Water-rock interaction ascribed to hyperalkaline mineral waters in the Cabeço de Vide serpentinized ultramafic intrusive massif (Central Portugal)

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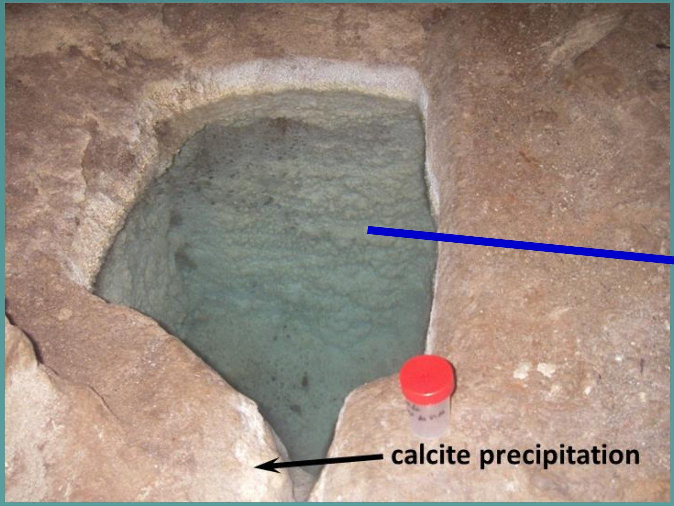
1. Introduction

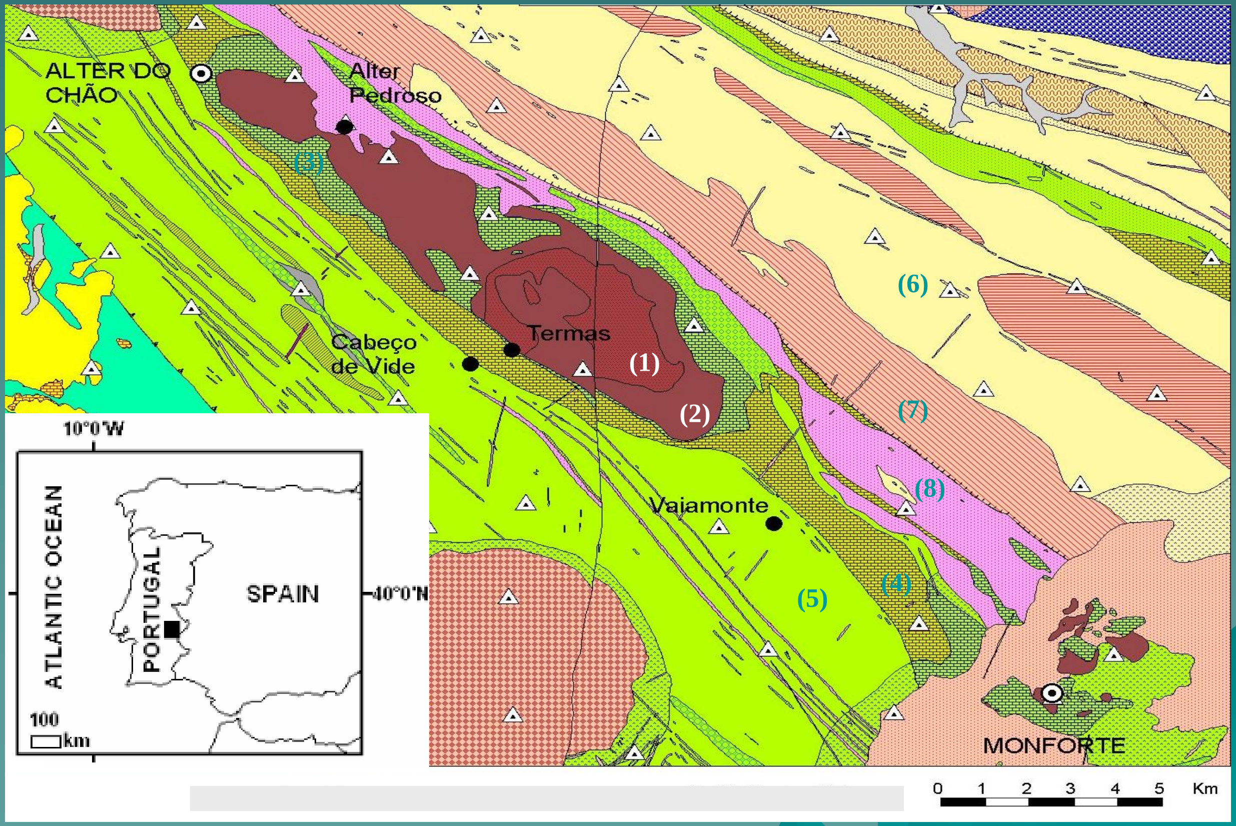
Methane with ^{13}C enriched composition has recently been discovered in hyperalkaline waters in Portugal, at Cabeço de Vide (Etiope et al., 2013).

