

RARE EARTH ELEMENTS AND URANIUM IN FOUNTAIN WATERS FROM DIFFERENT TOWNS OF THE IRON QUADRANGLE, MG, BRAZIL

Cláudia A. Ferreira^{1*}, Helena E. L. Palmieri¹ and Maria Ângela de B. C. Menezes¹

¹Centro de Desenvolvimento da Tecnologia Nuclear/Comissão Nacional de Energia Nuclear, CDTN/CNEN

*Pós-graduação em Ciência e Tecnologia das Radiações, Minerais e Materiais

Av. Presidente Antônio Carlos, 6627 Campus UFMG, CEP 31.270-970

Caixa Postal 941, CEP 30161-970, Belo Horizonte, MG

cferreiraquimica@yahoo.com.br, help@cdtn.br, menezes@cdtn.br

ABSTRACT

Rare earth elements (REE) and uranium were evaluated in 34 fountain waters collected in different towns of the Iron Quadrangle (IQ), Minas Gerais, Brazil. The IQ is one of the largest and most well-known mineral deposits in the world. Not only extensive iron deposits but also hydrothermal gold deposits are found in this region. Because of the toxicological properties of REE, monitoring of groundwater which is used for drinking water may be useful if relatively high concentrations of REE are expected. The total REE (Σ REE) concentrations in fountain water range from 3 to 33395 ng L⁻¹. It was observed that fountains with a pH value below 5 presented higher concentration values of the determined elements proposed in this work. This is due to the fact that waters exhibiting low pH values enhance the dissolution of these elements. Moreover, for uranium the values ranged from less than < 2 to 540 ng L⁻¹. The highest concentrations in waters were observed only in four cities. Statistical methods such as Pearson correlation, PCA and HCA analysis were applied to the data set to shed some light on the behavior of the elements in water in this study. Three major groups with similar characteristics were identified and six diagrams of REE signatures in fountain waters were plotted according to their groupings of subdivisions. Using the REE-Post-Archean Australian Shale (PAAS) normalized patterns it was possible to verify presence of distinct REE signatures and recognize that the two samples belong to the same aquifer type.

1. INTRODUCTION

Natural or human origins may lead to elevated levels of REE in groundwater. The importance of the determination of REE in fountain water is related to possible adverse health effects caused by REE in drinking water. In the Iron Quadrangle region, the public water supply is done mainly by the impound of water of watersheds. However, in some places, spring water and/or groundwater from closed mines are used for human consumption [1, 2].

The rare earth elements (REEs) lie in the last two rows of the periodic table. The REEs are divided into 3 subgroups: (i) those with lower atomic number and masses referred to as the light rare earth elements, LREEs (La, Ce, and Pr); (ii) those with higher atomic number and masses referred to as the heavy rare earth elements, HREEs (Tb, Dy, Ho, Er, Tm, Yb and Lu); and (iii) the middle rare earth elements (MREEs) that include Nd, Sm, Eu and Gd [3].

The unique and chemically coherent behavior of the rare earth elements has spawned considerable interest in their concentrations and are also of interest in hydrogeochemistry, because of their potential use to study water-rock interactions between groundwater and rocks hosting the aquifer and, in some cases, to trace the groundwater flow [4, 5].

Some investigations on the REE geochemistry have shown that groundwater exhibits typical signatures (aqueous REE normalized to a common rock standard) that closely resemble the rocks through which they flowed. REE-pattern similarities between groundwater and the parent rock suggest that the rare earth elements can be useful tracers of water–rock interaction processes. Aqueous rare earth elements geochemistry can be controlled directly or indirectly by different factors, such as redox conditions, solution chemistry, pH, complexation, colloidal and particulate matter transport. Several studies have reported the relevance of such factors on the REE signatures in groundwater, as compared to the REE signatures in parent rocks. Some authors suggest that depending on the considered system both rock source and solution chemistry can play important roles in controlling patterns and amount of REE in groundwater [3, 4, 5].

The REE-Post-Archean Australian Shale (PAAS) normalized patterns appear useful to recognize the aquifer type and suggest the possibility to use the REE as geochemical tracers [4,5].

Multivariate statistical techniques are efficient ways to display complex relationships among many objects. The data of this study were treated using multivariate statistical techniques such as principal component analysis (PCA) and cluster analysis. These techniques are used to explain the correlation amongst a large number of variables in terms of a small number of underlying factors without losing much information. The intention underlying the use of multivariate analysis is to achieve great efficiency of data compression from the original data. This method can also help indicate natural associations between samples and/or variables thus highlight the information not available at first glance [6, 7, 8].

