



Origins of high pH mineral waters from ultramafic rocks, Central Portugal

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ABSTRACT

This paper reviews the geochemical, isotopic (²H, ¹⁸O, ¹³C, ³H and ¹⁴C) and numerical modelling approaches to evaluate possible geological sources of the high pH (11.5)/Na–Cl/Ca–OH mineral waters from the Cabeço de Vide region (Central-Portugal). Water–rock interaction studies have greatly contributed to a conceptual hydrogeological circulation model of the Cabeço de Vide mineral waters, which was corroborated by numerical modelling approaches. The local shallow groundwaters belong to the Mg–HCO₃ type, and are derived by interaction with the local serpentized rocks. At depth, these type waters evolve into the high pH/Na–Cl/Ca–OH mineral waters of Cabeço de Vide spas, issuing from the intrusive contact between mafic/ultramafic rocks and an older carbonate sequence. The Cabeço de Vide mineral waters are supersaturated with respect to serpentine indicating that they may cause serpentization. Magnesium silicate phases (brucite and serpentine) seem to control Mg concentrations in Cabeço de Vide mineral waters. Similar $\delta^2\text{H}$ and $\delta^{18}\text{O}$ suggest a common meteoric origin and that the Mg–HCO₃ type waters have evolved towards Cabeço de Vide mineral waters. The reaction path simulations show that the progressive evolution of the Ca–HCO₃ to Mg–HCO₃ waters can be attributed to the interaction of meteoric waters with serpentinites. The sequential dissolution at CO₂ (g) closed system conditions leads to the precipitation of calcite, magnesite, amorphous silica, chrysotile and brucite, indicating that the waters would be responsible for the serpentization of fresh ultramafic rocks (dunites) present at depth. The apparent age of Cabeço de Vide mineral waters was determined as 2790 ± 40 a BP, on the basis of ¹⁴C and ¹³C values, which is in agreement with the ³H concentrations being below the detection limit.

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1. Introduction

The present study investigates the only occurrence of high pH (≈11) mineral waters, of Cabeço de Vide Spa (Fig. 1), from the Iberian Peninsula, which occur associated with ultramafic rocks. In nature, there are two primary types of high pH (≈ >10) waters: the so-called “saline” lake waters and groundwaters discharging mainly from ultra-

mafic rocks. Good examples of the “saline” lake waters occur at Lake Bogoria in the Kenya Rift System (Cioni et al., 1992) and at Mono Lake in eastern California (Jellison et al., 1998). Both lakes are associated with hot spring activity (Berry, 1980). In the Kenya Rift System, the saline lake waters are located near carbonatites, alkali basalts and phonolitic rocks and their pH is controlled by the hydrolysis of CO₃²⁻ (Cioni et al., 1992). In contrast, high pH waters associated with ultramafic rocks are usually dilute and have low carbonate contents. Their pH can be as high as 14 (e.g., Drever, 1982 – Agua de Ney, a spring in extreme northern California issuing from serpentinite has a

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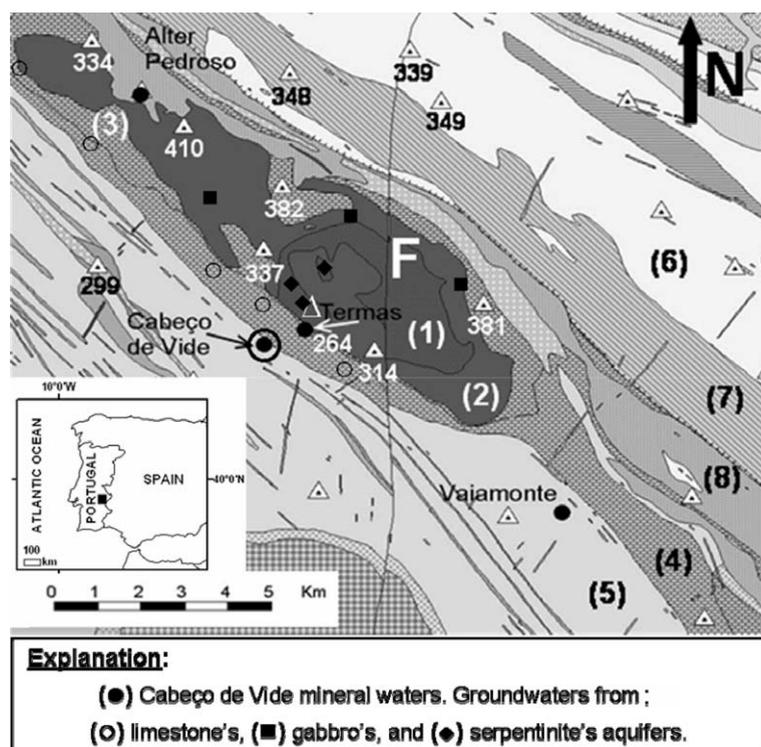


Fig. 1. Location and geologic map of Cabeço de Vide region (courtesy Fernandes, J., pers. Comm.). (1) serpentinitized ultramafic rocks; (2) mafic and ultramafic rocks; (3) hornfels; (4) carbonate rocks, displaying contact metamorphism; (5) Cambrian rocks: schists, quartzites and greywackes; (6) pre-Cambrian rocks: metamorphic schists and greywackes; (7) orthogneisses and (8) orthogneisses and hyperalkaline syenites. Termas stands for Cabeço de Vide spa. F stands for the main regional NNE–SSW trending fault. Altitude is given through the geodesics marks.

pH of 14). Barnes et al. (1978) reported waters from the United States, Oman, New Caledonia and Yugoslavia, showing geochemical evidence of modern low-temperature serpentinization, similar to those reported by Barnes and O'Neil, 1969. These waters are usually dilute, belong to the Ca–OH-type and are depleted in Mg due to precipitation of brucite and serpentine minerals. Goff and Lackner (1998) evaluated ultramafic bodies in the United States as sources of Mg for CO₂ sequestration (e.g., Del Puerto ultramafic mass and the Wilbur Springs serpentinite, California Coast Ranges). These ultramafic bodies occur structurally at the base of ophiolite sequences, which are the largest and most widespread of all ultramafic deposits (Coleman, 1977). The most saline spring in this region is Complexion Spring, which discharges from serpentinite (Barnes et al., 1973; Goff and Guthrie, 1999). Bruni et al. (2001, 2002) and Cipolli et al. (2004) reported cold dilute Ca–OH-type groundwaters with pH upto 12 from Genova, Italy, discharging from ultramafic rocks variably affected by serpentinization. Recently, Ramírez-Guzmán et al. (2004) reported high-pH thermal springs in the Pacific coast of Guerrero, Mexico. These waters (40–43 °C) discharge from oligocene (35–27 Ma) granitic plutons that outcrop along the coast near Acapulco and are characterized by low salinity (TDS < 0.5 g/kg) and high pH (9.5–10). Some analyses of the above mentioned high pH waters are shown in Table 1 for comparison.

