs* Cl and Li *vs* Cl diagrams for water samples collected at Caldas do Moledo area (1999 fieldwork campaign). Data from MARQUES *et al.* (2003).

content, indicating different underground flowpaths.

Another possible interpretation calls for the existence of mixing between a high-Cl endmember (Douro River waters) and a low-Cl component (Caldas do Moledo mineral waters). The possible mixing line seems to be also evident in the Li vs Cl plot (Fig. 2) where the typically conservative (mobile) Cl is compared with another rather conservative species that is Li. However, the thermomineral spring reflecting possible mixing (Poço Quente spring water) is located relatively far from the Douro River and at higher altitudes (500 m away and 40 m above the Douro River margin), indicating that the spread of points observed in Figure 2 can not be explained by a mixing mechanism of thermomineral waters with Douro River waters (see section 3.3).

3.2 **Chemical geothermometry**

Chemical geothermometry is one of the most important geohydrologic tools in the exploration of thermomineral resources. Reservoir temperatures are estimated from data related with chemical analysis of surface discharges. This methodology is based on the assumption that temperature-dependent chemical equilibrium is attained at depth, in the reservoir, and that re-equilibration during the rise of the thermomineral waters from the reservoir to the surface is not significant. However, chemical geothermometers should be applied with caution since chemical modifications associated with mixing and/or cooling in upflow zones could be large and element concentrations in natural spring waters could be mainly controlled by secondary reactions.

The results of the application of the SiO_2, Na-K-Ca and K-Mg chemical geothermometers to Caldas do Moledo thermomineral waters has been discussed in detail by MARQUES *et al.* (2003).

The mean Na-K-Ca and K-Mg temperatures indicated 71 ± 14°C and 71 ± 6°C, respectively, as the reservoir temperature, whereas the mean quartz temperature pointed on to higher temperatures (96 ± 5°C). The chalcedony geothermometer produced lower reservoir temperatures (65 ± 5°C). The results of the different geothermometers used favour a temperature of about 70°C as a reasonable estimate for the thermomineral fluids reservoir feeding Caldas do Moledo (Table 2).

Considering the mean thermomineral gradient value (32°C/km) for the studied region (HURTER & HAENEL, 2002), and using the mean reservoir temperature (71 ± 14°C) given by the K-Mg and Na-K-Ca geotermometers, the circulation depth reached by Caldas do Moledo system was estimated (1.8 ± 0.4km). This value was obtained considering that depth = (Tr - Ta) / gg, where Tr is the reservoir temperature, Ta the average annual temperature (15°C) and gg the thermomineral gradient.

In this paper, model calculations were used to estimate the circulation depth of the thermomineral waters as well as the nature and spatial extent of the ascent pathways. The model used (RYBACH, 1990) relates the heat delivered to the wallrock by the ascending thermomineral waters, which depends on the reservoir (T_r) and surface discharge (T_s) temperatures, to the flow rate (Q), maximum depth (D) and available heat exchange surface:

$$T_r - T_s = f\ (Q, D, \text{Geometry})$$

It should be applied preferentially to thermomineral areas where the hydrogeological regime is governed by considerable differences in hydraulic potential, due to the mountainous topography (Fig. 3).

The mathematical treatment is simplified by introducing the dimensionless variable θ:

$$\theta = (T_s - T_o) / (T_r - T_o) = \\ = f'\ (Q, D, \text{Geometry})$$

where T_o is mean annual surface temperature of the region (15°C in our case). The specific equation of the vertical pipe (cylindrical conduit) model is:

Table 2. Reservoir temperature (°C) of Caldas do Moledo thermomineral system, estimated from different chemical geothermometers (after MARQUES *et al.*, 2003).

Sampling site	*Date*	**Measured temperature**	**Quartz (1)**	**Chalcedony (2)**	**Na-K-Ca (3) (β=4/3)**	**K-Mg (4)**
Borehole AC1	4/1990	46.0	96	66	61	-
	7/1990	45.4	89	58	96	76
	4/1991	41.9	92	62	62	64
	7/1991	43.5	93	62	59	-
	11/1997	40.0	102	72	71	72
	6/1998	37.0	97	67	84	-
	4/1999	46.0	100	70	67	-
Mean		***43±3***	***96±5***	***65±5***	***71±14***	***71±6***

(1) TRUESDELL (1975) - cooling by conduction; (2) FOURNIER & TRUESDELL (1974) – *in* FOURNIER (1977);
(3) FOURNIER & TRUESDELL (1973); (4) GIGGENBACH (1988)

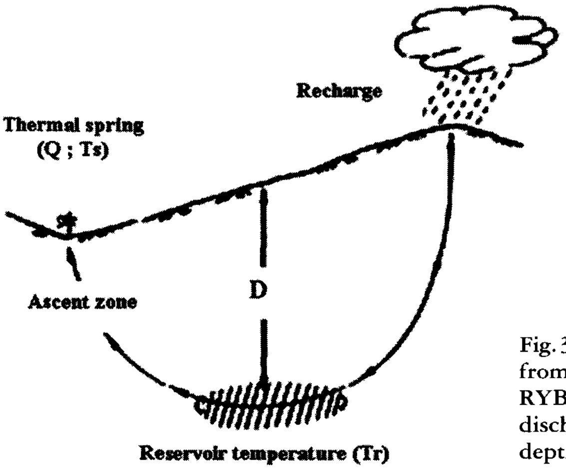

Fig. 3. Schematic thermomineral water flow path from recharge areas to discharge site (after RYBACH, 1990). Q stands for flow rate, T_s for discharge temperature and D for circulation depth.

$$\theta=(2\ Q\ c_w\ /\ \pi K_r\ D)\ (\ 1\ -\ \exp\ (-\pi K_r\ D/\ 2\ Q\ c_w))$$

where c_w is water heat capacity and K_r rock thermomineral conductivity. In Figure 4, the second equation is represented as master curves for the relationship $\theta = f(Q)$, with D the curve parameter. Master curves are calculated using $c_w = 4\ .\ 10^3\ Jkg^{-1}\ K^{-1}$ and $K_r = 3{,}0\ Wm^{-1}\ K^{-1}$ (RYBACH, 1990), which seem to be reasonable values for our case.

In Figure 4, Q/θ data point related to Caldas do Moledo thermomineral spring waters (Lameira 30 spring) have been plotted. The position in the diagram indicate that Caldas do Moledo thermomineral waters originate from a depth of about 4,0 km. Using this methodology we have arrived to a higher depth of circulation than that obtained by the chemical geothermometers and the thermomineral gradient.

In order to clarify the results obtained, the overall picture of Caldas do Moledo hydrogeological system must continue to be built up through a process of co-ordinated data synthesis and crosschecks. Since thermomineral water ascent at Caldas do Moledo seems to occur along narrow, steep conduits such as intersection of near-vertical faults, future studies supported by geophysical surveys (e.g. electromagnetic and magnetotellurics) should be carried in the region for delineating deep structures and determine its relation to probable groundwater pathways.

