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CHEMICAL COMPONENTS OF DEEP ORIGIN IN SULPHIDE WATERS OF THE PORTUGUESE SECTOR OF THE HESPERIAN MASSIF

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ABSTRACT. In the Portuguese sector of the Hesperian Massif a large number of springs occur which are characterized by the conspicuous presence of reduced forms of sulphur, high pH and high concentrations of fluoride and silica.

About one hundred springs or groups of springs were identified, the majority being derived from Hercynian granites, and frequently associated with regional Hercynian or tardi-Hercynian faults. Some of these faults were reactivated by the Alpine orogeny, and some have shown activity within the last 2 Ma.

From the springs a representative sample of 26 point sources was selected and the main physico-chemical parameters and several trace elements were analyzed.

Using multivariate analysis, a significant correlation was found between total reduced sulphur, bromide, fluoride, ammonium, total inorganic carbon, etc. These results, and hydrogeochemical modelling, allow one to conclude that there is an important enrichment of these components from a deep origin.

INTRODUCTION

The most important group of Portuguese mineral waters occurring in hard rocks are, by their total number (more than one hundred sources are identified) and by their relative homogeneity of chemical composition, the sulphide sodic alkaline waters. They are characterized by high pH, usually between 8 and 9.5, very low redox potential, low mineralization, presence of reduced species of sulphur and high contents of fluorine, usually between 10 and 25 mg/L.

In this paper, water analyses of 26 representative sources of these waters are discussed. The waters have been used for therapeutic purposes for some centuries, and in some cases analytical data from the last century up to now are available. These data show the waters to be chemically stable. All the analytical data discussed in this paper are very recent.

The main purpose of this paper is to show that the processes controlling the concentrations of total carbon, reduced sulphur, fluoride, etc. are related to the enrichment of the water with fluids of deep internal origin, namely CO₂, H₂S, HF, HCl.