Due to their uncommon chemical composition and complex geological and hydrogeological conditions, Cabeço de Vide mineral waters have attracted scientific attention for a long time (e.g., Portugal Ferreira and Mendonça, 1990; Costa et al., 1993).

During recent hydrogeological investigations performed at Cabeço de Vide region, several questions arose: (i) what causes the unusual high pH values of the mineral waters? (ii) are these mineral waters the result of meteoric water interaction with local ultramafic rocks? (iii) why do these waters have such low Mg and SiO₂ concentrations? and (iv) is there any interaction between the hydromineral system and the local Monforte–Alter do Chão carbonate aquifer?

The environmental problems associated with the use of low-temperature mineral waters are different, in many aspects, from those of utilising high-temperature thermomineral resources. In fact, spas are very dependent on both constant temperature and water quality. Thus, the existence of mixing between deep mineral waters and local shallow groundwaters is an important question. The development of reliable management practices based on the understanding of the resource will help to preserve the mineral water quality, creating public interest. In the case of the Cabeço de Vide hydromineral system improved understanding is necessary, considering the well known vulnerability of the local fractured carbonate rocks to

Table 1

Chemical composition (mg/L) of some high-pH waters associated with saline lakes, ultramafic rocks and a granite pluton

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
T°C	17.1	27.1	25.0	9.5	20	25	23	29	12	41
pH	10.71	10.10	10.15	12.07	11.54	11.5	10.8	11.75	11.86	9.98
Na	55.90	39300	28300	12000	19	230	14.6	35	23.7	88
K	5.22	547	1140	350	1.1	8	3	1.5	3.1	0.84
Ca	5.1	1.82	20	0.7	40	60	14.2	29	47.4	0.5
Mg	0.3	1.11	43	0.8	0.3	0.1	2.3	7	0.02	0.02
Cl	33.49	7460	17300	18200	63	280	22	20	21.2	61.3
HCO ₃	0.0	85400	20045*	7.1	0.0	0	0	0	1.3	37
SO ₄	12.60	144	9680	60	0.4	9	0.75	-	0.14	20
F	0.08	1350	41	0.5	0.0	<0.1	-	0.34	-	10.4
SiO ₂	5.6	378	30	24	4.0	0.1	0.4	1.9	1.5	57

Notes: (1) Ermida Spring, Cabeço de Vide, Portugal (this study) – ultramafic rocks; (2) Lake Bogoria, Kenya (Cioni et al., 1992) – alkaline volcanic rocks; (3) Mono Lake, F. Goff, unpublished data, collected October 1984 (* HCO₃⁻ + CO₃²⁻); (4) complexion Spring, California Coast Ranges, USA (Barnes et al., 1973) – serpentinite; (5) spring, Cazadero, California, USA (Barnes et al., 1978) – ultramafic rocks; (6) spring, Oman, Semail, Hahwalah, Wadi Jizi (Barnes et al., 1978) – ultramafic rocks; (7) spring, New Caledonia, La Coulée 1 (Barnes et al., 1978) – ultramafic rocks; (8) Yugoslavia, Kulasi, Bosnia (Barnes et al., 1978) – ultramafic rocks; (9) spring, Genova, Italy (Bruni et al., 2002) – serpentinites; (10) spring, Guerrero, Mexico (Ramírez-Guzmán et al., 2004) – granites.

contamination (Fernandes and Ribeiro, 2001; Fernandes and Françes, 2002).

2. Sampling procedures and analytical methods

Water samples were collected from streams, springs, dug wells and boreholes, for chemical and isotopic analysis. Temperature, pH (range: 0–14 pH units; accuracy ± 0.01 pH units), electrical conductivity and redox potential were determined in the field at the time of collection. The water samples were filtered by ultrafiltration before Al measurements. Total alkalinity was measured a few hours after collection. Major and minor elements in waters were determined at Laboratório de Mineralogia e Petrologia of Instituto Superior Técnico (LAMPIS), Portugal, using the following methods: atomic absorption spectrometry for Ca and Mg; emission spectrometry for Na, K, Li, Rb and Cs; colorimetric methods for SiO₂, Fe_{total}, F and Al; ion chromatography for SO₄, NO₃ and Cl; potentiometry for alkalinity. Trace element concentrations in waters were determined at Los Alamos National Laboratory (LANL) / USA, using ICP-MS. The ionic balance of major ion analysis ranges from –1.52% to 6.72%, depending on water mineralization. The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ measurements (vs. V-SMOW, Vienna-Standard Mean Ocean Water) were performed by mass spectrometry (SIRA 10–VG ISOGAS) at the Instituto Tecnológico e Nuclear (ITN – Portugal) following the analytical methods of Epstein and Mayeda (1953) and Friedman (1953), with an accuracy of $\pm 1\%$ for $\delta^2\text{H}$ and $\pm 0.1\%$ for $\delta^{18}\text{O}$. The ^3H water content (reported in Tritium Units, TU) was also determined at ITN, using electrolytic enrichment followed by liquid scintillation counting (standard deviation varies between ± 0.9 and ± 1.3 TU, depending on ^3H activity of the water samples). The $\delta^{13}\text{C}$ and ^{14}C determinations in waters were performed at the Geochron Laboratories/USA by accelerator mass spectrometry (AMS). The $\delta^{13}\text{C}$ values are reported in ‰ vs. V-PDB (Vienna-Pee-dee Belemnite) standard, with an accuracy of $\pm 0.1\%$. ^{14}C is given in pmC (per cent with respect to so-called “modern carbon”). Rock samples from local outcrops and from drill cores, from mineral water exploration boreholes AC1

and AC2, were selected for chemical (whole-rock) and mineral-petrographic characterization, as a comparison to the fluids, in order to assess water–rock interaction processes occurring at depth. Petrographic observations were complemented by IRS and XRD analysis, and whole-rock geochemical data was obtained by XRF at Los Alamos National Laboratory (LANL)/USA.

3. Geological setting

The study region (Fig. 1) is situated in the Ossa Morena Zone of the Iberian Hercynian belt. The Lower Cambrian carbonate sequence was metamorphosed by mafic and ultramafic intrusions forming a NW–SE cumulate-type structure of Ordovician age, which has been subjected to serpentinitization–rodingitization processes (Costa et al., 1993).

Cabeço de Vide mineral waters issue at the intrusive contact between the mafic/ultramafic rocks and the carbonate sequence, associated with the main regional NNE–SSW trending fault (Fig. 1). The ultramafic rocks range from partially serpentinitized dunites to serpentinites. The serpentinites contain some relict olivine. Most commonly, they contain only serpentine minerals (lizardite, antigorite and chrysotile), magnetite and residual chromite, plus brucite and carbonates. The mafic rocks adjacent to the ultramafics are mostly coarse- to fine-grained gabbros with Ca-plagioclase, Ti-clinopyroxene, olivine and some Al-hornblende (Costa et al., 1993).

Several other distinct geological formations can be observed in the surroundings of Cabeço de Vide spas. The most representative are: Precambrian metamorphic rocks (schists and greywackes), Cambrian chloritized schists, quartzites, greywackes and orthogneisses dated at 466 ± 10 Ma and some hyperalkaline syenites.