3.3 Environmental problems

The environmental problems associated with the use of low-temperature thermomineral waters are different, in many aspects, from those of utilising high-temperature thermomineral resources. For example, 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 thermomineral exploitations. Spas are very dependent on both constant temperature and water quality. Thus, in case studies associated with low-temperature thermomineral waters, the existence of mixing

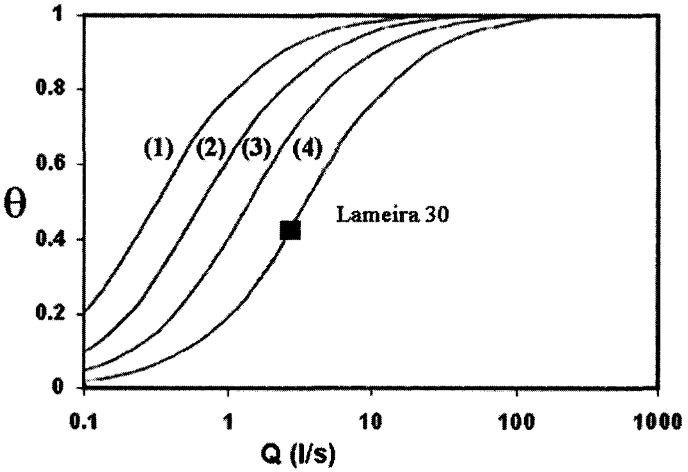

Fig. 4. Master curves for vertical pipe model (after RYBACH, 1990). Curve parameter is vertical pipe length. Curve 1 is for D = 0,5 km, 2 for 1,0 km, 3 for 2,0 km and 4 for 4,0 km.

between deep thermomineral and local shallow groundwaters is one of the main issues. The development of reliable management practices to preserve thermomineral water quality and remediation plans (in situations where thermomineral resources are already polluted), requires the identification of the sources of pollution and the processes affecting (in each particular situation) local concentrations.

Since Caldas do Moledo Spas are located in the region of the famous Port Wine vineyards, in the Douro River valley, special emphasis has been put on the identification of mixing processes between deep thermomineral waters and local cold shallow groundwaters (normal waters). In fact, during its flow through the soil zone and shallow geological strata, groundwater may pick up anthropogenic contaminants, from regional application of fertilisers and pesticides, resulting in the contamination of local thermomineral water resources (ALBU *et al.*, 1997). In the studied region, the agricultural diffuse pollution, especially the one related to the Port Wine vineyards, should be faced as one of the most important obstacles to achieve an environmentally sustainable exploitation of the local thermomineral resources.

Piper and Stiff diagrams have been used by ESPINHA MARQUES *et al.* (2003) to interpret the evolution of the chemical composition of groundwaters from Caldas do Moledo area (showing a trend towards high SO_4 and Ca waters as one passes from thermomineral to the cold shallow groundwaters). As stated by those authors, the intermediate position of some spring waters (Nova and Bica do Parque) in each of the three domains of the Piper Diagram is a clear sign of mixing between thermomineral waters (a low Ca-SO_4 endmember) and locally recharged cold shallow groundwaters (a high Ca-SO_4 endmember). As referred by COMANS *et al.* (1987), water samples from agricultural areas show a higher (Ca+Mg)/(Na+K) ratio and are characterised by higher

SO_4 contents, reflecting the intensive use of chemicals.

This trend can also be observed in the K *vs* Cl, Ca *vs* Cl, NO_3 *vs* Cl and SO_4 *vs* Cl diagrams of Figure 5, supporting the assumption of mixing between typical thermomineral fluids with local shallow groundwaters characterised by a relatively high concentration of K, Ca, NO_3, SO_4 and Cl. It should be stated that K, Ca, Cl, SO_4 and NO_3 are usual components of the most common fertilisers used in the vineyards, at the northern part of the country. Furthermore, in the vineyards is widely used a fungicide usually consisting of a solution of $CuSO_4$ neutralised with $CaCO_3$. Thus, the vineyard soils receive several chemicals (such as fertilisers and pesticides) that may be leached through the soil solution and, eventually, reach the aquifers by means of the infiltrating waters. However, it should be stated that the thermomineral waters from boreholes AC1 and AC2 (used for spas treatments) do not show any evidence of anthropogenic contamination.

In the Caldas do Moledo area, the existence of mixing between deep thermomineral fluids with local shallow groundwaters should be considered an extremely important environmental issue which should

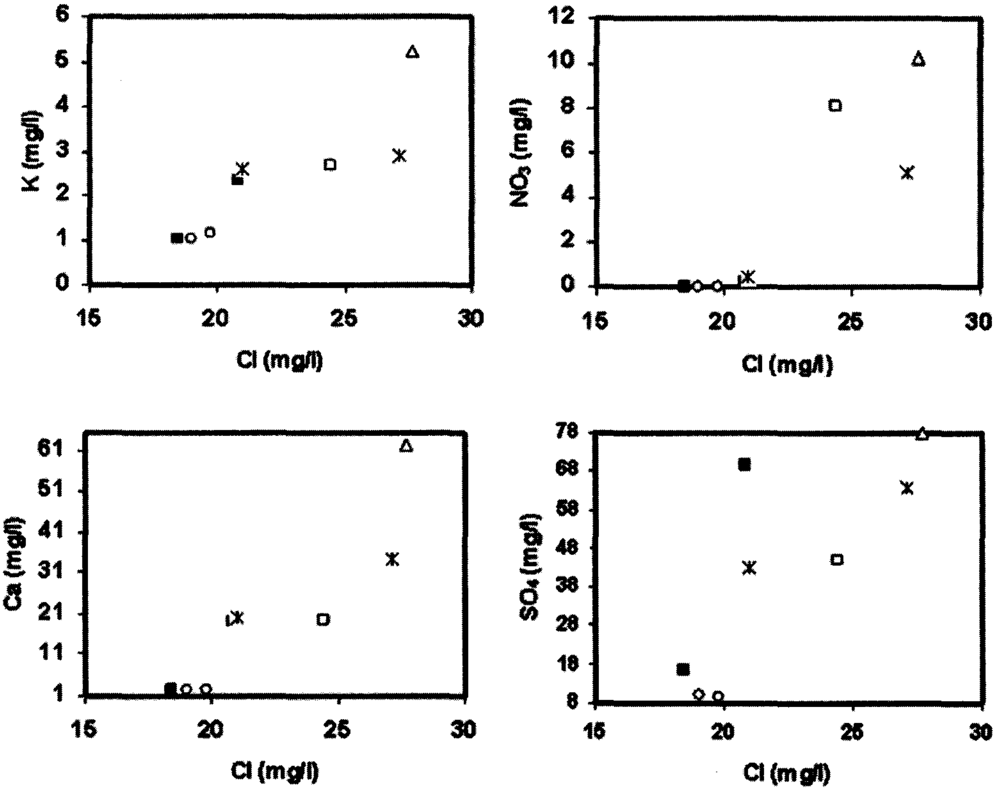

Fig. 5. K *vs* Cl, Ca *vs* Cl, NO_3 *vs* Cl and SO_4 *vs* Cl diagrams for water samples from Caldas do Moledo area. Data from MARQUES *et al.* (2003). Symbols as in Figure 2 (1999 fieldwork campaign).

be addressed either in the exploration and development of the studied thermomineral resources and in the delimitation of wellhead protection areas.