This study aims primarily to document the concentrations, patterns of the REEs in some water fountains of the IQ region and determine natural associations between fountain water samples and/or variables.

2. MATERIALS AND METHODS

2.1. Sampling and analytical methods

Rare earth elements, uranium and the physical-chemical parameters, such as pH, electric conductivity (EC), total dissolved solids (STD), oxidation/reduction potential (Eh), alkalinity and major cations and anions were determined in 34 fountain waters collected in March 2012 in different towns of the Iron Quadrangle (IQ), Minas Gerais, Brazil.

For the assessment of REEs elements, uranium and major cations and anions, water samples were collected and filtered through Millipore 0.45 μm filters and immediately acidified with nitric acid Fluka ($\text{pH} < 2$). Then they were stored in low density polyethylene bottles in a refrigerator before analysis. The concentrations of the REEs, uranium, calcium and magnesium were measured by ICP-MS with a Perkin Elmer ELAN DRC-e ICP-MS spectrometer equipped with an auto sampler (AS-93plus). The concentrations of these elements were analyzed in Mass Spectrometry Laboratory of CDTN/CNEN.

Multi-element Standard 2, Perkin Elmer Pure Plus N9300232 solutions containing Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sc, Sm, Tb, Th, Tm, Y, Yb (10.0 mg L^{-1}) were used for preparing

the calibration curves, and all the solutions and samples were prepared in 1% HNO₃ for ICP-MS. Ultra-pure water (18.2 MΩ.cm), and ultrapure HNO₃ 69.5% (w/w) (Fluka) were used for the preparation of all standard solutions and for the preservation and dilution of the samples.

Alkalinity was determined by titration method with mixed indicator and anions Cl⁻, SO₄²⁻, and as well as the cations Na⁺ and K⁺ were determined using ion exchange chromatography. Total dissolved solids (TDS), conductivity (EC), pH and oxidation/reduction potential were measured in the field using the portable meters Myron L Ultrameter II.

The principal component analysis and hierarchical cluster analysis were applied to the data for different water sample fountains, using MINITAB 16.

3. RESULTS AND DISCUSSION

3.1. Statistical analysis

3.1.1. Physicochemical characteristics

Table 1 shows an overview of the same data for the study area. The pH of the water samples varied from a minimum of 4.3 to a maximum of 7.5. Eh values for these samples ranged from 180 to 763 mV. Electrical conductivity (EC) ranged from 4 to 337 μS cm⁻¹. Total dissolved solids (TDS) varied from 2.9 to 238 mg L⁻¹.

In the present study, the detection limits were kept. Initially a univariate analysis of measured data in fields was done and multivariate analysis subsequent.

Pearson correlation matrices were used to find the relationship between the variables, for a 95 % confidence level. Only those with correlation values higher than 0.50 were considered. The results pointed out that there is a strong positive correlation between all REE in water samples collected in towns spread in the Iron Quadrangle region ($r = 0.592$ to $r = 1.000$). Moreover, there is a positive correlation between uranium with REE, except for Ce and Eu.

Strong correlations exist between the major elements. A strong positive correlation between Ba with Na⁺, K⁺, Cl⁻ and SO₄²⁻ ($r = 0.883$; $r = 0.649$; $r = 0.893$; $r = 0.782$, respectively) was observed.

HCO₃⁻ anion correlated with Ca²⁺ ($r = 0.915$) and Mg²⁺ ($r = 0.820$). One interpretation of these observations was that these ions in some groundwaters have similar hydrochemical characteristics in the study area. Ca-Mg-HCO₃ composition reflects most of the samples classified as calcium and magnesium bicarbonate.

The results also showed that cations and anions do not correlate with REE but among themselves.

Table 1: REE concentration and pH, Eh (mV), EC ($\mu\text{S cm}^{-1}$), TDS (mg L^{-1}) in fountain water samples

