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# Geochemical evolution of groundwater in metamorphic rocks of Trás-Os-Montes, Portugal

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**ABSTRACT:** Inverse and forward geochemical modelling were used in order to identify the water-rock inter-action processes that control the geochemical evolution of groundwater occurring in metamorphic rocks of Trás-os-Montes (Portugal). For such purpose, physical and chemical data from 30 water samples, collected in springs and wells in Paleozoic schists, quartzites and metavolcanics from hercynian shield in NW of Iberian Meseta (NE of Portugal). The results obtained suggest that calcium bicarbonate composition, characteristic of most of the samples, can be explained by plagioclase, biotite or chlorite and carbonate dissolution (the last one only present in rock cement) in an open system, with precipitation of clay minerals (usually kaolinite). A small group of samples shows a significant deviation from the general pattern, with enrichment in total mineralization, especially in DIC,  $\text{SO}_4^{2-}$  and  $\text{Na}^+$ . Isotopic data point to a significant contribution of a carbon source depleted of  $^{14}\text{C}$  and enriched in  $^{13}\text{C}$ . Modelling results suggest that the composition of this group could be explained by pyrite oxidation and by plagioclase and carbonate dissolution.

## 1. INTRODUCTION

This paper describes some of the results of a modelling study (Pereira 1999) to identify geochemical reactions controlling water chemistry in metamorphic rocks of hercynian shield in NW of the Iberian Peninsula (NE of Portugal).

Inverse and forward geochemical modelling were used in order to identify the most probable reactions that could explain the final composition of groundwaters, based on the knowledge of mineral composition of rocks, chemical data of water samples and speciation calculations.

## 2. GEOHYDROLOGIC SETTING

The geology of the area is rather homogeneous and is dominated by metasedimentary sequences (phyllites, greywakes, and quartzites) and metavolcanics. In the northern part of the area some hercynian granites are present.

The region is separated from the coast by the presence of two mountainous ridges, give a continental character to the climate. The mean annual precipitation ranges from 500 mm/year to 1300 mm/year and the mean annual temperature between 10 °C and 14 °C.

The wells located on metamorphic rocks are characterised by higher yields (1.5 L/s in average)

than the ones located on granites (0.2 L/s in average) (Pereira & Almeida 1994).

The chemical features of waters from metamorphic rocks were characterised on the basis of physical and chemical data from 30 water samples collected in springs and wells (Fig. 1).

Hydrochemical facies vary between sodium chloride, in a few springs, to calcium bicarbonate, in most of the well samples (Fig. 2). The electrical conductivity ranges from 30  $\mu\text{S}/\text{cm}$  to 1000  $\mu\text{S}/\text{cm}$  with a median of 250  $\mu\text{S}/\text{cm}$  and the pH between 5.5 and 9.3 with median of 7.

In order to evaluate the equilibrium state of the water in relation to the minerals present in rocks, speciation calculations were made using WATEQ (Plummer et. al. 1992).

The saturation indices obtained indicate oversaturation with respect to quartz and chalcedony and frequently to goethite and epidote.

A few cases of oversaturation with respect to calcite, dolomite, talc, and tremolite were also observed.

## 3. MASS BALANCE REACTION MODELS

Inverse modelling calculations provide a way to evaluate the most probable chemical reactions between water and minerals. The mass balance calculations were made using chemical data of the recharge water and downgradient wells, or between

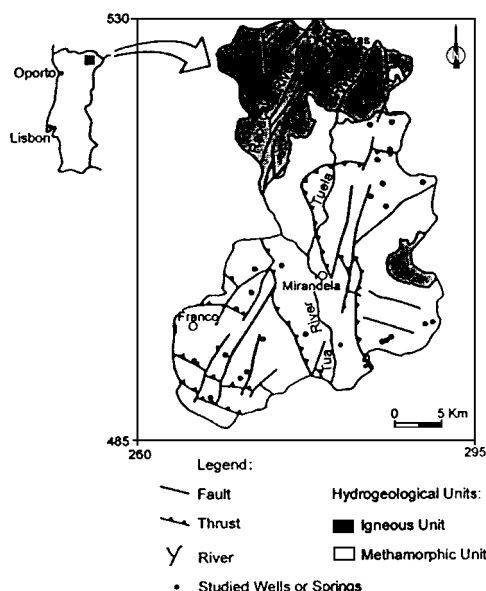


Figure 1. Map of the study area with location of sampling points. (Hydrogeological Units according to Pereira 1999).

