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THEMATIC ISSUE

Characterization of Portuguese thermo-mineral waters to be applied in peloids maturation

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Abstract Portugal has an old tradition of using thermo-mineral waters for thermal treatments. Near mineral water springs, traditional applications are made using clays mixed with mineral waters gushing up "in situ", which are employed for the treatment of skin and musculoskeletal disorders. Our research team has found that some of the studied Portuguese clays (and similar formations) have compositional and physico-chemical properties that partially explain their therapeutic qualities. In what concerns Portuguese mineral waters, only a few studies were made trying to characterize and better understand their beneficial effects on human health, when mixed with clays. In fact, the therapeutic efficiency of the obtained thermal products depends on the geochemistry of the mixed clay-mineral water peloid. In this study, a total of 28 thermo-mineral water samples were collected from springs/boreholes located at Portuguese spas or traditional healing baths. The aim of this study was the geochemical characterization of collected water samples, in order to select the most suitable thermo-mineral water samples, reduce the lack of information about the trace/hazardous elements and, also, contribute towards the revitalization of Portuguese thermalism. Results show a large range of chemical characteristics and diverse water types. Temperature, electrical conductivity and pH values are variable among samples. Different hydrochemical water types were obtained from Hill–Piper diagrams. In terms of potential application for maturation, we selected three Ca–SO_4 (T1, H1 and H2) and two Na–HCO_3 (T14 and T15) water samples as best candidates to produce desirable therapeutic effects on peloids.

Keywords Portuguese thermalism · Hydrochemistry · Hydrothermal mud · Maturation · Trace elements

Introduction

Portugal has an old tradition of using thermo-mineral waters for thermal treatments as well as in using clays as empirical medicine. In the last decade many thermal centers (spas) are increasingly requesting for the treatment of numerous afflictions of neuromuscular, gastrointestinal, epidermic/dermic, articular and respiratory nature, attributed to the particular physico-chemical characteristics of these waters (Gomes et al. 2003). Similarly, at several sites, the empirical application of "healing muds" has been observed for decades. These are made with outcropping clays and seawater, when applied at beaches, or with mineral waters gushing up "in situ" when applied near mineral water springs, and are employed especially for the treatment of skin and musculoskeletal disorders. In what concerns these disorders, and despite no medical studies having been made, our research team has found that some of the studied clays (and similar formations) have compositional and physico-chemical properties that partially explain their therapeutic qualities (Rebelo et al. 2005, 2010, 2011a). They also exhibit good consistency and adequate thermal properties that make them valuable for thermal treatments in Portuguese spas (Rebelo et al. 2011b).

In what concerns the Portuguese thermo-mineral waters, only a few studies were made trying to characterize and

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better understand their beneficial effects on human health (Gomes et al. 2003; Terroso 2005). Furthermore, some Portuguese thermal centers, such as Vale dos Cucos Spa (nowadays with suspended activity), developed combined application of the therapeutic properties of clays and waters.

In the last decade, various publications have studied the effects of different types of thermo-mineral waters used in Italian and Spanish spas in treatments that combine the therapeutic effects of clays and mineral waters. In these applications known as pelotherapy,[1] thermal muds[2] are applied after a suitable preparation defined as maturation (Sánchez et al. 2002; Veniale et al. 1999, 2004, 2007; Gámiz et al. 2009). The mixing of certain clays with thermo-mineral waters leads to the production of a peloid, a therapeutic mud used as a poultice in medical practice. The therapeutic efficiency of these thermal products was suggested to depend on both the maturation procedure [i.e. the (re)mixing practice and lasting time] and the geochemistry of the mixed salty thermo-mineral water (Sánchez et al. 2002; A.A.V.V. 2004; Veniale et al. 2004, 2007). In particular, the mixing of water with the solid phase was recommended to improve the peloid therapeutic activity and the required properties for their use in spas (Curini et al. 1990; Veniale et al. 1999).

In order to produce a matured thermal mud, it is recommended to assess the following suitable properties and active factors: water retention, consistency, bioadhesiveness, ease of handling, pleasant sensation while applied onto the skin, cooling kinetics (thermo-insulation and heat-retention) and exchange capacity through mud/skin interface, i.e., the mobile-soluble chemical elements and organic substances produced by the metabolic activity of growing micro-organisms (Veniale et al. 2007). In this last case, the different mobility of soluble salts existing in the thermo-mineral water contributes to peculiar properties such as water retention, swelling index, consistency, adhesiveness, activity and rheological parameters (Veniale et al. 2007; Tateo and Summa 2007). Therefore, in order to select the adequate thermo-mineral waters and produce peculiar peloids (i.e., peloids devised for specific therapies) it is important to somehow predict these improvements. Other improvements, such as the decreasing of virgin clayey material clay's fraction due to clay particle agglomeration, the degradation of certain clay minerals and the precipitation-growth of new mineral phases, can be achieved and were observed as consequence of the maturation process (Sánchez et al. 2002; Veniale et al. 2004).

As a matter of fact, the geochemistry of thermo-mineral waters used in the maturation treatment improve and influence properties such as cation exchange capacity, soluble salts, water retention, swelling index, activity, consistency parameters, heat capacity and cooling kinetic. Ca–SO_4, both ferruginous HCO_3-rich and SO_4-rich waters, e.g., were observed to increase the water retention, consistency and heat capacity, in an opposite trend from Br-I-salty, sulphurous and Ca–Mg–SO_4 waters (Sánchez et al. 2002; Veniale et al. 2004). Therefore, properties such as source temperature, pH, total dissolved solids (TDS), CO_2 and HCO_3^- content, sulphidric degree, sulphate, borate, chloride, bromide, iodide, fluoride and nitrogen amount, and Na^+, Ca^{2+}, Mg^{2+}, Li^+, Sr^{2+}, Ba^{2+} exchangeable cations strongly influence the characteristics and behaviour of peloids and should be surveyed (Veniale et al. 2004, 2007).

In this study, thermo-mineral waters were collected from springs/borehole located at Portuguese spas or traditional healing baths, commonly used for the treatment of skin and musculoskeletal disorders, where pelotherapy could be implemented as an innovative hydrology technique. The aim of this study was the geochemical characterization of these waters in order to: (a) select the most suitable thermo-mineral waters for the production of peculiar peloids devised for the treatment of specific pathologies; (b) reduce the lack of information about the trace/hazardous elements information and (c) contribute for the revitalization of Portuguese thermalism.

Materials and methods

Sampling and sampling preparation

The study area comprised two main regions situated along the Portuguese mainland located at different geologic environments (Fig. 1). The sampling sites were selected according to their thermal and therapeutic aptitudes used in the treatment of skin, rheumatic and musculoskeletal disorders (the most common application in pelotherapy). A total of 28 water samples were collected between March 2007 and July 2009: 23 thermo-mineral waters at 14 thermal centers with focused therapies for the referred disorders (T coded samples) and 5 thermo-mineral waters at traditional "healing baths" sites (H coded samples).

At the Hesperic Massif, a Palaeozoic shield which occupies the greater part of the territory, 18 samples were collected corresponding to spring and borehole waters from 11 thermal centers/spas: T5 (Moura Spa); T6, T7 and T8 (Cabeço de Vide Spa); T9 (Monte da Pedra Spa); T10

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[1] Local or generalized application of thermal muds (hot cataplasms called "peloids") for recovering rheumatism, arthritis and bone-muscle traumatic damages (Venialle et al. 2004).

[2] Hyperthermal muds produced by the primary or secondary mixing of a solid component (usually a clayey geomaterial) with thermo-mineral water.

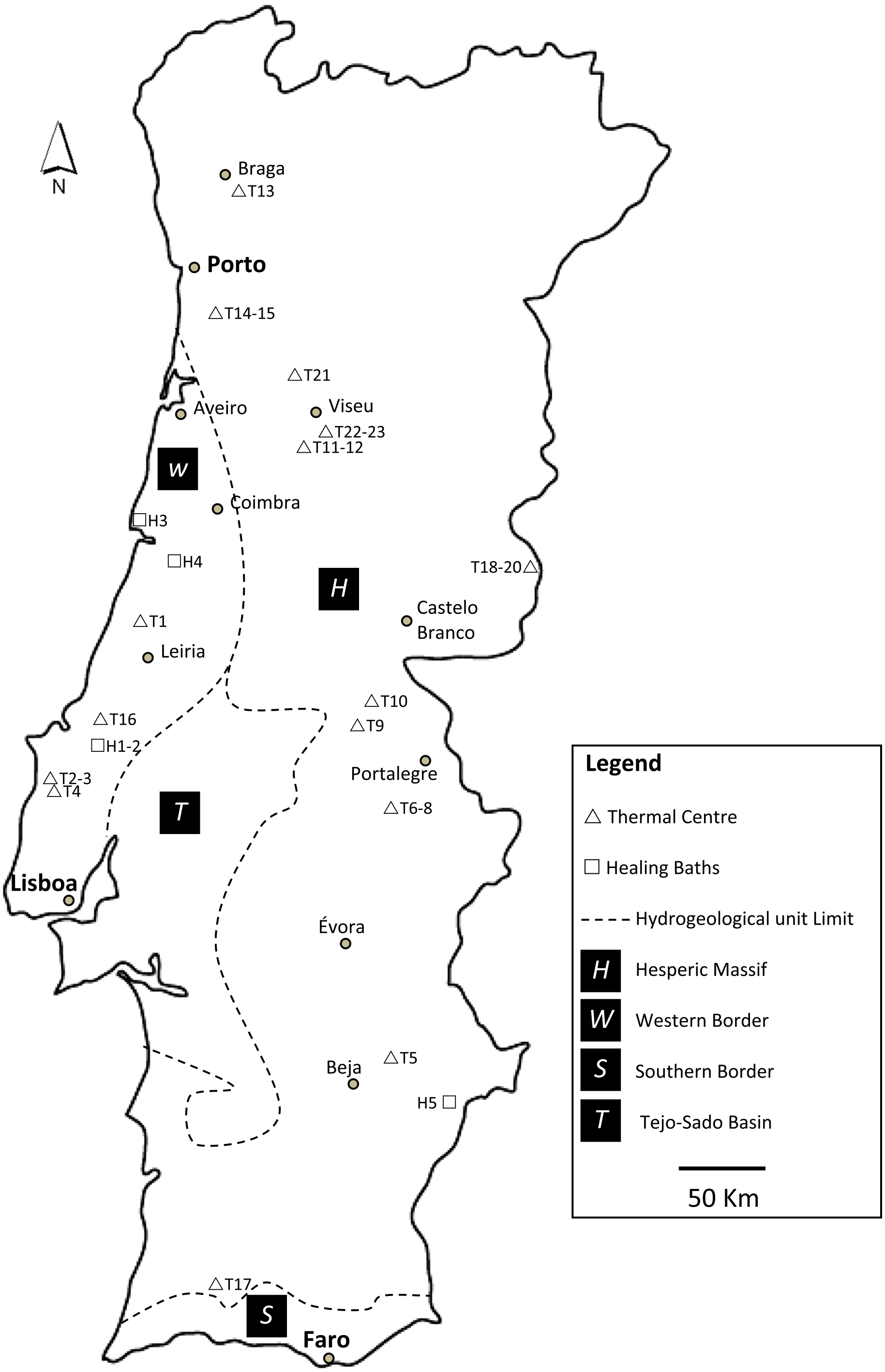


Fig. 1 Location of the mineral waters sampled in the Portuguese mainland and corresponding thermal centers (adapted from SNIRH-INAG 2000)

(Fadagosa de Nisa Spa); T11 and T12 (Caldas de Sangemil Spa); T13 (Caldas das Taipas Spa); T14 and T15 (São Jorge Spa); T17 (Caldas de Monchique Spa); T18, T19 and T20 (Monfortinho Spa); T21 (São Pedro do Sul Spa); T22 and T23 (Alcafache Spa). In addition, one sample (H5) was collected from a traditional healing bath (Ferradura healing baths). The remaining studied samples, in a total of nine, were collected at the Western Mesozoic–Cenozoic border (Fig. 1) and correspond to springs and boreholes from three thermal centers: T1 (Monte Real Spa); T2, T3 and T4 (Vimeiro Spa) and T16 (Caldas da Rainha Spa). In addition, four samples were collected at traditional healing baths sites: H1 and H2 (Quinta das Janelas healing baths); H3 (Ruaz healing baths) and H4 (Amieira healing baths). Generally, samples are quite well representative of the three main lithologies present in the Portuguese territory: 6

samples are located in metamorphic (M) rock regions, 9 samples are located in sedimentary (S) rock regions and 13 samples are located in igneous (I) rock regions.