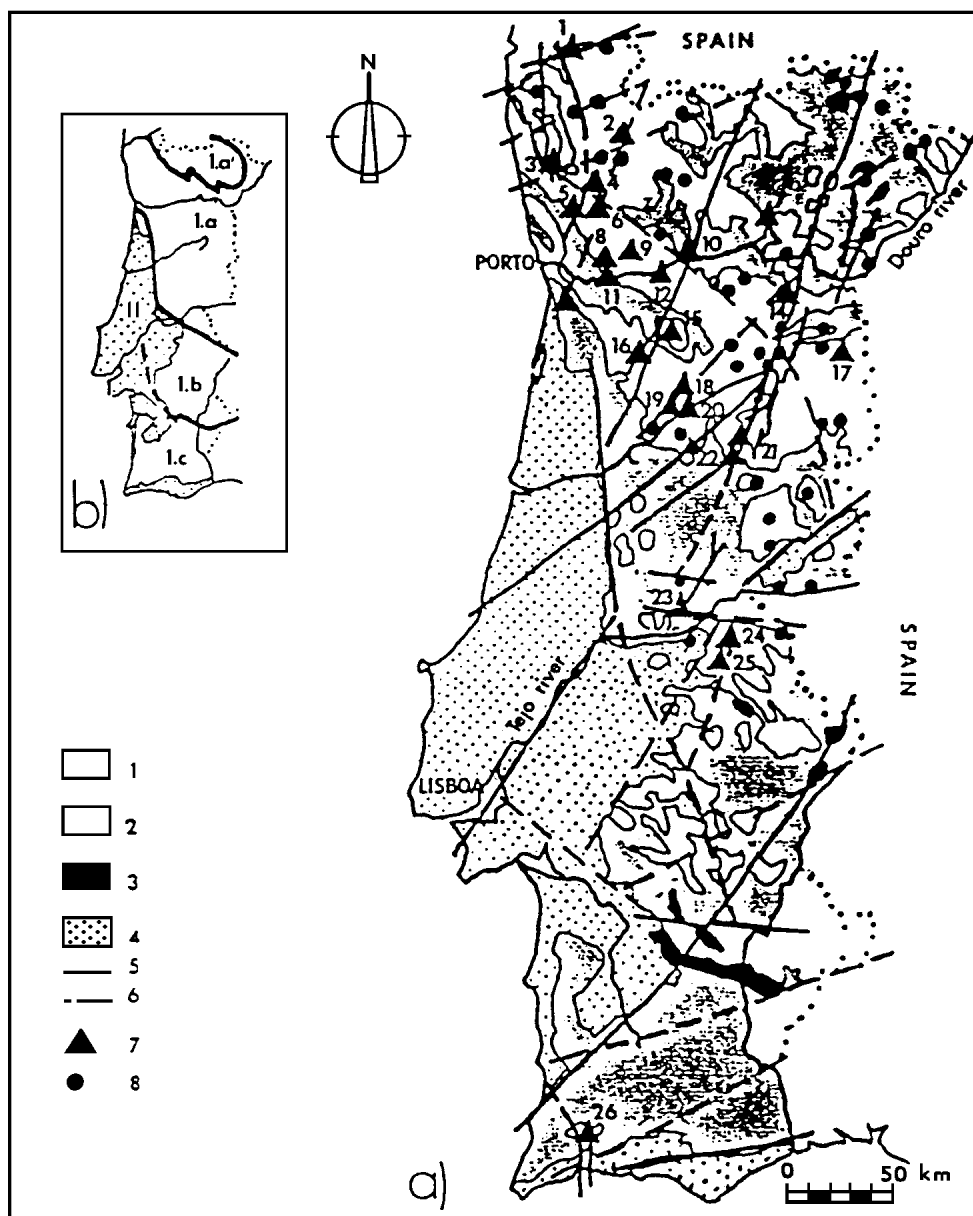


FIG 1. Distribution and geological environment of the Portuguese sulphide waters.

a) 1. metasediments; 2. acid and intermediate magmatic rocks; 3. basic and ultrabasic magmatic rocks; 4. Post-Paleozoic formations; 5. active fault; 6. probable active fault; 7. studied water (see table I); 8. other sulphide waters.
 b) I. Hesperian Massif: Ia. Central-Iberian Zone; Ia'. Sub-zone of Middle Galicia-Tras-os-Montes; Ib. Ossa-Morena Zone; Ic. South Portuguese Zone; II. Meso-Cenozoic sedimentary cover.

TABLE I

26 representative occurrences of Portuguese sulphide springs.

Table I

Ref.	Name	T °C	pH	TDS mg/L	$\Sigma\text{H}_2\text{S}$ mg/L
1	Monção	49.0	7.8	559.2	0.70
2	Gerês	47.0	9.2	281.8	0.54
3	Eirogo	24.1	8.7	491.5	8.21
4	Taipas	32.0	8.9	419.9	3.09
5	Caldinhas	26.5	8.8	568.1	14.56
6	Vizela	52.0	9.2	315.1	5.86
7	Carlão	28.9	8.2	433.5	3.12
8	S. Vicente	18.5	8.7	501.4	27.12
9	Canavezes	33.5	9.2	292.9	6.45
10	Moledo	45.4	9.3	247.3	2.86
11	Entre-os-Rios	19.3	8.6	471.6	25.22
12	Arêgos	57.5	8.9	312.2	5.60
13	S. Jorge	23.0	8.5	690.0	9.86
14	Longroiva	30.0	8.7	493.7	2.24
15	Carvalhal	28.5	9.2	331.8	3.79
16	S. Pedro Sul	67.0	8.9	341.2	3.70
17	Almeida	19.0	8.5	366.2	3.07
18	Alcafache	50.9	8.3	420.8	1.39
19	Sangemil	49.5	8.5	469.3	6.99
20	Felgueiras	31.2	8.1	396.1	0.45
21	Manteigas	45.5	9.5	176.5	1.58
22	Unhais da Serra	28.0	8.7	284.7	2.37
23	Mação	17.0	8.5	511.9	8.27
24	Nisa	18.8	8.3	380.1	3.66
25	Monte da Pedra	19.2	7.6	395.9	3.73
26	Monchique	32.0	9.4	340.3	0.27