As suggested by Costa et al. (1993), (i) serpentinitization of the ultramafics and rodingitization of the gabbros seem to be simultaneous, partly complementary hydrothermal mechanisms and (ii) serpentinitization–rodingitization processes in the Alter-do-Chão Massif took place at low-pressure conditions and over a wide range of temperatures,

evolving from amphibolite to upper prehnite–pumpellyite facies.

4. Conceptual model

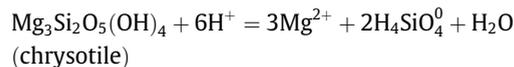
4.1. Water chemistry and mineral equilibrium

Different geological formations have led to the development of surface, shallow and groundwaters displaying different geochemical facies (see Table 2 and Fig. 2).

Groundwaters issuing within the Cambrian limestones are Ca–HCO₃-type waters, with neutral to slightly basic pH, and medium to high mineralization. In these waters, the Mg/Ca ratio is close to 0.5 reflecting the interaction with the calcites, the main mineral of the carbonate rocks (Fig. 3). The Mg concentrations can be attributed to the presence of dolomite.

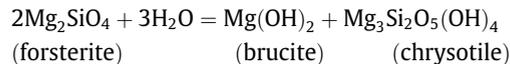
The groundwaters with HCO₃-Ca/Mg composition are neutral and have medium mineralization. This type of water is associated with gabbroic rocks and some springs are located at the geologic contact with the metamorphosed limestones.

The Mg–HCO₃-type waters constitute most of the surface (stream) and shallow groundwaters discharging from the serpentinites, suggesting that water chemistry is strongly host rock dependent. In particular, serpentine dissolution may explain the high Mg and SiO₂ concentrations found in Mg–HCO₃-type waters (e.g., Barnes et al., 1967; Barnes and O'Neil, 1969)



The Cabeço de Vide mineral waters have as their main chemical characteristics: (i) very alkaline pH values (between 10.5 and 11.5); (ii) Na–Cl/Ca–OH type; (iii) rather low mineralization (conductivity between 400 and 650 μS/cm); (iv) the concentration of C species (HCO₃⁻, CO₃²⁻, complexes and ions pairs of C), Mg and silica are extremely low (Fig. 4a and b); (v) the presence of reduced species of S (HS⁻ ≈ 0.7 mg/L); (vi) very high values of dissolved B.

Some authors (e.g., Barnes et al., 1967; Barnes and O'Neil, 1969) suggest that serpentinization of the ultramafic rocks might contribute to the mineral water chemistry through the reaction



which may explain the low Mg and SiO₂ concentrations found in the Cabeço de Vide mineral waters. Usually, as stated by Hostetler et al. (1966), serpentinization is not a single episode in the history of ultramafic bodies, but probably has occurred at various times and places for the same body of rock. The low Mg/Ca ratio of these waters may indicate the rodingitized rocks being leached (Coleman, 1977; Costa et al., 1993).

The higher B concentration observed in the Cabeço de Vide mineral waters can be attributed to leaching from metamorphic and igneous rocks, or even the dissolution of carbonates; B has a strong affinity with OH⁻ and the

aqueous speciation is mainly controlled by water pH. The formation of undissociated boric acid B(OH)₃⁰, and its conjugate B(OH)₄⁻ is the process that retains B in basic solutions.

Groundwaters from the limestones are in equilibrium with calcite, oversaturated in quartz but undersaturated with respect to amorphous silica (SiO₂ (a)), and Mg carbonates. Groundwaters from gabbros are undersaturated with respect to pyroxenes, forsterite and chrysotile. Groundwaters from serpentinites are in equilibrium with silicagel and oversaturated in calcite, as the result of the basic pH solution. Neutral Mg–HCO₃ waters are generally undersaturated with respect to the typical minerals of the ultramafic rocks and serpentinites, as well as brucite, sepiolite, and a variety of Mg–carbonates. These waters are oversaturated in calcite as a result of Ca–aluminosilicate dissolution and rising pH. In contrast, Cabeço de Vide mineral waters are strongly oversaturated with chrysotile, diopside and calcite, slightly undersaturated with respect to clinoenstatite and forsterite, and undersaturated in brucite and amorphous silica (Table 3).

4.2. Isotope geochemistry

Environmental isotopes (¹⁸O and ²H) were used to estimate the relative importance of locally infiltrated meteoric waters to the recharge of the Cabeço de Vide mineral waters. The long term weighted mean value (δ¹⁸O and δ²H) of precipitation collected in Portalegre meteorological station (597 m a.s.l./approximately 15 km NE of Cabeço de Vide) was used to help the interpretations. The relationship between the concentrations of the environmental stable isotopes ²H and ¹⁸O in all the water samples (Fig. 5) is similar to the relationship in the Global Meteoric Water Line (GMWL: δ²H = 8 δ¹⁸O + 10) defined by Craig (1961), indicating (i) that they are meteoric waters, which have not been subjected to surface evaporation (being directly infiltrated into the ground) and (ii) that there is no evidence of water/rock interaction at high temperatures, consistent with the low issue temperature (≈19.5 °C) of the Cabeço de Vide mineral waters.

Cabeço de Vide mineral waters, the local Mg–HCO₃ waters (issuing from the serpentinized dunites) and stream waters have similar δ²H and δ¹⁸O values (around –27‰ and –4.5‰, respectively), indicating a possible common meteoric origin (Fig. 5).

The shift observed between the GMWL and the isotopic composition of Cabeço de Vide mineral water could be due to the formation of hydrous minerals (e.g., clay minerals) and calcite precipitation leading to depletion in the water isotopic composition. These types of minerals are enriched in ¹⁸O but depleted in ²H compared to the water from which they precipitate at isotopic equilibrium (Chacko et al., 2001). Therefore, the residual Cabeço de Vide mineral waters should become progressively depleted in ¹⁸O and enriched in ²H, during the precipitation of hydrous minerals.