Points	Concentration in ng L^{-1}														pH	Eh (mV)	EC ($\mu\text{S cm}^{-1}$)	TDS (mg L^{-1})
	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu				
1	240	<1.3	28	127	27	119	51	10	83	24	83	11	63	10	6.0	322	326	230
2	1054	43	293	1313	331	11	431	61	316	64	172	21	105	17	5.8	340	109	73.5
3	58	<1.3	8	27	4	8	6	1	4	1	<1.1	<0.3	1	<0.2	6.1	338	81	54.5
4	39	81	10	41	9	4	9	1	7	1	5	1	5	1	6.3	338	9	6.0
5	221	383	59	234	40	9	39	4	19	3	8	1	8	1	5.0	373	6	4.1
6	29	18	4	15	3	1	2	0.3	<1.4	0.5	<1.1	<0.3	1	<0.2	5.2	372	65	44.2
7	7149	10472	2000	7941	1689	429	1532	201	879	152	437	60	395	59	4.3	379	100	67.4
8	<0.7	<1.3	<1.4	<2.6	<1.2	3	<1.2	<0.3	<1.4	<0.5	<1.1	<0.3	<0.5	<0.2	7.5	302	129	86.8
9	8401	5689	2121	7733	1557	140	1878	327	1924	362	1045	150	898	130	5.8	335	112	75.4
10	3	<1.3	<1.4	<2.6	<1.2	4	<1.2	<0.3	<1.4	<0.5	<1.1	<0.3	<0.5	<0.2	6.4	323	110	74.3
11	43	69	11	42	7	3	7	1	4	1	2	<0.3	3	<0.2	5.3	342	4	2.9
12	47	45	12	45	10	4	9	1	7	1	4	1	4	1	7.3	626	30	19.9
13	45	49	10	38	8	4	8	1	6	1	3	<0.3	4	1	7.0	637	27	18.3
14	84	114	19	79	17	5	18	2	11	2	7	1	6	1	4.8	433	36	24.2
15	38	27	9	35	7	4	6	1	4	<0.5	<1.1	<0.3	1	<0.2	5.7	306	6	4.3
16	93	157	24	95	18	6	19	2	12	2	6	1	6	1	4.8	600	16	10.5
17	22	32	6	23	5	3	4	1	4	1	2	<0.3	2	<0.2	6.0	681	15	10.4
18	93	3	17	81	16	7	25	4	22	5	16	2	9	0.2	6.1	615	48	30.1
19	6	3	<1.4	6	<1.2	3	<1.2	<0.3	<1.4	<0.5	<1.1	<0.3	1	<0.2	6.2	262	46	31.4
20	<0.7	<1.3	1.4	<2.6	<1.2	2	<1.2	<0.3	<1.4	<0.5	<1.1	<0.3	<0.5	<0.2	6.8	248	239	165
21	2	<1.3	<1.4	<2.6	<1.2	<0.5	<1.2	<0.3	<1.4	<0.5	<1.1	<0.3	1	<0.2	6.8	242	337	238
22	6	2	<1.4	4	<1.2	4	2	<0.3	<1.4	<0.5	<1.1	<0.3	<0.5	<0.2	5.8	278	39	26.7
23	19	51	4	17	2	3	3	<0.3	<1.4	<0.5	<1.1	<0.3	<0.5	<0.2	6.9	266	28	20.2
24	4	<1.3	<1.4	4	<1.2	3	<1.2	<0.3	<1.4	<0.5	<1.1	<0.3	<0.5	<0.2	5.8	280	30	19.7
25	11	2	2	11	2	3	3	0.3	2	<0.5	2	<0.3	1	<0.2	5.9	280	29	19.8
26	289	183	69	265	50	13	50	7	35	7	20	3	19	2	5.0	277	13	8.4
27	5	<1.3	<1.4	<2.6	<1.2	21	<1.2	<0.3	1.4	<0.5	<1.1	<0.3	<0.5	<0.2	6.8	763	202	138
28	26	52	6	23	5	<0.5	4	<0.3	2	<0.5	<1.1	<0.3	1	<0.2	5.2	246	4	2.9
29	22	35	5	16	3	5	4	<0.3	3	<0.5	2	<0.3	1	<0.2	6.9	180	22	14.5
30	227	15	26	96	14	52	17	2	9	2	5	1	3	<0.2	6.0	243	288	201
31	17	45	5	20	4	3	5	1	4	1	3	<0.3	2	<0.2	6.3	628	26	17.1
32	244	322	55	213	39	15	45	7	38	8	22	3	21	3	4.6	320	17	14.7
33	301	593	66	265	53	21	60	9	46	10	28	4	26	4	4.7	300	36	24.2
34	288	532	69	275	52	23	60	8	43	9	31	4	31	5	4.8	299	54	36.6

3.1.2. Principal component analysis

In order to obtain detailed statistical information, more robust statistical methods such as PCA and cluster analysis were applied to the data set to shed some light on the behavior of the elements in water in the present study.

PCA was applied to a matrix of concentrations of 27 parameters observed in 34 water samples including La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, U, Ba, Ca²⁺, Mg²⁺, Na⁺, K⁺, HCO₃⁻, Cl⁻, SO₄²⁻, pH, Eh, EC and TDS. Table 2 shows loadings including the eigenvalues of each PC, the percentage of explained variance and its cumulated values. The loadings are then evaluated to determine the variables that are responsible for these correlations. Variables with the greatest positive and negative loadings make the largest contribution. The loadings can, therefore, be examined to provide further insight into the processes that are responsible for the similarities in the variables. There were several criteria to identify the number of PCs to be retained in order to understand the underlying data structure.