Here we will focus on this new gas-bearing serpentinization site, summarizing and integrating the main results on water and gas chemistry in order to describe a general fluid circulation model applicable to other cases.



2. Site description

Cabeço de Vide spring and borehole mineral waters are located in the Alter-do-Chão pluton, a ring-like intrusion with NW-SE elongated shape, following the Variscan orientation. Mafic rocks (mainly gabbros) outcrop surrounding the ultramafic core including peridotites, serpentinized peridotites and serpentinites.



Location and geologic map of Cabeço de Vide area (1) serpentinized ultramafic rocks; (2) mafic and ultramafic rocks; (3) hornfels; (4) carbonate rocks, displaying contact metamorphism; (5) Cambrian rocks: schists, quartzites and greywackes; (6) pre-Cambrian rocks: metamorphic schists and greywackes; (7) orthogneisses and (8) orthogneisses and hyperalkaline syenites.

"Termas" stands for Cabeço de Vide spa and boreholes. F stands for the main regional NNE–SSW trending fault. Altitude (m a.s.l.) is given through the geodetic marks (△). Adapted from Marques et al. (2008) and Fernandes, J. (*pers. comm.*).

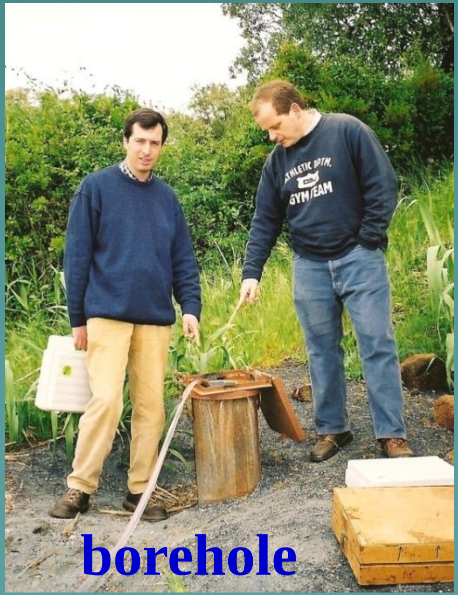
3. Chemistry of the waters

Local HCO_3-Mg-type waters constitute most of the surface (stream) and shallow (spring / borehole) groundwaters discharging from the serpentinites.

Serpentine dissolution explain the high Mg^{2+} and SiO_2 concentrations found in the local Mg-HCO_3-type waters (*e.g.*, Barnes et al., 1967).

$$\mathbf{Mg_3Si_2O_5(OH)_4 + 6H^+ = 3Mg^{2+} + 2H_4SiO_4^0 + H_2O}$$

(*chrysotile*)



3. Chemistry of the waters (cont.)

The Cabeço de Vide mineral waters discharge with a temperature between 17 and 20ºC, present very alkaline pH values (10.5 < pH < 11.5) and electrical conductivity values between 400 and 650 μS/cm.

Their main chemical characteristics are:
i) Na-Cl/Ca-OH *facies*;
ii) rather low mineralization (dry residuum around 200 mg/L);
iii) C_{total} < 3.0 mg/L; and vi) extremely low Mg^{2+} and silica concentrations, below 0.3 and 6.5 mg/L, respectively.

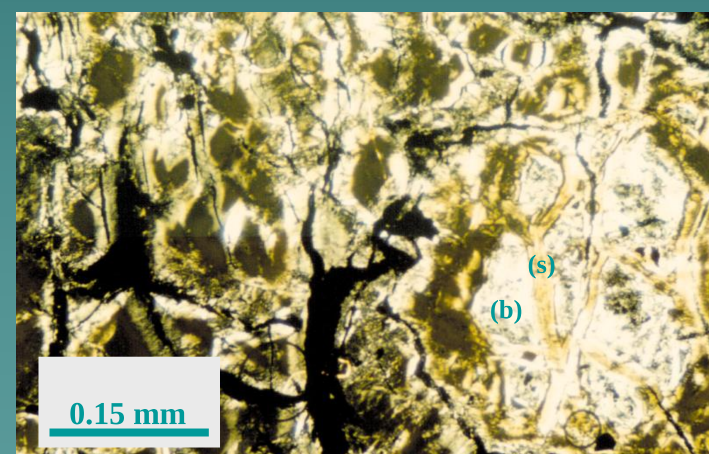
Borehole AC3

3. Chemistry of the waters (cont.)

Barnes et al. (1967) suggested that serpentinization of the ultramafic rocks contribute to the development of such type of mineral waters (low silica and Mg^{2+} concentrations).

