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THERMAL WATERS FROM SOUTH BULGARIA: A MULTIVARIATE APPROACH FOR EVALUATION AND INTERPRETATION OF ANALYTICAL DATA

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ABSTRACT

25 thermal and 6 cold waters from a granitic region of south Bulgaria were sampled and analyzed for a wide range of major and trace components. This generates a large data set, which was more accessible to interpretation by application of multivariate techniques. Cluster analysis and correspondence factor analysis (CFA) yielded a similar grouping of water samples, which was also confirmed by other interpretation strategies. From CFA, it was also possible to distinguish between two main groups of variables, which can be related to reservoir and surface conditions, respectively. Finally, an attempt was made to deduce information on reservoir temperatures from the calibration of the factor, which was, according to CFA, related to reservoir conditions.

INTRODUCTION

A series of groundwaters (cold and thermal) were sampled in the granitoid region of south Bulgaria. These waters were analyzed for major components as well as for trace elements by various chemical techniques. In this way, a large data set is created, which is difficult to interpret directly. Therefore, multivariate techniques were applied in order to describe the relationships between the variables (element concentrations) and the samples in a rigorous and comprehensive way.

The chemical composition of a groundwater is mainly related to the geological environment and the temperature and pressure prevailing at depth. Evaluation of the influence of these parameters on the chemical loading of a particular water is simplified when the range of water samples can be classified into categories, reflecting waters with a similar chemical composition. Therefore, cluster analysis, a multivariate technique that is often used in combination with chemical techniques generating large data sets (Bernard et al., 1986; Van Borm and Adams, 1988), was applied to the acquired data set. In this way, an attempt was made to put some order into the obtained data set and to uncover the structure residing within it.

During the ascent of a thermal water to the surface, the initial chemical composition may be changed due to, for example, incorporation of certain elements into secondary minerals or dissolution of minerals present in the surrounding rocks. Both processes are related to the temperature of the water, which decreases on the way to the surface. Some elements are very sensitive to the changing conditions during the ascent of the water, and will reequilibrate fast, according to the prevailing physicochemical conditions. Other elements are less affected by changing conditions and, thus, will still contain information on the deep reservoir situation. The latter elements are especially important, since they can be used, in principle, for calculation of the reservoir temperature, which in most cases cannot be assessed directly. In order to divide the elements into two main categories, those that reflect reservoir conditions and those connected to surface conditions, another multivariate technique was applied. Correspondence Factor Analysis (CFA) seemed an appropriate method, since it seeks for 'correspondence' between variables and creates dimensions (factors), which describe this correspondence.

GEOLOGICAL ENVIRONMENT, SAMPLING AND ANALYSES

The investigated thermal waters are associated with highly fissured granites and metamorphic silicate rocks in southwest Bulgaria. A map of the region is presented in Fig. 1. Natural discharges and shallow wells, drilled in the granitic rocks, produce alkaline, N₂-containing waters. These waters are of the Na-HCO₃-SO₄ type, with a low mineralization (0.1-0.8 g/l) and temperatures at the emergence ranging from 11 to 94 °C. Thermal waters from southwest Bulgaria are very similar to those emerging from granitic areas in the Eastern Pyrenees and the Vosges (France). These waters have been extensively studied by Blommaert (1983) and Vandelannoote (1984).

Waters from the investigated area were carefully sampled as closely as possible to the source, filtered (0.4µm) at the temperature of the emergence and stored in precleaned polyethene