4. ISOTOPE GEOCHEMISTRY

4.1 Stable isotopes (^{18}O, ^{2}H AND ^{13}C)

Isotope geochemistry has greatly contributed to the present understanding of Caldas do Moledo thermomineral system. In this chapter we discuss the use of stable isotope ratios ($^{2}H/^{1}H$ and $^{18}O/^{16}O$) to address questions associated Caldas do Moledo thermomineral waters, in particular to recharge, flow systems and mixing problems, emphasising that investigations that uses stable isotope data integrated with chemical and other relevant data (such as lithological or morphostructural characteristics) usually produce important results. 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 is determined. This difference is designated by the Greek letter δ 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 we can observe, positive values show the samples to be enriched in the heavy-isotope species with respect to the reference, and negative values correspond to samples depleted in the heavy isotopes. As the differences between samples and references are usually quite small, it is convenient to express the δ values in per mile differences, i.e.:

$$\delta = (^{o}/_{oo}) = \delta \times 1000$$

The standard universally adopted as reference for oxygen and hydrogen stable isotope variations in natural waters is the so-called Vienna Standard Mean Ocean Water (VSMOW). It corresponds to a water having both oxygen and hydrogen isotopic ratios similar to the mean isotopic ratios of ocean water, which have been evaluated by EPSTEIN & MAYEDA (1953) and by CRAIG (1961).

The isotopic compositions of hydrogen and oxygen in precipitation are covariant. This relationship is commonly represented by the Global Meteoric Water Line (GMWL) $\delta^{2}H = 8\ \delta^{18}O + d$, where $\underline{d}$ is the so-called deuterium excess. In 1961, Craig found that the global mean value of $\underline{d}$, in the case of natural waters, was $+10^{o}/_{oo}$. ROZANSKI *et al.* (1993) have proposed a new GMWL, based on isotopic data from the IAEA's global sampling network .

In the case of Caldas do Moledo area, all water samples lie on or close to the GMWL ($\delta^{2}H = 8.13\ \delta^{18}O + 10.8$) defined by ROZANSKI *et al.* (1993), indicating that the thermomineral and shallow groundwater samples are of meteoric origin (Fig. 6). The Local Meteoric Water Line (LMWL) was established using all the available data from local thermomineral and shallow groundwater systems (MARQUES *et al.*, 2003). The obtained equation of LMWL was: $\delta^{2}H = (9.28 \pm 0.84)\ \delta^{18}O + (20.21 \pm 4.20)$, ($n = 26$; $r = 0.89$). No oxygen isotope shift due to water-rock interaction at high temperatures was found.

Stable isotopes are, in many cases, used to identify the contribution of river waters to local groundwaters recharge. Rivers often carry waters derived from precipitation at much higher altitudes, which are depleted in heavy isotopes when compared to local precipitation as a consequence of the altitude effect (see section 5.1). In fact, isotope signatures from Douro River water samples indicate a depletion in heavy isotopes with respect to local shallow groundwaters, thermomineral springs, and thermomineral boreholes (Fig. 6). This isotope depletion found in Douro River samples could be explained by the fact that most of its waters proceed from higher elevation areas. In fact, Caldas do Moledo is situated at ca. 50m a.s.l., yet, most of the river Douro basin upstream Caldas do Moledo is characterized by elevations greater than 500m a.s.l., being the river source located in Spain at the Urbion mountains, near the city of Sória (1700m a.s.l.) — DGRAH (1986), LOUREIRO *et al.* (1986). Considering the isotopic composition of the thermomineral waters from Caldas do Moledo (ranging from –6.8 to –6.2 ‰ and –43 to –37 ‰ in ^{18}O and ^{2}H, respectively) we can conclude that the contribution of Douro River waters to the recharge of the thermomineral system ought to be extremely small or even inexistent.

Carbon-13 is an important isotopic tracer of groundwaters evolution due to the large variations in different carbon reservoirs. Like oxygen and hydrogen isotopes, the $^{13}C/^{12}C$ ratio is generally expressed as the difference in parts per thousand from a standard (VPDB – Vienna PeeDee Belemnite, a Cretaceous mollusc). The carbon dioxide present in thermomineral waters can be attributed to two main origins: organic and inorganic (PANICHI & TONGIORGI, 1975). Concerning the organic source, CO_2 can be produced from decay of organic matter with mean $\delta^{13}C$ values between -26 ‰ and –22 ‰ . Among the inorganic sources, carbon in hydrothermal systems may originate from: *i*) deep-seated (upper mantle) carbon showing $\delta^{13}C$ values ranging between -8 ‰ and –1 ‰ , *ii*) dissolution of marine limestones which have mean $\delta^{13}C$ values close to 0 ‰ , or *iii*) metamorphism of carbonates producing CO_2 with slightly positive $\delta^{13}C$ values (TRUESDELL & HULSTON, 1980).

At the northern part of Portuguese mainland, a great number of hot and cold CO_2-rich mineral waters flow from natural springs and boreholes concordant to the main NNE-SSW Régua–Verin fault system (e.g. MARQUES *et al.*, 1999a). Those CO_2-rich mineral waters present $\delta^{13}C_{(TIDC)}$ values ranging between -6.00 ‰ and -1.00 ‰ *vs* PDB indicating a deep-seated (upper-mantle) origin for most of the CO_2 (MARQUES *et al.*, 2000). As stated by BAPTISTA *et al.* (1993), the NNE-SSW Régua–Verin fault system should attain of about 30km depth in the northern part of the country. The 2-D resistivity models show low resistivity zones at great depth, suggesting deep water circulation, and that the tectonic setting could play an important role in CO_2 extraction and migration from the mantle to the surface (MONTEIRO SANTOS, 1994).

In the case of Caldas do Moledo AC1 borehole thermomineral waters, the $\delta^{13}C_{TDIC}$ = -15.45 ‰ *vs* PDB indicates a negligible contribution of carbon from a deep-seated origin. Although Caldas do Moledo thermomineral waters issue along the NNE-SSW Régua–Verin fault system, the

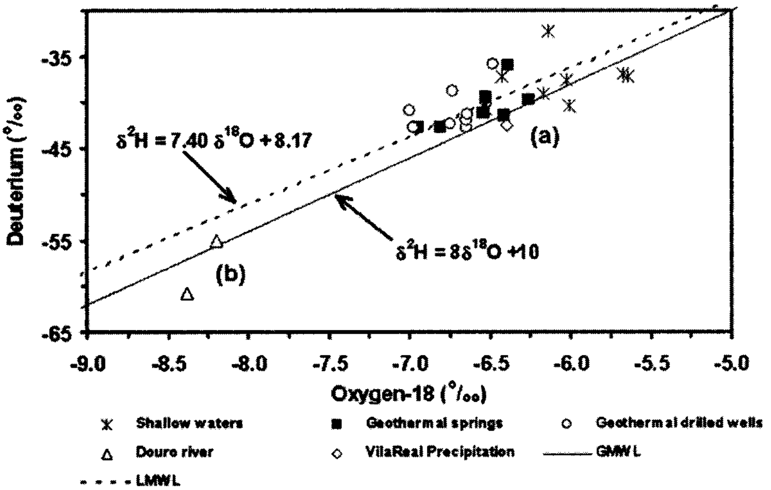

Fig. 6. δ^2H *vs* δ^{18}O plot for water samples from Caldas do Moledo area (after MARQUES *et al.*, 2003).

evolution of these thermomineral waters seems to be ascribed to a rather different regional geotectonic framework. In fact, the $\delta^{13}C_{TDIC}$ measured in Caldas do Moledo thermomineral waters seems to indicate that most of the carbon present in this thermomineral water system seem be attributed to the decay of organic matter.

4.2. Radioactive isotopes (^{3}H and ^{14}C)

Tritium (^{3}H) is the radioactive isotope of hydrogen, presenting a half-life of 12.32 a (LUCAS & UNTERWEGER, 2000). It is incorporated in the water molecule, and so is almost an ideal tracer for groundwater dating. When used as a tracer, ^{3}H is specially suitable for dynamic modelling of shallow groundwater systems, which usually are characterised by the presence of recently recharged water. Tritium concentrations are expressed as tritium unit (TU) where 1 TU = 1 ^{3}H per 10^{18} ^{1}H atoms.

