

Geochemical and isotopic controls of carbon and sulphur in calcium-sulphate waters of the western Meso-Cenozoic Portuguese border (natural mineral waters of Curia and Monte Real)

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Abstract The groundwater chemistry and stable isotopic composition of aqueous C- and S-bearing species were determined for mineral waters from Monte Real and Curia Spas. The results support dedolomitization -dolomite dissolution occurs as the gypsum dissolves and calcite precipitates- as a principal geochemical process controlling Ca - SO₄ facies of these waters. Soil CO₂ of atmospheric origin and carbonate weathering are the primary sources of dissolved inorganic carbon (DIC). However, dissolution / precipitation of carbonates, through incongruent dissolution of dolomite, is the controlling factor for the evolution of the C isotopic composition of DIC, as shown by $\delta^{13}\text{C}$ values of -11.8‰ (Monte Real) and -9.4‰ (Curia). When present, the dissolved sulphide species ($\delta^{34}\text{S}_{\text{H}_2\text{S}} = -36.1\text{‰}$ for Monte Real) appears to be derived from biogenic reduction of dissolved sulphate ($\delta^{34}\text{S}_{\text{SO}_4} = +16.1\text{‰}$ for Monte Real and +14.8‰ at Curia), itself derived from dissolution of Hettangian evaporites gypsum ($\delta^{34}\text{S}_{\text{Gy}} = +14.4\text{‰}$).

1 Introduction

Monte Real and Curia Spas are located in Central West Portugal (Fig. 1), benefiting from a Mediterranean climate with Atlantic influence. Those Spas use mineral waters that emerge at a temperature around 20°C, showing, therefore, a small thermal disequilibrium with the mean air temperature, which is 15°C for both locations. With a long balneotherapeutic tradition, they contribute to the preservation of the Spa culture, a heritage which is deeply rooted in the country.

The hydromineral circuits of the waters cropping out at Monte Real and Curia spas crosscut Mesozoic carbonate formations with associated Hettangian evaporitic rocks. The ubiquitous presence of carbonates (calcite and dolomite), sulphates (gypsum/anhydrite) and halides (halite) in both hydromineral systems point towards those minerals as responsible for the chemical composition of the waters studied. This paper deals with the geochemical interpretation of major elements and stable isotopes of carbon and sulphur for those mineral waters.

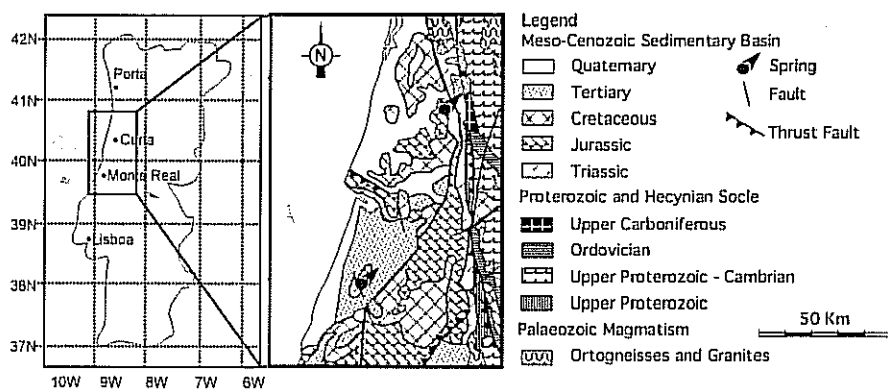


Fig. 1. Geographical location and generalized geological setting for the mineral springs Monte Real and Curia. Adapted from Carta Geológica de Portugal, 1/500000 (IGM 1992).

2 Geological and hydrogeological setting

The springs occur in the Western Meso-Cenozoic Portuguese border and emerge from Lower Jurassic formations (Teixeira and Gonçalves 1980; Neiva 1982; IGM 1992) in a hydrogeological context particularly influenced by Hettangian evaporites (Fig. 1).

Sediments of the Western Sedimentary Border lie on top of the ante-Mesozoic Massif. The "Grés de Silves", an Upper Triassic detrital complex largely formed by sandstones and conglomerates, is overlain by the "Margas da Dagorda", a unit of Hettangian age with clays, marls, masses of halite, and gypsum/anhydrite with lime-dolomite intercalations. These occurrences crop out in a more or less continuous band with North-South orientation. To the West, the Hettangian materials reappear in a patchy way in the middle of younger formations mostly associated with diapiric structures. Particularly in Monte Real, the migration of the evaporitic deposits to a diapiric anticline has reunited thick bodies of gypsum and halite, reaching great depths, as shown by the results of deep drilling for mineral exploration (Manuppella et al. 1978). The "Margas da Dagorda" is overlain by a Lower Jurassic carbonate unit made of dolomitic limestones, more or less argillaceous limestones, and marls.