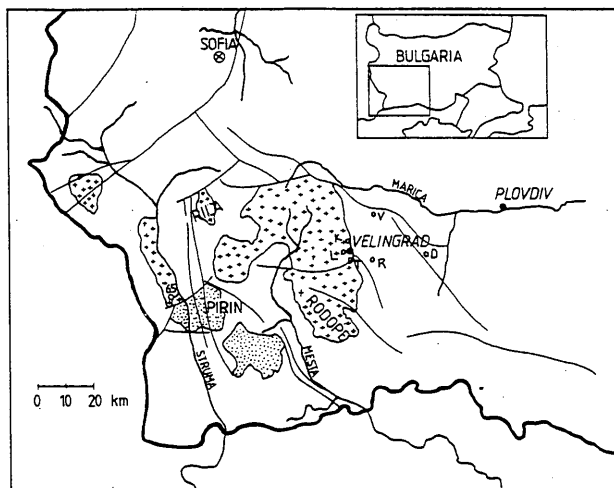


Fig. 1. Map of the investigated region. [+*]: Paleozoic granitoids; [:::]: Laramide granitoids; [—]: faults. Sampling stations are the following: K=Kamenitza, D=Draginovo, L=Ladjene, T=Tchechino, R=Rakitovo, V=Varvara.

bottles. Measurements in the field include temperature, pH and total alkalinity, from which HCO_3^- and CO_3^{2-} concentrations can be calculated.

Filtered water samples are further analyzed in the laboratory for main and trace components. Na, K and Li were measured by flame atomic emission; Ca and Mg by flame atomic absorption, using a Perkin Elmer 3030 spectrophotometer. Al was determined by graphite furnace atomic absorption spectrometry. Cl^- and SO_4^{2-} concentrations were obtained from ion chromatography measurements, using a $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ eluent (Dionex 4000i). F⁻ data were obtained by a direct measurement with a specific ion electrode (ORION 960900). Dissolved silica was analyzed by the heptamolybdate colorimetric procedure (Perkin Elmer/Lambda-UV/VIS spectrophotometer). B data resulted from an ICP-OES analysis. Further, trace elements (Sr, Rb, Cs, W, Mo) were analyzed by instrumental neutron activation analysis (INAA): after lyophilization, thermal water residues were irradiated in the nuclear reactor Thetis (University of Ghent), at a flux of 10^{12} neutrons. $\text{cm}^{-2}.\text{s}^{-1}$. Activation products were further analyzed by gamma-ray spectrometry, involving a solid state Ge(Li) detector. The applied INAA procedure is described in detail by Blommaert (1983).

The main characteristics of the investigated waters are summarized in Table 1.

Further, chemical element concentrations were obtained in the following ranges ($\mu\text{g/l}$): Li:5-500; SiO_2 :18000-95000; Na:7000-197000; K:400-8000; F:200-10000; Mg:4-10000; HCO_3^- :50000-300000; CO_3^{2-} :up to 35000; Cl^- :5000-30000; SO_4^{2-} :15000-250000; Ca:1000-90000; Al:5-70; Sr:up to 550; B:up to 370; Rb:up to 100; W:up to 30; Cs:up to 140 and Mo:up to 35.

Table 1. Summary of characteristics of Bulgarian ground waters.

no.	locality	Temp* (°C)	pH	TDS** (mg/l)
1	Tchechino	47.5	9.42	204
2	Tchechino	48.0	9.40	197
3	Tchechino	46.5	9.45	196
4	Tchechino	45.0	9.36	204
5	Tchechino	37.0	9.27	200
7	Grashovo	12.0	8.25	165
8	Ladjene	49.0	9.43	238
9	Ladjene	40.0	9.40	248
10	Ladjene	54.0	9.11	255
11	Ladjene	54.5	8.99	333
12	Ladjene	42.0	8.87	559
13	Kamenitza	65.0	8.01	658
14	Kamenitza	81.0	8.15	617
15	Kamenitza	89.0	7.84	750
19	Kamenitza	11.0	8.19	331
21	Draginovo	91.0	7.99	664
22	Draginovo	94.0	8.00	656
24	Draginovo	45.0	7.84	703
25	Draginovo	12.0	7.62	302
26	Rakitovo	51.0	9.59	328
27	Rakitovo	32.5	9.79	321
28	Rakitovo	11.0	7.82	399
29	Varvara	81.0	8.69	728
30	Varvara	14.5	7.47	320
31	Varvara	61.0	8.01	720
35	Ladjene	55.0	8.41	432
36	Ladjene	39.0	9.57	244
37	Rakitovo	11.0	9.66	311
38	Kamenitza	63.0	8.05	735
39	Kamenitza	82.0	8.27	657
40	Kamenitza	7.0	6.36	109