Table 2: Principal component loadings of the 27 variables

Variables	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6
La	0.264	-0.049	-0.010	0.076	-0.051	-0.052
Ce	0.233	-0.062	0.053	0.334	-0.246	-0.046
Pr	0.262	-0.053	-0.007	0.113	-0.081	-0.051
Nd	0.260	-0.053	0.003	0.141	-0.102	-0.051
Sm	0.259	-0.052	0.009	0.158	-0.116	-0.052
Eu	0.208	0.022	0.166	0.388	-0.326	-0.090
Gd	0.264	-0.047	-0.015	0.056	-0.036	-0.043
Tb	0.265	-0.044	-0.041	-0.037	0.034	-0.037
Dy	0.261	-0.039	-0.062	-0.124	0.099	-0.029
Ho	0.259	-0.033	-0.061	-0.147	0.118	-0.023
Er	0.260	-0.031	-0.059	-0.150	0.118	-0.022
Tm	0.259	-0.031	-0.064	-0.159	0.125	-0.025
Yb	0.261	-0.035	-0.059	-0.133	0.106	-0.023
Lu	0.261	-0.034	-0.056	-0.126	0.101	-0.023
pH	-0.062	0.127	-0.404	-0.270	-0.198	-0.703
Eh	-0.017	-0.069	0.022	-0.473	-0.769	0.203
EC	0.054	0.365	-0.091	0.062	-0.077	0.115
TDS	0.052	0.366	-0.088	0.066	-0.072	0.115
HCO ₃ ⁻	0.003	0.258	-0.446	0.076	-0.056	0.201
Ca ²⁺	0.054	0.306	-0.310	0.109	0.003	0.249
Mg ²⁺	-0.008	0.337	-0.212	0.190	0.056	-0.096
Na ⁺	0.073	0.316	0.230	-0.124	-0.116	-0.056
K ⁺	0.118	0.216	0.314	-0.121	-0.056	0.245
Cl ⁻	0.054	0.345	0.201	-0.006	-0.012	-0.084
SO ₄ ²⁻	0.078	0.250	0.327	-0.165	0.193	0.011
U	0.204	-0.000	-0.166	-0.338	0.121	0.312
Ba	0.027	0.292	0.317	-0.148	0.075	-0.361
Eigenvalues	13.908	6.870	2.498	1.207	1.066	0.497
% Variance explained	51.5	25.4	9.3	4.5	3.9	1.8
% Cumulative variance	51.5	77.7	86.2	90.7	94.6	96.5

In the present study, factors with eigenvalues greater than 1 were taken into account. Following this rule, the first five factors explained 94.6% of the total variance of the original

matrix. The first component (PC 1) was responsible for 51.5% of the total variance and was best represented by REE, U and appears to characterize the water–rock interaction (FIG. 1a). PC 2 explained 25.4% of the total variance in the hydrochemistry and is dominated by loadings in EC, TDS, HCO_3^- , Ca^{2+} , Mg^{2+} , Na^+ and Cl^- (FIG. 1a).

PC 3 has negative loadings for pH and HCO_3^- , positive loadings for K^+ , SO_4^{2-} and Ba which accounts for 9.3% of the total variance in the hydrochemistry at this location. The authors [3, 8, 9] have suggested that pH exerts an important control on REE concentrations by promoting higher concentrations at low pH. In this study, the REEs increase as the pH decreases. The mean REEs for pH values < 5, pH values 5–6, and pH values > 6 are 454.2 ng L^{-1} , 265.8 ng L^{-1} , and 35.2 ng L^{-1} , respectively.

PC 4 represents 4.5% of the total variance, where Ce, Eu and U contribute for the PC 4.

PC 5 explained 3.9% of the total variance being represents for redox potential. The loadings pH and Eh influence negatively the components.

