



Geochemical and isotopic controls of carbon and sulphur in Ca-SO₄ waters of the Western Meso-Cenozoic Portuguese sedimentary border (natural mineral waters from Curia and Monte Real).

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The groundwater chemistry and stable isotopic composition of aqueous inorganic C species (DIC) from Curia and Monte Real Spa's waters were determined.

These waters belong to the calcium-sulphate hydrochemical facies, and as such sulphate and calcium contents represent more than 80% of the total mineralization. They emerge in a hydrogeological context dominated by carbonate formations and Hettangian evaporites.

Calculated P_{CO_2} values are $10^{-2.4}$ atm. (Monte Real) and $10^{-1.8}$ atm. (Curia), which are typical soil P_{CO_2} in recharge environments. Therefore, carbonate dissolution has occurred in a system partially open to soil CO_2 .

Unity Na/Cl molal ratios for both waters reflect stoichiometry of halite dissolution. Similarly, Ca/SO₄ ratio of one would be expected if gypsum or anhydrite dissolution controlled calcium and sulphate. In fact, that is the case for Curia waters (Ca/SO₄ = 1,0), but not for Monte Real waters, which have Ca/SO₄ = 0,84. This ratio, however, becomes very close to 1 when considering calcium plus magnesium relative to sulphate (Ca+Mg/SO₄ = 0,93). This could indicate that the magnesium added to solution by incongruent dissolution of dolomite tends to equal calcium removed by calcite precipitation. This process could potentially be induced by the common-ion effect caused by dissolution of gypsum by calcite-saturated water.

Both waters are supersaturated with respect to calcite; in equilibrium (Curia) or weakly under-saturated (Monte Real) relative to the less soluble dolomite; in equilibrium (Monte Real) or under-saturated (Curia) in gypsum, and both of them are under-saturated in anhydrite.

The Dissolved inorganic carbon (DIC) $\delta^{13}C_{PDB}$ values are -11,8‰ (Monte Real) and -9,4‰ (Curia). Such enrichments in ¹³C relative to soil CO_2 dominated by C3 type vegetation could only be explained by transfer of carbon between reservoirs other than the dissolution of carbonates in a system more or less open to soil CO_2 .

$\delta^{34}S_{SO_4}$ is +16,1‰ and +14,8‰ relative to CDT standard, for Monte Real and Curia respectively. The source of dissolved sulphate is gypsum dissolution from Hettangian evaporites ($\delta^{34}S_{Gy} = +14,4‰$).

Where it is present the dissolved sulphide species ($\delta^{34}S_{H_2S} = -36,1‰$ for Monte Real) appears to be derived from biogenic reduction of sulphate ions.

We estimate that Monte Real water could be additionally enriched by 2 ‰ in $\delta^{13}C_{PDB}$ if biogenic sulphate reduction had not occurred.

From thermodynamic and isotopic considerations it is reasonable to admit that dedolomitization (*i.e.* dolomite dissolution and concomitant calcite precipitation driven by gypsum dissolution) is one of the major mechanisms controlling the chemical character and the isotopic evolution of C on those mineral waters.