Marques et al. (2003) estimated the altitude effect in the region on the basis of δ¹⁸O values of shallow groundwater samples collected at different altitudes, and the long term weighted mean value of precipitation collected in

Table 2
Representative physico-chemical data of waters from Cabeço de Vide region, Portugal

Reference	Source	T(°C)	pH	Cond ($\mu\text{S}/\text{cm}$)	Eh (mV)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Al (mg/L)	Fe (mg/L)	HCO ₃ (mg/L)	C _{Total} (mg/L)	OH (mg/L)	SO ₄ (mg/L)	Cl (mg/L)	NO ₃ (mg/L)	SiO ₂ (mg/L)	B (mg/L)
Rain water			6.00			0.3	0.01	0.16	0.04			14.8			3.50	2.97	0.63		
Alter-do-Chão (b)	○ (L)	19.4	6.96	724	26	100.0	26.50	14.30	0.96	0.002	n.d.	469.2	92.39	n.d.	20.56	16.68	19.48	24.6	0.008
Furo Pedreira (b)	○ (L)	18.8	7.04	663	22	95.2	22.10	12.80	0.77	0.005	n.d.	419.4	80.18	n.d.	29.03	12.18	9.22	27.0	0.008
Monte Mariolo (b)	○ (L)	18.9	7.18	599	-11	85.6	17.90	13.50	1.06	0.005	n.d.	383.7	75.56	n.d.	19.59	14.47	11.29	16.0	0.047
Monte do Holandês (b)	○ (L)	19.2	7.05	680	91	84.8	31.60	13.40	1.70	0.008	0.02	436.8	86.00	n.d.	18.79	14.92	19.24	15.6	0.044
Vale Fabiano (sp)	◆(Sp)	19.1	7.37	678	63	41.8	60.30	11.70	0.52	0.007	0.02	458.4	90.32	n.d.	17.82	10.99	11.89	59.5	0.011
Horta Tirana (sp)	■ (G)	19.1	6.98	675	78	79.0	31.80	17.00	0.83	0.011	n.d.	443.9	87.40	n.d.	20.76	12.38	12.08	30.0	0.009
Maria Rita (b)	◆(Sp)	19.4	8.04	741	33	16.5	74.30	27.80	8.36	0.004	n.d.	483.1	95.68	n.d.	17.40	20.18	17.92	43.0	0.068
Furo da Camara (b)	◆(Sp)	19.2	7.54	740	108	38.7	72.20	9.56	0.44	0.006	n.d.	542.9	107.06	n.d.	14.42	9.08	9.07	72.8	0.011
Horta de Fonte Vide (sp)	■ (G)	18.8	6.93	561	97	51.7	29.70	22.70	0.56	0.015	n.d.	372.9	73.40	n.d.	19.04	8.03	7.12	50.9	0.008
Ermida (*) (sp)	● (CV)	17.1	10.71	416	-39	5.1	0.30	55.90	5.22	0.100	n.d.	n.d.	2.82	7.97	12.60	33.49	7.60	5.6	0.230
AC3 (*) (b)	● (CV)	19.6	10.93	646	-177	22.5	0.16	49.00	5.04	0.230	n.d.	n.d.	1.38	33.02	5.18	32.14	6.22	5.5	0.290
Cabeço Vide stream	Δ (str)	18.5	8.23	735	48	31.5	78.80	10.40	0.44	0.004	n.d.	512.9	101.90	n.d.	14.50	11.57	7.32	60.3	0.170
Residêncial (b)	○ (L)	19.6	7.39	841	103	87.3	42.70	21.80	3.10	0.004	0.02	428.2	84.40	n.d.	30.79	22.33	69.10	15.6	0.036
Fontainhas (sp)	■ (G)	18.2	7.37	785	106	41.9	77.30	9.53	0.35	0.006	n.d.	540.3	106.48	n.d.	14.72	14.44	12.33	74.3	0.011
Santo Cristo (dw)	■ (G)	17.8	6.9	765	124	105.0	25.00	18.80	1.22	0.004	n.d.	423.8	85.21	n.d.	27.90	20.73	14.94	34.7	0.017
Sto. António Par. (dw)	■ (G)	17.5	7.03	785	134	112.0	24.40	18.40	0.91	0.021	n.d.	484.2	95.35	n.d.	22.60	20.10	12.32	48.8	0.013
AC5 (*) (b)	● (CV)	19.8	11.08	526	-115	20.8	0.02	37.00	4.15	0.180	n.d.	n.d.	1.14	27.88	0.96	25.79	5.57	6.1	0.250

Notes: n.d. – not detected (below detection limits); ○ (L) limestone aquifer; ■ (G) gabbro aquifer; ◆(Sp) serpentinite aquifer; ● (CV) Cabeço de Vide mineral waters; Δ (str) stream water; (b) borehole; (sp) spring; (dw) dug well. C total stands for total inorganic dissolved C.

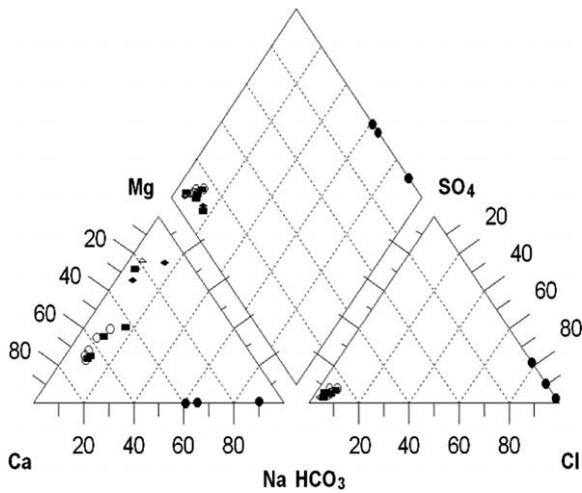


Fig. 2. Piper diagram: (●) Cabeço de Vide mineral water. Waters ascribed to different geological formations: (○) limestones; (■) gabbros; (◆) serpentinites; (Δ) Cabeço de Vide stream.

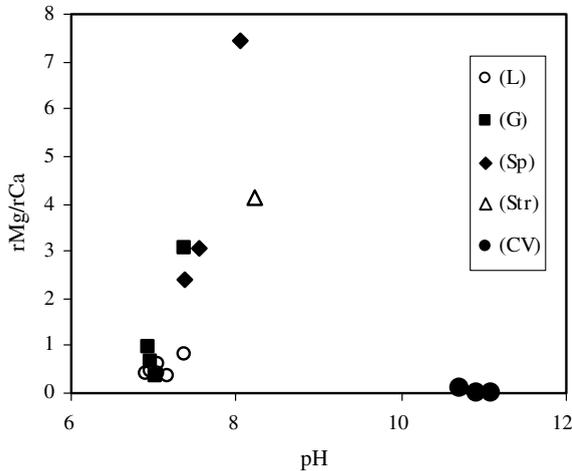


Fig. 3. rMg/rCa vs. pH plot of waters from different geological formations: (○) (L) limestones; (■) (G) gabbros; (◆) (Sp) serpentinites; (Δ) (Str) Cabeço de Vide stream. (●) (CV) Cabeço de Vide mineral waters.

Portalegre meteorological station ($\delta^2\text{H} = -32.2\text{‰}$; $\delta^{18}\text{O} = -5.44\text{‰}$; ITN, 2002). The shallow groundwater samples were assumed to represent the integrated isotopic composition of infiltrating precipitation above respective altitudes Marques et al. (2003). The magnitude of the altitude effect was $-0.28\text{‰}/100\text{ m}$ for $\delta^{18}\text{O}$, very similar to those values obtained in similar studies in the Portuguese mainland (Aires-Barros et al., 1994; Marques et al., 2000, 2001; Lima and Oliveira, 2000). Considering the long-term weighted mean isotopic composition of precipitation at Portalegre, it was concluded that the major source of recharge of the Cabeço de Vide mineral waters should infiltrate at lower elevation sites ($\approx 250\text{--}300\text{ m a.s.l.}$) located at the local mafic/ultramafic outcrop.

