

URANIUM, THORIUM AND RARE EARTH ELEMENTS DISTRIBUTION FROM DIFFERENT IRON QUADRANGLE SPRING WATERS

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ABSTRACT

This study was conducted to evaluate the concentrations of thorium, uranium and the rare earth elements (REE) in 26 spring waters, as well as the patterns of the REE of the samples from the Cercadinho, Moeda and Cauê aquifers in different municipalities of the Iron Quadrangle (Quadrilátero Ferrífero), located in the central-southeast of Minas Gerais state. The pH value of the ground waters ranged from 3.8 to 7.0, indicating an acid nature of most of the spring waters. The investigation of REE speciation showed that all the REEs exist in the free X^{3+} ionic forms, under the prevailing Eh and pH conditions. In the studied samples the uranium concentrations ($<2.3\text{--}1176\text{ ng L}^{-1}$) were below the guideline level set by Brazilian legislation (Ministry of Health 518-03/2004). Thorium concentrations ranged from $<0.39\text{--}11.0\text{ ng L}^{-1}$ and the sum of the REE ranged from 6.0 to 37657 ng L^{-1} . As there are no permissible limits related for the REE and thorium for different water quality standards in Brazil, more attention must be paid to the local residents' health risk caused by spring waters (REEs were $> 1000\text{ ng L}^{-1}$) originating from aquifers located in Sabará, Barão de Cocais, Santa Bárbara, Mário Campos, Congonhas and Lavras Novas. The REEs patterns in the spring waters from the Cercadinho, Cauê and Moeda aquifers are characterized by middle REE (MREE) enrichment compared to light REE (LREE) and heavy REEs (HREE), negative Ce anomalies (except for one sample) and positive Eu anomalies in all three aquifers studied.

1. INTRODUCTION

The importance of the rare earth elements (REEs), Th and U determination in waters is associated to possible adverse health effects caused by these elements in drinking water [1]. It is now well known that intake of REEs over a long period has harmful effects on human liver and kidneys, as well as negative effects on immunity [2]. When compared with the normal region, blood biochemical indices of human beings were abnormal in the REE high regions, and the effects of REE on males were a one-way irreversible process [2]. Despite the absence of permissible limits for REEs and thorium for different water quality standards in Brazil, more attention must be paid to the local residents' health risk caused by drinking water.

The large increase in groundwater consumption has required more rigorous quality controls and a better understanding of naturally occurring groundwater mineralization processes with respect to the REEs, Th, and U. These elements co-exist with elemental metals in minerals in

mining areas. Natural or anthropogenic origins may lead to elevated levels of REEs, Th and U in groundwaters [3].

Several studies have been carried out on REE geochemistry in groundwater and spring water resources worldwide [4, 5, 6]. Normally they document REEs concentrations, their probable sources in aquifers and have also shown that REEs in groundwater exhibit typical signatures (i.e. aqueous REE normalized to a common rock standard) that closely resemble the rocks through which they flowed. Anomalies of Ce are of particular importance because the anomaly's potential can be used as an indicator of water/rock interactions or as a hydrological tracer [5].

The Iron Quadrangle (IQ), located in the central-southeast of Minas Gerais state, stands out in the Brazilian scenario for the extraction of gold, iron and manganese. Since the discovery of gold in the late 17th century, the region of the IQ has been home to the largest urban concentration of Minas Gerais, with gold, iron and manganese mining, as its main economic activities. However, the intense exploitation of these mineral resources has had a great impact on nature, such as groundwater and soil pollution, biodiversity loss and erosion.

The public supply of water in the IQ is done mainly by water impound of watersheds, but, as today, in some historic towns, like Ouro Preto, Mariana, Congonhas, Sabará, spring waters are still used to supply the fountains located in churches, stately homes, monuments and cobbled streets of these historic towns. These waters are used by the local population and visitors who trust its drinking water quality.

As yet there is no data available on the quality of several of the spring waters used by the population in urban and rural areas of the IQ. Therefore, this study was undertaken in order to evaluate the concentrations of thorium, uranium, rare earth elements and the patterns of REEs in spring waters from the aquifers Cercadinho, Moeda and Cauê, within the Iron Quadrangle.

1.1. Some Properties of REEs

The REEs are divided into 3 subgroups: (i) those with lower atomic number and masses referred to as light rare earths elements, LREEs (La, Ce, Pr and Nd); (ii) those with higher atomic number and masses referred to as heavy rare earths elements, HREEs (Dy, Ho, Er, Tm, Yb and Lu); and (iii) the middle rare earth elements (MREEs) that include, Sm, Eu and Gd [5].

