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Geochemical processes affecting the composition of mineral waters in the South Portuguese Zone (Portugal)

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ABSTRACT: The Iberian Pyrite Belt is an important sector of the southernmost geostructural domain of the Iberian Peninsula Palaeozoic Massif, the South Portuguese Zone (SPZ). It is composed by metamorphic rocks of volcano-sedimentary origin, followed by the metasediments of the Mértola Formation, both formed in a submarine environment. In this sector several highly mineralised sulphide waters occur, having all a Na-Cl matrix. In order to evaluate the geochemical processes affecting the composition of these waters, forward and inverse geochemical modelling were used. The results show that the final composition could be the result of water/rock interaction of meteoric water with the following phases association: calcite, dolomite, pyrite, goethite, NaCl, CO₂ gas and cationic exchange. Minerals like calcite, dolomite, pyrite and NaCl are dissolving in an open system, as indicated by the large amounts of O₂ consumed during the evolution, accompanied by the precipitation of goethite.

1 INTRODUCTION

The South Portuguese Zone (SPZ) is the southernmost geostructural domain of the Iberian Massif. The presence of a Pyrite Belt (Iberian Pyrite Belt), of extraordinary economic importance for Portugal and Spain, and associated lithologies is related to several occurrences of highly mineralised sulphide waters (Calado & Chambel 1999).

The aim of this paper is to evaluate the geochemical processes controlling the composition of these waters, using forward and inverse geochemical models and considering the final composition as the result of the interaction between meteoric water and rocks.

2 GEOLOGICAL SETTING

The Iberian Massif is an important geological unit of the Iberian Peninsula and is sub-divided into several geostructural domains. The southernmost of these domains is the SPZ, characterised by the presence of three main units that are the result of the collision of the “middle European” and “North Europe/South Iberian” continents (Bard et al. 1980) accompanied by the closing of a Palaeozoic ocean just north of the SPZ (Fig. 1):

- the Pulo do Lobo Sub-Zone, in the northern part
- the Pyrite Belt
- the Baixo Alentejo Flysch Group, in the southern part

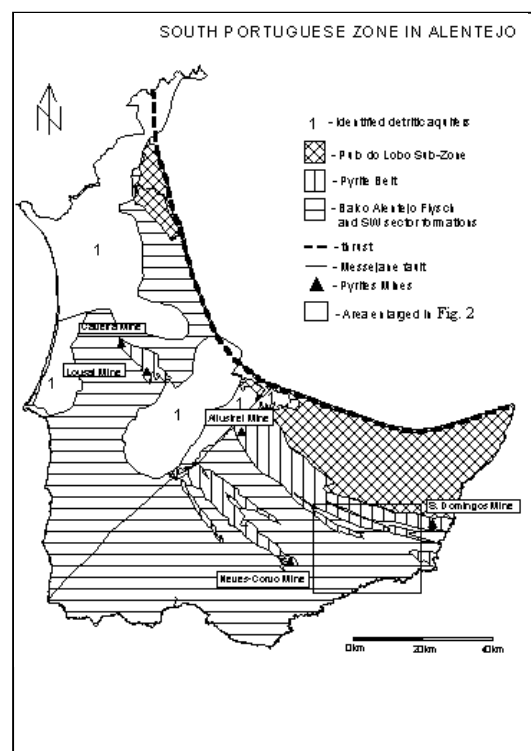


Figure 1. Tectono-stratigraphic unit of the South Portuguese Zone, in South Portugal, and its sub-divisions. The rectangle represents the area enlarged in Figure 2.

The Pulo do Lobo Sub-Zone is the oldest of all the units of the SPZ, consisting of phylites, quartzites and some layers of acid and basic volcanics. The Pyrite Belt consists of original sedimentary and volcanic rocks containing massive sulphides. It is composed of alternating decimetric to metric layers of acid and basic volcanic rocks, shales, graywackes, quartzowackes, siltstones, pellites, quartzites, sandstones, rare conglomerates and limestones and other types of rocks. South of the Pyrite Belt there are the most recent sediments of the SPZ, a turbiditic sequence corresponding to the Baixo Alentejo Flysch Group. The northernmost sub-division of this last Group is the Mértola Formation, followed by the Mira Formation and Brejeira Formation (Oliveira 1988, Silva 1989).

The collision was oblique and created an important left shear zone that forced, by transtension, the opening of grabens and the bimodal volcanism of the Pyrite Belt (Fig. 1).