At a local scale the natural emergences at Curia seem to be associated to fractures with a general NNE-SSW orientation which are visible in the outcrops of a karstified limestone. One of the wells exploring mineral water is 207 m deep and has intersected only Liassic formations e.g. limestone, dolomitic limestones, gypsum and marls (probably Sinemurian and Hettangian lithologies). The productive levels were some dolomitic formations found at 75 m depth (INAG 2001), providing the well ACP2 with a specific capacity of 28 L/s m. At Monte Real the mineral springs are also linked to a Lower Jurassic carbonate unit overlying the "Margas da Dagorda". Those springs are associated to the intersection of N-S to NNE-SSW faults limiting two diapiric structures (Neiva 1982). At the time of this study exploitation of the mineral aquifer was made by an 80 m deep artesian well.

3 Results and discussion

3.1 Facies and hydrochemical evolution

These waters belong to the calcium-sulphate hydrochemical facies, with sulphate and calcium contents representing more than 80% of the total mineralization. However, they present different anionic and cationic sequences:

- Monte Real: $r\text{SO}_4^{2-} \gg r\text{Cl}^- > r\text{HCO}_3^-$ and $r\text{Ca}^{2+} \gg r\text{Na}^+ > r\text{Mg}^{2+}$
- Curia: $r\text{SO}_4^{2-} \gg r\text{HCO}_3^- > r\text{Cl}^-$ and $r\text{Ca}^{2+} \gg r\text{Mg}^{2+} > r\text{Na}^+$

with *r* meaning concentration in meq/L.

The greater abundance of hypersaline evaporite minerals -particularly halite- in the diapiric region of Monte Real is directly reflected by the sodium and chloride contents of that water. This raises the solution's ionic strength, which in turn favours the continued dissolution of minerals as an effect of the decreasing ion activity coefficients, leading to a global increase of the salinity of the mineral water. The total dissolved solids (TDS) of Monte Real water (2.8 g/L) is about one and a half times that of Curia (1.9 gr/L) (Table 1).

Unity Na/Cl molal ratios for both waters reflects stoichiometric halite dissolution ($\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^-$). Similarly, a Ca/SO₄ ratio of one would be expected if gypsum or anhydrite dissolution controlled calcium and sulphate (e.g. anhydrite: $\text{CaSO}_4 \rightarrow \text{Ca}^{2+} + \text{SO}_4^{2-}$). That is, indeed, the case for Curia (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 (Sacks and Tihansky 1996; Sacks et al. 1995). This process could potentially be induced by the common-ion effect caused by dissolution of gypsum by calcite-saturated water.

Table 1. Chemical and isotopic data and saturation indices of Monte Real and Curia waters.

	Monte Real	Curia		Monte Real	Curia
Date	1996/09	1996/04	Date	1996/09	1996/04
Sampling Point	Well	Well ACP2	Sampling Point	Well	Well ACP2
Field Parameters			Calculated Parameters*		
Temperature, °C	19.0	20.6	Eh, mV	-218	n.c.
Conductivity, $\mu\text{S cm}^{-1}$	2600	1975	pCO ₂ , log atm	-2.44	-1.81
pH	7.40	7.10	DIC, mmol/L	2.08	4.48
Eh, mV	-111	+230	Total dissolved solids, mg/L	2840	1897
Constituents, mg/L			Isotopes		
Na ⁺	97.0	21.2	$\delta^{13}\text{C}(\text{DIC})$, ‰ vs PDB	-11.8	-9.4
K ⁺	3.6	2.0	$\delta^{34}\text{S}(\text{SO}_4)$, ‰ vs CDT	+16.1	+14.8
Ca ²⁺	628	445	$\delta^{34}\text{S}(\text{H}_2\text{S})$, ‰ vs CDT	-36.1	n.m.
Mg ²⁺	48.9	52.0	Saturation Indices*		
Fe ²⁺	<0.03	0.22	Calcite	0.34	0.29
Cl ⁻	160	29.5	Dolomite	-0.19	-0.07
HCO ₃ ⁻	124	238	Gypsum	0.02	-0.22
SO ₄ ²⁻	1759	1100	Anhydrite	-0.22	-0.45
HS ⁻	4.1	n.d.			

