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## **Extended Abstracts**

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**Hydrogeochemical characteristics of mineral and thermal waters**

title: **Stable isotopes of dissolved inorganic carbon and sulphur-bearing species in mineral and thermal waters from central Portugal**

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## 1. INTRODUCTION

There are many springs of mineral and thermal waters associated with the Hercynian Beiras Batholith granites of Central Portugal, which intruded meta-sedimentary rocks of Palaeozoic age. These low enthalpy thermomineral systems reflect the deep circulation of meteoric waters in fractured granites. All waters studied have similar chemical characteristics: pH varies between 8 and 9.3;  $\text{Na}^+$  is the dominant cation (representing over 90% of the total cations);  $\text{HCO}_3^-$  is the most representative anion, followed by  $\text{Cl}^-$  and/or  $\text{F}^-$  (always > 10 mg/L); and all of them are strongly reduced (as revealed by reduced sulphur ( $\text{HS}^-$ ) and reduced nitrogen ( $\text{NH}_4^+$ )) and have very low  $\text{Mg}^{2+}$  contents (usually < 0.15 mg/L). Temperature ranges between 18 and 66°C, and total dissolved solids between ~200 and ~500 mg/L. Both natural springs and boreholes as deep as 500 meters were studied.

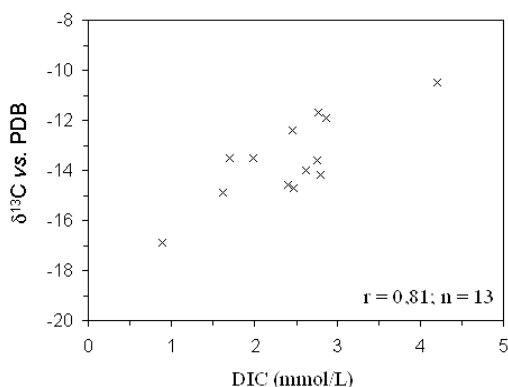
## 2. EXPERIMENTAL PROCEDURES

Samples for  $^{13}\text{C}/^{12}\text{C}$  measurements were obtained by precipitation of the total dissolved inorganic carbon (DIC) as  $\text{SrCO}_3$  by means of  $\text{SrCl}_2$ . The precipitate was filtered and dried without any contact with atmospheric air. Gas extraction was done by acidification with 103%  $\text{H}_3\text{PO}_4$  and purification by cryogenic distillation. Dissolved sulphide was collected as  $\text{ZnS}$  precipitated by addition of zinc acetate to the water, and later converted to  $\text{Ag}_2\text{S}$  by means of  $\text{AgNO}_3$ . Following filtration of the  $\text{ZnS}$ , the remaining water was acidified and treated with  $\text{BaCl}_2$  to precipitate dissolved sulphate as  $\text{BaSO}_4$ . All isotopic analyses were done at the Stable Isotope Laboratory, University of Salamanca. The isotopic values are reported in the usual delta notation ( $\delta\text{‰}$ ) relative to V-PDB ( $\delta^{13}\text{C}$ ) and CDT ( $\delta^{34}\text{S}$ ).

## 3. RESULTS AND DISCUSSION

### 3.1. $\delta^{13}\text{C}$ of the dissolved inorganic carbon

The  $\delta^{13}\text{C}_{\text{VPDB}}$  values of the total dissolved inorganic carbon (TDIC) in groundwaters range from -16.9 to -10.5‰. This range of  $\delta^{13}\text{C}_{\text{DIC}}$  values is accompanied by a large variation of TDIC contents. The observed linear relation between TDIC and  $\delta^{13}\text{C}$  (Fig. 1) suggest that inorganic carbon in the studied waters derives from more than one source: measured  $\delta^{13}\text{C}$  values can not be attributed to isotope fractionation between soil- $\text{CO}_2$  and DIC only.

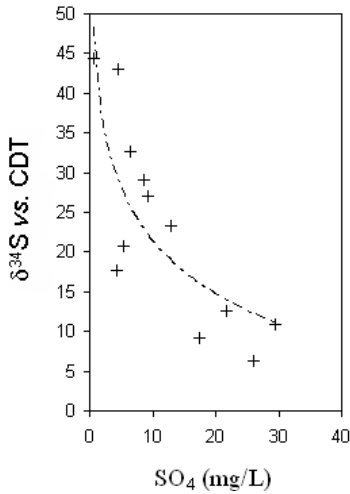


**Figure 1.** Relation between Total Dissolved Inorganic Carbon and  $\delta^{13}\text{C}$ .

A gaseous source, isotopically heavier than the organic C of soil-CO<sub>2</sub> (such as regional deep mantle-derived or metamorphic flux of CO<sub>2</sub>), must be invoked.

### 3.2. $\delta^{34}\text{S}$ of sulphur-bearing species ( $\text{SO}_4^{2-}$ ; $\text{HS}^-$ )

The  $\delta^{34}\text{S}$  of sulphur-bearing species shows a remarkable variability:  $\delta^{34}\text{S}_{\text{CDT}}$  ( $\text{SO}_4^{2-}$ ) ranges from +6 to +44 ‰;  $\delta^{34}\text{S}_{\text{CDT}}$  ( $\text{HS}^-$ ) ranges from -25 to +2‰. Sulphate is always enriched in  $^{34}\text{S}$  relative to reduced sulphur ( $\text{HS}^-$ ). This isotopic difference ( $\Delta^{34}\text{S} = \delta^{34}\text{S}(\text{SO}_4^{2-}) - \delta^{34}\text{S}(\text{HS}^-)$ ; mean value = 28.5‰) is interpreted as the result of biogenic reduction of sulphate occurring in these waters. An apparent reduction trend is seen on Figure 2.



**Figure 2.** Comparison of sulphate concentrations and  $\delta^{34}\text{S}$  values.



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