3 HYDROGEOLOGY

The hard rock aquifers of this area, represented by metamorphic rocks, are scarce in water resources. The median of the well yields is less than 1 L/s and the quality is poor, with high concentrations of dissolved ions, mainly chloride and sodium.

In this context, some special highly mineralised sulphide waters occur in the Pyrite Belt and in the Mértola Formation. They have a Na-Cl matrix and are used for medicinal purposes in several places (Calado & Chambel 1999).

The area corresponds to a semi-arid climate, with a yearly precipitation near the 500 mm, occurring mainly in winter times, and high rates of evapotranspiration. The potential evapotranspiration can exceed 800 mm per year.

4 GEOCHEMICAL MODELLING

In this study forward and inverse geochemical modelling were used in order to evaluate the geochemical processes influencing the composition of those mineral waters. The study was based on the evolution of a meteoric water collected in Mértola (Fig. 2) that will possibly achieve the composition of two of these special waters collected in wells: the Águas Santas da Morena and Águas Santas de Besteiros. The compositions of the three waters are in Table 1 and Table 2.

The program NETPATH was used for inverse modelling (Plummer et al. 1991), and for both final waters the following constraining phases were assumed:

CO₂ gas + Pyrite + Calcite + Dolomite + NaCl + Goethite

The possibility of a concentration process by evapotranspiration was also considered since this may be likely in the upper part of the soil where high temperatures are reached in this semi-arid climate.

Among the possible models resulting from the modelling exercise, the results show that the evapotranspiration is not needed to explain the composition after meteoric water interaction with the phases considered. In the two final waters the results were identical (Table 3), both involving the oxidation of pyrite, dissolution of calcite, dolomite and NaCl and precipitation of goethite.

The water of Água Santa da Morena seems to be more evolved than that of Águas Santas de Besteiros. The great amounts of NaCl needed for the dissolution can be justified by its presence in the meta-sedimentary rocks, resulting of the accumulation

Table 1. Analysis of rainwater collected in Mertola.

	Unit	Rain water
Electric conductivity	µS/cm	18
pH		7
Total hardness	mg/l	14
Cl ⁻	mg/l	1.59
NO ₃ ⁻	mg/l	0.62
SO ₄ ²⁻	mg/l	1.19
Ca ²⁺	mg/l	1.33
Mg ²⁺	mg/l	0.21
K ⁺	mg/l	0.69
Na ⁺	mg/l	1.31
SiO ₂	mg/l	0.3
Fe	µg/l	20.35
Al	µg/l	26.5

Table 2. Analysis of the groundwater of Águas Santas da Morena and Águas Santas de Besteiros.

	Unit	A S Morena	A S Best.
Temp.	°C	21.7	21.3
pH		7.45	7.19
Eh	mV	-172	-185
EC	µS/cm	2160	1595
Tot. alcal.	ml/l	72.3	66.6
SiO ₂	mg/l	16.4	18.9
F ⁻	mg/l	1.6	1.7
Cl ⁻	mg/l	464	320
HS ⁻	mg/l	0.2	0.4
SO ₄ ²⁻	mg/l	139	66
HCO ₃ ⁻	mg/l	441	406
NO ₃ ⁻	mg/l	<0.05	0.24
Li ⁺	mg/l	0.29	0.21
Na ⁺	mg/l	390	261
K ⁺	mg/l	4.1	2.2
Mg ²⁺	mg/l	35.8	30.5
Ca ²⁺	mg/l	64.8	60.2
NH ₄ ⁺	mg/l	0.26	<0.06
Br ⁻	µg/l	1750	1292
I ⁻	µg/l	34	17
B	µg/l	310	164
As	µg/l	24	28
Mn	µg/l	83	38
Fe	µg/l	70	13