The procedures for sampling and analysis followed standard methodologies (APHA 1992). At the spring, water sampling procedure consisted in the collection of the sample at the points of emission, while at the boreholes the water sampling and field measurements were undertaken after purging several borehole volumes. All samples were filtered in the field with 0.45 µm Millipore cellulose membrane filters and stored in clean 250 mL polyethylene bottles (ASTM 1984). Two sets of samples were collected at each site: (1) an acidified, down to $pH < 2$, adding ultrapure nitric acid; (2) an unacidified, for anion analysis. All of them were kept cool at 4 °C prior to laboratory analyses. All samples were placed in a portable cooler, with ice, immediately after collection to prevent bio alteration. In the laboratory, they were transferred and stored at 4 °C until analysis within the next 24 h (according to Working Party on Stabilization of Samples from the Hidrochemistry Team of the German Chemists Association 1980; EPA 1982; ASTM 1984).

Chemical analysis

Field parameters Unstable parameters such as temperature (*T*, °C), pH and electrical conductivity (EC, µS cm^{-1}, at 25 °C) were measured in situ, at each sampling location, using portable meters. The pH value was measured with a HI 8424 microcomputer pH meter, previously calibrated against supplied calibration standards (Titrisol standard solutions) at pH 4 and pH 7 with an accuracy of the pH measurement about ±0.05. Specific conductance referenced at 25 °C was measured using a HI8633 microcomputer electric conductivity meter. Alkalinity was also measured in the field by titration with H_2SO_4 at 0.16 N.

Chemical analyses Pre-concentration of water samples prior to analysis was not needed, but samples with lower pH and higher TDS required dilution. The analyzed elements include major anions (Cl, NO_3 and SO_4), major cations (Ca, K, Na and Mg), as well as a suite of dissolved trace metals (Ag, Al, As, B, Ba, Bi, Br, Cd, Co, Cr, Cs, Cu, Fe, Hg, Li, Mn, Mo, Ni, Pb, Rb, Sb, Sc, Si, Sr, U, W, V and Zn). Unacidified samples were analyzed using a Dionex 1000i ion chromatography (IC) workstation to determine the Cl, NO_3 and SO_4 concentrations. An isocratic elution with a sodium bicarbonate–sodium carbonate solution was employed together with a Dionex AS4-SC column. Although standards were prepared containing only the above anions, other anions would have been detected if present at levels greater than approximately 0.1 mg L^{-1}. Dilution was required for reliable anion analysis for concentrated samples. The HCO_3^- concentration was determined in situ by volumetric titration on filtered unacidified samples with sulphuric acid. The concentrations of major cations and trace elements in waters were determined using an inductively coupled plasma-atomic emission spectrometry method (ICP-MS) at ACME Analytical. ISO 9002 accredited lab, Canada. The detection limits for both major and trace elements in water samples were: 0.02 µg L^{-1} Co; 0.05 µg L^{-1} Ag, Bi, Cd, Sb; 0.1 µg L^{-1} Cu, Hg, Mo, Pb; 1 µg L^{-1} Al; 0.2 µg L^{-1} Ni; 0.5 µg L^{-1} As, Zn; and 10 µg L^{-1} Fe. The measurements taken on the studied thermo-mineral waters are reported in Tables 1 and 2.

Careful quality controls were achieved by checking sample containers and reagents for background concentration, preparing blank samples, and using duplicate or triplicate sub-samples (Ramsey et al. 1987). The geostandard WASTWATR3 was used by ACME to check the validity and reproducibility of the results. Typical uncertainties, including error sources, are under 6 % for all the trace elements whereas, for major anions, the uncertainties lie between 2 and 7 % depending on the concentration levels. The charge-balance errors of each sample, calculated considering the formula, show that the majority of the samples are within 10 % of balance.

Data analysis

Piper diagram Classifications of the water samples described in Table 1 were made according to principles of IAH (1979). Total equivalents of cations and anions separately were accepted as 100 % and ions with more than 20 % (meq L^{-1}) were taken into consideration in this classification.

Principal component analysis (PCA) statistical data analysis is a powerful tool in monitoring water properties and assisting in the interpretation of geochemical data. The analysis and interpretation of data, given by numerous variables, is difficult without the aid of multidimensional statistical analysis based on pattern recognition techniques, such as principal component analyses (PCA). In recent times, these multivariate statistical methods have been applied widely in hydrogeochemical studies (Join et al. 1997; Meng and Maynard 2001; Swanson et al. 2001; Cruz and França 2006), in order to establish the common relationships between measured hydrochemical variables, revealing patterns that may help to classify the original data. The PCA method aid in reducing the complexity of large-scale data sets, is currently widely used in environmental impact studies (Perona et al. 1999), elucidating relations among variables and identifying common underlying processes (Davis 1986; Webster and Oliver 1990; Wackernagel 1998). In the present study, a factorial analysis, PCA, was performed, allowing reducing the space

Table 1 Location of water sampling sites, and results of direct field measurements (temperature, pH and conductivity) and chemical analyses of the studied mineral waters

ID	Description	Cod	Type	Source	*T*	PH	EC	TDS	HCO_3^-	F[a]	Cl^-	NO_3^-	SO_4^{2-}	Na^+	S[b]	K^+	Mg^{2+}	Ca^{2+}	Si	ERB
T1	Monte Real	MR	sp	SD	20.6	7.3	2,052	3,420	138	0.0	424	1	1,954	275	20.2	4	46	705	8	−3.7
T2	Fonte Frades 1	FF	sp	SD	24.6	7.3	3,492	5,820	454	0.0	1,665	6	384	1,036	0	18	101	178	8	0.3
T3	Fonte Frades 2	FF	b	SD	23.8	7.1	3,858	6,430	434	0.0	1,934	2	391	1,194	0	15	104	206	9	1.0
T4	Vimeiro5	VM	b	SD	26.1	7.2	970	1,616	454	0.2	249	1	141	200	0	6	36	112	8	0.1
T5	Moura	MR	sp	MT	28.4	6.9	656	1,093	434	n.a.	143	32	27	51	0	2	40	66	11	−6.3
T6	Cabeço de Vide	CV	sp	MG	18.3	7.2	354	590	316	0.0	33	11	20	37	2.3	4	32	50	7	2.4
T7	Cabeço de Vide	CV	b	MG	19.8	11.3	354	590	177	0.0	45	2	18	48	2.3	4	m.d.l	11	3	−4.8
T8	Cabeço de Vide	CV	b	MG	19.8	11.2	296	493	118	0.0	38	2	1	37	2.3	3	m.d.l	15	3	−4.2
T9	Monte Pedra—Crato	MP	b	MG	22.3	7.8	307	512	197	n.a.	60	2	14	103	0	2	1	4	17	−4.0
T10	Fadagosa de Nisa	NI	b	MG	21.4	7.8	296	494	177	10.3	51	2	13	94	3.7	2	1	9	13	0.6
T11	Caldas de Sangemil HN1	SG	b	MG	45.0	8.3	352	586	197	17.1	58	1	15	129	43.7	4	0.1	5	49	7.1
T12	Caldas de Sangemil HN2	SG	b	MG	45.5	8.0	330	550	217	17.1	66	1	15	138	43.7	5	0.1	4	51	5.0
T13	Caldas das Taipas	TP	b	MG	29.9	8.1	185	308	130	5.2	23	1	33	55	8.2	1	1.	20	24	0.5
T14	São Jorge SJ1	SJ	sp	MG	24.2	8.5	564	940	631	17.2	207	1	36	227	61.6	10	0.3	4	35	−5.3
T15	São Jorge SJ2	SJ	b	MG	25.8	8.6	613	1,021	631	17.2	221	1	36	250	61.6	10	0.3	3	34	−2.6
T16	Caldas Rainha AC2	CR	b	SD	34.2	6.7	2,472	4,120	828	0.2	801	1	747	662	32.8	5	61	305	9	−2.5
T17	Caldas de Monchique	MO	sp	MG	28.6	9.4	288	480	316	1.4	43	1	63	119	2	2	m.d.l	1	7	−4.7
T18	Monfortinho AC3	MF	b	MT	31.2	5.4	25	42	10	0.5	3	1	3	3	0	1	1	1	7	−3.8
T19	Monfortinho AC6	MF	b	MT	30.9	5.4	25	41	15	0.5	2	1	3	3	0	1	2	1	9	0.8
T20	Monfortinho AC7	MF	b	MT	27.1	5.4	24	40	15	0.5	2	1	3	3	0	1	2	1	9	0.8
T21	S. Pedro Sul AC1	SPS	b	MT	64.8	8.4	312	520	138	17.1	26	1	24	83	15.5	3	m.d.l	3	28	4.7
T22	Alcafache 1	AL	sp	MG	52	8.2	325	541	197	17.8	34	1	3	96	5.1	2	0.1	5	24	2.7
T23	Alcafache 2	AL	b	MG	52	8.2	327	545	177	17.8	37	1	6	106	5.1	2	0.1	5	24	9.5
H1	Arrábidos 1	AR	sp	SD	30.6	6.8	1,902	3,170	335	n.a	533	1	972	389	4.2	4	67	335	13	−1.9
H2	Arrábidos 2	AR	sp	SD	30.5	6.9	1,848	3,080	335	n.a	493	1	992	394	4.2	4	66	323	12	−1.6
H3	Ruaz	RU	sp	SD	17.3	5.5	689	1,148	355	n.a	135	13	68	74	0	2	23	97	5	−4.9
H4	Amieira	AM	sp	SD	24.6	6.0	803	1,338	217	0.1	289	3	55	173	0	8	33	69	8	3.9
H5	Ferradura	FR	sp	MT	24.0	7.8	481	801	394	n.a	70	2	45	101	0	1	22	26	2	−3.2

b Borehole, *sp* spring, *T* temperature (°C), *EC* electrical conductivity (µS cm^{-1}), *TDS* total dissolved solids content calculated from EC content (Hem 1970), *MG*, Magmatic, *MT*, metamorphic, *SD* sedimentary, *m.d.l.* below method detection limit, *ERB* error balance