Prior to 1950, tritium in precipitation was the result its natural production in the upper atmosphere, mainly due to the bombardment of nitrogen by the flux of neutrons in cosmic radiation. The role of ^{3}H as an environmental tracer in the hydrological cycle is directly ascribed to the large quantities of tritium introduced by atmospheric thermonuclear testing in the 1950's and 1960's. By 1990's most of the "bomb-produced" tritium has been strongly cleaned from the atmosphere, and nowadays tritium levels in precipitation (≈ between 0 and 15 TU) are close to natural atmospheric production levels.

In the present paper, tritium data of thermomineral and shallow cold groundwaters was used in a qualitative way, bearing in mind that for continental regions (CLARK & FRITZ, 1997):

< 0.8 TU	submodern – recharge prior to 1952
0.8 to ≈ 4 TU	mixture between submodern and recent recharge
5 to 15 TU	modern (< 5 to 10 yr)
15 – 30 TU	some "bomb" tritium present
> 30 TU	considerable component of recharge from 1960s or 1970s
> 50 TU	dominantly the 1960s recharge

The determination of the age of a groundwater has strong implications on the groundwater resource management, contributing to its sustainable exploitation. The term "age of a groundwater" should only be applied in regional confined aquifers. Therefore, it is common to use the term "groundwater mean residence times" instead of "age of a groundwater". However, in this paper the term "age" will be used since many other authors have commonly adopted it.

In the case of Caldas do Moledo thermomineral waters, the low ^{3}H values (0 – 0.1 TU) found in AC1 and AC2 boreholes indicate relatively long mean residence time of the thermomineral groundwater. On the contrary, the ^{3}H data of Poço Quente spring waters (Table 1) seems to indicate that we are in the presence of an underground flow system, which could be, at the discharge area, strongly influenced by mixing with local cold shallow groundwaters presenting much higher ^{3}H concentrations. In the case of Caldas do Moledo thermomineral spring waters (Lameira 30 and Fresca springs), ^{3}H data seems to indicate that a component of recent recharge ought to be excluded. However, as stated by MARQUES *et al.* (1999b), the high ^{3}H concentrations and enriched δ^{18}O values found in Caldas do Moledo Nova spring waters could be mainly interpreted as the result of a mixing process with local cold shallow groundwaters.

Tritium is commonly applied with other geochemical and isotopic tracers in the identification of mixing processes where the different groundwater components have different residence times. Although classical geochemical methods usually give good indications of mixing processes between different groundwater bodies, coupled variations in geochemistry, stable isotopes and anthropogenic pollution (e.g. sulphate and nitrate) are important to support data interpretation. Thermomineral groundwaters associated with deep crystalline rocks have their salinities strongly related to water-rock interaction over long (in some cases geologic) time scales. So, in cases where measurable ^{3}H (above 1 TU) is detected, it should be faced as a important indication of the existence of hydraulic connection between a deep confined aquifer (associated to the thermomineral fluids) and a shallow and unconfined aquifer (associated to cold groundwater), with strong risk of contaminant transport.

From the observation of the diagram of Figure 7 we can conclude that, in the case of Poço Quente thermomineral spring waters, the high SO_4 concentrations associated with high ^{3}H values are a clear sign of mixing with locally recharged shallow groundwaters, flowing through the soil zone and shallow geological strata, and picking up anthropogenic contaminants from regional application of fertilisers and pesticides. On the other hand, the high sulphate concentration in Caldas do Moledo Fresca spring water should be mainly ascribed to water-rock interaction conditioned by a particular underground flow path associated

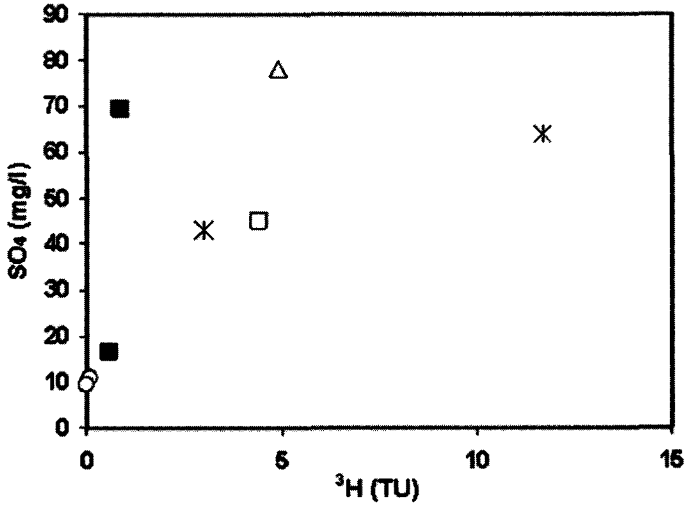

Fig. 7. SO_4 *vs* ^3H diagram for water samples from Caldas do Moledo area (data from 1999 fieldwork campaign). Symbols as in Fig. 2.

with different structural and geological conditions (e.g. sulphide bearing aplito-pegmatitic veins).

The identification of groundwaters that are sub-modern (recharged > 50 years ago) or older is an extremely important issue for renewability characterisation. As above mentioned, groundwater age dating should, in the first place, determine if they are ^3H-free, indicating no component of modern recharge. In the case of ^3H-free groundwaters, dating techniques should involve long-lived radionuclides. Among the radioactive isotopes with a half-life higher than 10^3 years, carbon-14 (τ= 5730 years) represents the most important tool in groundwater dating. This radioisotope is present in the atmosphere, soils, aquifer matrix, etc. The different sources of carbon incoming to the groundwater system make dating complicated. In the last decades, several attempts have been carried out in hydrothermal systems, in order to use ^{14}C content as a dating tool. Problems can arise when the measurements are performed in the Total Dissolved Inorganic Carbon (TDIC) due to different income of carbon to the water system. Small concentrations of carbon dioxide in the recharge waters derived from the atmosphere or from the geological environment could be masked by larger quantities of radiocarbon-free CO_2 introduced in the groundwater system, either from thermal metamorphism or from magma sources.

Several mathematical models are being used in the estimation of the initial ^{14}C activity of the total dissolved carbon that have been summarised by FONTES & GARNIER (1979) and by GALLAGHER *et al.* (2000). Models attempt to account for the dilution of ^{14}C by less active carbon and for isotopic exchange reactions, which may take place between the different carbon-bearing chemical species. Among these models two groups can be considered: a first one adopting a closed system based on chemical and isotopic mass balance and a second group of models based on the isotopic exchange in an open system. Several authors have used the combination of isotopic dilution and the exchange correction (MOOK, 2000).

In the case of Caldas do Moledo thermomineral waters, carbon-14 age calculation was based upon the assumption that:

I) the initial activity of the dating material is 100 % of modern CO_2 activity (100 pmc)

II) the $\delta^{13}C$ of aquifer matrix is 1 ± 1 ‰

III) the $\delta^{13}C$ for the CO_2 in the soil zone is –25 ± 2 ‰

IV) the fractionation factor $\varepsilon_{HCO3-CO2}$ ^{13}C is (8 ± 0.5) ‰ and

V) the error associated to the measurement of the TDIC is 0.5‰

using the closed system model proposed by SALEM *et al.* (1980). The apparent ^{14}C groundwater age (15.66 ± 2.86 ka BP) of Caldas do Moledo thermomineral waters was estimated using the ^{14}C content (13.97 ± 1.33 pmc) determined in the total dissolved inorganic carbon (TDIC) of AC1 borehole waters and the above mentioned values for correction.