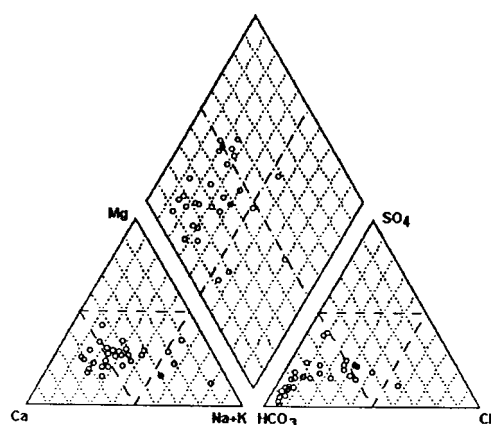


Figure 2. Piper diagram for waters from metamorphic rocks of NE of Portugal.

two wells situated in the same flowpath NETPATH (Plummer et al. 1992). The plausible phases were selected according to the mineralogical composition of the rocks and the results of the speciation model.

In order to verify the kinetic and thermodynamic consistency of results forward geochemical modelling was conducted using PHREEQE (Parkhurst et al. 1980) and the sequence of reactions needed to justify the mass balance obtained by the selected inverse model were chosen.

## 4. GEOCHEMICAL INVERSE MODELS

### 4.1 Sodium chloride waters

To simulate the evolution from rainwater and sodium chloride spring water we used chemical data for two samples: rainwater and a spring water from Franco village (Table 1).

Table 1. Chemical variation between rainwater and spring water of Franco village in Trás-os-Montes (Portugal).

Mineral element	Rain (mmol/L)	Spring (Franco) (mmol/L)	Variation (mmol/L)
C	0.1103	0.7442	0.6339
Al <sup>3+</sup>	-	-	-
Mg <sup>2+</sup>	0.0021	0.0391	0.0370
Na <sup>+</sup>	0.0152	0.1131	0.0979
K <sup>+</sup>	0.0036	0.0077	0.0041
Cl <sup>-</sup>	0.0099	0.1241	0.1142
Si <sup>4+</sup>	0	0.1215	0.1215

For the inverse modelling NETPATH program options were used to select mineral species, phases, evaporation and ion exchange according to the mineralogical composition of rocks and anticipated geochemical processes (Table 2).

Table 2. Chemical species, mineral phases and parameters selected to simulate the evolution between rainwater and NaCl spring water of Franco village in Trás-os-Montes (Portugal).

Species	Phases	Parameters
C, Cl <sup>-</sup> , Na <sup>+</sup>	Plagioclase (An <sub>38</sub> ),	Ion exchange (Ca/Na)
Mg <sup>2+</sup> , K <sup>+</sup>	Biotite, Chlorite,	Evaporation
Al <sup>3+</sup> , Si <sup>4+</sup>	CO <sub>2</sub> (g), Illite, Kaolin-ite, Silica, NaCl	

From several models obtained the following one is the most probable.

Minerals	Rain→Spring (Franco) (mmol/L)
Plagioclase (An <sub>38</sub> )	+0.127(*)
Biotite	+0.012
Kaolinite	-0.036
Illite	-0.051
NaCl	+0.053
Exchange Ca <sup>2+</sup> /Na <sup>+</sup>	-0.064
Concentration factor	7.188

\* + Dissolution of minerals

- Precipitation of minerals.

This model corresponds to plagioclase, biotite and sodium chloride dissolution and precipitation of kaolinite and illite. Some cation exchange between Ca<sup>2+</sup> and Na<sup>+</sup> is admitted.

The concentration factor corresponds to an infiltration rate of about 14%, which agrees with other methods of infiltration calculation (Pereira 1999).

### 4.2 Calcium bicarbonate waters

The geochemical evolution from rainwater to calcium bicarbonate water was modelled with four well samples.

The chemical composition of the well waters is presented in Table 3.

Table 3. Chemical composition of four calcium bicarbonate waters from wells located in metamorphic rocks of Trás-os-Montes (Portugal).

Mineral element	Passos (mmol/L)	Orelhão (mmol/L)	Pereira (mmol/L)	Carvalhal (mmol/L)
C	1.490	1.875	2.551	2.939
Ca <sup>2+</sup>	0.145	0.389	0.891	0.789
Al <sup>3+</sup>	-	-	-	-
Mg <sup>2+</sup>	0.111	0.243	0.276	0.309
Na <sup>+</sup>	0.213	0.526	0.535	0.801
K <sup>+</sup>	0.023	0.038	0.033	0.046
Cl <sup>-</sup>	0.104	0.127	0.172	0.200
Si <sup>4+</sup>	0.226	0.443	0.534	0.511

Chemical species, phases and selected parameters for NETPATH modelling are shown in Table 4. These are the same as in the last example, except for the inclusion of calcite, present in rock cement.