Tritium in most surface and shallow water samples was less than 7 TU, comparable to that of current precipitation

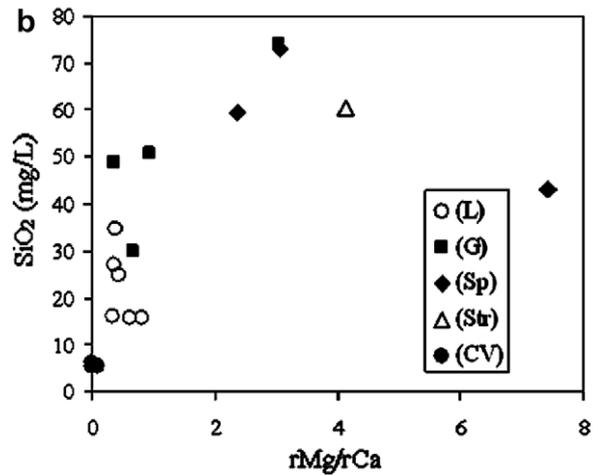
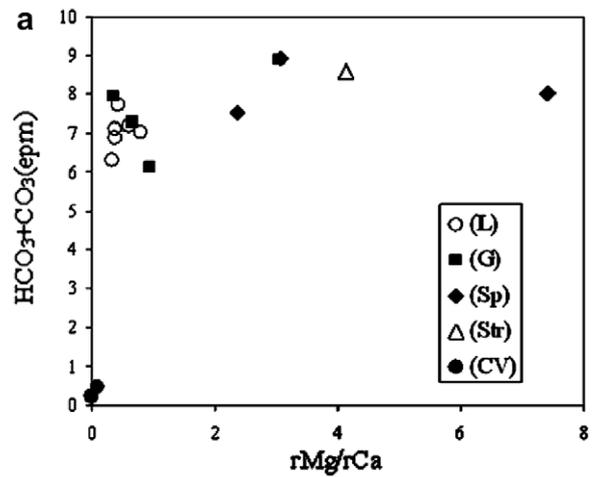


Fig. 4. (a) $\text{HCO}_3^- + \text{CO}_3^{2-}$ (epm) vs. rMg/rCa plot and (b) SiO_2 (mg/L) vs. rMg/rCa plot of waters from different geological formations: (○) (L) limestones; (■) (G) gabbros; (◆) (Sp) serpentinites; (Δ) (Str) Cabeço de Vide stream. (●) (CV) Cabeço de Vide mineral waters.

at the Cabeço de Vide Spa ($4.9 \pm 1.0\text{ TU}$). The absence of ^3H determined in the Cabeço de Vide mineral waters suggests that, using a simple decay model, recharge of Cabeço de Vide mineral system corresponds to an age older than 60 a. The high Cl concentrations and the absence of ^3H could be ascribed to an extended flow path and/or long residence time (Fig. 6).

Two samples of Cabeço de Vide mineral waters were collected for ^{14}C -age determinations (AMS determinations; Geochron Laboratories, USA). The values obtained range between $69.12 \pm 0.28\text{ pmC}$ and $65.24 \pm 0.35\text{ pmC}$ (AC5 and AC3 boreholes), indicating an apparent groundwater age between $3.6 \pm 2.3\text{ ka BP}$ and $6.0 \pm 2.2\text{ ka BP}$, respectively. The ^{14}C age calculations were based on a closed system model (Salem et al., 1980), on the assumption that the initial activity of the dating material is 100% modern CO_2 activity (100 pmC); for the $\delta^{13}\text{C}$ of the reservoir the value of $1 \pm 1\text{‰}$ was adopted (assuming that part of the CO_2 is related to the dissolution of the carbonate rocks); the $\delta^{13}\text{C}$ for the CO_2 in the soil zone is $-25 \pm 2\text{‰}$; the fractionation

Table 3
Saturation indices for key minerals

Reference	Anorthite	Brucite	Calcite	Chrysotile	Clinoenstatite	Diopside	Dolomite	Forsterite	Magnesite	Sepiolite	SiO ₂ (a)
Alter-do-Chão	-4.28	-6.47	-0.04	-7.42	-4.25	-5.25	0.38	-10.86	-0.91	-4.56	-0.63
Furo Pedreira	-3.36	-6.42	-0.02	-7.16	-4.16	-4.99	-0.40	-10.73	-0.95	-4.29	-0.58
Monte Mariolo	-3.72	-6.22	0.07	-7.00	-4.18	-5.00	-0.27	-10.54	-0.90	-4.57	-0.81
Monte do Holandês	-3.41	-6.22	-0.03	-7.06	-4.20	-5.29	-0.22	-10.57	-0.75	-4.64	-0.82
Vale Fabiano	-2.65	-5.31	0.03	-3.16	-2.71	-2.90	0.49	-8.17	-0.10	-1.07	-0.24
Horta Tirana	-2.67	-6.36	-0.14	-6.91	-4.06	-5.04	-0.40	-10.57	-0.83	-4.06	-0.54
Maria Rita	-3.79	-3.87	0.33	0.83	-1.43	-0.83	1.59	-5.44	0.70	1.33	-0.39
Furo da Camara	-2.61	-4.90	0.23	-1.76	-2.21	-2.02	1.02	-7.26	0.22	0.01	-0.16
Horta de Fonte Vide	-2.18	-6.49	-0.44	-6.82	-3.96	-4.98	-0.86	-10.60	-0.98	-3.60	-0.31
Residencial	-3.97	-5.40	0.33	-4.63	-3.39	-3.79	0.63	-8.93	-0.26	-3.04	-0.83
Fontainhas	-2.54	-5.28	0.07	-2.80	-2.57	-2.70	0.66	-7.99	0.03	-0.61	-0.14
Santo Cristo	-3.38	-6.72	-0.15	-7.76	-4.33	-5.33	-0.67	-11.2	-1.08	-4.44	-0.46
Santo António Par.	-1.46	-6.50	0.07	-6.77	-3.96	-4.53	-0.28	-10.60	-0.90	-3.52	-0.31
Ermida	-4.78	-1.04	0.46	6.07	-0.27	3.41	-0.08	-1.46	-1.09	2.09	-2.10
AC3	-3.96	-0.72	0.76	6.34	-0.25	4.38	-0.39	-1.11	-1.72	1.71	-2.36
AC5	-4.39	-1.32	0.69	4.32	-0.95	3.86	-1.43	-2.41	-2.68	0.19	-2.46

Note: Symbols as in Table 2.

