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Andrzej Zuber
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Ewa Kmieciak



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Hydrogeochemical characteristics of mineral and thermal waters

title: **Distribution and variation of geochemical signatures in mineral waters from the Portuguese mainland**

author(s): **Hans G. M. Eggenkamp**
Centro de Petrologia e Geoquímica, Instituto Superior Técnico, Universidade
Técnica de Lisboa, Portugal, hermanus.eggenkamp@ist.utl.pt

José M. Marques
Centro de Petrologia e Geoquímica, Instituto Superior Técnico, Universidade
Técnica de Lisboa, Portugal, jose.marques@ist.utl.pt

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ABSTRACT

In the present study we propose the use of the chemical composition of mineral/thermal waters as a tool for geochemical mapping. In this case, unlike conventional geochemical mapping, where surface samples (such as stream water, sediments and soils) are analysed, by analysing mineral and thermal waters, the deeper geology and the chemical processes that take place at depth are monitored. Using this approach it is shown that chemical characteristics of mineral/thermal waters follow regional variations ascribed both to the geology and geochemical processes that take place in the mapped area. This approach is tested in the Portuguese mainland, a country with a very high density in mineral and thermal waters. The preliminary results presented here show that the chemical composition of mineral and thermal waters reflects the chemical geology of the country.

INTRODUCTION

Inventories of the richness in mineral and thermal springs in Portugal were already made centuries ago. Henriques (1726) published the first countrywide overview of waters with therapeutic characteristics. This list was recently reviewed at the Institute of Social Sciences of Lisbon University, who published an on-line database of 668 locations with one or more waters with therapeutic qualities, mainly according to local tradition (Bastos, 2008). The chemistry of the most important of these “medicinal-mineral” waters have been analysed from early on, starting in the 19th century. Most mineral and thermal waters with a concession were analysed by Charles Lepierre and António Herculano de Carvalho in the first half of the 20th century (see e.g. Acciaiuoli, 1952). Several modern studies are known, but they all only have a local/regional focus (e.g. Marques et al. 2003, 2006, 2008, 2010). Therefore, we believe that it is extremely important to have a countrywide overview of the chemistry of mineral and thermal waters.

Mineral waters can be defined as natural (spring) waters that show a distinct chemistry and which composition and temperature are not varying over time, indicating a deep source. Mineral waters normally are issued along faults and have a recharge area which is often several kilometres from the springs/boreholes. The water gets its chemical composition as a result of water-rock interaction between the recharge area and the discharge location. Using stable isotope ratios of hydrogen and oxygen Aires-Barros et al (1995) showed that the original infiltrating water in the recharge areas is rainwater which contains only very little dissolved solids. Marques et al (2003, 2006, 2008, 2010), using this technique, showed that the recharge area in many Portuguese cases (e.g. Caldas do Moledo, Chaves, Cabeço de Vide, Caldas da Rainha) is rarely more than 10 km from the mineral springs/boreholes. As such, the chemistry of the mineral waters represents only the results of water-rock interaction of this relatively small area fairly close to the springs/boreholes. This way the water is representative for the water-rock interaction in an area close to the springs, and as such it could potentially be used for geochemical mapping.

Geologically the Portuguese mainland can roughly be divided in two regions (Figure 1). Along the west and south coasts Mesozoic and Cenozoic sedimentary rocks are found. To the east and north of this region, Proterozoic and Palaeozoic bedrocks are found which are intruded in large areas (especially widespread in the north) with Palaeozoic magmatism.