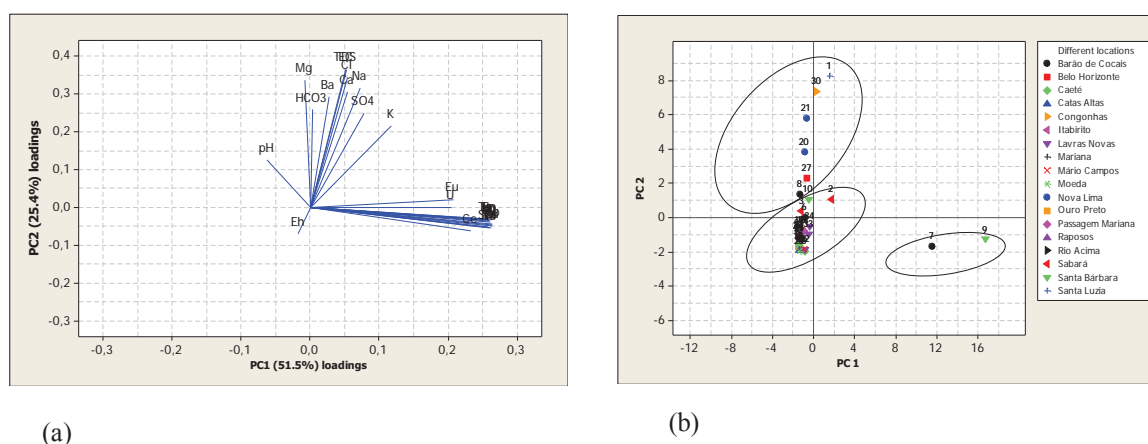


Figure 1: a) Contribution of each element to the PC loadings obtained by the principal component analysis. b) Principal component scores for 34 fountain water samples.

Figure 1b shows the score plot for the first two PCs, explaining 76.9% of the total variance. Three main groups are visible from the principal component analysis in diagram of the scores for PC 1 versus PC 2. The total REE ($\sum\text{REE}$) concentrations in fountain water range from 3 to 33395 ng L^{-1} . The highest concentrations (i.e. $\sum\text{REE} > 1000 \text{ ng L}^{-1}$) were observed in waters from Barão de Cocais (33395 ng L^{-1} , sample 7), Santa Bárbara (32355 ng L^{-1} , sample 9), Sabará (4232 ng L^{-1} , sample 2), Lavras Novas (1486 ng L^{-1} , 1430 ng L^{-1} , 1035 ng L^{-1} , sample 33, 34, 32 respectively), Caeté (1029 ng L^{-1} , sample 5), and Mário Campos (1012 ng L^{-1} , sample 26).

For uranium the values ranged from less than < 2 to 540 ng L^{-1} . The highest concentrations in waters were observed in four cities: Santa Bárbara (540 ng L^{-1} , 280 ng L^{-1} , sample 9, 10 respectively), Caeté (160 ng L^{-1} , sample 5), Belo Horizonte (120 ng L^{-1} , sample 27) and Barão de Cocais (110 ng L^{-1} , sample 7).

3.1.3. Cluster analysis

Cluster analysis groups a system of variables into clusters on the basis of similarities (or dissimilarities) such that each cluster represents a specific process in the system. Hierarchical cluster analysis is the most widely applied technique in the earth sciences and is used in this study. The levels of similarity at which observations are merged are used to construct a dendrogram. HCA is a powerful tool for analyzing water chemistry data. In this study, a standardized and Euclidean distance and the Ward's method are used [6, 7].

Fig. 3 presents the dendrogram from the HCA for Iron Quadrangle fountain water samples. Distinctive clusters of the variables were defined. The distinction between clusters in this analysis is quite clear from the dendrograms. It was observed that the REE are characteristic and grouped on the same side, while the physicochemical parameters are on opposite sides.

Two main groups are visible from the cluster analysis that can be grouped into three types. Group 1 comprises La, Pr, Gd, Nd, Sm and Ce, Eu which divided into Tb, Dy, Yb, Lu, Ho, Er, Tm and U. Group 2 is made up of pH, Eh, EC, TDS, Mg^{2+} , HCO_3^- , Ca^{2+} which is divided into (Na^+ , Cl^- , Ba, K^+ , SO_4^{2-}) sub groups.

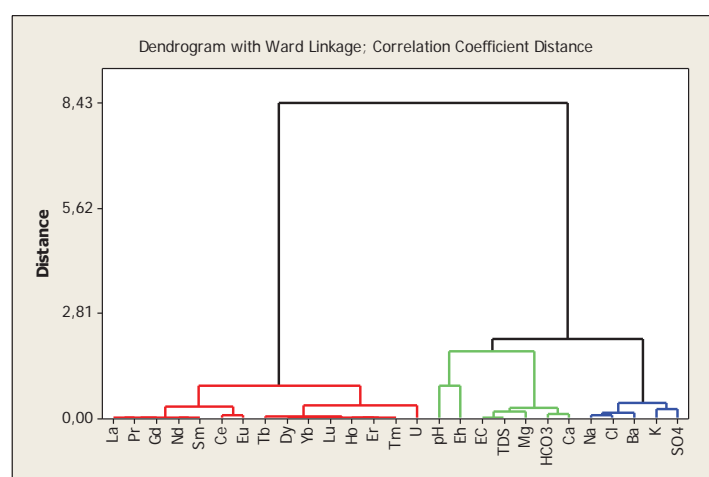


Figure 3: The dendrogram showing the clusters of the variables

The result of the hierarchical cluster analysis for the samples was given as a dendrogram (Fig. 4). As can be seen from Figure 4, the samples collected were clustered together. The first group is comprised by samples 1, 30, 8, 10, 27, 20, 21. The second cluster is represented by samples subdivisions (2, 6, 33, 14, 34), (3, 19, 22, 25, 24, 23, 29), (4, 11, 15, 26, 28, 32, 5), (12, 13, 16, 17, 31, 18) and the third group by samples (7 and 9).