GEOGRAPHICAL DISTRIBUTION AND GEOLOGICAL ENVIRONMENT

The Portuguese sulphide waters occur only in the Hesperian (or Iberian) Massif, which is the most extensive segment of the Hercynian basement in Europe (Ribeiro *et al.*, 1979). The Hesperian Massif consists of pre Mesozoic formations, essentially metasediments and plutonic rocks, mainly granites. There are also effusive rocks, abundant in the southern part of the massif.

As can be seen from fig. 1 and table I, all the sources, with the exception of Caldas de Monchique (26), are located in the Central Iberian Zone (Julivert *et al.*, 1972). The available data do not indicate the presence of such waters either in the Ossa-Morena Zone or in the South Portuguese Zone (Calado, 1992).

Ribeiro & Almeida (1981) pointed out that the occurrence of hot waters is related to zones of uplift during the Quaternary (the vertical movement was about 500m in the northern part and between 100 and 300 m in the south of Portugal) and they propose a mechanism of seismic pumping to explain the ascension of hot fluids to the surface (Fig. 2). Indeed the occurrence of all the sulphide waters, not only the hot ones; seems to be associated, at least when seen at a small scale, with megafractures active in the last 2 Ma (Cabral & Ribeiro, 1988). Although in the field the distance between the sources and the megafractures can sometimes reach many kilometers, detailed hydrogeological studies have revealed the presence of transverse secondary faults, confirming the suggestion of Ribeiro & Almeida (1981). These secondary faults control the flow regime near the spring sites.

CHARACTERIZATION AND ANALYTICAL TECHNIQUES

The Portuguese alkaline sulphide waters can be characterized by the following main features:

- pH rather high, usually between 8 and 9;
- median total mineralization usually in the range of 200 to 500 mg/L; i.e. higher than the typical waters of the granitic regions where almost all are issuing;
- the dominant anion (more than 50%) is in general bicarbonate, more rarely chloride. In some cases there is no dominant anion, bicarbonate and fluoride being the most important ones;
- sodium is always the dominant cation, usually more than 80% of the cations;
- conspicuous presence of reduced species of sulphur, very low Eh and sulphate in low concentrations;
- high content of fluoride, usually above 10 mg/L; this anion is often the second most important one;
- silica content representing more than 15 % of the total mineralization;
- ammonium is always present, usually below 0.5 mg/L; nitrate and nitrite absent;
- significant presence of boron, bromide and tungsten;
- very low concentrations of heavy metals;

- nitrogen is the dominant gas in solution;
- discharges are generally below 1 L/sec with minor seasonal fluctuations. The highest discharge (S. Pedro do Sul, 16) is 10 L/sec, and is also the hottest sulphide water (68 °C).

Almost all the analytical results used in this study come from the D. G. Geol. e Minas laboratory. Sampling and analytical techniques are described in detail by Machado (1988, 1991). In addition to temperature, Eh, pH, conductivity (after rapid cooling when the temperature exceeds 30 °C), sulphide and dissolved oxygen were measured in the field.

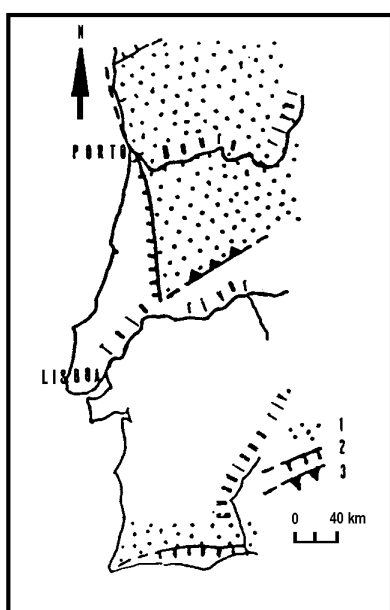


Fig. 2. Quaternary uplifted areas (adapted from Ribeiro & Almeida, 1981).
 1 – Uplifted areas;
 2 – Normal fault;
 3 – Inverse fault.