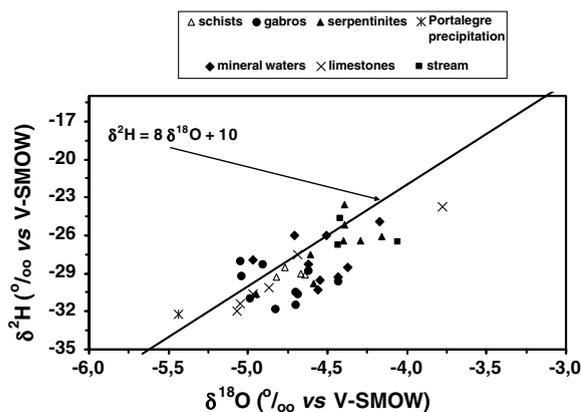


Fig. 5. $\delta^2\text{H}$ vs. $\delta^{18}\text{O}$ relations in water samples from the Cabeço de Vide area.

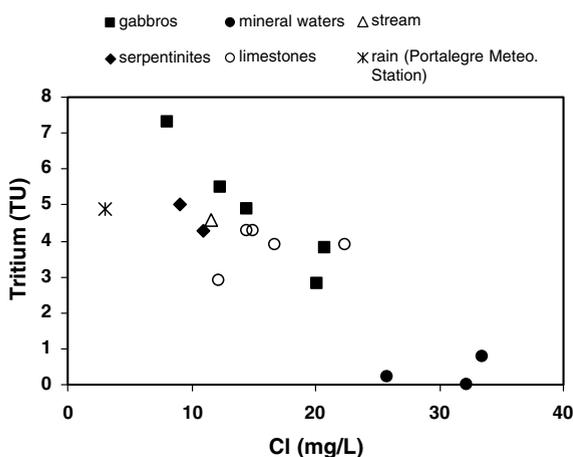


Fig. 6. Plot of ^3H (TU) vs. Cl (mg/L). Adapted from Marques et al. (2004).

factor ϵHCO_3 is $8 \pm 0.5\text{‰}$ and the error associated with the measurements of the TDIC is 0.1‰ . The chosen mathematical model, therefore, includes a mixture with the soil CO_2

(main source) and a minor contribution of the CO_2 from carbonate rock dissolution.

The $\delta^{13}\text{C}$ values of -22.9‰ and -18.0‰ for Cabeço de Vide mineral waters (boreholes AC3 and AC5, respectively) suggest (i) an organic origin for the C in the Cabeço de Vide mineral waters, and (ii) a negligible contribution from the local carbonate rocks ($\delta^{13}\text{C}$ values $\approx 1.48\text{‰}$).

In order to support these interpretations, a water sample from a borehole exploiting the Alter-do-Chão carbonate aquifer was also sampled for C (^{13}C and ^{14}C) determinations. ^{14}C values of 103.11 ± 0.41 pmC indicate that these waters are modern and $\delta^{13}\text{C}$ values of -14.8‰ indicate a mixture of soil CO_2 with CO_2 derived from water–rock interaction with the local carbonate rocks at a 1:1 ratio (Mook, 2000).

A simple conceptual circulation model of Cabeço de Vide mineral waters, using both geochemistry and isotope hydrology indicates that Mg-HCO_3 waters are generated in an initial step, under open CO_2 conditions, due to meteoric water–serpentinite interactions in a shallow environment, whereas the Cabeço de Vide mineral waters are produced in a subsequent step, under closed CO_2 conditions. In this second step, the increased pH values (due to water–dunite interaction at depth) will favour calcite precipitation. The carbonate deposits occurring along veins of drill cores from Cabeço de Vide corroborate this model, with most of the Mg retained in serpentines and vein brucite. Calcium concentrations should increase proportionally in waters during the evolution of the Mg-HCO_3 -type waters towards the Cabeço de Vide mineral water end member.

5. Numerical model

To better understand the geochemical processes responsible for the Na–Cl/Ca–OH mineral waters of Cabeço de Vide, irreversible water–rock mass transfer was simulated using chemical speciation, mineral–solution equilibrium, and reaction path modelling. The calculations were carried out by means of the PHREEQC software code (Parkhurst and Appelo, 1999), using the WATEQF (Ball and Nordstrom, 1991) thermodynamic database of 2005.

The simulations were run at a temperature of 21 °C, close to the average spring temperature and because Cabeço de Vide wells are relatively shallow (maximum depth of 190 m). Reaction path calculations were performed in titration mode, which means adding at each step of the reaction progress (variable) a corresponding amount of a mineral, and only the chemical composition of the solid reaction was considered (*i.e.*, both reaction kinetics and reactive surfaces of solid phases were not considered).

5.1. Serpentinite dissolution modelling

Since serpentinites are almost monomineralic rocks, stoichiometric serpentine ($\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$, chrysotile) dissolution was carried out at open- and closed-system conditions with respect to CO_2 (g). The average rainwater composition in the Cabeço de Vide region (Marques et al., 2004, represented in Table 2) was used as the initial solution. During the reaction path modelling, a limited number of solid phases were allowed to precipitate. These phases are in equilibrium or oversaturated in the mineral water and are those found in the drill cores: calcite, brucite, magnesite, and amorphous silica.

The pH variation and the amount of dissolved species produced through chrysotile dissolution at open-system conditions with (PCO_2) of $10^{-2.5}$ atm (*i.e.*, the average value found in the regional groundwaters) are shown in Fig. 7. The water pH and dissolved Mg and total C become stable from 0.6 mmol dissolved chrysotile, as a result of magnesite precipitation. After dissolution of 0.8 mmol of this mineral the silica is removed from the solution as amorphous silica.

The general agreement between the theoretical path and the analytical data indicates that progressive interaction of surface- and groundwaters with chrysotile leads to the formation of the Mg- HCO_3 type waters, under open-system conditions with respect to CO_2 . The concentration of Mg, SiO_2 and total C in the groundwaters flowing through serpentinites is close to the theoretical values obtained for the dissolution of 0.7 mmol of chrysotile. Sequential chrysotile dissolution under closed-system conditions to CO_2 (g) was simulated using as initial solution the slightly basic composition of Mg- HCO_3 type water obtained in the open-system dissolution path, and PO_2 in the system of $10^{-5.0}$ atm in order to reproduce the average redox conditions prevailing in the mineral water reservoir. The amount of dissolved species produced through reaction of 10 mmol of chrysotile and the water pH variation are shown in Fig. 7.

Water saturation in chrysotile is quickly reached, because the formation of Mg-rich solid phases, such as magnesite, dolomite and brucite does not remove the Mg and Si dissolved species in sufficient quantity to maintain continuous dissolution. In this way, the pH of the solution does not reach values as high as those observed in the mineral water of Cabeço de Vide and the concentrations of Mg and SiO_2 are too high.