5. CONCEPTUAL CIRCULATION MODELS

5.1 Hydrogeologic conceptual models

A model of a natural system is, by definition, a formal and simplified representation of a certain reality, phenomenon or group of phenomena. The use of models may be indispensable for understanding complex systems, by means of an abstraction process which takes in consideration those features regarded as fundamental.

The formulation of a preliminary conceptual model is one of the first and most important steps of the modelling process. This model (expressed by ideas, words and figures) is the foundation of subsequent mathematical models and strongly influences the type of computer code to be used and the design and priority of the site characterisation activities (NAP, 2001). In fact, the quality of the results obtained from the use of mathematical models is greatly influenced by the quality of the prior conceptual model.

A hydrogeologic conceptual model consists of an evolving hypothesis in identifying important features, processes and events related to a hydrogeologic system. The conceptualisation process implies the comprehension of the aquifer nature, its broad characteristics and the physical and chemical processes involved. Some of the most important features to consider include lithology, the geologic and geometric characteristics of the system's limits, the spatial variability of hydraulic parameters, hydrogeochemistry, surface-groundwater interactions, recharge, discharge, piezometry, among others.

The conceptual model detail depends on its scale and purpose. Frequently, in the initial phase of research, the available data may not consent the creation of a satisfactory model. In those cases, the collection of further data and the results provided by mathematical modelling may contribute to improve the preliminary conceptual model.

5.1 The isotopic approach

The use of geochemical and isotopic methods in thermomineral exploration is very useful because of the relatively low cost involved as compared to geophysical surveys and subsurface investigations by drilling. With relatively low costs, chemical and isotopic analysis of groundwater can give important information to produce more reliable conceptual circulation models of thermomineral water systems on both local and regional scales. Although the elaboration of hydrogeologic conceptual models requires the identification and characterisation of the different components of the hydrologic cycle, such as precipitation input, surface waters, shallow and deep groundwaters (as discussed above), most of the studies are strongly supported on the altitude dependence of the isotopic composition of the meteoric waters, due to a relationship between altitude and condensation temperature of precipitation.

According to GAT (1980) and YURTSEVER & GAT (1981) the isotope gradients vary between 0.15 - 0.5 $^{o}/_{oo}$ $\delta^{18}O$/ 100 m, pointing to an average rate of depletion of –0.26 $^{o}/_{oo}$.

Precipitation and groundwater isotopic data correspond well in many areas (CLARK & FRITZ, 1997). Since the weighted $\delta^{18}O$ mean values for precipitation are close to that of local groundwaters, conceptual circulation models are often elaborated using locally derived groundwaters (springs and shallow wells) instead of resorting to direct precipitation sampling. In fact, in the present case, the long-term weighted mean value of precipitation (ITN data base / IAEA, 1994), collected in Vila Real meteorological station (approximately 25km NE from Caldas do Moledo) is reasonably similar to the isotopic composition of the local shallow groundwaters (see Figure 6).

5.2 Caldas do Moledo thermomineral system: a case study

The hydrogeochemical signature of Caldas do Moledo thermomineral waters, combined with the morphostructural data, made it possible to establish the limits of a possible recharge area, situated between 5,5 and 8,5 km to NW and WNW of the discharge area, with altitudes around 1000 m a.s.l.. This recharge area is closely related to the WNW-ESE Vigo–Régua shear zone.

The altitude dependence of the isotopic composition of Caldas do Moledo thermomineral waters was estimated by $\delta^{18}O$ and $\delta^{2}H$ values of shallow groundwaters issuing from springs in the thermomineral discharge area and its bordering mountains (Donsumil - 850 m, Águas Mortas - 700 m, Gavião - 500 m and Valcovo - 150 m a.s.l.). As stated by MARQUES *et al.* (1999b), the isotopic gradient for $\delta^{18}O$ in Caldas do Moledo thermomineral area is -0.12 $^{o}/_{oo}$ / 100 m of altitude, reflecting the influence of geographical parameters depending on the local climate and topography (Fig. 8).

The referred recharge altitudes were determined by considering the isotopic signatures of Caldas do Moledo borehole waters ($\delta^{18}O_{mean}$ = –6.75 ± 0.25 $^{o}/_{oo}$ *vs* VSMOW). These elevations occur at the Laivos do Monte granitic outcrop, suggesting that the NW-SE Vigo-Régua shear zone should play an important role in groundwater recharge and deep circulation towards the NNE-SSW Régua-Verin fault, which seems to act as the most likely channel way for thermomineral waters ascent at

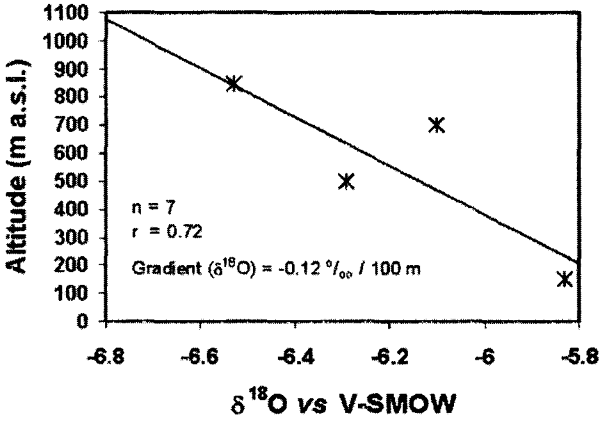

Fig. 8. Relation of $\delta^{18}O$ (mean values) to altitude of sampling sites in Caldas do Moledo area (after MARQUES *et al.*, 1999b).

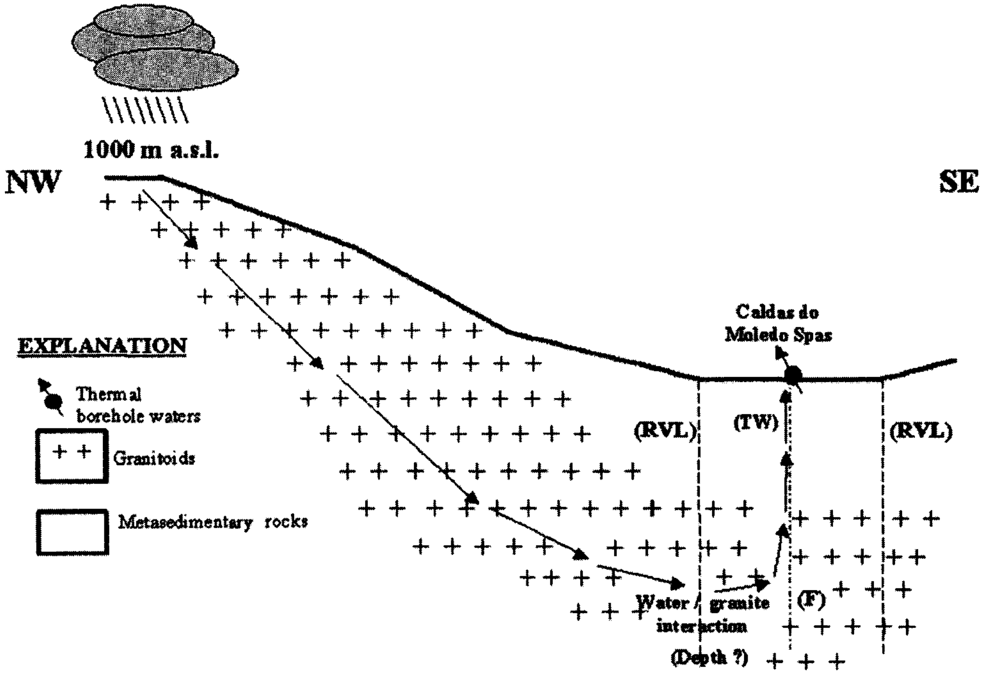

Fig. 9. Schematic NW-SE regional cross-section of Caldas do Moledo thermomineral water circulation from recharge to discharge. (RVL) Régua–Verin lineament; (F) fault; (TW) thermo-mineral borehole waters (adapted from MARQUES *et al.*, 2003).