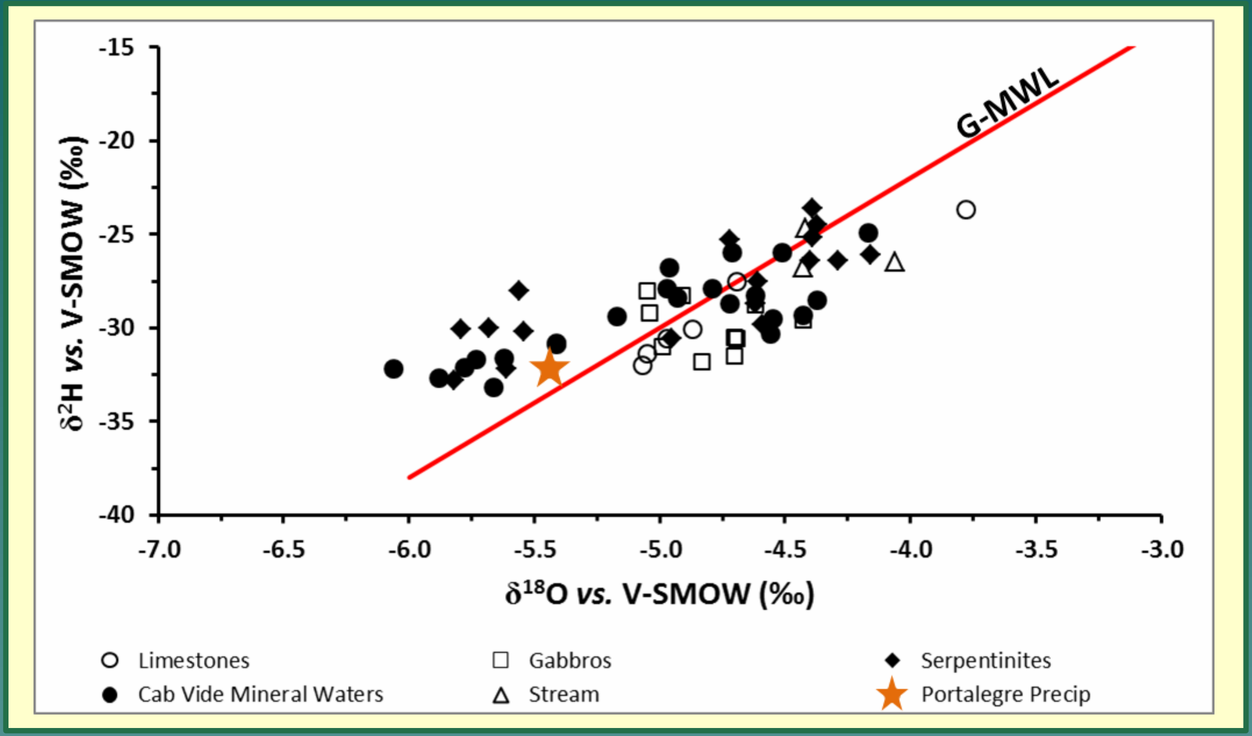
$$\mathbf{2Mg_2SiO_4 + 3H_2O = Mg(OH)_2 + Mg_3Si_2O_5(OH)}$$

(*forsterite*) (*brucite*) (*chrysotile*)



Drillcore from borehole AC2 (Cabeço de Vide Spa). Serpentinized dunite, showing the presence of serpentine (s) and brucite (b) along fractured zones.

4. Water isotopic composition



The local shallow HCO_3-Mg groundwaters, discharging from the serpentinized dunites, and the Cabeço de Vide mineral waters have similar δ^2H and $\delta^{18}O$, indicating that the mineral waters could have evolved ascribed to the deep infiltration of the shallow HCO_3-Mg groundwaters.

- *SIRA 10 mass spectrometer from VG ISOGAS;*
- *laser spectroscopic analysis, LGR-24d.*

5. Gas chemistry and microbiology

Laboratory (JPL /INGV) analyses confirmed:
-the presence of methane and ethane (1.2 and 0.03 mg/L, respectively);
-the lack of CO_2 and very low H_2.