n.d.: not detected; n.c.: not calculated; n.m.: not measured

*Computed with Wateq4F, version 2.63 (2004) (Ball and Nordstrom, 1991)

Plotting those waters on a modified Langelier-Ludwig diagram (Pastorelli et al. 1998) illustrates the hydrochemical characteristics, and the geochemical processes resulting from groundwater circulation through carbonate- evaporite rocks. In this graph (Fig. 2a) percentages of equivalent units for the main ionic solutes (*i.e.*, Ca²⁺, Mg²⁺, HCO₃⁻ and SO₄²⁻) are plotted in adjusted scale in a way that the coordinate values of three vertices fits the theoretical composition of calcite, dolomite and anhydrite.

The studied waters plot close to the anhydrite vertex, and near the anhydrite-dolomite tie-line, reflecting the determinant role of these minerals in the structural chemistry of the waters. On the other hand, water composition shifts away from the calcite vertex, which may be caused by calcite precipitation. This analysis is consistent with the geochemical indices presented and the saturation state of the waters with respect to the minerals considered, according to data in Table 1 and Figure 2b.

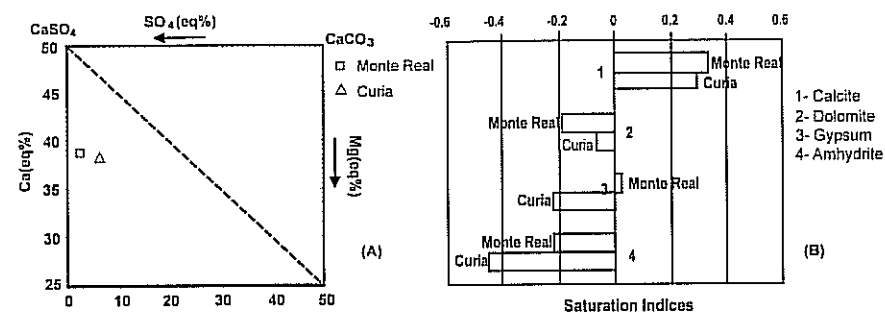


Fig. 2. a. Modified Langelier-Ludwig diagram for the studied waters b. Saturation states of the waters with respect to selected mineral phases.

Both waters are supersaturated with respect to calcite; in equilibrium (Curia) or slightly 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. From thermodynamic and isotopic considerations it is reasonable to admit that dedolomitization is one of the major mechanisms controlling the chemical character and the isotopic evolution of C on those mineral waters (see next section). Dedolomitization is the process by which incongruent dolomite dissolution occurs as gypsum dissolves and calcite precipitates (Deines et al. 1974; Hanshaw and Back 1979; Appelo and Postma 1994; Sacks et al. 1995). The Ca²⁺ common-ion effect, induced by gypsum dissolution, can cause supersaturation of calcite, and consequently its removal from the solution. That will promote incongruent dissolution of dolomite, and as a result, an increase in calcium, magnesium and sulphate of the solution.

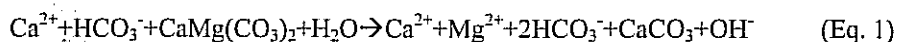
3.2 Stable carbon isotopic geochemistry of dissolved inorganic carbon

The dissolved inorganic carbon (DIC = mH₂CO₃ + mHCO₃⁻ + mCO₃²⁻) exists almost entirely as HCO₃⁻, as indicated by the near neutral pH values of the mineral waters. HCO₃⁻ is the second most abundant anion in Curia water, where it is more abundant than at Monte Real, indicating that more calcite has been dissolved. Identical magnesium contents for both waters imply sub-equal quantities of dolomite dissolved, if that mineral was the only source of magnesium in solution.

This interpretation is coherent with calculated P_{CO_2} values (Table 1), that are higher at Curia ($10^{-1.8}$ atmospheres) than at Monte Real ($10^{-2.4}$ atm). Both values are within the range typical for soil P_{CO_2} in recharge environments with vegetal cover ($10^{-1.5}$ - $10^{-2.5}$; Freeze and Cherry 1979; Appelo and Postma 1994). Therefore, carbonate dissolution has occurred in a system partially open to soil CO₂.

filtration to the saturated zone, isolating the water from the gaseous phase and/or encountering sulphate minerals in an initial stage of its hydrochemical evolution, thus very soon attaining calcite supersaturation and preventing the dissolution of the most soluble carbonates.