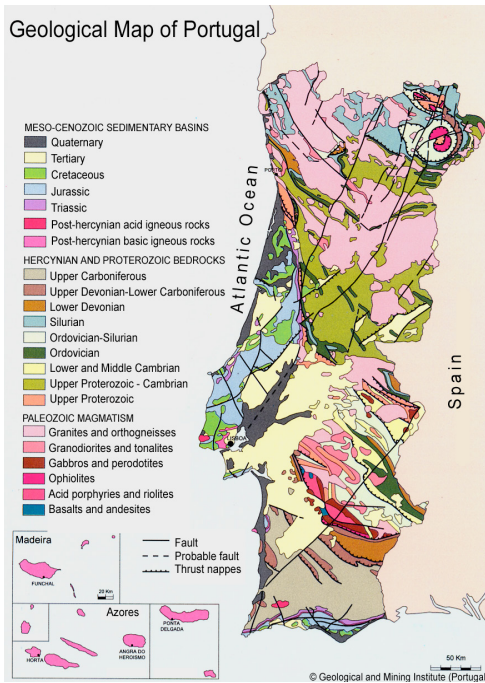


Figure 1. Geological map of Portugal.

Geochemical mapping using mineral and thermal waters is potentially a good complement to the more conventional geochemical mapping techniques. In conventional geochemical mapping techniques the chemical composition of surface materials, such as stream water, stream sediments or soils (Inácio et al., 2008) is normally analysed. As water–rock interactions take place to depths of about 2 kilometres or more (Marques et al., 2003) mineral and thermal waters give us the possibility to take into account chemical processes that take place at a greater depth, and show effects of the deeper geology.

DATA COLLECTION

Analyses from Portuguese mineral and thermal waters were collected, from published literature and the internet. We collected 822 analyses from 606 springs from about 500 locations on the Portuguese mainland. Multiple analyses from the same source (from different years) were averaged. Compositions from sources from which multiple analyses are available (sometimes representing a period of over 100 years) generally showed only little variation over time, showing that mineral and thermal waters have constant compositions, and also that older analyses are of equal quality as more modern analyses. Data were analysed using Golden Software's Surfer® program to produce maps showing the distribution of the parameters over the country. The oldest analysis is from 1850 (Pimentel, 1852), and the majority of data have been taken from important classic publications such as Luzes et al. (1930, 1934, 1935), Acciaiuoli (1952) and Almeida & Almeida (1966, 1970, 1975, 1988) which represent the period from about 1890 until 1970. More recent data are taken from papers reporting individual areas (e.g. Marques et al., 2003, 2006, 2008; Ferreira Gomes, 2001; Calado & Chambel, 1999). Most data from the

Alentejo region in the south of Portugal are taken from ERHSA (2000). Considering the great variety of the publications it is to expect that the quality of the dataset is very diverse. For example from virtually all analyses only a limited number of parameters have been measured. Most importantly many of the “general” parameters (e.g. NO_3^- , F^- and HS^-) often are below the detection limit. Other parameters are just not measured for all samples. For example in the works by Almeida and Almeida (1966, 1970, 1975, 1988) the standard analyses consisted of Na, Ca, Mg, Fe, Cl, HCO_3^- and SO_4^{2-} , while NO_3^- , F and HS were only determined (or reported) while above the detection limit. Most strikingly K is not normally reported. In this contribution we present maps for Total Dissolved Solids (TDS), determined for each spring by adding up analytical results for all known parameters, and for Na, Cl, Ca, $\text{HCO}_3^- + \text{CO}_3^{2-}$ (total carbonate) and F. Of these only the F concentration is not known for the majority of springs. In those cases where F is not known it is assumed that it was not measured or reported because the value is below the detection limit, and in the database the value of 0.01 mg/l is entered for F. Na, Cl and Ca are known in almost all locations, while the carbonate content is calculated from the ion balance. The reason for doing this is that, in several (mainly older) analyses, the carbonate content is reported including the free carbon dioxide, and as such the sample was way out of balance. As most analyses have an acceptable ionic balance, the total carbonate content is determined by calculating the ion balance without the carbonate species, and subsequently balanced by adding carbonate species. For the majority of samples the calculated and measured sum of carbonate species is in very good agreement, indicating the acceptability of this approach.