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 CI chondrite, the chondritic meteorite, and the Post Archaean Australian Shales (PAAS) [5].

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.

2. MATERIALS AND METHODS

2.1. Studied Area

The Iron Quadrangle (Quadrilátero Ferrífero) covers an area of approximately 7000 km² in the central-southeast of Minas Gerais state, Brazil, and is internationally recognized as an important Precambrian terrane with significant mineral resources, particularly gold and iron. The geology of the Iron Quadrangle comprises an Archean greenstone belt sequence, represented by the Rio das Velhas Supergroup, surrounded by Archean granite-gneiss terrains which are overlaid by a Paleoproterozoic sedimentary succession, i.e., the Minas Supergroup [13].

This region is rich in water resources, hosting the headwaters of the basins of the Rivers Velhas and Doce, two of the main Brazilian watersheds, with wide diversity of biomes, including remnants of the Atlantic Forest, Cerrado stretches and rupestrian fields [13]. The underground water potential in this region has been known since the early occupation of the area due to the abundance and quality of its spring waters. Data available [14] indicate the existence of large reserves of groundwater in various geological formations of the IQ: the hematites and itabirites of the Cauê Formation, the quartzites ferruginous of the Cercadinho Formation, the dolomites of the Gandarela Formation and the quartzites of Moeda Formation. The Cauê aquifer is the main groundwater reservoir in the IQ, with a high storage capacity.

Forty-four spring water samples were collected in the municipalities of Sabará, Caeté, Barão de Cocais, Santa Bárbara, Catas Altas, Mariana, Ouro Preto, Congonhas, Moeda, Nova Lima, Rio Acima, Raposos, Itabirito, Mário Campos and four artesian well water samples in the municipalities of Santa Bárbara and Belo Horizonte. Fig. 1 shows the sample sites in the various municipalities as well as the main aquifers in the Iron Quadrangle region. The geoprocessing program used was the ArcGIS (ESRI), version 10.2.2, [15]. Six sampling sites (4, 5, 7, 8, 16 and 17) fell into the Cercadinho Formation (quartzitic ferruginous aquifer), one (14) in the Cauê Formation (aquifer in iron formations) and one (28) in the Moeda Formation (quartzitic aquifer).

2.1. Sampling and Analytical Methods

Natural spring waters and artesian well waters samples were collected in two different surveys, i.e., March 2015 (wet season) and August 2015 (dry season). The well samples were included in our study due to the fact that these waters were also used for human consumption (fig. 1). Eh and pH were measured in the field using a multiparameter (Myron L Company Ultrameter).

Samples for Th, U, and REEs analysis were collected into washed polyethylene narrow-mouth bottles with screw cap. Before sample collection, the bottles were rinsed with spring water filtered through 0.45 µm membrane (mixed cellulose esters-Merck Millipore). After

collecting the samples were immediately acidified to pH<2 with ultrapure nitric acid and then stored at 4°C before analysis. The concentrations of Th, U, and REEs, were determined by inductively coupled plasma-mass spectrometry (ICP-MS) (Perkin-Elmer Elan DRCE equipped with an auto sampler (AS-93plus).