Table 4. Chemical species, mineral phases and parameters selected to simulate the evolution between rainwater and calcium bicarbonate waters from wells located in metamorphic rocks of Trás-os-Montes (Portugal).

Species	Phases	Parameters
C, Cl <sup>-</sup> , Na <sup>+</sup>	Plagioclase (An <sub>38</sub> ),	Ion exchange (Ca/Na)
Ca <sup>2+</sup> Mg <sup>2+</sup>	Biotite, Chlorite, Cal-	Evaporation
K <sup>+</sup> , Al <sup>3+</sup>	cite, CO <sub>2</sub> (g), Illite,	
Si <sup>4+</sup>	Kaolinite, Silica, NaCl	

Although the concentration of aluminium was unknown this element was included in the inverse models. This is justified because aluminium is usually conserved in the weathering reactions and so the changes in the solutions are in general negligible when compared with mass transfer among phases.

The four samples, Passos, Orelhão, Pereira and Carvalhal, have different degree of mineralization (80, 182, 253 and 252 µS/cm respectively) but have undergone similar geochemical evolution. For that reason the same species, phases and parameters were used to model the evolution between rainwater and each of the samples.

The selected models obtained using NETPATH show that the plausible reactions include:

- dissolution of CO<sub>2</sub>, NaCl, Calcite, Plagioclase (An<sub>38</sub>) and Biotite;
- precipitation of Kaolinite and Illite;
- cation exchange, between Ca<sup>2+</sup> and Na.

The concentration factor corresponds to an infiltration rate varying between 15 % and 5% of annual precipitation.

## 5 FORWARD MODELS

The forward models were based on the inverse models obtained by using NETPATH and were per-

formed using the PHREEQE program. They included:

1. Evaporation, with a concentration factor of 13 times
2. Dissolution of 0.922 mmol of plagioclase (An<sub>38</sub>) and 0.212 mmol of biotite maintaining the equilibrium with kaolinite and goethite and allowing the dissolution of calcite (up the saturation index of -1.2). The CO<sub>2</sub> partial pressure considered was 10<sup>-2.1</sup> atm. This reaction was added in six steps: 8%-20%-40%-60%-80%-100%.

In Table 5 are the results of these models for sodium, carbon and pH.

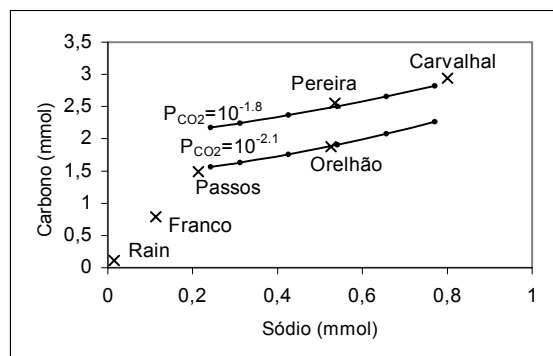


Table 5. Results of forward models proposed for evolution from rainwater to groundwater in metamorphic rocks of Trás-os-Montes.

% of reaction added	Sodium (mmol)	Carbon (mmol)	pH
8%	0.242	1.563	6.98
20%	0.311	1.631	7.00
40%	0.426	1.760	7.04
60%	0.541	1.908	7.08
80%	0.656	1.077	7.13
100%	0.711	1.265	7.17

Figure 3 presents the carbon and sodium values for the water samples and the evolution line for the proposed geochemical models.

Figure 3. Geochemical evolution of groundwater associated with metamorphic rocks in Trás-os-Montes.

Trend lines represent the modelled water compositions and the x symbols observed compositions.

Sodium chloride water from Franco spring has low values of sodium and carbon, since it is near the beginning of the evolution path. Orelhão groundwater results from evolution of Passos water.

In the case of Pereira and Carvalhal, the evolution process seems to be related to different infiltration conditions.

A soil with a higher content of organic matter could explain the more elevated carbon present in the water. Based in this assumption, the same model was run using a partial pressure of CO<sub>2</sub> of 10<sup>-1.8</sup> atm.

The respective evolution line, present in Figure 3, shows that Carvalho is the evolution of Pereira groundwater.