* Temperatures recorded at the surface

** Total dissolved solids calculated taking into account Na, Ca, Cl^- , SO_4^{2-} , HCO_3^- , CO_3^{2-} and SiO_2 concentrations

MULTIVARIATE METHODS

Hierarchical clustering techniques

Clustering techniques seek to form 'clusters', 'groups' or 'classes' of individuals, such that individuals within a cluster are more similar than individuals from different clusters. We shall concentrate here on a particular set of clustering methods, in which some clusters are nested within other clusters; these are known as hierarchical techniques. One subtype of the hierarchical clustering method is the agglomerative one, which proceeds by a series of successive fusions of the n individuals into groups. The results from this clustering may be presented in the form of a dendrogram, this being a two dimensional diagram illustrating the fusions which have been made at each stage of the procedure.

A large number of agglomerative hierarchical cluster algorithms have been developed (Massart and Kaufman, 1983). They differ from each other in the way of defining distance (or similarity) between an individual and a group containing several individuals, or between two groups of individuals. The clustering strategies used in this work were the following: nearest neighbor, furthest neighbor, group average, centroid and Ward's method. These methods are extensively described in the literature (Massart and Kaufman, 1983). Cluster programs are incorporated in a software package developed by Van Espen (1984).

Correspondence factor analysis

Correspondence Factor Analysis (CFA) is a multivariate technique that seeks for similarities in 'behavior' between the various characters that constitute an initial data matrix. CFA has a different field of application than the more commonly used principal component analysis (PCA). PCA is often used on heterogeneous data sets, while CFA works well on contingency tables (data tables composed of dependent variables and individuals). Because of a possible simultaneous incorporation of certain elements in a mineral phase, chemical element concentrations will, at least partially, be correlated to each other.

By use of CFA, the variation in the data can be represented in such a way that, without losing significant information, the dimensionality is reduced. To achieve this, new variables are constructed, according to a linear combination of the original variables. This is done in such a way that the newly formed variables (factors) are uncorrelated and factors are constructed with decreasing degree of importance. CFA, in the context of water chemistry, was combined with multi element chemical analysis by Vandelannoote et al. (1983). CFA is performed by means of a commercial computer program, in which a CFA algorithm is incorporated.

RESULTS AND DISCUSSION

The different cluster procedures that can possibly be used for the classification of individuals were compared with respect to their ability to differentiate the series of thermal and cold Bulgarian waters described above. The evaluation was rather intuitive and based on a satisfactory compromise between:

- description of the data matrix by a minimum number of groups
- maintenance of a maximum of geochemically relevant information. A criterion for this was a first separation into groups between, on the one hand, the cold waters, and on the other hand, thermal waters.

Clustering was performed taking into account normalized values of pH, temperature and major ion concentrations (SiO_2 , Na, K, Li, Ca, Mg, F^- , Cl^- , SO_4^{2-}). These variables were selected because they are known for all investigated waters well above the detection limits. This is not always obvious, since cold surface waters are often depleted in trace elements specific for thermal waters from a granitic area. It appeared that the furthest neighbor clustering technique gave the most satisfactory results in terms of the purpose formulated above. The corresponding dendrogram is presented in Fig. 2.



Fig. 2. Dendrogram resulting from cluster analysis of cold and thermal waters from south Bulgaria.

