

Hydrochemical and isotopic interpretation of thermal waters from the Felgueira area (Central Portugal)

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ABSTRACT: The hydrothermal system of Felgueira has long been appreciated for the recreational and therapeutic benefits of the thermal baths. In order to protect and maintain these thermal resources it is necessary to understand the characteristics of these waters and determine its origin and that of its solutes. In this paper we use chemical and isotopic data as tools for addressing some of those questions. Early Holocene meteoric waters reacted, at low reservoir temperatures, with minerals from a granite aquifer, in an environment with available deep CO₂, thus acquiring a sodium bicarbonate-chloride composition, with alkaline and strongly reducing characteristics. Biogenic sulphate reduction results in a wide variation of the S isotopic composition of both oxidized and reduced sulphur species. The drawdown imposed by exploitation wells results in some degree of vulnerability of the hydrothermal system.

1 INTRODUCTION

Caldas da Felgueira is an active thermal spa whose waters have been used for medicinal purposes since ancient times. Located at Central Portugal (Fig. 1), it has a mild climate, with an average rainfall of 1100 mm and a mean annual air temperature of 15°C.

There are two natural spring discharges, one with a water temperature of 32.5°C, which serves as Buvette of the spa, and a cold spring with a temperature of 18°C. For balneological activities, 32.0°C water was obtained from a 16 m deep excavated well until the 90's of the last century. Since then, 3 wells have been drilled in order to satisfy the development of the spa, with increased consumption of thermal water.

A considerable amount of chemical data is available from 1991 until present, derived from monitoring programs of those wells. Additionally, two sampling campaigns for isotopic determinations were made in 1996 and 2008, as reported on Table 1.

The overall goal is to obtain a geochemical model of the hydrothermal system based on chemical and isotopic data.

2 HYDROGEOLOGICAL SETTING

Caldas da Felgueira region is located onto fractured granitic rocks intruding a metamorphic complex of low Palaeozoic age, belonging to the Central Iberian geotectonic zone of the Hesperian Massif. The area was cut by large, deep faults during the Hercynian orogeny, some of which were reactivated during Alpine times, allowing for extensive deep circulation

of meteoric waters which resulted in several hydrothermal fields, including Caldas da Felgueira.

The locally significant features of the hydrogeologic setting are shown in Figure 1 (map after Rodrigues et al. 2000). The rock exposed in the neighbourhood of the thermal springs is porphyritic medium to fine-grained two-mica granite, gradually passing into a coarser grain size. These granites belong to the calc-alkaline series and are associated to a post-tectonic Hercynian pluton. A dense fracture network affects the crystalline basement, with the main fault system -trending ENE-WSW- controlling the spring occurrences. It was along this structurally controlled corridor that 3 wells were drilled; namely AC1, a 64 m deep flowing well with a water temperature of 35.8°C; AC2 (250 m; 26,7°C) and the deepest AC3 well (306 m) with water at 33.2°C. All the wells yield warm water whose chemical and physical characteristics are similar to those of the spring waters, but with a minor mixing with surficial waters. This suggests that the waters emerge from the same aquifer system and follow identical flow paths, and are subjected to similar geochemical processes during its trajectory in the hydraulic circuit.

3 ORIGIN AND “AGE” (MEAN RESIDENCE TIME) OF THERMAL WATERS

The meteoric origin of these waters has been established by comparison of $\delta^{18}\text{O}$ and δD values (Fig. 2) with those of the World Meteoric Water Line (WMWL) for rainfall as defined by Craig (1961). The lack of significant deviation of the

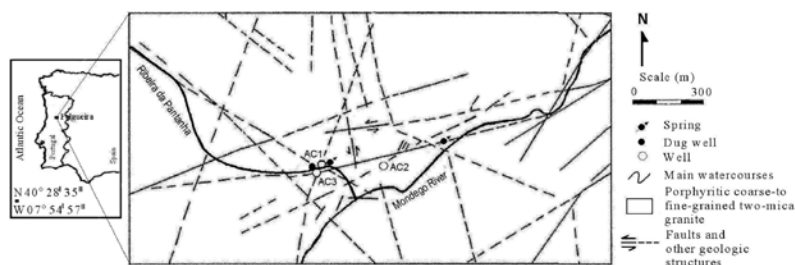


Figure 1. Location and geologic map of the Felgueira area (modified from Rodrigues et al. 2000).