[a] Total sulphur content in ml of I_2 0.01 N (expressed in mg L^{-1} of H_2S) determined by several authors (INETI 2006)

[b] n.a., data not available in the literature

Table 2 Minor and trace elements composition (in μg L^{-1}) of the studied mineral waters

Ref.	Name	Al	*As*[a]	*B*	Ba	*Br*	*Cr*	Cs	*Cu*	Fe	Li	*Mn*	Mo	Rb	Se[1]	Sr	U	W	V	*Zn*
T1	Monte Real	5	b.d.l.	b.d.l.	13	422	14	0.9	4	382	23	33	0.5	7.9	b.d.l.	2,681	0.1	0.1	2.7	2.5
T2	Fonte Frades 1	5	12	257	50	5,198	54	1.9	1	50	51	1	0.5	25.3	48	1,935	0.25	0.2	24.1	2.5
T3	Fonte Frades 2	19	14	258	81	5,127	55	1.6	b.d.l.	50	75	33	1.4	20.5	46	2,532	0.32	0.1	26.9	14.6
T4	Vimeiro5	0.5	2	99	65	798	35	0.4	1	5	15	b.d.l.	0.7	5.5	8	650	1.13	0.1	3.4	0.3
T5	Moura	0.5	4	15	61	646	9	0.0	1	40	3	b.d.l.	0.1	0.8	4	187	0.17	0.0	0.4	1.0
T6	Cabeço de Vide	7	2	96	38	133	11	0.1	1	16	6	b.d.l.	0.3	10.0	1	432	0.45	0.0	0.7	0.5
T7	Cabeço de Vide	112	b.d.l.	210	12	200	3	0.1	0.3	5	1	b.d.l.	0.3	9.1	1	195	0.01	0.0	0.1	0.3
T8	Cabeço de Vide	163	b.d.l.	158	11	181	2	0.1	0.2	5	1	b.d.l.	0.05	8.6	b.d.l.	158	0.01	0.0	0.1	3.6
T9	Monte Pedra—Crato	15	5	606	0.1	421	5	31.0	1	5	446	31	0.05	28.5	1	84	0.04	53.5	0.1	0.3
T10	Fadagosa de Nisa	2	31	468	0.1	370	4	67.2	0.2	5	350	46	0.1	37.3	1	118	0.01	34.3	0.1	0.3
T11	Caldas de Sangemil HN1	7	8	857	0.7	416	7	257.8	1	5	157	9	2.2	94.4	2	60	0.1	142.5	0.6	1.3
T12	Caldas de Sangemil HN2	3	7	843	1	426	7	274.9	1	11	1,561	6	2	108.8	2	61	0.04	148.1	0.5	1.9
T13	Caldas das Taipas	3	56	67	92	131	6	4.4	1	51	111	17	3.3	13.2	1	315	0.01	11.4	0.2	1.8
T14	São Jorge SJ1	1	13	2,715	4	1,268	9	235.5	1	46	978	23	0.4	128.7	7	421	0.01	413.6	2.5	0.3
T15	São Jorge SJ2	1	1	2,854	4	1,292	9	244.0	1	5	1,021	31	0.1	132.7	7	472	0.01	470.9	2.8	0.3
T16	Caldas Rainha AC2	13	6	b.d.l.	38	399	21	3.0	4	5	67	19	0.05	10.5	b.d.l.	4,618	0.19	2.0	8.7	13.7
T17	Caldas de Monchique	88	6	32	0.5	113	8	0.0	0.2	5	1	0.1	19.9	5.7	1	97	0.01	9.7	0.7	0.3
T18	Monfortinho AC3	0.5	1	5	9	15	1	0.4	b.d.l.	5	5	1	0.05	3.0	b.d.l.	8	0.03	0.0	0.9	4.4
T19	Monfortinho AC6	0.5	1	5	7	15	1	0.4	b.d.l.	5	4	0.4	0.05	3.6	b.d.l.	10	0.01	0.0	1.0	2.9
T20	Monfortinho AC7	0.5	1	b.d.l.	7	16	1	0.4	b.d.l.	5	4	0.4	0.05	3.5	b.d.l.	9	0.01	0.0	0.9	3.6
T21	S. Pedro Sul AC1	57	5	434	62	160	1	56.8	16	112	549	2	1.4	56.7	b.d.l.	70	0.03	67.5	0.1	8.8
T22	Alcafache 1	8	6	145	242	267	6	123.6	1	5	764	5	5.6	54.6	b.d.l.	81	16.30	68.3	0.1	0.3
T23	Alcafache 2	61	10	141	16	272	2	126.4	21	89	751	6	5.5	55.3	b.d.l.	88	8.55	56.3	0.1	8.9
H1	Arrábidos 1	23	b.d.l.	81	25	315	32	2.6	5	161	77	b.d.l.	0.5	9.8	b.d.l.	5,873	0.01	0.1	4.4	0.3
H2	Arrábidos 2	5	b.d.l.	74	24	305	32	2.4	3	50	72	b.d.l.	0.5	9.0	b.d.l.	5,619	0.01	0.1	3.9	2.5
H3	Ruaz	0.5	1	40	74	464	26	0.0	1	5	9	0.1	0.1	1.7	5	216	0.76	0.1	1.3	0.3
H4	Amieira	1	3	70	33	998	25	0.1	–	5	9	b.d.l.	0.2	13.5	9	200	2.12	0.1	4.2	0.3
H5	Ferradura	4	5	9	36	479	9	0.1	2	48	1	0.2	1.1	0.3	2	1,601	1.35	0.0	0.4	2.3

Italics represents elements/ions associated to anthropogenic sources of contamination (Berner and Berner 1996; Adriano 2001); (b.d.l.) below the detection limit

[a] Hazardous elements for cosmetic purposes (Veniale et al. 2007)

size of the variables (Massart and Kaufman 1983). The main goal of PCA is to define the principal components, known as eigenvectors, of a variance–covariance or a correlation matrix from a data set corresponding to a raw matrix of N rows of observations by p columns of variables (Davis 1986). The underlying structure of the data is revealed by the eigenvectors that yield the orientation of the principal axis of the ellipsoid, which result from the geometrical interpretation of the variance–covariance matrix, and the respective magnitude, i.e., the eigenvalues. This standardization procedure tends to increase the influence of variables whose variance is small, and reduce the impact of variables whose variance is large. Furthermore, it eliminates the effect of using different units of measurement, and makes the data dimensionless, transforming the data into a small number of independent factors (principal components) which synthesize the associations between variables. As such, the referred factors (or PCs) are orthogonal linear combinations of the variables and are related with common processes that affect the variables through expert knowledge of the problem in hand. The number of significant principal components for interpretation is selected on the basis of the Kaiser criterion with eigenvalue higher than 1 (Kaiser 1960) and a total of explained variance equal or higher than 70 %. The computer program Statistica 9.0® was used to conduct several multivariate statistical techniques including cluster analysis and principal components analysis.

Results and discussion

Geological and hydrogeological setting of the studied samples

Most of samples collected at Hesperic Massif emerge from Hercynian Granites (Fig. 1) outcropping at Porto, Viseu and Portalegre regions and are related with deep fractured reservoirs with localized permeability occurring along the main active faults (Aires-Barros and Marques 2000). In particular, water samples from Caldas de Sangemil Spa (T11, T12), and Alcafache Spa (T22 and T23) are associated with a coarse- to medium-grained two-mica porphyritic granite, the Vouzela Granite (Teixeira et al. 1961; Bento 1986; GEOESTUDOS 1990; CAVACO 1991). Water sample from Caldas das Taipas Spa (T13) is associated with a coarse-grained porphyritic biotitic granite, the Celeirós and Vieira do Minho Granite (D'Almeida and De Almeida 1988; CAVACO 1981). Water samples from São Jorge Spa (T14 and T15) are associated with an important metalliferous vein (Beiras Metalliferous Vein), occurring in this brecciated milky-quartz vein that stays in contact with a medium-grained porphyritic granite, the São Jorge-Fiães Granite (Medeiros et al.1964; CAVACO 1983). Finally, water samples from Monte da Pedra Spa (T9) and from Fadagosa de Nisa Spa (T10) are associated with the Nisa Eruptive Complex, coarse-grained porphyritic two-mica granite, rich in uraniferous minerals (Calado and Franco 2006). Furthermore, associated with an eruptive complex, is a sample collected at Caldas de Monchique (T17), this emerging from the contact of syenite rocks of the Monchique Eruptive Complex (subvolcanic alkaline ring complex of Cretaceous Age) with the surrounding schists of Brejeira Formation (GEOESTUDOS 1992).

The remaining Hesperic Massif sampled waters emerge from metamorphic geologic environments (Fig. 1). In particular, sample from São Pedro do Sul Spa (T21) emerges from sillimanite-rich schist bodies occurring in the middle of fine- to medium-grained two-mica granites, the São Pedro do Sul Granite. The presence of uraninite and the association of uranium–thorium in some accessory minerals are associated with the radioactivity of these granites (Basham et al. 1982; Pereira and Ferreira 1985; Lemos et al. 1992). In another metamorphic context (Fig. 1) are samples from Monfortinho Spa (T18, T19 and T20), emerging from the Arenigian quartzite complex of the Penha Garcia syncline (GEOESTUDOS 1993; CAVACO 1994; Sequeira et al. 1999).

Associated with the metamorphic rocks of the southern part of the Hesperic Massif, some carbonated systems may occur and correspond to important aquifers (Almeida et al. 2000; Chambel et al. 2006). According to Marques et al. (2008) the Cabeço de Vide mineral waters (T6, T7 and T8) issue at the intrusive contact between the mafic/ultramafic rocks and the carbonate sequence, associated with the main regional NNE–SSW trending fault. The ultramafic rocks range from partially serpentinized dunites to serpentinites. Finally, samples collected at Ferradura healing baths (H5) and Moura Spa (T5) are associated with the flow in dolomitic marbles and dolomites of the Ficalho-Moura volcanic-sedimentary complex which underlies the Miocene detritic carbonated deposits of Moura region (Marques da Costa et al. 2005).