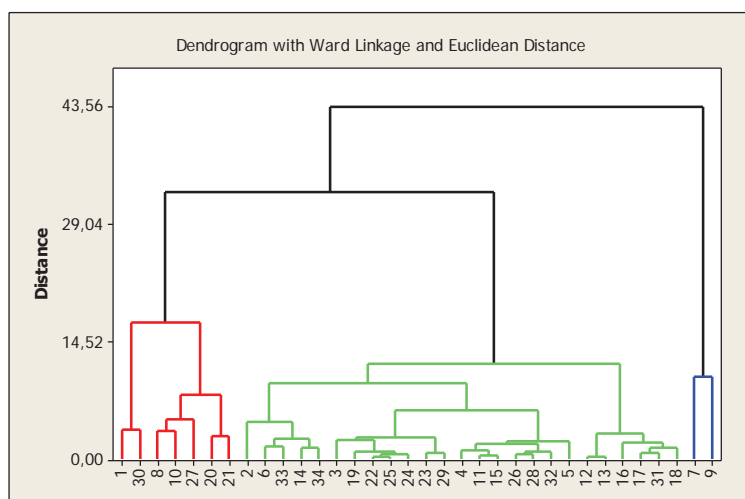


Figure 4: The dendrogram of the hierarchical cluster analysis using the Ward method showing the clustering of 34 fountain water samples

3.1.4. REE patterns in filtered water samples

The distribution of REEs in natural materials and their variations caused by geochemical behavior can be illustrated by plotting the relative abundances versus the atomic number. Due to the different abundances of odd and even atomic numbers of elements within the REE group, a simple plot of their content produces a saw tooth pattern with decreasing slope toward the highest atomic numbers.

Thus, the REE behavior is better presented if the values are normalized and reported as a relative abundance plot. This means that the concentrations of REEs found in the sample are divided by the same REEs contained in a reference material. Examples of such reference materials include de Cl chondrite, the chondritic meteorite, and the Post Archaean Australian Shales (PAAS) [3].

The advantage of this method is that the abundance variation between REEs of odd and even atomic numbers is eliminated, and any fractionation that has occurred among the REEs will be detected. Hence, the abundance peaks (positive and negative) in the normalized REE pattern reflect the geochemical history of the sample. Generally, the abundance of REEs in natural waters is usually extremely low in comparison to the levels found in most rocks.

Fig. 5 shows the concentrations of each REE in the filtered fountain water samples normalized to the corresponding concentration in the PAAS [5]. The samples were grouped according to the cluster analysis carried out in item 3.2.3, FIG. 4. Three major groups with similar characteristics were identified and six diagrams of REE signatures in fountain waters were plotted according to their groupings of subdivisions. Samples tend to have distinct REE signatures.

Despite some similarities, a closer inspection of patterns shows found different REE signatures. Fig. 5a shows REE patterns for the samples 1, 30, 8, 10, 27, 20, 21. The REE pattern of these samples shows a marked negative Ce anomaly and a more marked positive Eu anomaly. The samples are characterized by enrichment in HREE. The negative Ce anomaly is