The 26 waters which are studied in this paper can be considered representative of the type of waters that have been described, with one exception (Caldas de Monchique, 26). Caldas de Monchique water has a much lower content of fluoride, sulphide and silica (which represents less than 4% of the total mineralization). However, this water occurs in a geological environment quite different from the others: a syenitic massif, Mesozoic in age, intruded into carboniferous formations of the South Portuguese Zone. The other waters are located in (or not far from) Hercynian granitoids of the Central Iberian Zone.

It must be emphasized that despite the fact that the presence of alkaline sulphide waters has been noted in several other areas such as Spain (Galicia, Castilla-Leon, Extremadura), France (Pyrenees, Vosges, Corsica), Sweden, Bulgaria and Italy (Michard, 1990, Calado, 1992) and despite their rather conspicuous characteristics,

they were not considered in the classification proposed by Ivanov (1979). In fact, the sulphide waters considered by Ivanov are related to areas of active or recent volcanism or to sulfate reduction, criteria that cannot be applied to the kind of waters under discussion here.

GEOOTHERMOMETRY AND MINERAL EQUILIBRIA

By applying geothermometer estimations to the data, rather scattered values of reservoir temperature were obtained. These values are synthesized in a graphical form (fig. 3) where the interval between the 1st and 3rd quartile is represented.

Considering the geological context, the Na-Li (Fouillac & Michard, 1981) and Na-K-Ca (Fournier, 1981) geothermometers can be excluded because they gave too high temperatures.

Other geothermometers seem to be more realistic, although the Na/K one (Fournier & Truesdell, 1973) give a rather large range pointing in the direction of low temperatures.

The common range of values obtained by the more appropriate geothermometers gives temperatures between 70 °C and 100 °C, seeming to be acceptable.

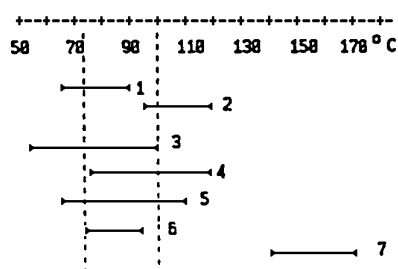


FIG 3. Interquartile range of reservoir temperatures given by geothermometers.

1 = Chalcedony, Fournier (1977); 2 = Quartz (AS=O), *ibid.*; 3 = Na-K, Fournier & Truesdell (1973); 4 = Na-K, Arnorsson *et al.* (1983); 5 = Na-K, Ellis (1970); 6 = Mg-Li, Kharaka & Mariner (1989); 7 = Na-K-Ca, Fournier (1981).

In order to carry out equilibrium calculations an appropriate program, HIDSPEC (Carvalho & Almeida, 1989), was used. The results obtained can be summarized as follows.

Carbonate minerals

More than 50% of the waters are in equilibrium with calcite and/or aragonite. The remainder are generally near equilibrium. With respect to dolomite almost all are undersaturated.

Silica minerals

All waters are supersaturated with respect to quartz. With respect to chalcedony and cristobalite, supersaturation predominates, although some cases of equilibrium were observed.

About 50% of the waters are in equilibrium with silica gel, which suggests that their cooling is accompanied by precipitation of that mineral. If so, the temperatures calculated with silica geothermometers can be underestimated.

Fluorite

About 50% of the waters are supersaturated with respect to fluorite and some cases of equilibrium were observed. However, the majority of waters are in equilibrium when the calculations are carried out at the reservoir temperatures estimated from geothermometers.