Table 1. Chemical and isotopic data and saturation indices for Felgueira thermal waters.

Sampling Point	AC1	AC1	AC2	AC3	AC3
Date	96/09	08/07	96/09	96/09	08/07
Field Parameters					
Temp., °C	35.5	35.1	23.3	33.5	34.1
Cond., S cm ⁻¹	680	528	580	690	529
pH	8.10	8.00	7.85	8.05	8.17
Constituents, mg/L					
Na ⁺	109	107	104	108	108
K ⁺	1.6	2.4	2.2	2.6	2.4
Ca ⁺⁺	5.3	5.1	7.2	6.2	5.0
Mg ⁺⁺	0.11	0.11	0.38	0.2	0.13
Li ⁺	1.06	0.99	1.06	1.12	0.99
NH ₄ ⁺	0.12	0.10	0.07	0.17	0.08
Cl ⁻	51.8	50.7	49.0	51.8	48.6
HCO ₃ ⁻	143	148	138	145	149
SO ₄ ⁼	26.0	16.8	36.9	27.6	20.3
F ⁻	15.1	15.7	13.0	14.7	15.5
HS ⁻	0.6	0.7	0.3	0.5	0.3
NO ₃ ⁻	0.24	<0.10	0.27	0.33	0.10
SiO ₂	50.5	52.2	50.4	52.2	56.2
Calculated Parameters*					
Eh, mV	-303	-297	-258	-295	-303
TDS, mg/L	404.4	399.9	402.8	410.4	406.6
Isotopes					
Stable**					
δ ¹⁸ O(H ₂ O)	-5.0	-5.4	-5.3	-5.1	-5.0
δ ¹⁸ O(SO ₄)	+10.9	-	+7.3	+10.3	-
δ ² H(H ₂ O)	-	-34.3	-	-	-34.8
δ ¹³ C(DIC)	-14.6	-13.8	-14.5	-13.6	-14.0
δ ³⁴ S(SO ₄)	+6.4	+9.0	-1.3	+6.0	+10.6
δ ³⁴ S(H ₂ S)	-25.1	-23.5	-29.9	-25.2	-25.3
Radioactive					
T., TU	<d.l.	n.m.	0.82	<d.l.	n.m.
¹⁴ C, pMC	17.9	n.m.	31.2	18.5	n.m.
Saturation Indices					
Calcite	-0.33	-0.43	-0.62	-0.33	0.28
Fluorite	0.17	0.20	0.31	0.23	0.18
Chalcedony	0.35	0.37	0.49	0.39	0.41
Quartz	0.74	0.77	0.93	0.79	0.81

*Calculated with Wateq4F version 2.63 (2004), (Ball & Nordstrom, 2001). Eh calculated with the pair HS/SO₄.

** δ¹⁸O ‰ vs VSMOW; δ²H ‰ vs VSMOW; δ¹³C ‰ vs PDB; δ³⁴S ‰ vs CDT; n.m.—not measured; <d.l. below detection limit of 0.7 TU.

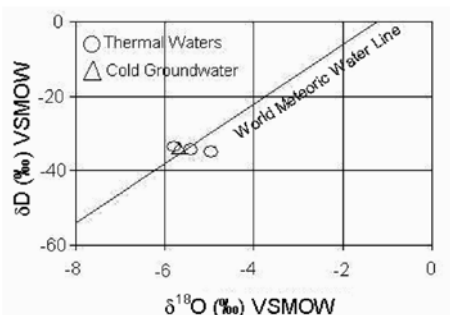


Figure 2. The relationship between δ¹⁸O and δD values in the thermal and cold water samples from the study hydrothermal system.

δ¹⁸O values of the thermal waters from WMWL (“oxygen isotope shift”) limits the reservoir temperatures to a maximum of 150°C (Ellis & Mahon 1977), suggesting a low enthalpy hydrothermal system corresponding to the deep circulation of meteoric water in a fractured granite of Hercynian age. Tritium is absent from wells AC1 and AC3, while the small con-tent measured at well AC2 gives an indication of a major vulnerability to phreatic waters (Table 1). That hint is corroborated by ¹⁴C content: AC1 and AC3 have the same content of ¹⁴C, and are the less hybrid fluids of the system, while ¹⁴C contents of well AC2 are significantly larger. The value of the initial activity of ¹⁴C was calculated with the isotopic mixing model of Pearson (Pearson & Hanshaw 1970). Applying the decay equation to the measured ¹⁴C activities of the waters, an adjusted radiocarbon age of 10.3 Ka is derived for AC1 and AC3 waters.