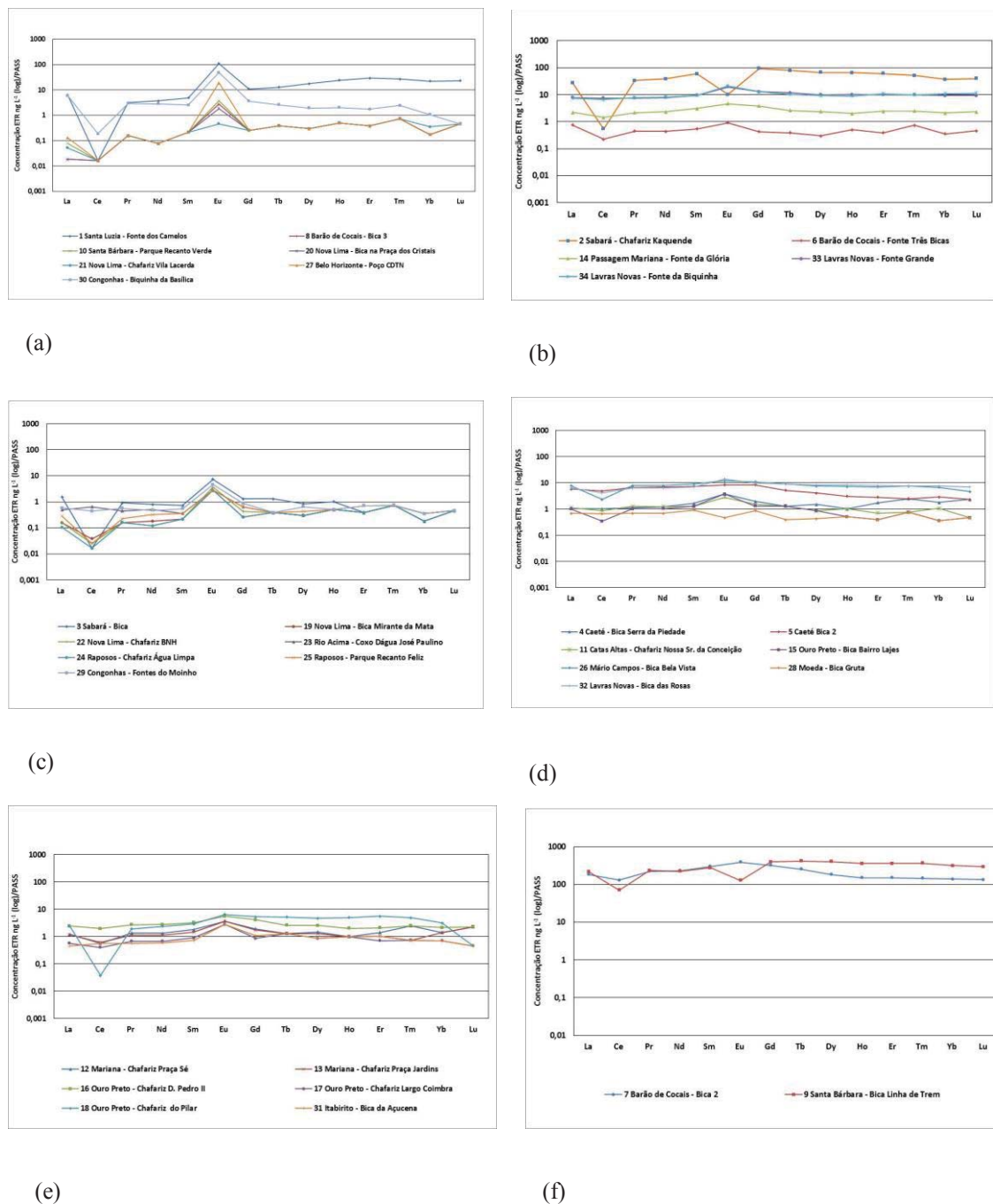


Figure 5: Patterns of REE for 34 fountain waters, samples taken in March 2012 in the IQ. Concentrations normalized to the Post-Archean average Australian Shale (PAAS).

frequently observed in groundwater under oxidizing conditions, and results from the preferential retention of Ce in solid phases, due to the poor solubility of Ce^{4+} species [10]. The HREE enrichments reflect the greater solubility of the HREE as compared with the LREE [1].

All the 14 REEs (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) are strongly electropositive and exist in the trivalent oxidation state. However, Ce, Eu, Sm and Yb can also exist, respectively, in Ce^{4+} , Eu^{2+} , Sm^{2+} and Yb^{2+} oxidation states [3, 11].

The PAAS-normalized plots (FIG. 5b) show patterns with small Ce and Eu anomalies except for sample 2 (Sabará- Kaquende fountain). The water samples 33 and 34 features the same REE signatures, being indicative of samples that belong to the same aquifer.

FIG. 5c shows the negative Ce and positive Eu anomaly. The results obtained for the REE signatures in Fig. 5c show normalized patterns and slightly enriched in heavy REE (HREE).

A slight middle enrichment relative to the LREEs over HREEs has been observed in Fig. 5d. We observed for most samples a small negative Ce anomaly and a more positive Eu anomaly, except for sample 28.

The graph in FIG. 5e shows a negative Ce anomaly and a small positive Eu anomaly and a slight enrichment to HREE.

The REE signatures in the graph in FIG. 5f show Eu inverse anomalies and the samples 2, 28 and 9 (FIG. 5b, 5d, 5f respectively) were the only samples which exhibited negative Eu anomalies. Samples 2 and 9 exhibited also negative Ce anomalies and enrichment in HREE.