The remaining studied samples were collected at the Western Mesozoic–Cenozoic border (Fig. 1), mainly on limestone and sandstone formations locally intercepted by volcanic intrusions and extensive lava flows (Chambel et al. 2006). Deep groundwaters occur in this part of the territory, associated with circulation along major faults or through deep-seated strata associated with the diapiric structures. Not so deep waters are well controlled by uniform horizontal pathways formed by relatively undisturbed sedimentary rocks (Aires-Barros and Marques 2000). All samples are located at different aquifers which occur in a great variety of geological formations (Almeida et al. 2000; SNIRH-INAG 2005; Chambel et al. 2006). Sample T1

(Monte Real Spa) is situated in the Leirosa-Monte Real aquifer next to the Monte Real Diapir, and emerges from Plio–Pleistocene sandstones overlaying this diapir. Samples collected at Vimeiro Spa (T2, T3 and T4) are located in the Torres-Vedras aquifer above the Upper Jurassic limestones outcropping in the E limb of Vimeiro diapir. The main recharge area of the Caldas da Rainha thermo-mineral system (represented by sample T16) seems to be related to the geological formations located at the E border of the Candeeiros Mountains. The discharge zone is located at the W border of the regional syncline, controlled by the locally oriented N–S oblique fault (60°E). In the Caldas da Rainha discharge flow area the thermo-mineral water flows through the limestone strata. In this area, the flow evolves from east to west, following the reverse inclination of limestone layers (Marques et al. 2013). The Arrábidos healing baths (H1 and H2) are located in the Caldas da Rainha-Nazaré aquifer and emerge from Lower Jurassic formations outcropping at the E limb of the Caldas da Rainha diapir. Finally, a sample from Ruaz healing baths (H3) emerges from Upper Jurassic sandstones, marls and limestones of the “Carboniferous Complex” exploited during 200 years in the carbon mine of Cabo Mondego (Kullberg et al. 2006), and a sample from Amieira healing baths (H4) emerges from the Upper Cretaceous Limestones of Verride anticline.

Physico-chemical characteristics of the studied waters

Descriptive statistics for the IC and ICP water analysis of temperature (T), electrical conductivity (EC), HCO_3, Cl, NO_3 and SO_4, Na, K, Mg, Ca, as well as a suite of selected dissolved trace metals (Ag, Al, As, B, Ba, Bi, Br, Cd, Co, Cr, Cs, Cu, Fe, Hg, Li, Mn, Mo, Ni, Pb, Rb, Sb, Sc, Si, Sr, U, W, V and Zn) are listed in Table 3.

The pH values vary from 5.4 (sample T19) to 11.3 (sample T7) with a median value of 7.5. According to these values, 68 % of studied waters (from magmatic and metamorphic sources) were considered alkaline and remaining waters (from sedimentary sources) exhibited an acidic character (Fig. 2).

Temperature in the springs ranges between 17.3 °C (sample H3) and 64.8 °C (sample T21), with a median value of 52 °C. Adopting the Lisbon Hidrology Institute classification (Carvalho et al. 1961) the majority of studied samples (82 %) presented characteristics of mesothermal (T 25–35 °C) and hypothermal waters ($T < 25$ °C). Only a few (18 %) exhibited temperatures typical of thermal waters (T 35–45 °C), as observed in samples T11 and T12, and hyperthermal waters ($T > 45$ °C), as observed in samples T21, T22 and T23 (Fig. 2).

Electrical conductivity varied between 40 $\mu S\ cm^{-1}$ (sample T20) and 6,430 $\mu S\ cm^{-1}$ (sample T3), with a median value of 590 $\mu S\ cm^{-1}$. The total dissolved solids (TDS) content was calculated according to Hem (1970) for all samples and ranged between 24 $mg\ L^{-1}$ and 3,858 $mg\ L^{-1}$, with a median value of 864.2 $mg\ L^{-1}$. Adopting the Portuguese Geological and Mining Institute (now LNEG) classification (Lourenço and Ribeiro 2004), 68 % of studied waters correspond to low mineralized waters once their TDS varied between 100 and 1,000 $mg\ L^{-1}$ and only a few presented parameters typical of hypersaline (samples H1, H2, T1, T2, T3 and T16) and hyposaline (samples T18, T19 and T20) thermo-mineral waters (Fig. 2). The waters from sedimentary sources present the highest EC median value (3,170 $\mu S\ cm^{-1}$) while the waters from metamorphic and magmatic sources show similar median value (520 and 543 $\mu S\ cm^{-1}$, respectively). The obtained results are in accordance with those published by Lourenço and Cruz (2006). Both thermal centers and healing bath samples corresponded to hypothermal and mesothermal waters, with low mineralization and alkaline pH. In what concerns healing-bath waters, they were included in the group of hypersaline (H1 and H2) and low mineralized waters (H3, H4 and H5).

According to the results, the dominant anions were HCO_3 and Cl, with median values of 217 and 63 $mg\ L^{-1}$, respectively, and followed by SO_4. Sodium is the dominant cation and Ca was also abundant, although exhibiting lower concentrations (median value = 13 $mg\ L^{-1}$). The waters from the sedimentary sources show the highest values when compared with the waters from the metamorphic and magmatic sources. The less abundant elements were Mg, Si, K and NO_3, with values not exceeding 50 $mg\ L^{-1}$. Higher concentrations of NO_3, in samples T5, T6 and H3, can indicate more reducing environmental conditions. Although the S content was not determined in this work, the available information on investigated thermal centers depict the sulphurous character of most of the studied waters and their exclusive curative properties. In fact, analysis made by Lourenço and Cruz (2006) confirmed the existence of sulphurous content in some of the studied waters (Table 1), with the highest median values being observed in waters related to magmatic sources.

The main minor and trace elements identified in the studied waters, and respective detection limits, are presented in Table 2. According to the results of Table 3, the elements Br, Sr, B, Li and Ba were the most abundant minor elements. Water samples from sedimentary sources (especially H1, H2 and T16) are enriched in Sr, reaching about 5 $mg\ L^{-1}$ (median value of 2,532 $\mu g\ L^{-1}$). In these waters, Br is also abundant, exhibiting major quantities particularly in samples T2 and T3, where it reached the same concentration as Sr. B and Li exhibited lower contents, reaching major values in samples T14, T15 (for B)

Table 3 Descriptive statistics for the IC and ICP water analysis of field parameters (pH, EC, T), major, minor and trace elements

Parameter	Units	Global data ($n = 28$)				Sedimentary ($n = 9$)				Metamorphic ($n = 9$)				Magmatic ($n = 10$)			
		Mean	Med	Min	Max	Mean	Med	Min	Max	Mean	Med	Min	Max	Mean	Med	Min	Max
pH	–	7.6	7.5	5.4	11.3	6.8	6.9	5.5	7.3	7.7	7.2	5.4	11.3	8.2	8.2	7.8	8.6
EC	μs cm^{-1}	1,440.3	590.0	40.0	6,430.0	3,349.1	3,170.0	1,148.0	6,430.0	467.8	520.0	40.0	1,093.0	597.7	543.0	308.0	1,021.0
T	°C	30.1	26.6	17.3	64.8	25.9	25.0	17.3	34.2	29.4	27.1	18.3	64.8	34.7	29.3	21.4	52.0
HCO_3	mg L^{-1}	287.1	217.0	10.0	828.0	394.4	355.0	138.0	828.0	179.7	138.0	10.0	433.9	287.1	197.1	130.0	631.0
Cl	mg L^{-1}	274.5	63.0	2.0	1,934.0	724.8	493.0	135.0	1,934.0	40.2	33.0	2.0	143.0	80.0	54.5	23.0	221.0
SO_4	mg L^{-1}	217.1	30.0	1.0	1,954.0	633.6	390.5	55.0	1,954.0	16.0	18.0	1.0	45.0	23.4	15.0	3.0	63.0
S	mg L^{-1}	11.38	2.300	0.000	61.60	6.822	0.000	0.000	32.80	2.489	0.000	0.000	15.50	23.47	6.65	0.000	61.60
Na	mg L^{-1}	220.3	112.5	3.0	1,194.0	488.6	389.0	74.0	1,194.0	50.4	45.0	3.0	130.0	131.7	112.5	55.0	250.0
K	mg L^{-1}	4.5	3.5	1.0	18.0	7.3	5.0	2.0	18.0	2.2	2.0	1.0	4.0	4.0	2.0	1.0	10.0
Mg	mg L^{-1}	22.9	1.5	0.1	104.0	59.7	61.0	23.0	104.0	11.0	2.0	0.1	40.0	0.4	0.2	0.1	1.0
Ca	mg L^{-1}	91.6	13.0	1.0	705.0	258.9	206.0	69.0	705.0	19.3	11.0	1.0	66.0	6.0	4.5	1.0	20.0
Al	μg L^{-1}	21.7	5.0	0.5	163.0	8.0	5.0	0.5	23.0	38.4	4.0	0.5	163.0	18.9	5.0	1.0	88.0
As	μg L^{-1}	7.3	4.2	0.3	56.0	5.0	2.5	0.8	14.0	2.0	0.8	0.3	5.1	14.3	7.4	1.3	56.0
B	μg L^{-1}	377.5	97.5	2.5	2,854.0	100.7	74.0	2.5	258.0	103.8	15.0	2.5	434.0	872.8	537.0	32.0	2,854.0
Ba	μg L^{-1}	35.9	20.2	0.1	242.4	44.7	38.1	12.7	80.7	27.0	11.6	7.1	62.2	36.1	2.6	0.1	242.4
Br	μg L^{-1}	744.5	384.5	15.0	5,198.0	1,558.4	464.0	305.0	5,198.0	205.0	160.0	15.0	646.0	497.6	393.0	113.0	1,292.0
Cr	μg L^{-1}	14.0	8.5	0.6	55.3	32.5	31.7	13.5	55.3	4.1	1.8	0.6	10.6	6.4	6.6	1.7	9.1
Cs	μg L^{-1}	51.28	1.74	0.01	274.85	1.44	1.58	0.02	3.01	6.48	0.14	0.04	56.75	136.47	124.99	0.01	274.85
Cu	μg L^{-1}	2.4	0.7	0.1	21.4	2.1	1.0	0.3	5.1	2.4	0.3	0.1	16.4	2.7	0.7	0.2	21.4
Fe	μg L^{-1}	38.4	5.0	5.0	382.0	79.2	50.0	5.0	382.0	14.9	5.0	5.0	48.0	22.7	5.0	5.0	89.0
Li	μg L^{-1}	304.6	59.0	0.6	1,579.1	44.1	51.4	8.7	76.5	63.5	3.8	0.6	548.5	756.0	757.3	0.7	1,579.1
Mn	μg L^{-1}	9.4	0.9	0.0	45.9	9.7	0.3	0.0	33.3	0.5	0.2	0.0	2.1	17.3	12.7	0.1	45.9
Mo	μg L^{-1}	1.7	0.5	0.1	19.9	0.5	0.5	0.1	1.4	0.4	0.1	0.1	1.4	3.9	2.1	0.1	19.9
Rb	μg L^{-1}	30.7	10.3	0.3	132.7	11.5	9.8	1.7	25.3	10.6	3.6	0.3	56.7	65.9	54.9	5.7	132.7
Se	μg L^{-1}	5.5	1.5	0.3	47.8	13.7	4.6	0.3	47.8	0.9	0.3	0.3	3.8	2.2	1.2	0.3	7.4
Si	μg L^{-1}	15.5	9.4	1.2	51.0	8.7	8.1	4.9	12.6	8.8	6.8	1.7	28.3	27.7	24.2	7.0	51.0
Sr	μg L^{-1}	976.8	191.0	8.2	5,872.5	2,702.4	2,531.6	200.2	5,872.5	136.7	158.5	8.2	432.5	179.7	92.6	60.3	472.1
U	μg L^{-1}	1.1	0.0	0.0	16.3	0.5	0.3	0.0	2.1	0.2	0.0	0.0	1.4	2.5	0.0	0.0	16.3
W	μg L^{-1}	52.8	0.1	0.0	470.9	0.3	0.1	0.1	2.0	7.5	0.0	0.0	67.5	140.8	62.3	9.7	470.9
V	μg L^{-1}	3.3	0.8	0.1	26.9	8.8	4.2	1.3	26.9	0.5	0.4	0.1	1.0	0.8	0.4	0.1	2.8
Zn	μg L^{-1}	2.8	1.6	0.3	14.6	4.1	2.5	0.3	14.6	3.0	2.9	0.3	8.8	1.5	0.3	0.3	8.9