From Fig. 2 it can be seen that cold and thermal waters are clearly separated by use of the furthest neighbor linkage approach. Further, it is possible to distinguish at least two main groups of thermal waters. The first group comprises Tchepino, Ladjene and Rakitovo thermal waters; Draginovo, Kamenitza and Varvara waters are included in the second group. According to Table 1, the first group corresponds to relatively low temperature-low TDS waters, while the latter group is characterized by a higher temperature and mineralization. Sample 37, although it has a low temperature at the surface, is incorporated within the thermal cluster. This suggests the water to be of thermal origin.

As results obtained by clustering techniques depend on the kind and number of variables selected and on the particular clustering method that is applied, it is recommended to involve additional interpretation strategies. Therefore, Rb/Cs and Li/Cs ratios, which are, according to Pentcheva (1967), characteristic for N_2 -containing thermal waters, are calculated (see Table 2). From these ratios, a similar grouping as the one concluded from cluster analysis can be deduced. Rb/Cs ratios appeared to be >1 for the first group (Tchepino, Ladjene and Rakitovo) and <1 for the second one (Kamenitza, Draginovo and Varvara). Li/Cs ratios for group 1 waters are >10 and <10 for group 2 waters. Exceptions are samples 10, 11, 12 and 35, which will appear to be 'special' (see further). Varvara waters show a slightly higher Rb/Cs ratio (1.4 and 1.5), than expected from their incorporation in group 2.

Further, a similar grouping of thermal waters is obtained by Michard et al. (1986). These authors made a classification of a series of Bulgarian thermal waters, based on the saturation with chalcedony at emergence conditions. Tchepino and Rakitovo waters were found to be saturated with chalcedony, while Draginovo and Ladjene waters are supersaturated. Kamenitza waters were not considered. The Ladjene water considered by Michard et al. (1986) corresponds with sample 11 in this work, which shows an intermediate behavior (see further). It is suggested that waters, saturated with chalcedony, flow out at a temperature close to the one at deep levels, while the other waters are cooled during ascent from the reservoir to the surface. Varvara waters were found to be only slightly cooled.

Table 2. Rb/Cs and Li/Cs ratios for south Bulgarian thermal waters.

no.	locality	Rb/Cs	Li/Cs
1	Tchepino	3.9	80
2	Tchepino	7.5	98
3	Tchepino	5.4	82
4	Tchepino	3.5	79
5	Tchepino	6.5	160
8	Ladjene	3.0	48
9	Ladjene	3.5	58
10	Ladjene	0.99	9.6
11	Ladjene	0.89	7.3
12	Ladjene	0.68	5.3
13	Kamenitza	0.64	4.3
14	Kamenitza	0.71	4.3
15	Kamenitza	0.67	3.7
21	Draginovo	0.76	3.9
22	Draginovo	0.76	4.1
24	Draginovo	0.96	5.7
26	Rakitovo	14	170
27	Rakitovo	-	1073
29	Varvara	1.4	7.8
31	Varvara	1.5	5.5
35	Ladjene	0.61	5.7
36	Ladjene	1.9	41
37	Rakitovo	-	-
38	Kamenitza	0.71	3.6
39	Kamenitza	0.72	3.9

- : not determined

In parallel to cluster analysis, a second multivariate technique, CFA, was applied, from which it is also possible to deduce a certain classification of the individuals (water samples). On the other hand, also information on the behavior of the variables can be obtained. Since a grouping of variables into reservoir and surface dependent elements is required, CFA was performed on thermal water samples, omitting the cold waters (7, 19, 25, 28, 40) as well as sample 37, which, although probably of thermal origin, forms a definite outlier as compared to the other thermal waters, when included in CFA. The variables that are included are the following : SiO₂, Na/K, Li, Rb, Cs, B, W, Mg, Al, Mo and Sr. SiO₂ and Na/K, which are commonly used in geothermometers, are included to facilitate

interpretation, since they are known to correlate with reservoir temperatures. In this case, also trace elements could be considered, since only thermal waters were involved, for which trace element data are available.