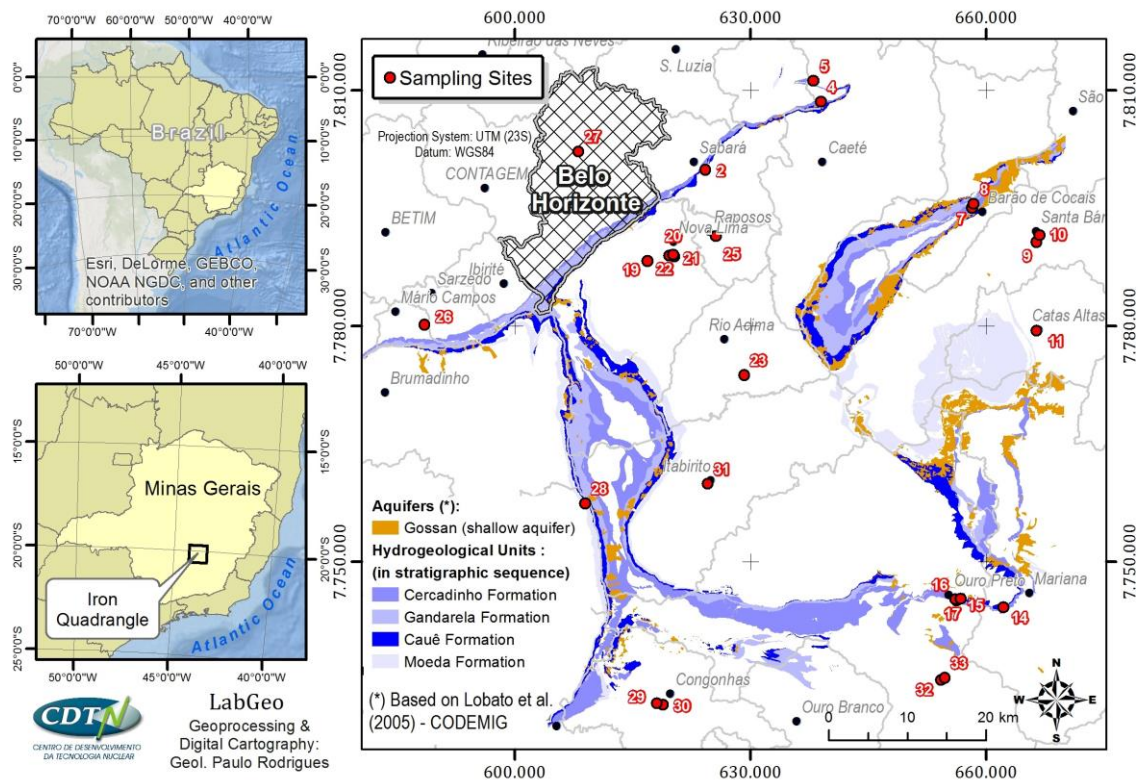


Figure 1: Map of the study area with the sample sites in the various municipalities and the main aquifers in the Iron Quadrangle region.

3. RESULTS AND DISCUSSIONS

3.1. REEs, pH and Speciation

The results of pH, Eh (mV), REE, U e Th (ng L⁻¹) and Σ REE in the spring water samples collected in March (M) and August (AG) 2015 are shown in Tables 1 and 2. In the studied samples the uranium concentrations (<2.3–1176 ng L⁻¹) were below the guideline level (30 000 ng L⁻¹) set by Brazilian legislation (Ministry of Health 518- 03/2004). Thorium concentrations ranged from <0.39-11.0 ng L⁻¹ and the sum of the REEs varied considerably, ranging from 6 to 37657 ng L⁻¹ (Tables 1 and 2). The highest concentrations (Σ REE >1000 ng L⁻¹) were observed in spring waters from Sabará, Barão de Cocais, Santa Bárbara, Mário Campos, Congonhas and Lavras Novas.

Table 2: Results of pH, Eh (mV), REE, U e Th (ng L⁻¹) and Σ REE in the spring water samples collected in August (AG) 2015