Iron minerals

With respect to haematite, magnetite, marcassite and pyrrhotite all waters are strongly supersaturated. This is also the case with respect to goethite, with the exception of three cases which are undersaturated.

Aluminosilicates

With respect to this group only seven cases could be used, because in the others the aluminium was below the detection limit (0.01 ppm) or was not analyzed. All those waters are strongly supersaturated with respect to microcline, muscovite and pyrophyllite. With respect to other minerals no clear trend was observed.

DISCUSSION

Comparing the Portuguese alkaline sulphide waters with typical groundwaters of Portuguese granites, it is noted that the total concentrations of carbon, sulphur, fluoride, chloride etc. are significantly higher in the former. The quantities of those components that originate from dissolution of the rock can be considered negligible, therefore an enrichment by fluids such as CO₂, HS, HCl, HF and probably NaCl from a deep origin must be assumed.

Total carbon (C^T)

Carvalho et al. (1990), have shown that the concentration of C^T in alkaline groundwaters, which is about 6 times greater than the concentration found in typical shallow groundwaters in granites in the same area, is compatible with solution processes at equilibrium with a partial pressure of CO₂ higher than 10^{-1.5} bar. The

corresponding pressure in typical shallow granite groundwater ranges between 10^{-2} and $10^{-2.5}$ bar.

Some cases where the concentration of C^T is near the values found in typical granite groundwaters can be explained by assuming dilution with those waters.

As one can neglect the contribution of C from the dissolution of the rock, taking into account the geological environment, the above facts suggest a contribution of CO_2 from a deep origin.

CO_2 is one of the main factors controlling the concentration of major elements, as it is the main source of H^+ (which is involved in many of the reactions of dissolution). Indeed the relationship between pH and C^T (fig 4) shows that CO_2 is the main factor controlling the pH. It also correlates with the concentration of Na (fig. 5). This cation also shows a good correlation with chloride.

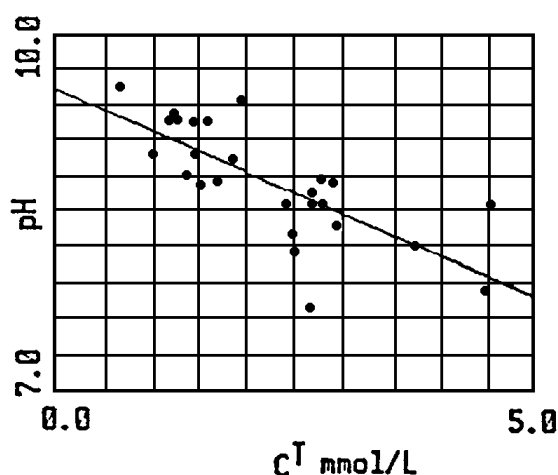


FIG 4. pH vs Dissolved Inorganic Carbon

The above comments concerning C^T can also be applied to chloride, which is present in concentrations well above those found in superficial waters. Two different mechanisms can be proposed in order to explain the correlation between Cl and Na; (i) mixing with solutions of NaCl and (ii) contribution due to the dissolution of albite, orthoclase and other silicates by HCl. The dependence of Na on Cl and C^T can be seen when we plot Na-Cl versus C^T .

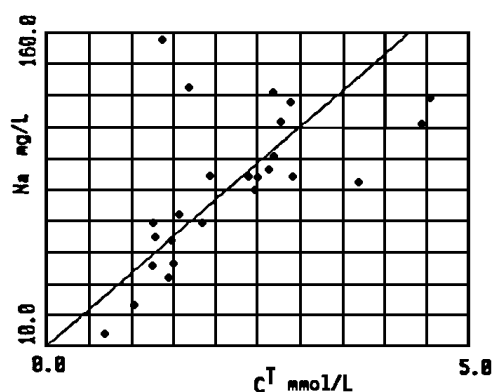
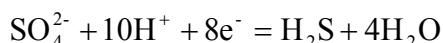


FIG 5. Dissolved Inorganic Carbon vs Sodium.