4 CLASSIFICATION OF THERMAL FLUIDS

Chemically, Felgueira thermal waters (Table 1) have low mineralization (total dissolved solids around 400 mg/L), pH in the alkaline range (around 8.10) and a strong negative calculated redox potential (always < -250 mV), which allow for measurable quantities

of NH_4^+ and HS^- species, representing nitrogen and sulphur at lower oxidation states. Nitrate and magnesium are usually low. Additional main constituents are Cl^- (50 mg/L), F^- (15 mg/L) and Li^+ (1 mg/L). The mean values of sulphate concentration were ca. 25 mg/L. Na represent 90% of cations ($r\text{Na} \gg r\text{Ca} \gg r\text{Mg}$), but none of the anions clearly dominates ($r\text{HCO}_3^- > r\text{Cl}^- > r\text{SO}_4^{2-}$), thus belonging to a sodium-bicarbonate-chloride type. The observed characteristics give a complex chemical structure, rendering these waters very susceptible to aging effects.

5 MINERAL-SOLUTION EQUILIBRIA AND GEOTHERMOMETRY

The composition in terms of cations (Na^+ , K^+ and Mg^{++}) plotted on the triangular diagram of Giggenbach (1988) and Giggenbach & Corrales (1992) is used to classify the state of rock-water interaction of these waters as partially equilibrated at 70–140°C with hydrothermally altered rock in the geothermal reservoir (Fig. 3).

However, the most probable temperature range for the reservoir system is 70–80°C, as calculated with some degree of confidence by independent temperature estimates using chemical geothermometers (chalcedony: Fournier 1991, Na-K-Ca: Fournier & Truesdell 1973, *in* Fournier 1991, Na-K: Nieva & Nieva 1987, *in* Fournier, 1991, and K-Mg: Giggenbach 1988).

The saturation indices were calculated using the thermodynamic equilibrium model from the geochemical software Wateq-4F (Ball & Nordstrom 2001) for minerals assumed to be relevant for the aquifer. Waters are oversaturated with respect to quartz, chalcedony and fluorite, and undersaturated with respect to calcite. At the temperature of the reservoir these waters approach equilibrium with calcite and chalcedony; are slightly undersaturated in fluorite, and slightly oversaturated in quartz.

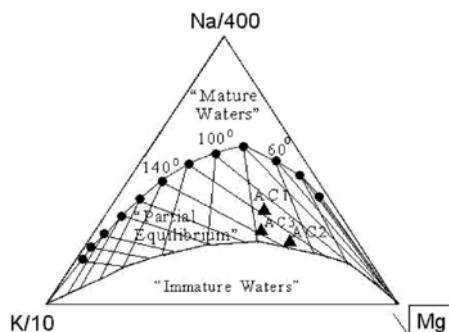


Figure 3. Triangular diagram of $\text{Na}/400\text{-K}/10\text{-}\sqrt{\text{Mg}}$ for the thermal waters (modified from Giggenbach, & Corrales 1992).

The investigation of the fluid-mineral equilibrium for aluminosilicates employed activity diagrams constructed at reservoir temperatures, for primary minerals like microcline, albite and anorthite. According to these diagrams, thermal waters plot in the stability field of microcline, and are most likely to produce montmorillonites (Na and Ca) as alteration minerals.

6 ISOTOPIC STUDIES

If groundwater circulates in an aquifer with apparent absence of carbonate minerals, and in a system closed to CO_2 , its C isotopic ratios do not evolve far beyond those of the soil CO_2 contribution, *i.e.* $\delta^{13}\text{C}$ around -23 to -25‰ for C3 type vegetation in temperate climate (Clark & Fritz 1997). However, dissolved inorganic carbon (DIC) $\delta^{13}\text{C}$ values at Caldas da Felgueira, approach ca. -14‰ . This probably records a contribution of isotopically heavy carbon from a source external to the granite aquifer. We can only speculate about this source as being metamorphic carbon or mantle derived CO_2 .