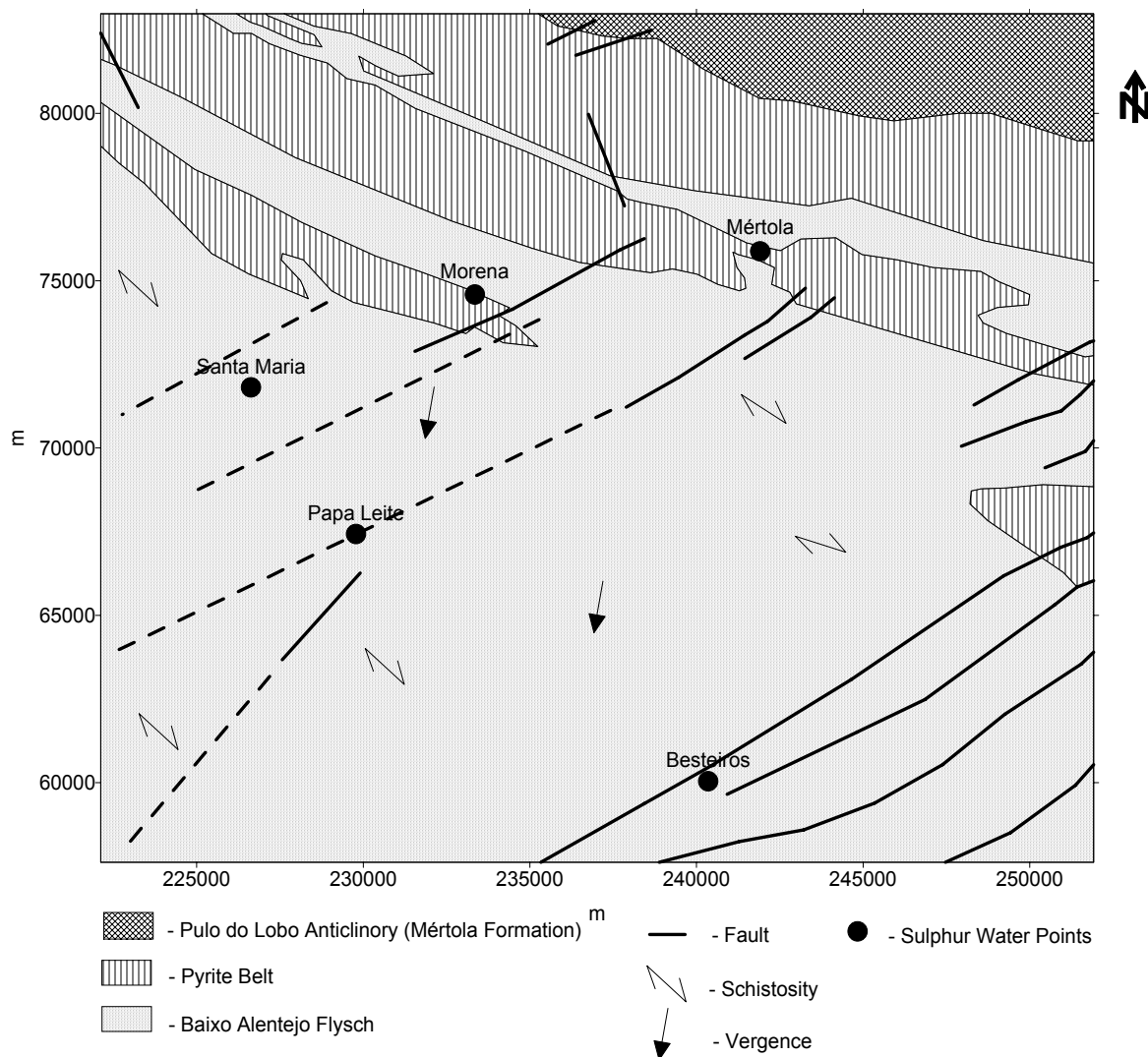


Figure 2. Map of the studied area, with the geological units and the water points identified.

of brines in Palaeozoic times during orogenesis.

The great amount of oxygen consumed in pyrite oxidation (each mole of pyrite needs 3.5 moles of oxygen) shows that this reaction occurs in an open system.

The product of pyrite FeS_2 oxidation, are iron and sulphate. The NETPATH interpretation shows that all the iron resulting from pyrite dissolution is used to form goethite:



To test the thermodynamic consistency of the reactions obtained by the NETPATH program, the geochemical modeling program PHREEQE (Parkhurst et al. 1980) was used. This is a model that can execute a great number of geochemical calculations and allows evaluating how the water composition

changes in response to reactions (mineral dissolution, gases phase equilibria, etc.) or to temperature changes, for example.

Table 3. Mass transfer values (α) for each mineral, calculated for the evolution of the rain water till reach the composition of two waters collected in Águas Santas da Morena and Águas Santas de Besteiros. The results were obtained with the program NETPATH (Plummer et al. 1991). Positive values represent dissolution and negative values precipitation (in mmol/kg).