RESULTS AND DISCUSSION

Total dissolved solids (TDS)

To show the general variation in composition, distribution of the total dissolved solids over the country is shown in Figure 2a. Clear differences are shown over the country. Highest TDS values are found in areas where salt deposits from the Lower Jurassic Margas da Dagorda formations do occur. These formations are mainly ascribed to the western basin north of Lisbon and along the south coast (Algarve region). Highest TDS values are found in locations where salt diapirs do approach the surface very closely such as in Rio Maior where the diapir is so shallow that the spring contains 137 g/l TDS (containing 98% NaCl) and is used to extract and commercialise the salt (Eggenkamp et al., 2010).

Na/Cl

Comparing the two maps representing the distribution of Na and Cl (Fig. 2b and 2c) in the mineral and thermal waters one can conclude that while in the south and the west of the country the two maps are more or less similar, in the north of the country large regions with very low Cl concentrations are found, while Na is in many samples significantly more concentrated. These differences can be explained by the large difference in geology and structure of the two parts of the country. In the south and the west both Na and Cl are regulated by dissolution of salt deposits from the lower Jurassic. In the north the geology is dominated by granite rocks which intruded into Palaeozoic rocks, which are heavily folded and metamorphised. In this area many very deep faults are found. Through these faults mantle CO_2 and other gases escape to the surface and dissolve in the shallower groundwaters (Carreira et al., 2010).

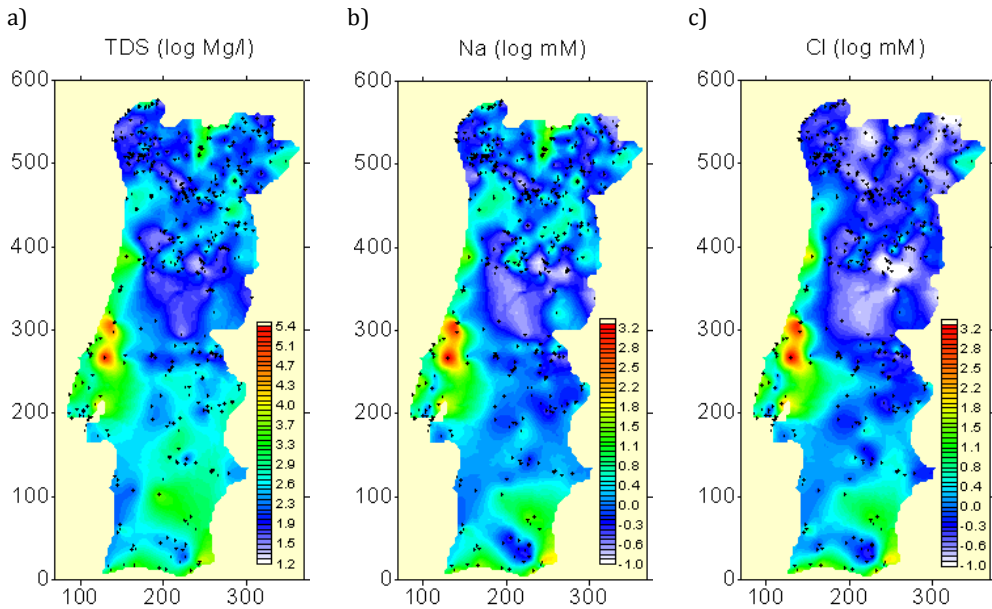


Figure 2. Distribution of a) TDS; b) Na; c) Cl in mineral and thermal waters from the Portuguese mainland.

As granitic rocks contain more Na than Cl, in this area water-rock interaction results in relatively increased Na contents in waters. Mantle CO₂ balances the Na mainly as HCO₃ in this water, resulting in Na-HCO₃ dominated waters. Along the deepest faults the amount of CO₂ escaping can be so high that the waters are supersaturated in CO₂ and can be described as Na-HCO₃-CO₂ type waters (Marques et al., 2006). As Na is the major cation in the majority of mineral and thermal waters issuing in the Portuguese mainland there is a good agreement between the TDS and the Na maps for the Portuguese mainland. Only in the northern part of the Alentejo region (southern half of Portugal, north of the Algarve) Ca is the dominant cation in most mineral and thermal waters, resulting in one of the few divergences between the TDS and Na maps.