Med Median value, *min* minimum value, *max* maximum value

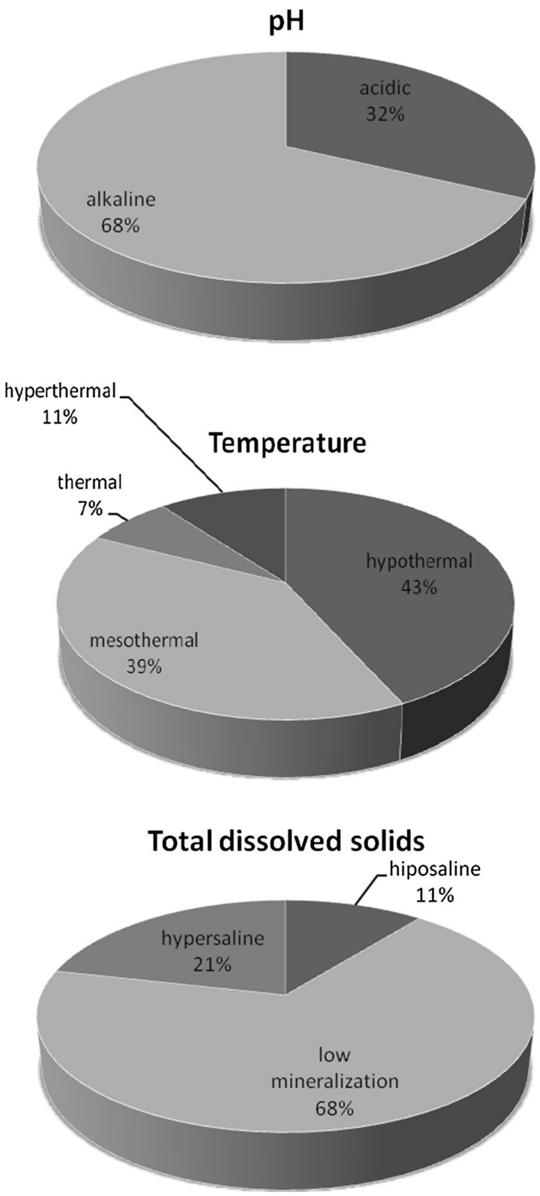


Fig. 2 Pie charts showing the distribution of the sampled mineral waters based on the main physicochemical parameters

and T11, T12, T15 (for Li) which ranged between 1 and 2 mg L^{-1}. The remaining elements occur naturally in groundwater as essential and/or potentially toxic elements (Custodio and Llamas 2001).

In all the selected samples the concentrations of Pb and Cd were below the detection limit of the method. Punctually, were observed in some samples, concentrations of certain elements: Co at Monte Real and Vimeiro samples (0.44 and 0.32 µg L^{-1}, respectively); Sb at Cabeço de Vide (0.67 µg L^{-1}), Sangemil (0.46–0.57 µg L^{-1}) and Alcafache samples (1.42–1.61 µg L^{-1}) and, finally, Tl at Vimeiro (0.13–0.43 µg L^{-1}) and Caldas da Rainha samples (0.34 µg L^{-1}).

Water hydrochemical facies

The hydrochemical data were plotted in a Piper diagram (Piper 1944) and different hydrochemical types were obtained for the studied waters (Fig. 3).

According to the figure, the majority of the waters were included in the Na–HCO_3 type (Group D). The remaining samples were classified as Na–Cl waters (Group C: samples T2, T3, T4, T16 and H4), Ca–SO_4 waters (Group A: samples T1, H1 and H2) and other group, with intermediate characteristics (located in the center of the cationic triangle), included samples characterized as Ca/Mg–HCO_3 waters (Group B: samples T5, T6, T19, T20 and H3).

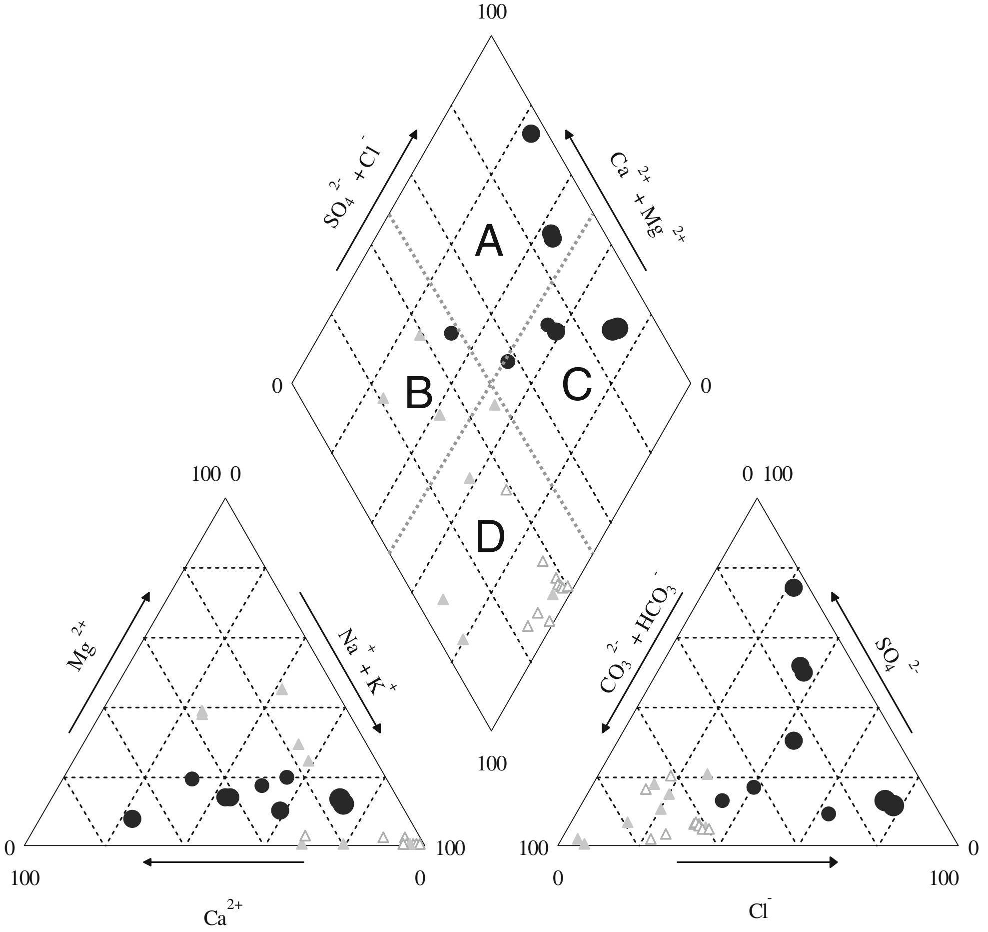
It was also observed that the distribution of the studied waters in the Piper diagram was conditioned by their hydrogeological environment (Table 1). The waters collected at magmatic sources showed Na–HCO_3 facies, whereas samples collected at sedimentary sources (with exception of sample H3) presented Na–Cl or Ca–SO_4 facies. The remaining samples, collected at metamorphic sources (with exception of samples T7, T8 and T21) presented more intermediate characteristics (Ca/Mg–HCO_3 facies).

Determining major hydrochemical characteristics using PCA

Principal component analysis (PCA), carried out based on the correlation of all hydrochemical data, made possible the reduction of data set structure. Table 4 lists the eigenvalues of the first five principal components (PC), their percentage of variance and cumulative percentage of variance. According to the Kaiser criterion, the number of significant principal components with eigenvalue higher than 1 was selected (Davis 1986; Manly 1994). As well, PCA enabled the extraction of five principal components explaining 86.6 % of the total variance in the sets of data (Table 4).

The absolute values of factor loadings over 0.5 were considered as a strong correlation and were marked in Table 4 with bold typeface to elucidate the relationships between the factors and the hydrochemical data. The first component (PC1), explaining 33.10 % of the total variance, defines two groups of variables: a first group (Mg, EC, Cl, Na, Ca, SO_4 and Br) with high positive loadings and a second group (Li, Si and Rb) with negative loadings. Rb and Si show the highest loadings in PC2 and SO_4 in PC3. In PC1 are also associated, as supplementary variables, Cr, V, Sc, Sr with positive loadings and W with negative loadings. The PC2, explaining 26.92 % of the total variance, shows high positive loadings on Rb, H_2S, B, K, Cs, Li, Si, HCO_3, Na, Br, Mn. The PC3, which describes 11.37 % of the variance, has a high negative factor loading

Fig. 3 Piper's diagram showing the chemical composition of studied mineral waters. Four main groups of waters are defined: **a** Cl and/or SO_4 (Ca and or Mg) type waters, **b** HCO_3 (Ca and/or Mg) type waters and **c** SO_4 and/or Cl(Na) type waters; **d** HCO_3 (Na). Samples codes: *solid triangles* samples collected at the Hesperic Massif (metamorphic); *open triangles* samples collected at the Hesperic Massif (eruptive); *solid circle* samples collected at the W Meso-Cenozoic Border



for Fe, SO_4 and Ca variables. A fourth component (PC4), explaining 8.40 % of the total variance, has a high factor loading for Al and P. At last, PC5, explaining 4.78 % of the total variance, has a high negative factor loading for Temperature (already explained in PC1).

The overview of the most representative variable projections allows differentiating existing proximity and oppositions (Cardoso 1995). In Fig. 4 a graphical projection of the PCA results shows the position of the 32 selected variable coordinates, representing the correlation coefficients between the variables, in the different factorial plans. Here, six groups of variables can be identified in the four factorial plans. Factor scores were computed from hydrochemical data on springs and mapped to illustrate the characteristics of the factors based on the geological origins. Figure 5 displays the score distributions based on the location, geological origin and type facies.