There is a strong difference in solubility among the carbonate minerals presumably in contact with water since its infiltration. Even admitting simultaneous calcite and dolomite dissolution, it is generally agreed that dissolution of magnesium carbonates (dolomite, but also magnesian calcite) only takes place significantly within the saturated zone, under closed-system conditions (Freeze and Cherry 1979; Appelo and Postma 1994; Clark and Fritz 1997). In those circumstances, if calcite equilibrium was attained, dolomite dissolution could only occur incongruently, as represented by the reaction (Clark and Fritz 1997):



The loss of carbon from solution, concomitant with calcite precipitation, removes some of the isotopically heavy carbon (enrichment factor $\epsilon^{13}\text{C}_{\text{CaCO}_3 - \text{HCO}_3} = +2.0\text{‰}$ at 25°C; Deines et al. 1974), causing a reduction in $\delta^{13}\text{C}_{\text{DIC}}$. However, that effect is largely compensated by addition of carbon enriched in ^{13}C from dissolution of dolomite ($\delta^{13}\text{C}_{\text{Dol}}$ frequently near 0‰), which in a global balance determines a ^{13}C enrichment of the initial DIC.

Models concerning the isotopic evolution of dissolved carbon in waters are widespread (as an example, Wigley et al. 1978; Clark and Fritz 1997). These use as premises the isotopic evolution of carbon in water at equilibrium with soil CO_2 ($\delta^{13}\text{C}_{\text{CO}_2} = -23\text{‰}$ at our latitudes) and then dissolving marine carbonates ($\delta^{13}\text{C} \approx 0\text{‰}$) in open or closed system conditions for various P_{CO_2} pressures. (see, for example, Clark and Fritz 1997; their Figure 5-6).

None of those models can explain the isotopic composition of dissolved carbon shown by the waters studied ($\delta^{13}\text{C}_{\text{DIC}} = -11.8\text{‰}$ for Monte Real and -9.4‰ for Curia) (Table 1). In a first approach, expected values for $\delta^{13}\text{C}_{\text{DIC}}$ (Clark and Fritz 1997) would be around -15‰ (at 25°C) to -14‰ (at the mean annual temperature of 15°C in the region). Therefore, measured values must result from additional reactions occurring in the saturated zone.

Incongruent dolomite dissolution is an important mechanism of carbon transfer between reservoirs, which results in a significant ^{13}C enrichment of DIC. Dedolomitization, and the associated carbon isotopic evolution, is discussed by Wigley et al. (1978). Carbon isotope data reported in this study are compatible with such a process, favouring the thesis of incongruent dissolution in the aquifer.

DIC species derive from soil CO_2 and from interaction of water with carbonates. However, an additional source, derived from biological sulphate reduction, contributed to Monte Real water.

According to the stoichiometry of sulphate reduction (Equation 3) and considering the total sulphide measured on the water, a HCO_3^- contribution of 0.248 mmol/L can be estimated, which would represent about 12% of the actual DIC of

Monte Real water. Given its organic carbon origin, this secondary addition of a carbonate species causes a decrease of the heavy stable carbon isotope and contributes to water saturation with respect to calcite. The role of this carbon source in the DIC isotopic evolution can be modelled using the following mass balance equation:

$$\delta^{13}\text{C}_{\text{Final}} \cdot \text{mDIC}_{\text{Final}} = \delta^{13}\text{C}_{\text{Initial}} \cdot \text{mDIC}_{\text{Initial}} + \delta^{13}\text{C}_{\text{Organic}} \cdot 2\text{mHS}^- \quad (\text{Eq. 2})$$

For an approximate $\delta^{13}\text{C}_{\text{Organic}}$ value of -25‰ , and knowing the final isotopic composition of carbon ($\delta^{13}\text{C}_{\text{Final}}$), the above equation can be resolved in order to determine the isotopic composition of DIC prior to sulphate reduction ($\delta^{13}\text{C}_{\text{Initial}}$). The calculated value of -10‰ indicates that the DIC could be enriched by about 2‰ in $\delta^{13}\text{C}$, had biogenic sulphate reduction not occurred.