Caldas do Moledo (Fig. 9). As stated by the ^3H contents, by the apparent ^{14}C groundwater age and by the geothermometry results, the thermomineral water circuit seems to be several thousands of years long and about 1.8 ± 0.4 km deep.

The discharge area (situated at Caldas do Moledo) of the aquifer system includes a deep confined thermomineral aquifer, a shallow confined cold aquifer and a shallow unconfined cold aquifer. Hydrogeochemical features pointed out the existence of mixing between shallow groundwater and deep thermomineral waters.

In fact, from the observation of the diagram of Figure 10 (including data from the same water points of Figure 8) we can conclude that the shallow groundwaters showing less negative $\delta^{18}O$ values (associated with springs located at low altitude sites) are those presenting higher (SO_4+NO_3) concentrations, probably as the result of intensive land use (e.g. for agriculture/ vineyards). On the other hand, those shallow groundwaters characterised by lower (SO_4+NO_3) values are associated with springs located at higher altitude sites, corresponding to forest and/or uncultivated areas.

MARQUES *et al.* (1999b) have already suggested that the specific isotopic signatures of Caldas do Moledo Nova thermomineral spring result from mixing with local shallow groundwaters. The mixing patterns shifted the thermomineral spring waters towards enriched isotopic (δ^2H and $\delta^{18}O$) values. This trend requires the waters diluting Moledo thermomineral waters to be derived from local infiltration at low altitude sites to explain the less negative $\delta^{18}O$ values. This mixing process could be responsible for the increase of K, Ca, Mg and SO_4 in the thermomineral spring waters. The flow rate of Moledo Nova thermomineral spring tend to be very low suggesting that there has been ample opportunity for mixing of the deep thermomineral component with cold shallow groundwaters.

So, at a local scale, some thermomineral spring waters [C] (see fig. 11) of Caldas do Moledo area (e.g. Nova spring) should be faced as the result of mixing between two end-members (see Fig. 11): [A] deep thermomineral waters — HCO_3-Na *facies*; light isotopic (δ^2H; $\delta^{18}O$) composition —; [B] local shallow groundwaters — HCO_3-(Na, SO_4) *facies*; heavy isotopic composition. The hydrogeochemistry indicates that the thermomineral end-member corresponds to a deep granitic (uncontaminated) aquifer as the local shallow groundwater end-member is related to metasedimentary aquifers contaminated through agriculture activities.

6. CONCLUDING REMARKS AND FUTURE RESEARCH DIRECTIONS

In this paper special emphasis has been put on the contribution of hydrogeochemical methods and isotope techniques to establish a hydrogeologic conceptual model. The model presented considers the recharge, the deep circulation and the discharge of thermomineral system, and identifies the regional and local flowpaths of the groundwaters associated to Caldas do Moledo Spas (northern Portugal). Special attention was dedicated to the relationships between local cold shallow groundwaters and deep thermomineral waters. The low $\delta^{18}O$ values of Caldas do Moledo thermomineral waters ($\delta^{18}O_{mean}$ = −6.75 ± 0.25 ‰ *vs* VSMOW) indicate that these waters are meteoric waters infiltrated at high altitude areas (around 1000 m a.s.l.). These elevations suggest

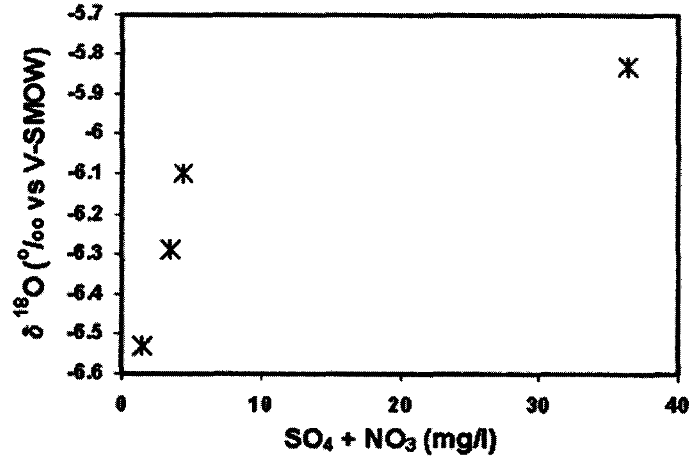

Fig. 10. $\delta^{18}O$ *vs* (SO_4+NO_3) diagram (mean values) for shallow groundwaters from Caldas do Moledo area. Data from the same water points of Figure 8.

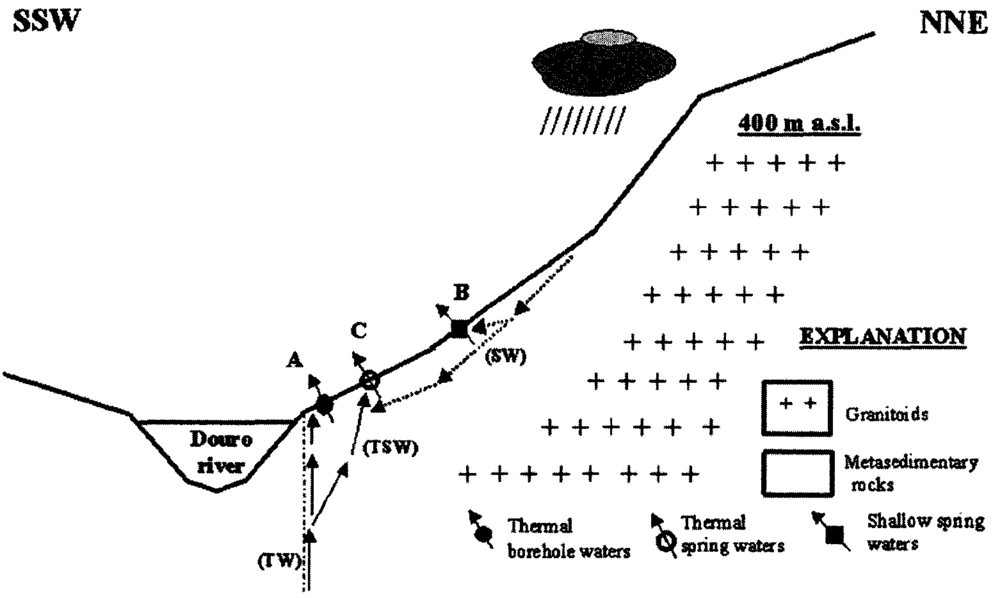

Fig. 11. Schematic NNE-SSW cross-section showing local mixing processes in the surroundings of Caldas do Moledo area. (TW) thermomineral borehole waters; (TSW) thermomineral spring waters; (SW) shallow groundwaters waters (adapted from MARQUES *et al.*, 2003).

that the NW-SE Vigo-Régua shear zone should play an important role in groundwater recharge and circulation towards the NNE-SSW Régua-Verin fault system, which seems to act as the most likely channel way for thermomineral waters ascent. The existence of mixing between deep thermomineral waters and local cold shallow groundwaters may explain the highest K, Ca, Mg, SO_4 and NO_3 concentrations detected in some of the Caldas do Moledo thermomineral spring waters. Local cold spring waters showing the higher SO_4 concentrations were found at low elevation areas. These low elevation areas correspond to the famous Port Wine vineyards, in the River Douro Valley. In contrast, the waters from wells AC1 and AC2 (used for spa treatments) do not show any evidence of anthropogenic contamination.