In the first factorial plan (PC1/PC2), representing 60.02 % of the global information of the data set, the selected variables could be separated into two large clusters (Fig. 4a) but, three different groups (I, II and III) of variables can be identified, two of them with strong associations with PC1 and one correlated with PC2. Group I (EC, Cl, Na, K, Br, HCO_3) and Group II (SO_4, Ca) have positive loadings in PC1 and in PC2, revealing a strongly correlated association of elements ($r_{EC/Cl} = 0.95$; $r_{Cl/Na} = 0.99$; $r_{SO_4/Ca} = 0.98$; $r_{Na/Br} = 0.88$, $p < 0.05$). These groups appear to be controlled by the circulation of the water contacting with sources of evaporitic chlorides and sulphates such as the evaporites (Upper Jurassic limestones outcropping in the E limb of Vimeiro diapir), resulting in high Cl and Na contents in the spring water, or the Lower Jurassic formations outcropping at the E limb of the Caldas da Rainha diapir resulting in high SO_4 and Ca contents. For example the presence of HCO_3, Ca and Mg is related to water–limestone interactions, while Na, Cl and SO_4 concentrations are mainly associated with the dissolution of halite and gypsum lenses found along the regional syncline. On the other hand, the magmatic sources are known to provide CO_2-rich vapours to aquifers. That's why the resulting Na–HCO_3 fluids are commonly observed in the periphery of geothermal fields and are typical of early stages of interaction between meteoric water and rocks (Cruz et al. 2010). In what concerns the group of variables

Table 4 Eigenvalues of the first five principal components (PC), their percentage of variance and cumulative percentage of variance

	Variables	PC 1	PC 2	PC 3	PC 4	PC 5
Variables for analysis	pH	−0.331	0.164	0.108	**−0.844**	0.104
	EC	0.869	0.455	0.020	−0.063	−0.146
	T	−0.441	0.166	−0.115	0.077	**−0.770**
	HCO_3	0.298	**0.575**	0.208	0.104	0.371
	Cl	0.807	0.490	0.239	−0.053	−0.178
	NO_3	0.155	−0.211	0.258	0.404	0.296
	SO_4	0.625	0.149	**−0.735**	−0.102	−0.014
	S	−0.430	**0.783**	−0.227	0.013	0.193
	Na	0.756	**0.565**	0.213	−0.085	−0.183
	K	0.483	**0.724**	0.365	−0.096	−0.011
	Mg	0.922	0.256	0.077	0.104	−0.127
	Ca	0.709	0.139	**−0.662**	−0.053	0.010
	Al	−0.130	−0.277	0.178	**−0.877**	−0.070
	B	−0.432	**0.748**	0.051	−0.030	0.400
	Br	0.610	**0.554**	0.448	−0.037	−0.114
	Cs	−0.661	**0.711**	−0.078	0.058	−0.059
	Fe	0.425	0.096	**−0.793**	−0.134	0.029
	Li	−0.666	**0.660**	−0.101	0.057	−0.217
	Mn	0.064	**0.510**	−0.282	−0.087	0.399
	Rb	−0.587	**0.797**	−0.020	−0.004	0.002
	Si	−0.640	**0.650**	−0.142	0.138	−0.263
Supplementary variables	As	−0.054	0.126	0.006	−0.005	0.021
	Ba	0.114	−0.043	0.147	0.152	−0.304
	Cr	**0.807**	0.355	0.236	0.093	−0.136
	Cu	−0.122	0.032	−0.235	−0.145	−0.479
	Mo	−0.163	−0.110	0.049	−0.227	−0.204
	Se	**0.648**	0.477	0.456	−0.019	−0.156
	Sr	**0.645**	0.213	−0.357	−0.033	−0.116
	U	−0.199	−0.029	−0.009	0.017	−0.379
	W	**−0.508**	**0.730**	−0.003	0.016	0.329
	V	**0.754**	0.474	0.353	−0.035	−0.200
	Zn	0.340	0.191	0.068	−0.113	−0.395
Eigenvalue		6.95	5.65	2.39	1.76	1.43
% Total variance		33.10	26.92	11.37	8.40	6.80
Cumulative % of variance		33.10	60.02	71.39	79.79	86.59

Most significant values are given in bold

III (Rb, Li, Si, Cs, B, H_2S), it is associated mostly with the waters from the Hesperic Massif (both from metamorphic or magmatic sources) which are mainly of sulphurous type (Fig. 5a).

The second factorial plan (PC1/PC3), representing 44.47 % of total variance, is dominated by the association of Ca, SO_4 and Fe variables (Group II) and the association of Cl, Na, Br and K (Group I). This plan separates the waters characterized by Cl–Na facies from the SO_4–Ca facies (Figs. 4b, 5b).

The third factorial plan (PC1/PC4), representing 41.50 % of the total variance, evidences the association between the Al and pH variables (Group IV) (Figs. 4c, 5c). This association is related mainly to the Cabeço de Vide mineral waters and their main chemical characteristics, such as: (1) very alkaline pH values (11.3 and 11.4); (2) NaCl/CaOH type; (3) rather low mineralization; (4) extremely low concentration of HCO_3, Mg and silica; (5) presence of reduced S species; (6) very high values of dissolved B. Some authors (such as Barnes and O'Neil 1969) suggest that serpentinization of the ultramafic rocks might contribute to the chemistry of these waters through the reaction $2Mg_2SiO_4 + 3H_2O = MgOH_2 + Mg_3Si_2O_5(OH)_4$, which may explain the low Mg (0.05 mg L^{-1})

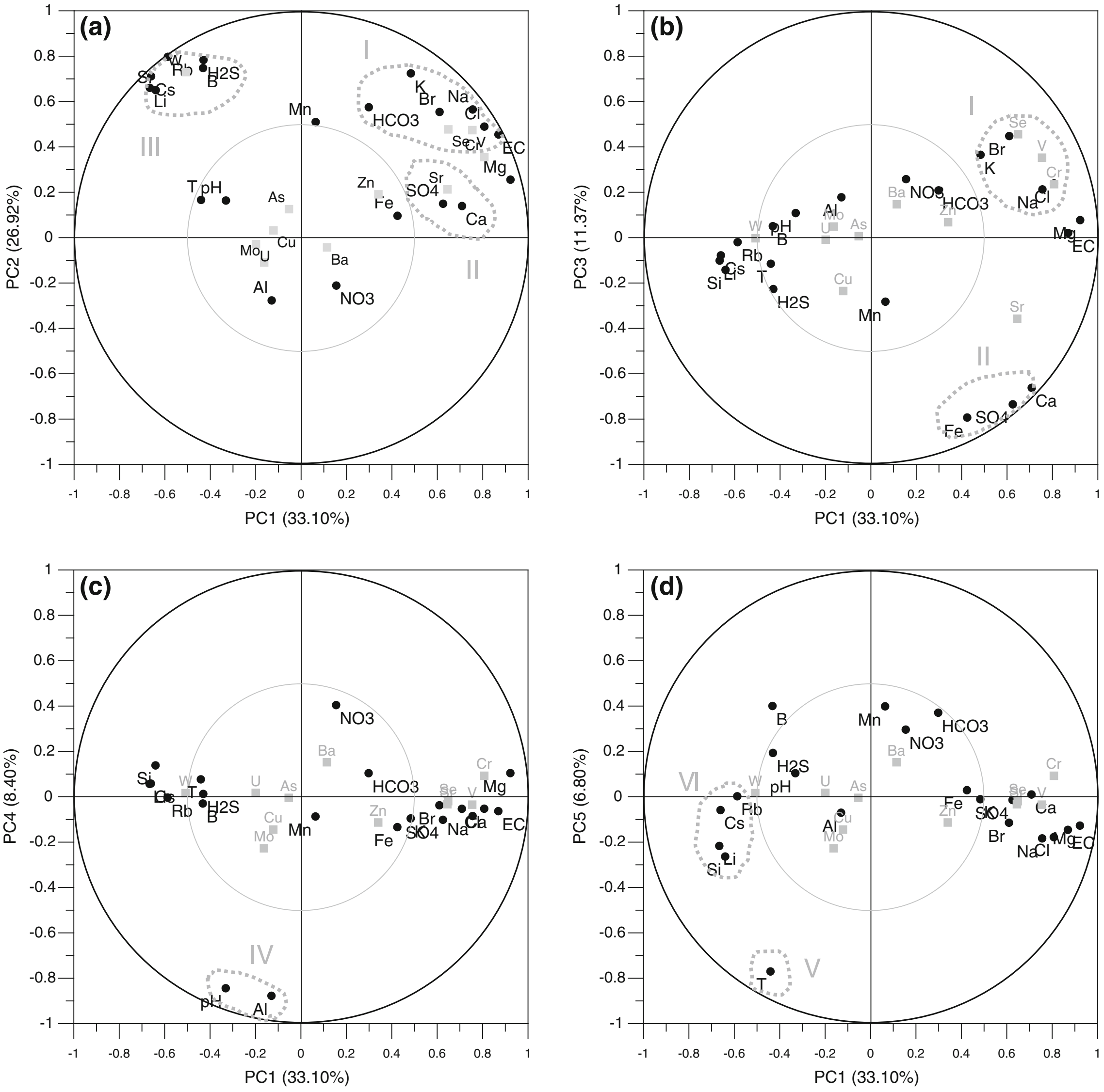


Fig. 4 - Graphical projection of the PCA results showing the position of the selected 32 variables coordinates (*black dots* variables for analysis; *grey dots* supplementary variables; from Table 4)

and SiO_2 (1.4 mg L^{-1}) concentrations found in the Cabeço de Vide thermo-mineral waters. On the other hand, higher B concentration observed in the Cabeço de Vide thermo-mineral can be attributed to leaching from metamorphic and igneous rocks, or even the dissolution of carbonates. In fact, B has a strong affinity with OH^- and the aqueous speciation is mainly controlled by water pH. The formation of undissociated boric acid BOH_0^3, and its conjugate BOH_4^-, is the process that retains B in basic solutions. According to Marques et al. (2008), 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. Moreover, most spring waters emerging from magmatic and metamorphic sources exhibit slightly acidic properties.