The first two factors from CFA are extracted and presented in a two dimensional plot. Factor 1 explains 65% of the variance, while factor 2 explains another 15% of the remaining variance. Fig. 3 shows the 'loadings' of each variable on the first two factors. From this picture, it is clear that B, Rb, Li, SiO₂, W, Cs and Na/K are closely related to factor 1. Al and Mg, on the other hand, are related to factor 2. Sr and Mo show an intermediate behavior. Since SiO₂ and Na/K are known to correlate with temperature at depth, factor 1 is suggested to reflect reservoir conditions. Factor 2, which is mainly influenced by the Al and Mg concentration, can be attributed to processes occurring on the way to, or near the surface, as Al and Mg both reequilibrate rapidly when physicochemical conditions change (Michard et al., 1979).

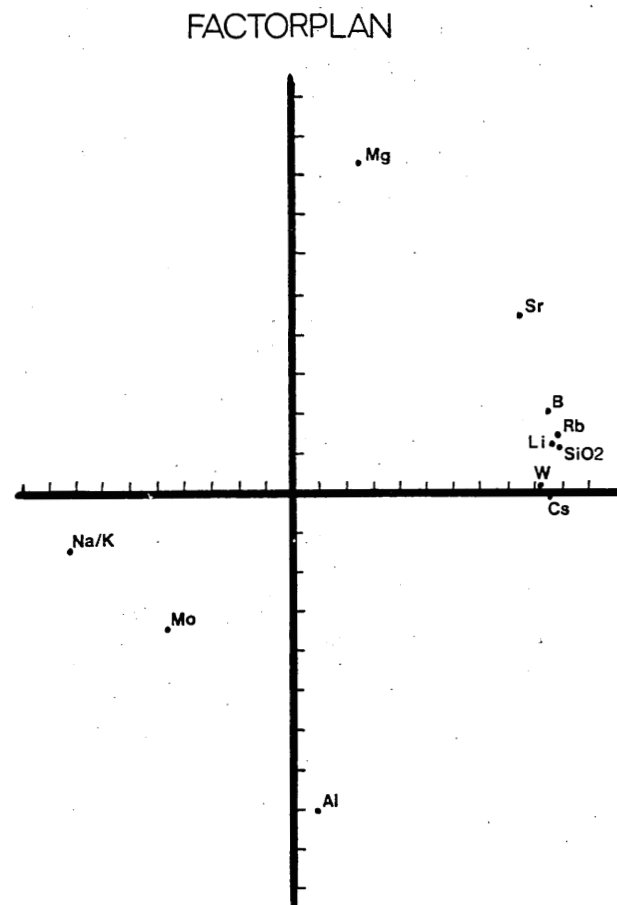


Fig. 3. Loadings of the involved variables on the first two factors obtained from CFA.

Fig. 4 shows the 'score' of each water sample on factors 1 and 2. The loading of a sample on factor 1 indicates the deep reservoir influence, while the loading on factor 2 points to near surface reactions. In this picture, samples that are more similar are situated closer to each other. According to factor 1, a similar classification, as compared to the one obtained from clustering techniques, can be deduced. Samples 11, 12 and 35, which are incorporated into the 'colder' group, according to clustering techniques, are rather intermediate between the two groups from CFA. From Table 2, a similar conclusion can be drawn. Calculations based on SiO₂, Li, Cs, Rb and W concentrations point to a mixing of Ladjene and Kamenitza waters. This may explain the intermediate position of samples 11, 12 and 35 on the factorscore plot. When looking to the sample loadings on factor 2, samples 24 and 31 are found to score highly positive. This is due to their rather high Mg concentration, which points to mixing with a cold water.