4. CONCLUSIONS

This study showed that groundwater samples from different Iron Quadrangle aquifers have distinct REE signatures. The most striking feature in these patterns in these samples is the marked positive Eu anomalies as negative Ce anomalies. The results also show a direct positive correlation between all REEs in water samples collected in towns spread in the Iron Quadrangle region. Moreover, a positive correlation between uranium with REE, except for Ce and Eu.

The statistical methods such as Pearson correlation, PCA and HCA analysis were applied to the data set to shed some light on the behavior of the elements in water in this study. Three major groups with similar characteristics were identified and six diagrams of REE signatures in fountain waters were plotted according to their groupings of subdivisions. Using the REE-Post-Archean Australian Shale (PAAS) normalized patterns it was possible to verify presence of distinct REE signatures and recognize that two samples belong to the same aquifer type.

Total REE (\sum REE) concentrations in fountain waters ranged from 3 to 33395 ng L⁻¹. The highest concentrations (\sum REE > 1000 ng L⁻¹) were observed in eight fountain waters from Barão de Cocais, Santa Bárbara, Sabará, Lavras Novas, Caeté and Mário Campos. In this study it was found the REEs increase as the pH decreases. The mean REEs for pH values < 5, pH values 5–6, and pH values > 6 are 454.2 ng L⁻¹, 265.8 ng L⁻¹, and 35.2 ng L⁻¹, respectively.

However, the present study pointed out that uranium values ranged from less than < 2 to 540 ng L⁻¹. The highest concentrations in waters were observed only in the cities: Santa Bárbara, Caeté, Belo Horizonte and Barão de Cocais.

ACKNOWLEDGMENTS

The authors thank Nuclear Technology Development Center (CDTN), Brazilian Nuclear Energy Commission (CNEN) and Research Support Foundation of the State of Minas Gerais (FAPEMIG) for their financial support (APQ-02575-13) and PhD scholarship.

REFERENCES

1. J. L. M. de Boer, W. Verweij, T. van der Velde-Koerts, W. Mennes, Levels of rare earth elements in dutch drinking water and its sources. Determination by inductively coupled plasma mass spectrometry and toxicological implications. A pilot study, *Wat. Res.* **Vol. 30**, pp. 190-198, 1996.
2. P. R. Borba, B. R. Figueiredo, J. A. Cavalcanti. Arsênio na água subterrânea em Ouro Preto e Mariana, Quadrilátero Ferrífero (MG), *Rev. Esc. Minas.*, Ouro Preto, **Vol. 57**, n.1, pp.45-51, 2004.
3. A. E. EDET. A preliminary assessment of the concentrations of rare earth elements in an acidic fresh groundwater (south-eastern Nigeria), *Applied Earth Science*, **Vol.113**, pp.100-109, 2004.
4. R. Biddau, M. Bensimon, R. Cidu, A. Parriaux. Rare earth elements in groundwater from different Alpine aquifers, *Chemie der Erde*, **Vol. 69**, pp.327-339, 2009.
5. P. Kralj, P. Kralj. Rare earth in thermal water from the Sob-1 well, Murska Sobota, NE Slovenia, *Environ. Earth Sci.*, **Vol. 59**, pp.5-13, 2009.
6. K. Chen, J. J. Jiao, J. Huang, R. Huang. Multivariate statistical evaluation of trace elements in groundwater in a coastal area in Shenzhen, China, *Environmental Pollution*, **Vol. 147**, pp.771-780, 2007.
7. S. M. Yidana, D. Ophori, B. B. Yakubo. A multivariate statistical analysis of surfasse water chemistry data-The Ankobra Basin, Ghana, *Journal of Environmental Management*, **Vol.86**, pp.80-87, 2008.
8. C. Lourenço, L. Ribeiro, J. Cruz. Classification of natural mineral and spring bottled waters of Portugal using Principal Component Analysis, *Journal of Geochemical Exploration*, **Vol. 107**, pp.362–372, 2010.
9. G. Protano, F. Riccobono. High contents of rare earth elements (REEs) in stream waters of a Cu-Pb-Zn mining area, *Environ. Pollut.*, **Vol. 117**, pp.499–514, 2002.
10. E. R. Sholkovitz. Chemical evolution of rare earth elements: fractionation between colloidal and solution phases of filtered river water, *Earth and Planetary Science Letters*, **Vol. 114**, pp.77–84, 1992.
11. R. P. T. Janssen, W. Verweij. Geochemistry of some rare earth elements in groundwater, Vierlingsbeek, The Netherlands, *Water Research*, **Vol. 37**, pp.1320–1350, 2003.