The fourth factorial plan (PC1/PC5) explains 39.9 % of the total variance (Fig. 4d) with strong loadings of temperature (Table 3). Truesdell and Fournier (1975) and also Swanberg and Morgan (1979, 1985) documented that temperatures of spring waters could be presumed by contents of aqueous silica. Although their works showed a non-linear relationship between temperature and SiO_2 content, in this study the linear correlation between them was moderate ($r = 0.60$, significant at $p < 0.05$), and accordingly, factor 5 is termed the factor of spring temperature. The increase of Si is accompanied by B ($r = 0.62$, significant at $p < 0.05$), Li ($r = 0.96$, significant

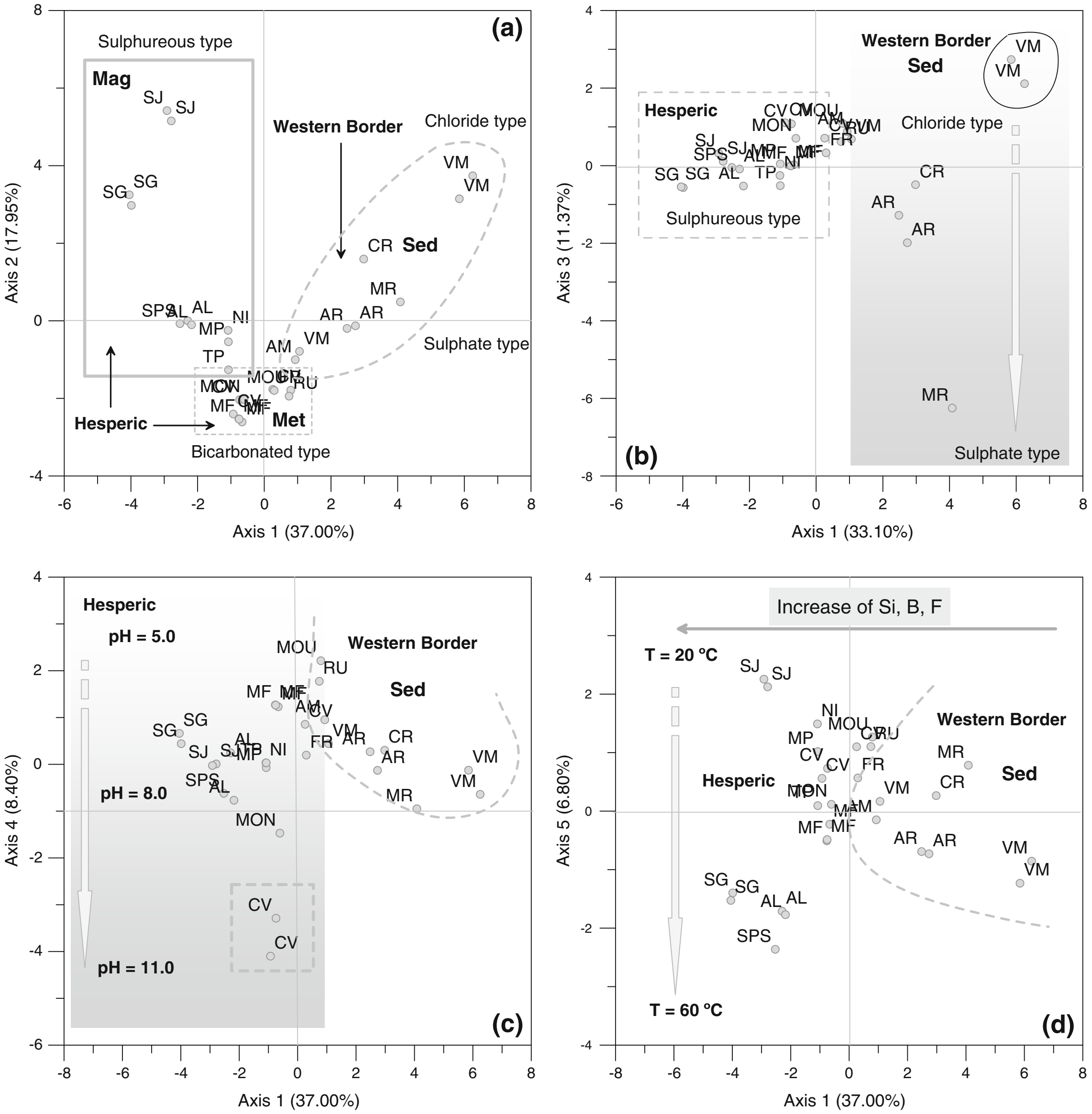


Fig. 5 Score distributions based on the location, geological origin and type facies. Spa/healing baths abbreviations: *AL* Alcafache, *AM* Amieira, *AR* Quinta das Janelas, *CR* Caldas da Rainha Spa, *CV* Cabeço de Vide, *MF* Monfortinho, *MON* Caldas de Monchique, *MOU* Moura, *MP* Monte da Pedra, *MR* Monte Real, *NI* Fadagosa de Nisa, *RU* Ruaz, *SG* Caldas de Sangemil, *SJ* São Jorge, *TP* Caldas das Taipas, *VM* Vimeiro, *SPS* São Pedro do Sul

at $p < 0.05$) and Rb ($r = 0.89$, significant at $p < 0.05$) that enhances weathering, for example of silicates in the igneous rocks, that also release Li.

Boron is found in very different geological environments, associated with the presence of geothermal processes, and with materials deposited in a very saline environment (Leeman and Sisson 1996). The high values recorded in thermal waters may be due to the alteration of rocks and hydrothermal activity (Risacher 1984; Risacher and Fritz 1991). In this case, the influence of temperature on its release has been already reported by Arnorsson and Andresdottir (1995). The dissolution of evaporite rocks has been considered also to be a possible source of boron (Rose et al. 2000). Other authors consider that the high boron concentration in some waters is directly related to the content of Li (Macpherson and Land 1989). In this study the correlation between B and Li was moderate ($r = 0.64$, significant at $p < 0.05$).

In fact, according to Chan et al. (1994), the high mobility of Li is related to temperature. It is found in high concentrations in thermal waters and for this reason it is a good tracer for use in geochemical investigations of hydrothermal systems (Brondi et al. 1973, 1983). In addition, some groundwater associated with regional flows

Table 5 Saturation indices of various mineral phases in the water samples

ID	Name	Albite-low	Anhydrite	Calcite	Ferrihydrite	Quartz	SiO_2 (am)	Gypsum
T1	Monte Real		−0.16	0.32	2.00	0.24	−0.81	0.06
T2	Fonte Frades 1		−1.29	0.39		0.20	−0.83	−1.12
T3	Fonte Frades 2	2.04	−1.26	0.22		0.28	−0.76	−1.08
T4	Vimeiro5		−1.59	0.34		0.15	−0.87	−1.43
T5	Moura		−2.40	−0.14	−0.03	0.29	−0.72	−2.27
T6	Cabeço de Vide	0.09	−2.67	−0.19	0.08	0.20	−0.86	−2.43
T7	Cabeço de Vide	−4.23	−3.34	1.21		−1.70	−2.76	−3.12
T8	Cabeço de Vide	−3.79	−4.34	1.07		−1.58	−2.63	−4.12
T9	Monte Pedra—Crato	1.89	−3.74	−0.77		0.54	−0.50	−3.54
T10	Fadagosa de Nisa	0.71	−3.42	−0.44		0.44	−0.60	−3.22
T11	Caldas de Sangemil HN1	1.75	−3.43	0.08		0.71	−0.23	−3.45
T12	Caldas de Sangemil HN2	1.48	−3.52	−0.21	0.68	0.74	−0.20	−3.54
T13	Caldas das Taipas	0.93	−2.58	0.15	1.76	0.59	−0.42	−2.46
T14	São Jorge SJ1	1.83	−3.52	0.24	1.45	0.82	−0.22	−3.35
T15	São Jorge SJ2	1.68	−3.66	0.26		0.76	−0.26	−3.50
T16	Caldas Rainha AC2	0.92	−0.69	0.44	−1.08	0.12	−0.87	−0.61
T17	Caldas de Monchique	0.65	−3.85	0.16		−0.11	−1.12	−3.72
T18	Monfortinho AC3	−4.11	−4.70	−4.79	−2.01	0.05	−0.95	−4.59
T19	Monfortinho AC6	−3.80	−4.71	−4.67	−2.15	0.20	−0.81	−4.60
T20	Monfortinho AC7	−3.84	−4.75	−4.71	−2.20	0.23	−0.79	−4.60
T21	S. Pedro Sul AC1	0.73	−3.25	−0.01	1.70	0.24	−0.63	−3.43
T22	Alcafache 1	0.44	−4.03	0.07	0.74	0.34	−0.58	−4.10
T23	Alcafache 2	1.36	−3.73	0.04	1.75	0.33	−0.58	−3.81
H1	Arrábidos 1	−13.22	−5.61	−5.32	0.08	−2.68	−3.68	−5.49
H2	Arrábidos 2		−0.52	0.16		0.29	−0.72	−0.41
H3	Ruaz		−1.95	−1.59		0.08	−0.99	−1.71
H4	Amieira	−15.93	−7.59	−7.01		−2.79	−3.83	−7.41
H5	Ferradura	−1.77	−2.55	0.24	0.98	−0.47	−1.50	−2.37

contains increased quantities of Li (Fidelibus et al. 1992). Given its small ionic ratio, Li is retained in clay minerals and can even exchange with Na or K, although small changes in temperature are sufficient to release it from the mineral matrix (Paropkpari 1990). The highest B and Li values in water are reached in aquifers with large residence time and, also, after enough interaction between water and rocks at high temperatures (Delgado-Outeiriño et al. 2010).

Saturation state of studied thermo-mineral waters

Saturation indexes with respect to some mineral species were calculated at the measured discharge temperature using hydrogeochemical software PHREEQC® (Parkhurst and Appelo 1999), and are listed in Table 5. In general, studied waters are undersaturated in anhydrite and when the concentration of SO_4 increases the saturation index is increasing toward the equilibrium (Fig. 6a). This fact indicates that anhydrite is contributing with SO_4 for the solution. Similarly, a strong correlation between SO_4 and Ca concentration was observed (Fig. 6b), revealing that anhydrite is also controlling the Ca content on solution. In fact, concerning calcite saturation indexes (Table 5), studied samples are very close to the equilibrium indicating that their geochemistry is mostly controlled by the anhydrite rather than calcite. Confirming this statement, is the 1:1 correlation of SO_4 and Ca contents, indicating that anhydrite is the one controlling the Ca concentration in solution (Fig. 6b). A tendency for an increase of $p_{(CO_2)}$ with HCO_3 content was also observed (Fig. 6c), revealing that CO_2 has contributed for HCO_3 content in the studied waters.