With the collaboration of Yuichiro Ueno (Department of Earth and Planetary Sciences, Tokyo Inst. of Techn., Japan), H_2 was detected in small amounts in the mineral waters (around 10^{-2}, concentration in vol. % - Yuichiro Ueno *pers. comm*.).

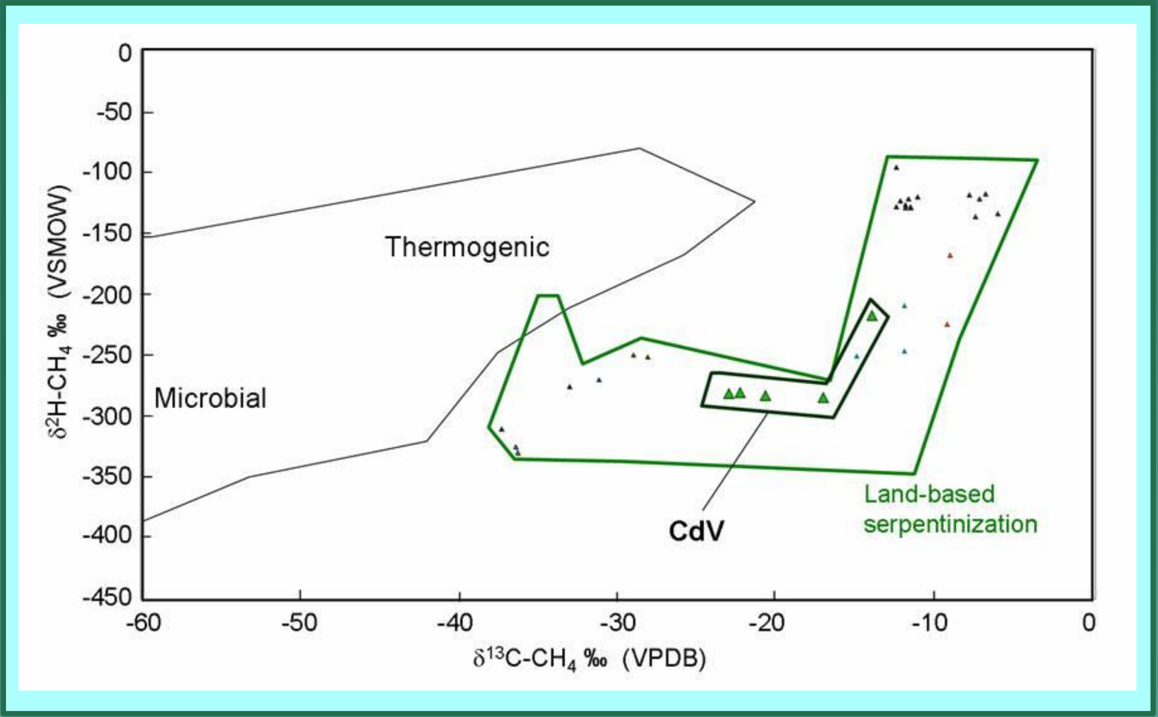
$$\textbf{olivine + pyroxene + } H_2O \longrightarrow \textbf{serpentine} \pm \textbf{brucite} \pm \textbf{magnetite + } H_2$$

In this framework, microbial analysis has indicated that microbial H_2 consumption likely occurs in the Cabeço de Vide mineral waters since the most dominant microbe found in the mineral waters (AC3 borehole) has been close to *Serpentinomonas*, a well-known hydrogen oxydizing bacterium (e.g. Tiago and Veríssimo, 2012) .

Methanogenic Archaea has not been detected in Cabeço de Vide mineral waters (e.g. Tiago and Veríssimo, 2012), indicating that microbial methanogenesis is not occurring in this spring as suggested from isotopic gas analysis of methane.

5. Gas chemistry and methane isotopic composition (cont.)

The CH_4 isotopic composition is substantially different from that of typical microbial or thermogenic gas, falling in the range of typical abiotic gas found in other serpentinizing sites. The origin of ethane is unknown at this stage.



$\delta^{13}C_{CH4}$ *vs.* $\delta^{2}H_{CH4}$ diagram of Cabeço de Vide mineral waters compared with the fields of all biotic- *vs.* abiotic-driven gases so far documented (data from Etiope et al., 2013, and references therein).