## 6 SULPHATE ENRICHED WATER SAMPLES

A few water samples are characterised by much higher mineralization (about 1000  $\mu\text{S}/\text{cm}$ ) due to special enrichment in DIC,  $\text{SO}_4^{2-}$  and  $\text{Na}^+$  (Pereira & Almeida 1996).

Hydrochemically they are of sodium bicarbonate type and are all associated with sulphide mineralization present in quartz veins in the schists.

The principal chemical components of one selected sample (Freixeda) are compared with rain-water composition in Table 6.

Table 6. Chemical variation between rainwater and sodium bicarbonate groundwater of Freixeda in Trás-os-Montes (Portugal).

Element	Rain (mmol/L)	Freixeda well (mmol/L)	Variation (mmol/L)
C	0.110	5.90	5.79
$\text{Ca}^{2+}$	0.008	0.5	0.492
$\text{Al}^{3+}$	-	-	-
$\text{Mg}^{2+}$	0.002	0.68	0.678
$\text{Na}^+$	0.015	8.97	8.955
$\text{S}^{6+}$	0.01	2.2	2.19
$\text{Fe}^{3+}$	0.001	0.002	0.001
$\text{Si}^{4+}$	0	0.31	0.31

The results of geochemical inverse model are:

1. Carbon dioxide dissolution.
2. Pyrite oxidation by  $\text{O}_2$ , in open system, with precipitation of goethite.
3. Calcite and dolomite dissolution.
4. Plagioclase dissolution, with kaolinite and silica precipitation.
5. Ionic exchange  $\text{Ca}^{2+}/\text{Na}^+$ .

Oxidation of pyrite, requires an elevated quantity of oxygen to occur (about 120 mg of  $\text{O}_2$  is necessary to oxidise 1 mmol of pyrite) which means that it should happen in an open system.

This reaction is responsible by the high content in sulphate and, as a proton donor, promotes the dissolution of silicates (with precipitation of kaolinite and silica) and carbonates.

All these reactions led to a mineralization that is very distinct from the normal compositions of the area.

To explain the elevated concentration of carbon in this water, isotopic analyses of  $^{13}\text{C}$  and  $^{14}\text{C}$  were conducted (Pereira & Almeida 1997). A value of 6.75 TU indicates modern water.

Carbon isotopes indicates a low  $^{14}\text{C}$  content ( $\delta^{14}\text{C} = 37.88$  pmc) and a source of heavy carbon ( $\delta^{13}\text{C} = -8.49$  ‰). These values indicate source of older carbon without  $^{14}\text{C}$  and enriched in  $^{13}\text{C}$ , such as by dissolution of carbonate minerals.

The geochemical simulations give thermodynamically consistent results which compare well with real values, including isotopic data.

## 7 HYDROCHEMICAL FACIES VERSUS GEOCHEMICAL EVOLUTION

Based on geochemical modelling results and observed hydrochemical facies, different evolution stages were defined for groundwater related to metamorphic rocks in NW Portugal:

### A. SODIUM CHLORIDE WATERS:

Have low degree of evolution and a shallow circulation.

Dissolution of very small quantities of plagioclase and biotite with precipitation of illite and kaolinite is consistent with the water chemistry.

### B. CALCIUM BICARBONATE WATERS:

Correspond to a higher degree of geochemical evolution and a deeper circulation.

Hydrolysis of silicates and dissolution of carbonates could explain the composition and the higher mineralization.

### C. SODIUM BICARBONATE WATERS:

These waters have a very high conductivity (1000  $\mu\text{S}/\text{cm}$ ) and are associated with oxidation of sulphide minerals in schists where some carbonate minerals are present in rock cement.

## 8 CONCLUSIONS

The most frequent rock-water interactions in metamorphic rocks of Trás-os-Montes (Portugal) are the dissolution of plagioclase and biotite or chlorite, which induce the precipitation of clay minerals, usually kaolinite.

In some lithologies, carbonate minerals (calcite) are present as cementing material and, in these cases, the mineralization of water samples is higher and attributed to the easy dissolution of carbonates.

When sulphide minerals are present, associated with mineralised quartz veins, the oxidation of these minerals gives a high concentration of dissolved sulphate and the  $\text{H}^+$  ions released during oxidation promote the dissolution of silicate minerals and carbonates. Under such hydrogeologic conditions, the waters have a high concentration in inorganic carbon,  $\text{SO}_4^{2-}$  and  $\text{Na}^+$ .

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