This paper demonstrates the applicability of hydrogeochemistry and isotope hydrology in the improvement of the hydrogeologic conceptual model of Caldas do Moledo low-temperature thermomineral system. The methodology adopted is strongly related with one of the main issues of the UNESCO International Hydrological Programme: the *"Joint International Isotopes in Hydrology Programme – JIIHP"* which main objectives can be summarised as follows:

I) develop tools for better understanding specific hydrological processes, improving the assessment, development and management of water resources;

II) support national, regional and international programs in water resources through isotope techniques;

III) integrate isotopic data in hydrological databases at national, regional and global scales.

Isotope hydrology strongly contributes to such kind of investigations as an additional tool to be used in a multi-technique approach together with hydrogeology, tectonics, geomorphology, geochemistry, geophysics (among other scientific domains). Isotopic (δ^2H; $\delta^{18}O$) composition of water should be used, in each particular case, as a natural tracer on the origin of groundwaters, while radioisotopes decay will provide a qualitative and/or quantitative approach of groundwater circulation time. Combining information ascribed to the geochemical and isotopic signatures of groundwaters, hydrogeologists can strongly support their conclusions on the origin of waters and recharge areas, groundwater quality and contaminant processes, water-rock interactions occurring at depth and resource renewability.

Such approach has been most useful to improve the thermomineral system's management. The hydrogeochemical results have proven to be suitable to aid the decision making related to thermomineral water exploration in several aspects, such as the sustainability of well discharge rates (since excessive rates could increase the referred mixing between different groundwater facies with undesired effects over the thermomineral water quality) or the delineation of wellhead protection areas.

In a near future, the research activities to be performed in Caldas do Moledo region must be addressed towards "new" isotopic techniques ($^{87}Sr/^{86}Sr$ and $^{37}Cl/^{35}Cl$ stable isotope ratios in waters and rocks) that have already demonstrated to be promising in such particular groundwater studies (MARQUES *et al.*, 2001; ANDRADE, 2003). Finally, efforts should be made to include geophysical surveys (e.g. electromagnetic and magnetotellurics) for delineating probable groundwater pathways and its linkage to regional and local deep structures.

ACKNOWLEDGEMENTS

This work has been supported by the 'Centro de Petrologia e Geoquímica' of Instituto Superior Técnico (CEPGIST) and by the 'Centro de Geologia da Universidade do Porto'. The authors also acknowledge H. I. Chaminé (ISEP, MIA-UA) for detailed reviews helping the improvement of the final manuscript.

Recibido: *10-4-2004*
Aceptado: *20-7-2004*

REFERENCES

ALBU, M., BANKS, D. & NASH, H. (1997). *Mineral and thermal groundwater resources.* Chapman and Hall, London, UK, 447 pp.

ANDRADE, M. P. L. (2003). *A geoquímica isotópica e as águas termominerais. Contribuição dos isótopos do Sr (*^{87}*Sr/*^{86}*Sr) e do Cl (*^{37}*Cl/*^{35}*Cl) na elaboração de modelos de circulação. O caso de algumas águas gasocarbónicas do N de Portugal.* Instituto Superior Técnico, Lisboa, 104 pp. (MSc Thesis).

BAPTISTA, J., CABRAL, J. & RIBEIRO, A. (1998). Seismotectonics of Chaves and Moledo mineral springs in Penacova-Régua-Verin Fault Zone. In: AZERÊDO, A., eds., Actas do V Congresso Nacional de Geologia, *Comunicações do Instituto Geológico e Mineiro,* Lisboa, 84 (1): 69–72.

BAPTISTA, J., COKE, C., DIAS, R. & RIBEIRO, A. (1993). Tectónica e geomorfologia da região de Pedras Salgadas–Vidago e as nascentes minerais associadas. In: CHAMBEL A. (eds.) *Comunicações da XII Reunião de Geologia do Oeste Peninsular,* Universidade de Évora, 1: 125-139.

BERNARDO DE SOUSA, M. & SEQUEIRA, A. J. D. (1989). *Notícia explicativa da Carta Geológica de Portugal,* escala 1/50 000. Nº 10-D (Alijó). Serviços Geológicos de Portugal, Lisboa, 59 pp.

CABRAL, J. (1995). Neotectónica em Portugal Continental. *Mem. Inst. Geol. Min.,* Lisboa, 31: 1-265.

CARVALHO, J. M. (1996a). Mineral water exploration and exploitation at the Portuguese Hercynian massif. *Environmental Geology,* 27: 252-258.

CARVALHO, J. M. (1996b). Portuguese geothermal operations: a review. *European Geologist,* EFG: 21-26.

CLARK, I. & FRITZ, P. (1997) *Environmental Isotopes in Hydrogeology.* Lewis Publishers, New York: 328 pp.

COMANS, R. N. J., van der WEIJDEN, C. H. & VRIEND, S. P. (1987). Geochemical studies in the drainage basin of the Rio Vouga, Portugal. IV. Impact of land use on the hydrogeochemistry of natural waters in the Vouzela Region. *Environ. Geol. Water Sci.,* 9 (2): 119-129.

CRAIG, H. (1961). Isotopic variations in meteoric waters. *Science,* 133: 1703-1704.

D.G.R.A.H [Direcção-Geral dos Recursos e Aproveitamentos Hidráulicos] (1986). *Monografias hidrológicas dos principais cursos de água de Portugal Continental,* Lisboa: 569 pp.

EPSTEIN, S. & MAYEDA, T. (1953). Variation of ^{18}O content of waters from natural sources. *Geochim. Cosmochim. Acta,* 4: 213 - 224.

ESPINHA MARQUES, J., CHAMINÉ, H. I., CARVALHO, J. M. & BORGES, F. S. (2001a). Tectónica regional do sector de Caldas do Moledo–Granjão–Cidadelhe (Falha de Penacova–Régua–Verín, N de Portugal): implicações no controlo das emergências hidrominerais. *Comunicações Instituto Geológico e Mineiro,* Lisboa, 88: 203-212.

ESPINHA MARQUES, J., MARQUES, J. M., CHAMINÉ, H. I., GRAÇA, R. C., CARVALHO, J. M., AIRES-BARROS, L. & BORGES, F. S. (2001b). The newly described 'Poço Quente' thermal spring (Granjão–Caldas do Moledo sector, N Portugal): hydrogeological and tectonic implications. *Geociências,* Rev. Univ. Aveiro, 15: 19-35.

ESPINHA MARQUES, J., MARQUES, J. M., CHAMINÉ, H. I., GOMES, A. A., FONSECA, P. E., CARVALHO, J. M., CARREIRA, P. M., GRAÇA, R. C., AIRES-BARROS, L. & BORGES, F. S. (2003). Nascente termal do Poço Quente (Granjão-Caldas do Moledo, N de Portugal): morfoestrutura, geoquímica e hidrogeologia. *Cadernos Lab. Xeolóxico de Laxe,* A Coruña, 28: 147-172.