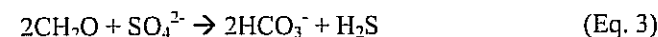
3.3 Stable sulphur isotopic geochemistry of dissolved sulphate and sulphide

The reducing character of Monte Real water is manifested by the presence of reduced sulphur species (mainly HS^- , but also H_2S) co-existing with species of a higher oxidation state, such as sulphate.

Measured redox potential is -111 mV , while the value calculated by the redox couple sulphate/sulphide is -218 mV (Table 1). Measurement errors associated to analytical difficulties and/or absence of equilibrium between aqueous redox couples (Appelo and Postma 1994; Stumm and Morgan 1996) may lie behind the differences between calculated and measured values. Nevertheless, both values agree qualitatively, indicating reducing conditions at Monte Real water, in contrast with the oxidizing character of Curia water (field measured value of $\text{Eh} = +230\text{ mV}$, emphasizing the absence of reduced sulphur forms from its chemical composition).

Aqueous sulphate at Monte Real has $\delta^{34}\text{S} = +16.1\text{‰}$ and that at Curia is $+14.8\text{‰}$ (Table 1). Those values are close to $\delta^{34}\text{S} = +14.4\text{‰}$ measured on a sample of Hettangian gypsum, which in turn is within the range of admissible values for sulphates of that age (Triassic - Jurassic transition; Claypool et al. 1980; Clark and Fritz 1997). Gypsum dissolution is essentially a non-fractionating process (Everdingen et al. 1982; Clark and Fritz 1997; Hoefs 2004); therefore sulphate content of spring water is unequivocally derived from evaporite gypsum (or anhydrite), contributions of other sources being negligible.

In the absence of oxygen, some bacteria, such as *Desulfovibrio desulfuricans*, can metabolize organic matter using aqueous sulphate as electron acceptor, giving bicarbonate and sulphide as by-products (Freeze and Cherry 1979; Hoefs 2004):



Since the light isotope forms weaker bonds, $^{32}\text{SO}_4^{2-}$ is preferentially used, resulting in isotopically light sulphide, and, by mass balance, a residual sulphate with higher $\delta^{34}\text{S}$. Kinetic fractionation factors of up to about 50‰ are known from laboratory experiments and field studies (Krouse 1980; Everdingen et al. 1982; Hoefs 2004).

$\delta^{34}\text{S}_{\text{HS}}$ measured at Monte Real was -36.1‰, resulting in an apparent fractionation between SO_4^{2-} and HS^- of 52.2‰. This value is similar to those frequently attributed to bacterial sulphate reduction.

From the actual contents of sulphate and sulphide of Monte Real waters, about 1% reduction of sulphate would suffice to account for the sulphide observed. Considering a closed system, and applying the isotopic mass balance equation:

$$\delta^{34}\text{S}_T = (\delta^{34}\text{S}_{\text{SO}_4^{2-}} m_{\text{SO}_4^{2-}} + \delta^{34}\text{S}_{\text{HS}} m_{\text{HS}^-}) / (m_{\text{SO}_4^{2-}} + m_{\text{HS}^-}) \quad (\text{Eq. 4})$$

would result in $\delta^{34}\text{S}_T = 15.7\text{‰}$ for total sulphate before reduction. This value is closer to that measured at Curia, where no reduction is evidenced, or to that of the outcrop gypsum sample.

4 Conclusions

The hydrothermal circuits of the waters cropping out at Monte Real and Curia spas crosscut Mesozoic carbonate formations with associated Hettangian evaporite rocks.

Molar ratios $\text{Ca}^{2+}/\text{SO}_4^{2-}$, $(\text{Ca}^{2+} + \text{Mg}^{2+})/\text{SO}_4^{2-}$, Na^+/Cl^- and thermodynamic equilibrium calculations show that dissolution of evaporitic rocks and interaction with carbonate formations controls the structural chemistry of those waters.

$\delta^{13}\text{C}$ evolution of the DIC is accounted for by the contributions of C in the soil gas phase together with that of carbonate minerals of marine origin, modified by subsurface precipitation of secondary calcite due to the incongruent dissolution of gypsum and dolomite.

Both waters present $\delta^{34}\text{S}$ values of dissolved sulphate which are comparable to those of Hettangian gypsum. The presence of reduced sulphur species (H_2S and HS^-) in Monte Real water records oxidation-reduction reactions.

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