The $\delta^{34}\text{S}$ values of SO_4 from AC1 and AC3 waters are positive and between $+6$ and $+10\text{‰}$, while $\delta^{34}\text{S}$ in the associated dissolved sulphide is around -25‰ . Keeping in mind the values reported in Table 1, the S isotope ratios for those waters could be explained by some bacterial reduction of SO_4^{2-} which results in an enrichment in ^{34}S of the remaining SO_4^{2-} ; $\Delta \text{SO}_4^{2-} - \text{HS}^- \approx +30$ to $+35\text{‰}$ (van Everdingen et al. 1982, Hoefs 2004). Moreover, the $\delta^{18}\text{O}_{(\text{SO}_4)}$ values of $+10$ to $+11\text{‰}$ are enriched in ^{18}O relative to $\delta^{18}\text{O}_{(\text{H}_2\text{O})}$ ($\approx -5\text{‰}$), which is also to be expected in the reduction process of dissolved SO_4^{2-} (Fritz et al. 1989). The negative $\delta^{34}\text{S}$ value and increased content of SO_4^{2-} (oxidized S) in water from well AC2 possibly reflects a contribution from oxidation of dissolved sulphide derived by more significant mixing of the thermal waters with phreatic waters. The lower value of $\delta^{18}\text{O}_{(\text{SO}_4)}$ relative to waters from wells AC1 and AC3 also supports this interpretation.

7 CHEMICAL MONITORING

Time series plots of the chemical data obtained from the monitoring programme exhibit a consistent increase in dissolved sulphate concentrations up to 1998, followed by a decrease later on. This variation is relative to “historical” mineral water composition, *e.g.* data from 1951 analysis (Fig. 4). Other parameters hardly changed, although small variations in concentrations with time of some elements have been carefully analysed for the period 1991–98 by Morais (2008). Such contamination by sulphates is attributed to the impact of the extraction and ore processing of uranium at Urgeiriça mine, located

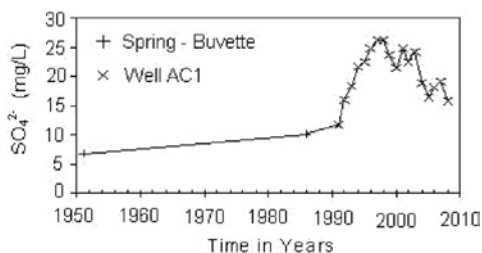


Figure 4. Evolution in sulphate concentrations in the thermal waters during the period 1951–2008.

4 kms to the NW of Caldas da Felgueira. The mining area is drained by the Ribeira da Pantanha watercourse that flows through the Caldas da Felgueira area, transporting wastewater from the treatment plant of Urgeiriça. This plant used components like sulphuric acid to benefit the ore. In a sample collected in September 1996 the content of sulphates in water from Ribeira da Pantanha were 968 mg/L, with a value of $\delta^{34}\text{S}$ of +4.57‰. The significant increase of sulphate levels in water after the construction of the wells is consistent with admixture with contaminated surficial waters, as a consequence of the new dynamic equilibrium in water pressures within the productive geological structure imposed by pumping the wells. Extraction and treatment of uranium began in 1951, declined towards 1991 and completely ended in 2004. Although anthropogenic impacts are now much diminished, initial sulphate values have not yet recovered (Fig. 4).

8 CONCLUSIONS

The Felgueira hydrothermal system flows through a fractured granite aquifer, heating early Holocene aged water to a maximum temperature of 70–80°C. Its chemistry is controlled by the interaction of meteoric water, enriched in deep CO_2 , with the minerals of the granite aquifer. The stable carbon isotopic composition reflects both organic and inorganic carbon sources for DIC, in a system partially open to inorganic CO_2 . Biogenic reduction of dissolved sulphate is the process which significantly determines the isotopic geochemistry of sulphur. The medicinal utilization of Felgueira water was hampered from 1951 onwards by the coexistence at its neighbourhood of environmentally aggressive uranium mining. Drawdown caused by wells pumping the thermal water resulted in surficial sulphate rich waters, derived from mining activities, entering the system, which result in a marked increase in sulphate contents of the water. The adverse effect of mining activities still continues, although environmental restoration began in 2006 by sealing of mill tailings.

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