In what concerns silicates (plagioclases and quartz) a strong correlation was found between quartz and Si concentrations (Fig. 6d). In addition, studied samples are undersaturated with quartz and SiO_2 (amorphous),

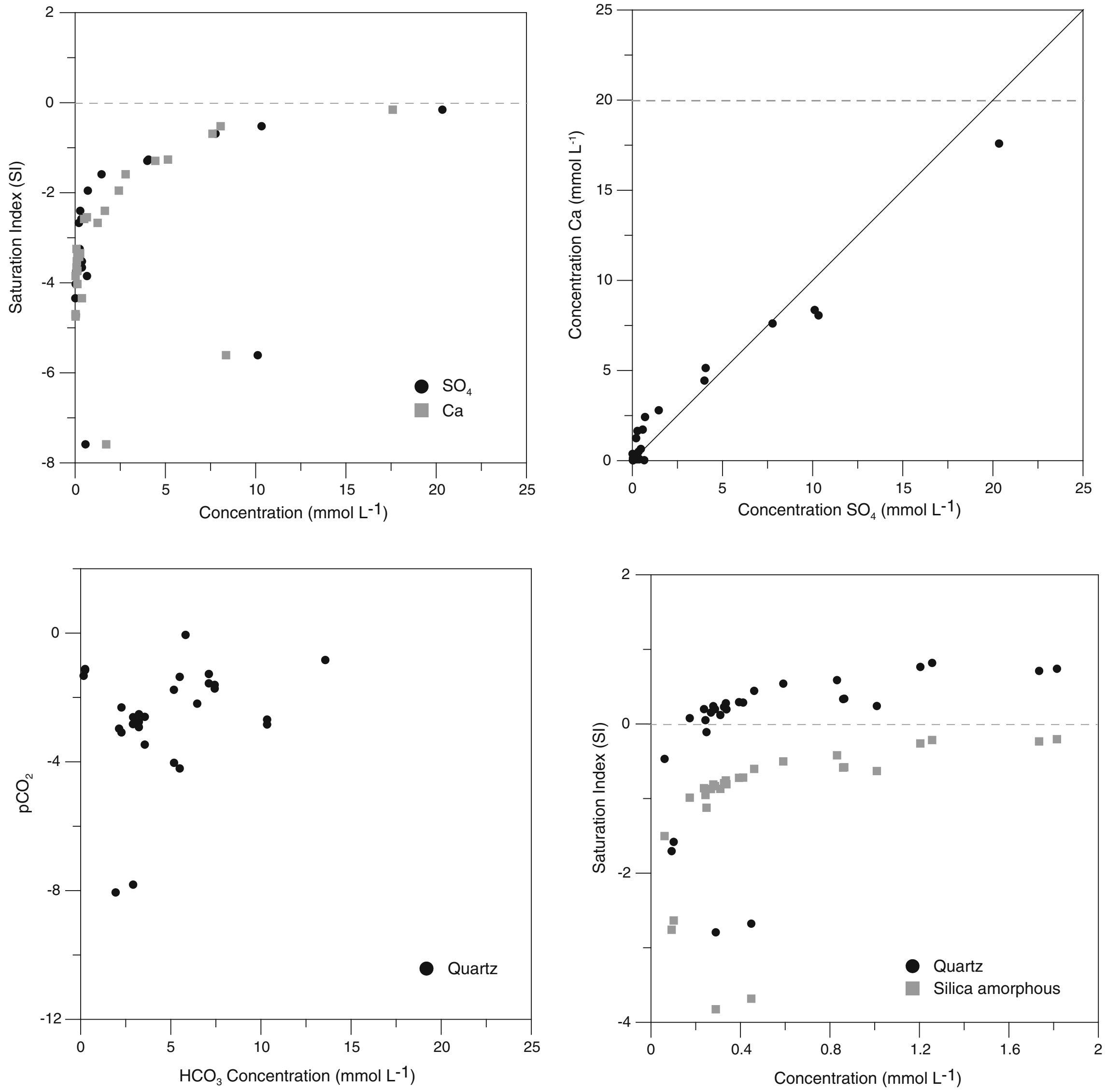


Fig. 6 Saturation state of studied mineral waters

indicating that this mineral phase contributes for the Si content dissolved in the studied waters.

Potential application in pelotherapy

In what concerns the potential application of the studied waters in pelotherapy, some aspects may be taken into account. Temperature information is important for Spa-management especially when high energy-costs have to be met for the peloid heating. A high-moisture peloid conciliated with a thermal or hyperthermal water is capable to supply 40–45 °C when applied in the patient's body for 20–30 min, the adequate duration of treatment (Veniale et al. 2007). Thus, samples T11, T12 (Sangemil Spa), T21 (S. Pedro Sul Spa), T22 and T23 (Alcafache Spa) are the most adequate to provide good temperatures when peloid is applied.

Concerning pH, alkaline environments increase plasticity and activity of peloid and decrease bacteria/germ activity (Veniale et al. 2007). However, the resulting peloid pH depends on both the virgin clay and mineral water pH. To produce peloids with high plasticity and low bacteria activity with the analysed waters, attention must be paid to the more acidic ones (T18, T19, T20, H3 and H4), because they can produce acidic environments if mixed with a low-pH virgin clay/mud.

In respect to mineralization, higher ionic concentration improves the peloid therapeutic activity as more exchangeable cations are available (Gámiz et al. 2009). However, a large quantity of ions (as succeeds in highly saline waters) may act as bridges between clay minerals particles, decreasing porosity and making more difficult the adsorption/absorption of substances in the application of the peloid onto the skin. Because none of the analysed waters presented highly saline characteristics, all of them were considered adequate for applications without compromising the therapeutic properties of the peloids. Furthermore, in some cases, was verified that least saline waters accumulated the most heat, which consequently is released more slowly (Gámiz et al. 2009).

Studies carried out by several authors (Veniale et al. 2004, 2007; Sánchez et al. 2002; Gámiz et al. 2009) have demonstrated the influence of various water types in the suitable properties and active factors of a peloid. As a result, properties such as consistency, exchangeable cations, water retention and heat capacities resulted improved when Ca–sulphate waters were used in opposition to sulphurous waters which affected negatively the consistency of the peloids (Veniale et al. 2004). Similar results were obtained in plasticity index and cooling rate of peloids maturated with a Fe-bicarbonate- and sulphate-rich water (Sánchez et al. 2002). Because of their similar Ca–sulphate hydrochemical facies with those observed by Sánchez et al. (2002), samples T1, H1 and H2 were selected as the most adequate to produce suitable peloids. Comparing the Cl and Na contents, they are higher in the studied samples representing a higher beneficial effect, as those ions are involved in the adsorption/absorption mechanisms between clay and water (Gámiz et al. 2009).

In respect to the studied bicarbonate waters, they were also compared with the one studied by Sanchéz et al. (2002). The studied waters are very distinct from those studied by Sanchéz et al. (2002) and even the most identical bicarbonate-rich waters (such as samples T14 and samples T15) exhibit significant lower contents in various dissolved species such as HCO_3, SO_4, Mg, Ca and, especially, in Fe. Even though, samples T14 and T15 were considered as the best candidates for the maturation of peloids with bicarbonate-rich waters.

In what concerns the studied chloride waters, recent studies performed with high chloride content waters suggested that peloid properties are negatively affected by the large concentration of this ion. In particular, they originate less porous fabrics, traduced in more massive peloids with low consistency, great water losses and consequently reduced heat retention capacities (Veniale et al. 2004; Gámiz et al. 2009). When compared with these studies, all the studied chloride waters have lower ionic concentration, but attention should be paid in the maturation process with samples T3, T2 and T16.

Concerning trace metals, the study of collected waters was focused in the elements that could be present in matured muds with mineral waters (As, Se, Cd, Tl and Pb). On the other hand, were considered the elements that are prohibited by the European Laws for cosmetic products as well as other traces suspected to be human toxicants (Cr, Cu, Mn and Ni) or that should be absent in water for human consumption (Mn, Ni, Sb, Ba, Cu) (WHO 1996; EU 1998; EPA 2002).

Ba and Cr occur in concentrations usually below 100 $\mu g\ L^{-1}$, except in sample T22 with higher Ba content, and the highest Cr contents were identified in samples T2 and T3, rounding 55 $\mu g\ L^{-1}$. Mn, As and Se contents were usually under 50 $\mu g\ L^{-1}$, with sample T13 presenting a higher content in As. Samples T2 and T3 showed the highest values of Se while sample T10 exhibited the highest concentration in Mn. Ni and Cu were the less abundant minor elements, with concentrations ranging between 1 and 20 $\mu g\ L^{-1}$. Concerning the trace elements Be, Sb, Tl, Hg and Pb, the concentrations did not exceed 2 $\mu g\ L^{-1}$ or were below the detection limits in the majority of the samples. NO_3 and NO_2 were also detected but only in isolated cases. NH_4 was identified in samples T10, H1 and H2 whereas NO_2 occurred only in sample T6, revealing the influence of an anthropogenic source of contamination (Berner and Berner 1996; Adriano 2001).

The risk of toxicity was evaluated considering the social use of the studied waters, once they will be in contact with the skin or eventually mucous membranes, in the form of a hypothermal mud (Mance et al. 1984; Jordana and Batista 2004). In opposition to the drinking-waters regulations, there are no specific rules that can be easily applied when waters are used exclusively for dermal exposure (WHO 2011). However, the World Health Organization Guidelines for drinking-water quality (WHO 1993, 1998) can provide a starting point for deriving values that could be used to make a screening level risk assessment under specific circumstances. This approach considers that a substance occurring in waters for social (or recreational) use at a concentration ten times that stipulated by drinking-water guidelines may merit further consideration. With exception of F, in sample T13, which exhibited a concentration slightly above than the recommended by WHO and the EU (concentration normally found in fresh water, surface water and ground water—1.5 mg L^{-1}; health based guideline—1.5 mg L^{-1}), all the remaining samples presented safe values. In this case, where the corresponding values for F were exceeded, it does not necessarily imply that a problem exists. Rather, it suggests the need for a specific evaluation of the contaminant, taking into consideration local circumstances and conditions of the recreational water area (WHO 2011).

Concerning the potential hazardous effect of the analyzed elements in the matured peloids, recent studies suggested that more important than to know the bulk chemistry of studied waters, was considering that the leaching solutions exerted during application affect the mobility of hazardous elements (Tateo and Summa 2007). As a result, elements such as As, Se and Tl which occur at trace levels, as salts, in the studied thermo- mineral waters may present different mobility when applied. Therefore, although the studied samples present no concern about their toxicity, further research should be developed in order to study the mobility of the referred elements to prevent possible harmful effects. In addition, it is the presence of some trace elements in groundwater that causes its therapeutic properties, which are in general beneficial for human health, being often considered as essential elements (Jordana and Batista 2004).

Concluding remarks and outlook

In this paper the concentrations of major and trace elements in 28 thermo-mineral waters were analyzed and discussed. Principal component analysis (PCA) were applied to classify data and distinguish significant variables as grouping predictors and to determine the number of fundamental properties represented in the data set. PCA results point out that waters used in SPA or in baths in the Portuguese mainland could are related to rock dissolution (Tertiary Bassin of the Tagus and Sado rivers, Meso-Cenozoic Margins and the south part of the Hesperian Massif); or controlled by deep fluids, generated in metamorphic and/or magmatic processes (Center Iberian Zone of the Hesperian Massif). Spring waters emerging from acid-sulfate igneous rocks are high temperatures, characterized by abundant dissolved SiO_2 concentrations and strongly acid while spring waters emerging from sedimentary rock contain substantial amount of Cl^-, HCO_3^- and Na^+ ions and low temperatures. Springs controlled by active faults (some of them with very high temperatures) show some abnormal levels of fluorine, boron, bromine, and ammonium.

The thermo-mineral waters characterization performed allows us to consider them as appropriate water-type to complement peloid activity. Therefore, these thermal-mineral waters can be regarded as worth developing because of their human health implications and, if thermal tourism is promoted, their importance to the local economy. The geochemical results of this study contribute for the development of new opportunities for the Spas. Considering the global results, in terms of application potential for maturation, the a priori best candidate waters to produce desirable effects on peloids were samples T1, H1 and H2 as $Ca–SO_4$ waters and samples T14 and T15 as $Na–HCO_3$ water type. Their overall suitability analysis is a basis for a future certification protocol.

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