FONTES, J. CH. & GARNIER, J. M. (1979). Determination of the initial activity of the total dissolved carbon. A review of existing models and a new approach. *Water Resources Research,* 12: 399-413.

FOURNIER, R. O. (1977). Chemical geothermometers and mixing models for geothermal systems. *Geothermics,* 5: 41-50.

FOURNIER, R. O. & TRUESDELL, A. H. (1973). An empirical Na-K-Ca geothermometer for natural waters. *Geochim. et Cosmochim. Acta,* 37: 1255-1275.

FRIEDMAN I. (1953). Deuterium content of natural waters and other substances. *Geochim. Cosmochim. Acta,* 4: 89-103.

GALLAGHER, D., McGEE, E. J., KALIN, R. M. & MITCHELL, P. I. (2000). Performance of models for radiocarbon dating of groundwater: an appraisal using selected Irish aquifers. *Radiocarbon,* 42 (2): 235-248.

GARCIA, D. (1986). *Étude isotopic et géochimique des eaux thermales des Vosges Méridionales, application géothermique.* Université des Sciences et Techniques du Languedoc. Académie de Montpellier, Document BRGM, 167 pp. (Thèse de 3^{e} cycle).

GAT, J. R. (1980). The isotopes of hydrogen and oxygen in precipitation. In: FRITZ P. & FONTES J. Ch., eds., *Handbook of Environmental Isotope Geochemistry*, 1: 21-47.

GIGGENBACH, W. F. (1988). Geothermal solute equilibria: derivation of Na-K-Ca-Mg geoindicators. *Geochim. Cosmochim. Acta*, 52: 2749-2765.

HURTER, S. & HAENEL, R. (2002). *Atlas of Geothermal Resources in Europe. European Commission* – Research Directorate – General. Publication No. EUR 17811.

I.A.E.A [International Atomic Energy Agency] (1994) *Environmental Isotope Data No. 10: World Survey of Isotope Concentration in Precipitation (1988-1991).* Technical Reports Series 371.

LLANA-FÚNEZ, S. & MARCOS, A. (2001). The Malpica–Lamego Line: a major crustal-scale shear zone in the Variscan belt of Iberia. *J. Struct. Geol.*, 23, (6/7): 1015-1030.

LOUREIRO, J. J. M., MACEDO, M. E. Z., ALMEIDA, M. C. L. & MARTINS J. C. S. (1986). Bacia hidrográfica do rio Douro. *Monografias Hidrológicas dos Principais Cursos de Água de Portugal Continental.* D.G.R.A.H, Lisboa, pp. 147-205.

LUCAS, L.L. & UNTERWEGER, M.P. (2000). Comprehensive review and critical evaluation of the half-life of tritium. *J. Res. Natl. Inst. Technol.*, 105: 541-549.

MARINI, L. & SUSANGKYONO, A. E. (1999). Fluid geochemistry of Ambon Island (Indonesia). *Geothermics*, 28: 189-204.

MARQUES, J. M., AIRES-BARROS, L. & GRAÇA, R. C. (1999a). Geochemical and isotopic features of hot and cold CO_2-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. (1999b). Isotopic and chemical signatures of low-temperature sulphurous mineral waters (Northern Portugal): preliminary results. *Geothermal Resources Council Transactions*, 23: 327 - 332.

MARQUES, J. M., ANDRADE, M., AIRES-BARROS, L., GRAÇA, R. C., EGGENKAMP, H. G. M. & ANTUNES DA SILVA, M. (2001). $^{87}Sr/^{86}Sr$ and $^{37}Cl/^{35}Cl$ signatures of CO_2-rich mineral waters (N-Portugal): preliminary results. In: SEILER K-P. & WOHNLICH S., eds., *New approaches characterizing groundwater flow*, A. A. Balkema, pp. 1025-1029.

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. *Environmental Geology*, 40 (1/2): 53 - 63.

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: 189-201.

MONTEIRO SANTOS, F. A. (1994). *Interpretação integrada de dados de resistividade e magneto-telúrica: aplicação ao estudo de reservatórios geotérmicos de baixa entalpia.* Universidade de Lisboa, 280 pp. (Tese de Doutoramento).

MOOK, W. G. (2000). *Environmental isotopes in hydrological cycle. Principles and applications.* IHP-V, Technical Documents in Hydrology, N° 39.

N.A.P [National Academy Press] (2001). *Conceptual models of flow and transport in the fractured vadose zone.* Washington, D.C., 374 pp.

PANICHI, C. & TONGIORGI, E. (1975). Carbon isotopic composition of CO_2 from springs, fumaroles, moffetes and travertines of Central-Southern Italy: a preliminary prospection method of geothermal area. *Proceedings of the Second United Nations Symposium on the Development and Use of Geothermal Resources*, S. Francisco, C.A, pp. 815-825.

RIBEIRO, A., QUESADA, C. & DALLMEYER, R. D. (1990). Geodynamic evolution of the Iberian Massif. In: DALLMEYER R. D. & MARTÍNEZ-GARCÍA E., eds., *Pre-Mesozoic Geology of Iberia,* Berlin, Heidelberg. Springer-Verlag, pp. 397-410.

ROZANSKI, K, ARAGUÁS-ARAGUÁS, L. & GONFIANTINI, R. (1993). Continental Isotope Indicators of Climate. Isotopic patterns in modern global precipitation. *Am. Geophys. Union Monograph*, 78: 1-36.

RYBACH, L. (1990). Determination of thermal water circulation depth, with examples from the Valaisan Alps, Switzerland. *Memoires of the 22nd Congress of IAH*, Vol. XXII. Lausanne, pp. 608-615.

SALEM, O., VISSER, J. M., DEAY, M. & GONFIANTINI, R. (1980). Groundwater flow patterns in western Lybian Arab Jamahitiya evaluated from isotope data. In: INTERNATIONAL ATOMIC ENERGY AGENCY, eds., *Arid* *zone hydrology: investigations with isotope techniques*, 165-179.

SEIFERT, H. (1967). *Caldas de Moledo: consequências da construção da Barragem de Carrapatelo sobre as nascentes termais e projecto de novas captações*. Geo-Hidrol– Gabinete de Estudos Geológicos e Hidrológicos, Lda, Lisboa. 13 pp. Unpublished report.

TEIXEIRA, C., FERNANDES, A. P. & PERES, A. (1967). *Notícia explicativa da Carta Geológica de Portugal* na escala 1/50 000. Folha 10-C (Peso da Régua). Serviços Geológicos de Portugal, Lisboa. 60 pp.

TRUESDELL, A. H. (1975). Summary of Section III. Geochemical techniques in exploration. *Proceedings of the Second United Nations Symposium on the Development and Use of Geothermal Resources*. San Francisco, California, USA, 53-79.

TRUESDELL, A. H. & HULSTON, J. R. (1980). Isotopic evidence on environments of geothermal systems. In: FRITZ P. & FONTES J. Ch. (eds.) *Handbook of Environmental Isotope Geochemistry, The Terrestrial Environment,* 1: 179-226.

YURTSEVER, Y. & GAT, J. R. (1981). Atmospheric Waters. In: International Atomic Energy Agency, eds., *Stable Isotope Hydrology. Deuterium and oxygen-18 in the water cycle,* Technical Reports Series nº 210, pp. 103-142.