Ca/HCO₃/F

The distribution of Ca (Fig. 3a) in the Portuguese mineral and thermal waters is also clearly related to the geology of the country. Roughly three regions can be recognised: high concentrations in the west, low concentrations in the north and intermediate concentrations in the south. The high concentrations in the west are also the result of dissolution of evaporite minerals (mainly gypsum) from the Lower Jurassic *Margas da Dagorda* formation. In the southern half of the country Ca concentrations are intermediate due to dissolution of carbonate minerals. In this area, the HCO₃ concentrations (Fig. 3b) are also relatively high (with the same order of magnitude as Ca), while in the western part of the country HCO₃ is significantly lower. In the north of the country Ca shows very low concentrations. This is the result of water-rock interaction between water and calcium-poor rocks (e.g. granites and schists). In the northeast of the country ultramafic Ca-rich rocks are present, which is reflected in the slightly higher Ca concentrations in mineral and thermal waters from that area. It is encouraging that the Ca distribution on this mineral and thermal water map correlates well with the Ca distribution on the soil geochemical map (Inácio et al., 2008).

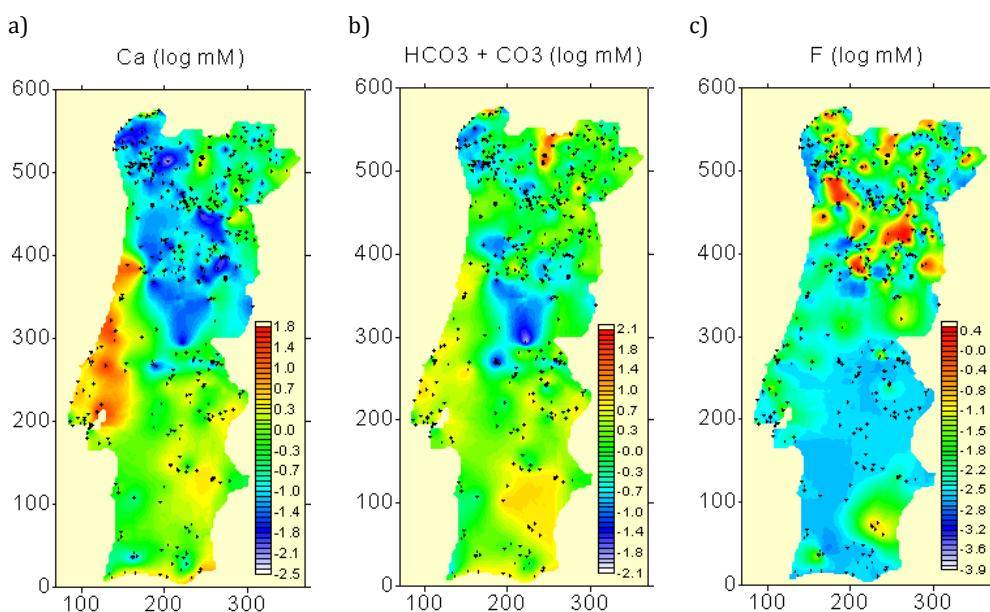


Figure 3. Distribution of a) Ca; b) (bi)carbonate; c) F in mineral and thermal waters from the Portuguese mainland.

High bicarbonate concentrations which are found in some areas in the north of the country are related to very deep faults where mantle CO_2 escapes to the surface. Fluoride concentrations in mineral and thermal waters are normally restricted by Ca due to the low solubility product of fluorite (CaF_2). As Ca has very low concentrations in mineral and thermal waters from north Portugal, there is potential for higher F concentrations. Indeed higher F concentrations are found in this area (Figure 3c). Fluoride concentrations are especially high along major faults in the granitic areas, with maximum values above 20 mg/l.

CONCLUSIONS

It is shown that maps prepared from the chemical composition of mineral and thermal waters do describe the geology and chemical processes properly. Variations in chemical parameters found on maps can be explained with the known variations in geology in the studied regions. Based on the present dataset more maps can be produced and it is encouraged that new analyses will be done on mineral and thermal waters preferably by ICP-MS so that also minor and trace components can be determined.

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