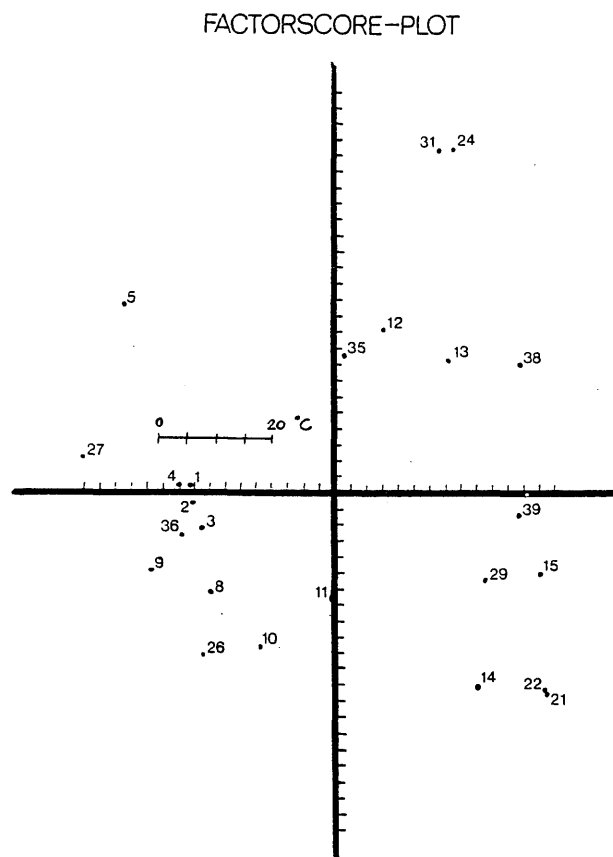


Fig. 4. Scores of the investigated thermal water samples on the first two factors obtained from CFA.

As factor 1 was found to be related to reservoir conditions, an attempt was made to derive, from CFA, quantitative information on the particular reservoir temperatures. Therefore, factor 1 was calibrated, taking into account reservoir temperatures of samples 9 and 21, calculated by use of the silica geothermometer. Since it is generally accepted that dissolved silica is controlled by chalcedony solubility at temperatures < 100°C, and by quartz solubility at higher temperatures, a chalcedony based temperature is used for sample 9, while the temperature obtained by use of the quartz geothermometer is used for sample 21. Evidence for this assumption is given by Michard et al. (1986). In this way, temperatures at depth are estimated by use of a 'mixed' geothermometer, taking into account several variables that may attribute some reservoir temperature information. Especially when trace elements are involved, this may be a useful approach, since small concentrations are more easily subject to element specific variations or measurement faults. A summary of the calculated reservoir temperatures according to the classic geothermometers, on the one hand and CFA, on the other hand, is presented in Table 3. From Table 3, it can be seen that the temperatures obtained from CFA are in the same range as those from the classical geothermometers. At T < 100°C, temperatures calculated from the Na/K(T3) and Na/K/Ca(T4)-geothermometer, in most cases, yield values that are low, compared to the other data. According to Michard et al. (1986), a small degree of under- or supersaturation can yield errors of about 25°C for the Na/K and 15°C for the chalcedony thermometers. Michard et al. (1986) calculated reservoir temperatures based on a computer simulation of the chemical changes induced by cooling. This yields temperatures at depth in the range of 102-110 and 139-145°C for Varvara (sample 29) and Draginovo waters (sample 21) respectively. For the other waters, considered in this work, no simulation was performed. Temperatures cited above are similar to the ones obtained by CFA (125 and 136°C, respectively). According to Michard et al. (1986), waters 2 (Tchepino) and 26 (Rakitovo) have reservoir temperatures that are close to temperatures at the surface. This would suggest that Na/K, Na/K/Ca and/or Na/Li geothermometers, for these waters, yield more accurate results, as compared to silica and CFA estimates. Temperatures recorded at 54m depth for water 2 and at >790m depth for water 26 are 48 and 57°C, respectively.