5.2. Sequential serpentinite/dunite dissolution modelling

The dunite dissolution simulation was performed assuming that the olivine end-member forsterite

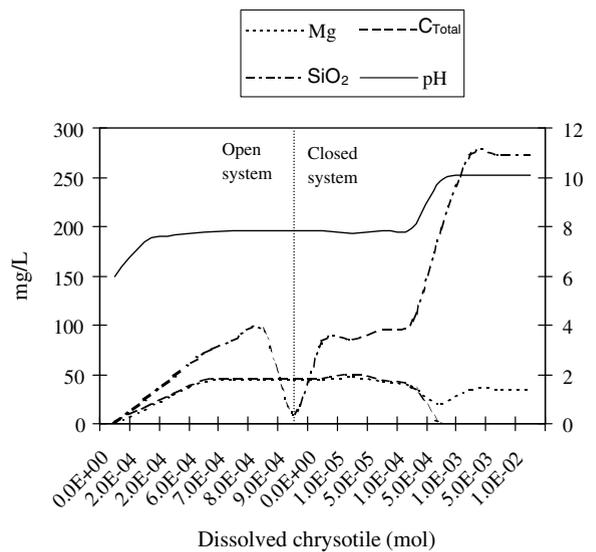


Fig. 7. Mass transfer and pH evolution as a function of the amount of chrysotile dissolved, during the reaction path in open-system conditions with respect to PCO_2 of $10^{-2.5}$ atm and closed system at highly reducing conditions.

(Mg_2SiO_4) is the main rock constituent and it dissolves stoichiometrically over a wide range of solution pH (Gíslason and Arnórsson, 1993). The simulation was carried out at PO_2 of $10^{-5.0}$ atm, after the dissolution of chrysotile in open-system conditions, and considering that chrysotile, magnesite, calcite, brucite and amorphous silica could be formed at thermodynamic equilibrium. The amount of dissolved species produced and the water pH are shown in Fig. 8. The final water composition is very close to the Cab-

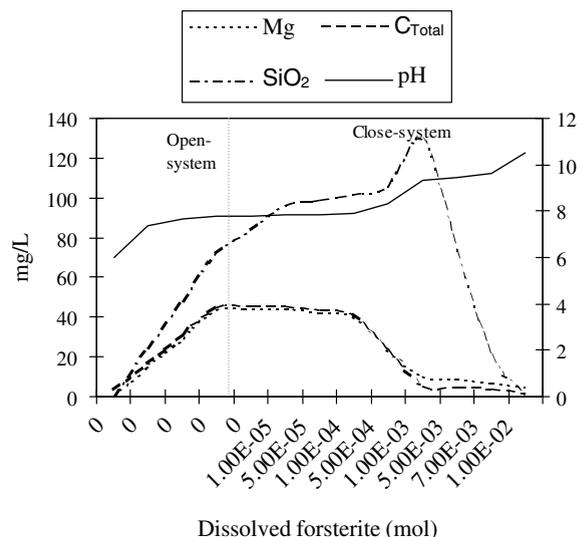


Fig. 8. The pH evolution and the amount of dissolved species produced through the sequential dissolution reaction path of chrysotile (0.0007 mol) in open-system to CO_2 (g) and 10 mmol of forsterite in highly reducing closed-system conditions.

ço de Vide mineral water composition, except for the SiO_2 content. Even modelling the forsterite reaction path under other environmental conditions such as the temperature, the redox state, the product solid phases or the solution equilibrium related to the different minerals, the amount of dissolved SiO_2 obtained is always 10–100 times less than the analytical values. This difference can be related to the kinetic reaction of solid phase dissolution and precipitation.

The numerical modelling shows that, during progressive forsterite dissolution under closed-system conditions to CO_2 (g), calcite, magnesite, amorphous silica, chrysotile and brucite can precipitate in this order. Brucite formation limits the pH increase, since this mineral starts to precipitate when the pH becomes stable. Calcite precipitation is the main process that depletes the aqueous solution in C and Ca species, allowing the water to acquire a Na–OH type geochemistry. The precipitation of amorphous silica is controlled by the water pH and the chrysotile precipitation. When this last solid phase starts to form, silica precipitation is inhibited.

Under natural conditions, the Cabeço de Vide mineral water system is oversaturated in chrysotile. There are limitations in thermochemical calculations of natural geological processes, especially at low temperatures. Kinetics of mineral dissolution and mineral precipitation at low temperature often is too slow for attaining water–rock equilibrium within a reasonable time scale. The low rate of chrysotile precipitation can explain the water oversaturation and the higher SiO_2 values in the natural water system than those obtained during the simulations.

Pokrovsky and Schott (2000) found the initial stage of forsterite dissolution is always non-stoichiometric with preferential Mg release at $\text{pH} \leq 8$ but preferential Si release at $\text{pH} \geq 10$, with silica concentrations up to 100 times higher than those of Mg. The preferential Si release from

forsterite grain surfaces in observed minerals and the interaction between this rock and regional groundwaters was simulated. The water composition from the limestone aquifer (Fig. 9, Furo da Pedreira), gabbro aquifer (Fig. 10, Horta de Fonte de Vide) and serpentinite aquifer (Fig. 11, Maria Rita) were used as initial solutions.

It is found that chrysotile and brucite formation control the extremely high water pH and the water undersaturation in relation to forsterite, allowing extensive dissolution

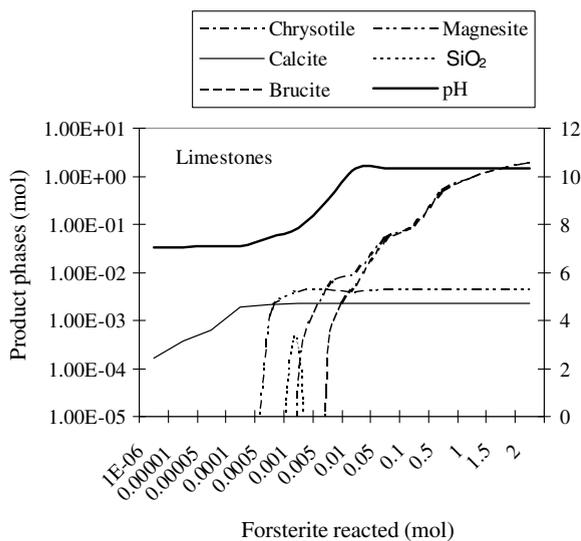


Fig. 9. Amounts of solid phases produced by the forsterite dissolution, at closed-system to CO_2 (g), by a water flowing through limestones rock aquifer with chemical composition similar to the Furo da Pedreira water.

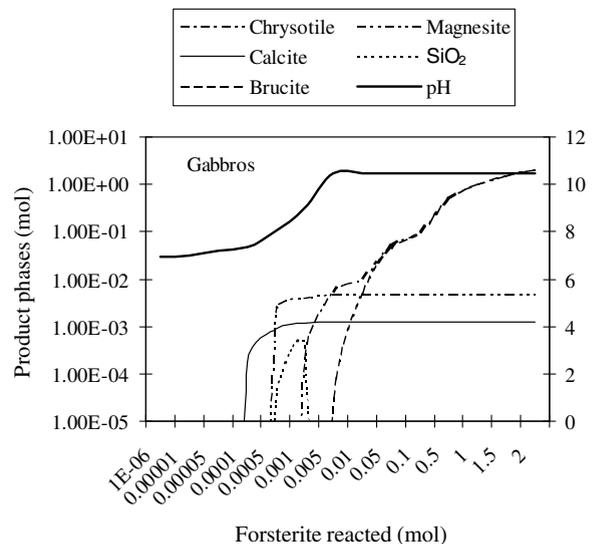


Fig. 10. Amounts of solid phases produced by forsterite dissolution, at closed-system to CO_2 (g), by a water flowing through gabbroic rock aquifer with chemical composition similar to the Horta de Fonte de Vide water.