	A S Morena	A S Besteiros
CO_2	2.716	3.619
Pyrite	0.718	0.338
Calcite	2.055	1.382
Dolomite	1.466	1.247
Ionic change	1.935	1.159
NaCl	13.063	8.992
Goethite	-0.718	-0.338

In the present case, the goal was to verify if the meteoric water interacting with the mineralogical component, indicated by the NETPATH program, and with all the hydrochemical reactions that could possibly arise along the way, could result in the final composition of the two waters under consideration.

These types of models are able to calculate the equilibrium composition of the aqueous solutions with the minerals, add reagents and calculate the pH and electronic activity as function of the reactions, temperature or gas pressure changes.

The PHREEQE program had proved that the set of reactions obtained by inverse modelling with NETPATH is thermodynamically plausible. So, the proposed reactions are acceptable and seems likely that all the mineral weathering is occurring without the influence of the evapotranspiration (Table 4). The final composition achieved is very similar to the composition of the final waters for some selected ions (see Table 3).

Although it is not possible to confirm that this model is the only one that can explain the observed compositions, the set of reactions is thermodynamically feasible and the phase associations plausible in the local environment where the waters occur.

Table 4. Estimated values, based on the hydrochemical model program PHREEQE (Parkhurst et al. 1980), using as initial water the rain water of Table 1 and considering its interaction with the mineralogical association defined as possible by the NETPATH program, referred to in the text. The results of some ions show that the estimated values are close to the real results presented in Table 2.

	Units	A S Morena		A S Besteiros	
		Real	Estimated	Real	Estimated
Ca ²⁺	mg/l	64.8	56.8	60.2	58.2
Mg ²⁺	mg/l	35.8	31.3	30.5	32.1
Na ⁺	mg/l	390	377	261	244
Cl ⁻	mg/l	464	462	320	321
SO ₄ ⁻	mg/l	139	115	66	54.5
HCO ₃ ⁻	mg/l	441	386	406	365

5 CONCLUSIONS

Inverse and forward geochemical modelling shows that the special type of composition represented by the Morena and Besteiros mineral waters can be explained by the dissolution of calcite and dolomite which provides a source of carbon, calcium and magnesium, pyrite oxidation, which provides a source for sulphur and enhances carbonate dissolution by proton release, ionic exchange and halite dissolution.

REFERENCES

- Bard, J. Burg, J. Matte, P. & Ribeiro, A. 1980. La Chaîne Hercynienne d'Europe Occidentale en termes de tectonique des plaques: *Mem. Bur. Rech. Geol. Min. Fr.* 6(26): 233-246.
- Calado, C. & Chambel, A. 1999. Un unexpected mineral sulphide water type in the Iberian Pyrite Belt (South Portugal), In M. Fendeková & M. Fendek (eds), *Hydrogeology and land use management* - Proc. XXIX Congress of IAH, Bratislava, 6-10 September 1999: 671-676. Bratislava: IAH.
- Chambel, A. 1999. Hidrogeologia do concelho de Mértola. *Doctoral Thesis*. Évora: Universidade de Évora.
- Oliveira, J.T. 1988. Contribuição para o Conhecimento da Evolução Tectono-Estratigráfica da Zona Sul Portuguesa em Portugal. *Doctoral Thesis*. Lisboa: Serviços. Geológicos de Portugal.
- Parkhurst, D.L. Thorstenson, D.C. & Plummer, L.N. 1980. PHREEQE - A computer program for geochemical calculations: *U.S. Geological Survey Water-Resources Investigations Report*: 80-96
- Plummer, L.N. Prestemon, E.C. & Parkhurst, D.L. 1991. An interactive code (NETPATH) for modeling net geochemical reactions along a flow path: *U.S. Geological Survey Water-Resources Investigations Report*: 91-4087
- Ribeiro, A. 1979. Le cadre structural et géotectonique; Essay de reconstitution paléogéographique par cycles orogéniques. Le cycle hercynien. In A. Ribeiro et al. (eds) *Introduction à la géologie générale du Portugal*: 8-45. Serviços Geológicos de Portugal.
- Silva, J.B. 1989 Estrutura de uma Geotransversal da Faixa Piritosa: Zona do Vale do Guadiana. Estudo da Tectónica Pelicular em Regime de Deformação Não Coaxial. *Doctoral Thesis*. Lisboa: Universidade de Lisboa