Reduced sulphur

The presence of reduced species of sulphur (H_2S , HS^- , S^{2-} , $\text{S}_2\text{O}_3^{2-}$) can be controlled by the supply of H_2S from internal origin, or by the reduction of sulphates according to the equation:



When equilibrium is not reached, the direction of the reaction can be assessed by computing the variation of free energy or Eh. In the case under discussion, the Eh calculated from the redox pair $\text{H}_2\text{S}/\text{SO}_4^{2-}$ is always below the Eh measured, indicating that the reaction is proceeding in the direction of oxidation of H_2S , thus discouraging the hypothesis that the reduced sulphur originates from sulphate reduction. This departure from equilibrium could be due to the sluggish kinetics of this reaction. The relationship between the disequilibrium index (Eh measured minus Eh calculated) and temperature (fig. 6) shows a fairly significant correlation, suggesting that in more rapidly ascending waters (i.e. with higher temperature), the system has not yet adapted to the new conditions created by an entry of H_2S .

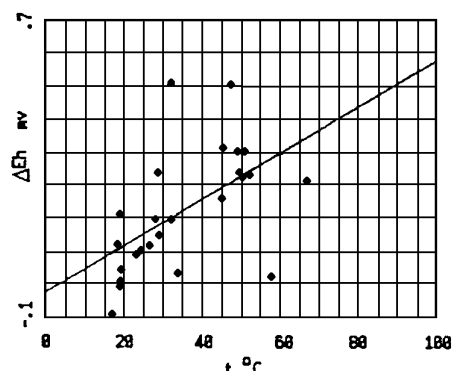


FIG 6. Temperature vs (measured Eh minus calculated Eh).

Silica

Silica shows a weak correlation with those components that can contribute H^+ , and therefore to the reactions of dissolution where this ion participates. This can be due to the fact that silica concentration is also controlled by other processes as dissolution and/or precipitation of quartz and chalcedony, which can be important in waters reaching relatively high temperatures.

Fluoride

The alkaline waters of Portugal have high concentrations of F^- . If this anion had originated from dissolution of fluorite, a positive correlation between F^- and Ca^{2+} should be expected. In the present case the opposite relationship is observed (fig 7),

which can be explained by an entry of HF into the system and a consequent loss of calcium due to the precipitation of fluorite. The fact that many waters are in equilibrium with fluorite at the temperatures of the reservoir supports this assumption.

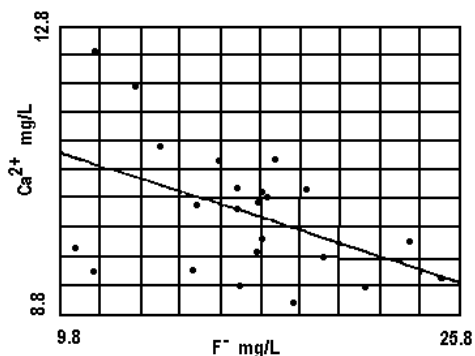


FIG. 7. Fluoride vs Calcium

Other componentes

A high degree of correlation between total carbon, reduced sulphur and chloride and some components frequently thought of as having a deep origin, such as bromide, boron and ammonium, was found.

A significant correlation between tungsten and bromide, boron, reduced sulphur and chloride was also noted.

CONCLUSIONS

The chemical composition of the Portuguese alkaline sulphide waters cannot be explained only by water-rock interactions, as some components cannot be supplied by the mineral constituents of granitic rocks.

The outlet and reservoir temperatures, calculated using geothermometers, point to depths of circulation greatly exceeding the depths reached by normal groundwaters in granitic massifs. There is an obvious spatial correlation between the occurrence of sulphide waters and some fractures, mainly active faults present in regions of uplift. All these facts are consistent with the hypothesis that the specific mineralization of the Portuguese sulphide waters is controlled by the waters enrichment by fluids such as CO₂, H₂S, HCl, HF and probably NaCl of deep origin.

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