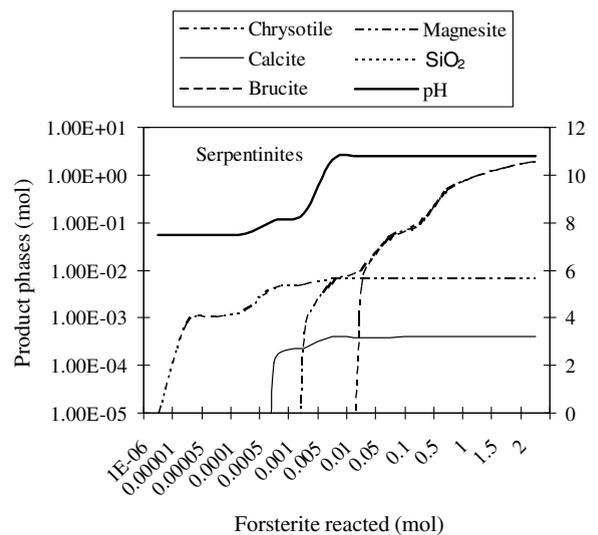


Fig. 11. Amounts of solid phases produced by forsterite dissolution, at closed-system to CO_2 (g), by a water flowing through serpentinite rock aquifer with chemical composition similar to the Maria Rita water.

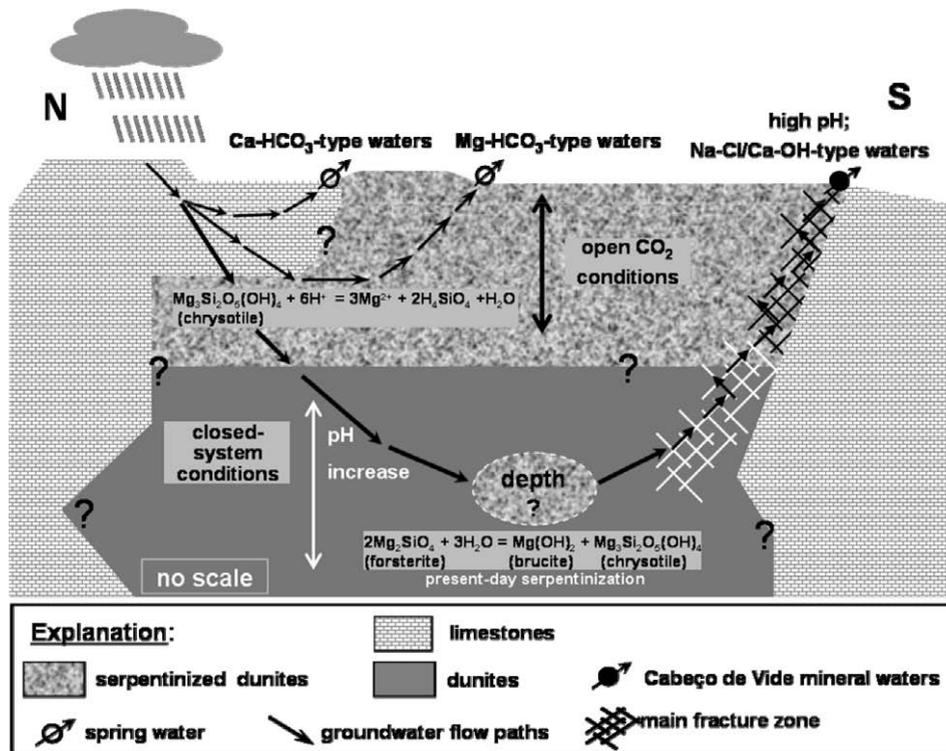


Fig. 12. Hydrogeological conceptual model of Cabeço de Vide mineral waters, showing the evolution of the local Mg–HCO₃-type waters (generated under open CO₂ conditions) towards the Cabeço de Vide mineral waters (high pH; Na–Cl/Ca–OH-type waters), as the result of water–dunite interaction under closed-system conditions at depth.

of this mineral. In the Cabeço de Vide region the serpentinization of the mafic and ultramafic rocks has been associated with metamorphic processes, occurring at low-pressure conditions under a great range of temperatures, from amphibolite facies to prehnite–pumpellyite facies (Costa et al., 1993). However, since 1967 studies on serpentinized rocks have found that modern serpentinization of ultramafic rocks occurs at low temperatures, where the formation of lizardite–chrysotile is observed (Barnes et al., 1967, 1978; Barnes and O’Neil, 1969; Wenner and Taylor, 1971, among others). The formation of these minerals is associated with Ca–OH type fluids oversaturated in chrysotile, brucite, diopside and undersaturated relative to forsterite and enstatite (Barnes and O’Neil, 1969).

6. Conclusions

The results obtained in this study increase knowledge regarding the hydrogeologic conceptual model of the Cabeço de Vide mineral waters, which seem to be dominated by interactions between locally recharged meteoric waters and ultramafic rocks. The local Mg–HCO₃-type waters are generated under open CO₂ conditions. The high-pH, Na–Cl/Ca–OH type waters from Cabeço de Vide are depleted in Ca, Mg, total C and SiO₂. These geochemical signatures can only be obtained with sequential and progressive interaction with serpentinites under open-system condi-

tions with respect to CO₂ followed by dissolution of dunite at highly reducing closed-system conditions (Fig. 12).

The irreversible water–rock mass transfer leading to these chemical changes in the aqueous phase is attained by the formation of solid phases as the water becomes oversaturated along the reaction path: calcite, magnesite, amorphous silica, chrysotile and brucite. Minerog-petrographic observations from drillcores provide strong evidence that considerable Mg precipitation occurs when surface waters infiltrate and react progressively with the ultramafic rocks. Cabeço de Vide mineral waters are unsaturated with respect to Mg–olivine [forsterite–Mg₂SiO₄] but supersaturated with serpentine [chrysotile–Mg₃Si₂O₅(OH)₄] indicating that the precipitation of Mg-rich minerals controls aqueous Mg concentrations. Serpentinization does not represent a single episode in the history of Cabeço de Vide ultramafic body, but probably indicates many episodes at various times and places for the same body of rock.

The Cabeço de Vide mineral waters would be responsible for serpentinization at low temperature conditions of the ultramafic rocks present at depth. There is general agreement between these theoretical reaction paths and the mineral assemblages observed in the cores from mineral water boreholes. These hydrogeological signatures are being used by the concessionaire of Cabeço de Vide spas for the redefinition of well-head and aquifer protection areas, drilling strategies, and future development

plans. At Cabeço de Vide region, these spas should be considered as one of the main sources of local/regional development, contributing to an increase in lodgings, commerce, services, etc., promoting social/economic growth.

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