CONCLUSION

Cluster analysis yields a grouping of water samples, based on the similarity in their chemical composition. Especially in combination with other validation methods, this technique may be a source of information. Correspondence factor analysis confirms the general trends found by clustering techniques. From CFA, also a grouping of the variables is obtained. These groups can be

Table 3. Reservoir temperatures calculated by use of classic geothermometers and by CFA.

no.	locality	T1 T2 T3 T4 T5 T6					
		—(°C)—					
1	Tchepino	92	72	33	45	80	74
2	Tchepino	92	71	35	45	85	74
3	Tchepino	91	70	40	46	86	76
4	Tchepino	90	70	41	39	78	72
5	Tchepino	90	69	20	37	77	62
8	Ladjene	88	67	16	57	62	78
9	Ladjene	88	67	5	49	60	67
10	Ladjene	96	76	22	61	71	86
11	Ladjene	107	89	66	110	105	99
12	Ladjene	122	105	134	154	125	108
13	Kamenitza	124	107	96	128	135	119
14	Kamenitza	128	112	86	128	109	124
15	Kamenitza	134	119	92	130	123	135
21	Draginovo	136	122	95	133	113	136
22	Draginovo	131	116	107	138	128	136
24	Draginovo	132	117	124	138	127	120
26	Rakitovo	100	81	55	105	57	76
27	Rakitovo	84	63	16	68	38	55
29	Varvara	125	108	338	207	316	125
31	Varvara	129	113	118	140	96	117
35	Ladjene	113	95	74	111	142	101
36	Ladjene	81	60	6	47	64	72
38	Kamenitza	135	121	116	139	141	132
39	Kamenitza	133	118	108	137	139	131

T1 : quartz; $T(^{\circ}\text{C}) = (1315 / (5.205 - \log \text{SiO}_2)) - 273.15$
(Mazor et al., 1980; $[\text{SiO}_2]$ in ppm)

T2 : chalcedony;
 $T(^{\circ}\text{C}) = (1051.1 / (4.655 - \log \text{SiO}_2)) - 273.15$
(Mazor et al., 1980; $[\text{SiO}_2]$ in ppm)

T3 : Na/K; $T(^{\circ}\text{C}) = (908 / (0.7 + \log(\text{Na}/\text{K}))) - 273.15$
(Ellis, 1970; $[\text{Na}]$ and $[\text{K}]$ in mol/l)

T4 : Na/K/Ca;
 $T(^{\circ}\text{C}) = 1647 / (2.24 + \log(\text{Na}/\text{K}) + \beta \log(\text{Ca}^{1/2}/\text{Na})) - 273.15$
(Fournier and Truesdell, 1973; $[\text{Na}]$, $[\text{K}]$ and $[\text{Ca}]$ in mol/l)

$\beta = 1/3$ for $T > 100^{\circ}\text{C}$

$\beta = 4/3$ for $T < 100^{\circ}\text{C}$

T5 : Na/Li; $T(^{\circ}\text{C}) = (1000 / (0.38 + \log(\text{Na}/\text{Li}))) - 273.15$
(Fouillac and Michard, 1979; $[\text{Na}]$ and $[\text{Li}]$ in mol/l)

T6 : CFA (see text)

interpreted as 'reservoir' and 'surface' dependent. Reservoir temperatures can be estimated by calibration of the factor, which is related to reservoir conditions. It is expected that the use of various elements instead of only one or two for predicting deep reservoir temperatures, yields results which are less influenced by element specific secondary effects.

A further study will include the following

- a) As temperatures calculated from CFA are dependent on the calibration procedure, further calibrations, based on alternative deep reservoir temperature data, will be tested

- b) Application of multivariate techniques to a similar data set, obtained by chemical analysis of another series of Bulgarian waters

- c) Calculation of reservoir temperatures for a range of thermal waters from a similar area (Eastern Pyrenees, France), using the 'Bulgarian' calibration of the reservoir related factor.

From this, a first conclusion on 'how general' this approach is, can be drawn.

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