6. Gas-water circulation model

The conceptual model can be summarized as follows:

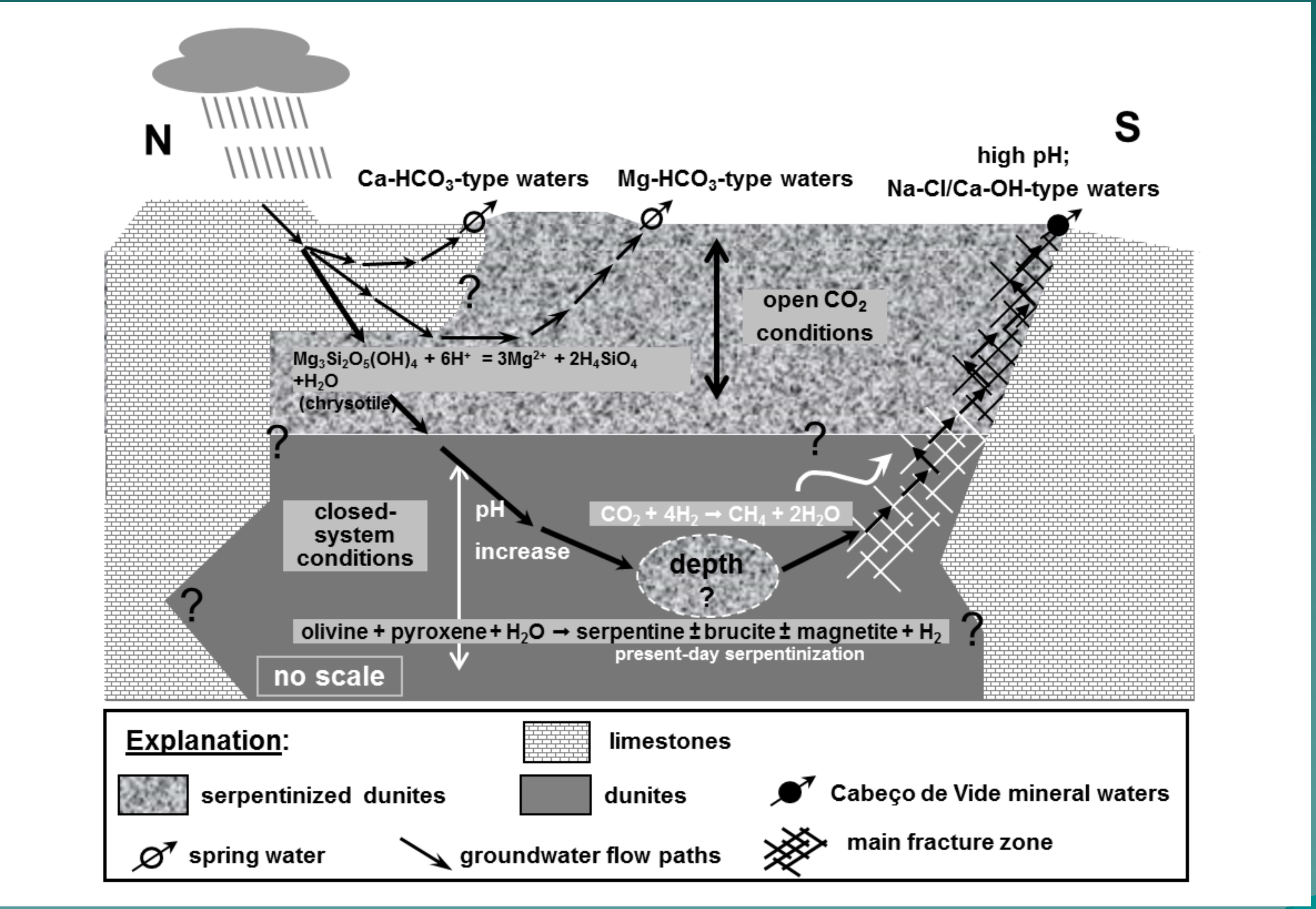
(a) Local shallow groundwaters are generated in a first step, under open CO_2 conditions, due to meteoric water-serpentinite interactions; these are the HCO_3-Mg-rich waters;

(b) The mineral waters are produced in a later step, under closed CO_2 conditions, due to water-dunite interaction at depth;

(c) Under these deep and closed conditions, CO_2 exsolves from the water due to the high calcium levels. In addition CO_2 is likely consumed by hydrogenation to form CH_4;

(d) Methane produced by CO_2 hydrogenation in deep serpentinized rocks enters the waters and is transported to the surface.

6. Gas-water circulation model (cont.)



Hydrogeological conceptual model of Cabeço de Vide mineral waters, showing the evolution of the local Mg–HCO_3-type waters (generated under open CO_2 conditions) towards the Cabeço de Vide mineral waters (high pH; Na–Cl/Ca–OH-type waters), as the result of water–dunite interaction at depth, under closed-system conditions (Adapted from Marques et al. 2008).

Many thanks for your attention

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