Water samples/Parameters	pH	Eh	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	U	Th	Σ REE
AG2 Sabará	5.9	175	1100	50	275	1370	318	102	425	57	293	63	166	24	108	21	16.4	2.00	4372
AG4 Caeté	6.3	200	24.8	78.9	6.71	23.9	5.26	2.14	5.8	0.92	5.13	1.07	2.97	0.86	2.53	0.47	3.06	3.98	161
AG5 Caeté	5.3	209	41.3	43.3	10.7	43.9	8.66	3.17	9.47	1.34	6.6	<0.31	3.41	<0.25	3.05	<0.23	23.2	4.08	175
AG7 Barão de Cocais	4.5	242	5386	7316	1340	5621	1188	298	1092	131	591	106	304	45	278	44	89.1	6.00	23740
AG8 Barão de Cocais	7.0	196	5.24	10.6	1.37	<1.4	< 0.95	<0.30	<1.3	<0.17	< 0.91	<0.31	<1.1	0.44	<0.61	<0.23	40.1	5.08	18
AG10 Sta. Bárbara	6.2	217	4.96	8.13	0.9	2.53	< 0.95	<0.30	<1.3	<0.17	0.78	<0.31	1.1	<0.25	0.61	<0.23	155	3.79	18
AG11 Catas Altas	6.5	222	18.7	29.2	4.62	17.4	3.49	<0.30	4.17	0.57	2.13	<0.31	<1.1	0.53	1.21	<0.23	4.65	3.97	82
AG14 Mariana	4.6	224	74.7	121	19.7	82.7	17.1	4.86	17.4	2.34	11.8	2.48	6.07	1.21	5.44	0.64	6.34	4.00	367
AG15 Ouro Preto	6.9	280	21.2	24.4	5.78	24.6	5.37	2.12	4.65	<0.17	1.8	<0.31	<1.1	<0.25	1.14	<0.23	5.54	5.15	91
AG16 Ouro Preto	4.9	700	81.5	159	22.1	82.5	16.5	4.73	17.2	2.32	12.3	2.17	5.9	1.11	5.91	0.89	13.1	4.60	414
AG17 Ouro Preto	5.4	726	41.7	75.4	11.1	41.6	8.57	2.63	<1.3	1.12	5.7	<0.31	3.2	<0.25	3.67	<0.23	7.64	3.84	195
AG20 Nova Lima	6.6	85	9.71	16.9	1.95	7.52	< 0.95	0.67	1.87	0.54	< 0.91	<0.31	<1.1	<0.25	<0.61	0.16	15.6	6.01	39
AG21 Nova Lima	6.5	138	6.14	7.77	1.05	4.14	<0.95	<0.30	1.25	<0.17	<0.91	<0.31	<1.1	<0.25	0.92	<0.23	37.8	4.49	21
AG22 Nova Lima	6.0	164	13.1	11.8	2.25	7.24	<0.95	1.95	2.66	0.76	1.61	<0.31	<1.1	<0.25	< 0.61	<0.23	<2.3	3.19	41
AG23 Rio Acima	6.5	192	20.5	47.7	4.55	16.8	3.82	1.25	4.05	0.77	<0.91	<0.31	0.69	<0.25	< 0.61	< 0.23	<2.3	3.16	100
AG25 Raposos	6.0	199	70.2	74.3	19	78	17.2	5.16	19.9	2.71	12.6	2.7	9.11	1.23	6.97	1.05	2.94	3.24	320
AG26 Mário Campos	4.7	221	394	239	88.9	335	66.9	16.3	64.4	8.96	48.9	9.54	25.4	3.43	23.6	3.31	17.9	1.25	1328
AG27 Belo Horizonte	6.3	265	7.47	10.7	1.22	4.04	<0.95	11.5	2.05	0.51	< 0.91	<0.31	<1.1	<0.25	< 0.61	<0.23	118	3.96	37
AG28 Moeda	5.3	213	36.7	68.5	8.62	30.9	6.14	1.26	5.02	0.97	2.4	0.39	<1.1	<0.25	< 0.61	<0.23	7.88	4.45	161
AG29 Ft. Congonhas	6.4	208	215	688	45.8	160	30.4	9.39	31.4	4.04	20.9	4.03	12	1.67	9.86	1.26	13.2	7.96	1234
AG30 Congonhas	6.0	241	130	19.8	15.4	49.2	7.58	32.5	9.42	1.48	4.49	1.00	3.08	0.39	< 0.61	<0.23	3.95	4.12	274
AG31 Itabirito	6.2	680	20.5	46.8	5.02	17.2	4.13	1.5	<1.3	1.03	<0.91	<0.31	2.2	0.33	1.69	<0.23	4.38	7.92	100
AG32 Lavras Novas	4.3	294	285	393	65.8	253	52.5	17.3	58.6	8.38	48.9	10.3	30.6	4.62	29	4.1	37.1	2.53	1261
AG33 Lavras Novas	4.8	282	223	444	52.7	213	44.5	16.9	52.4	8.13	43.1	9.32	26.7	4.17	25.1	3.46	10.1	<0.39	1166
Minimum	4.3	85.0	4.96	7.77	0.90	<1.4	0.95	<0.30	<1.3	<0.17	<0.91	<0.31	<1.1	<0.25	<0.61	<0.23	<2.3	<0.39	18
Maximum	7.0	726	5386	7316	1340	5621	1188	298	1092	131	591	106	304	45.0	278	44.0	155	7.96	23740
PASS values			38.2	79.6	8.83	33.9	5.55	1.08	4.66	0.774	4.68	0.991	2.85	0.405	2.82	0.433			

The pH value of groundwater in the study area ranged from 3.8 to 7.0 indicating an acid nature of most of the spring water samples, which could enhance the dissolution of some elements, including the REEs present in the soils or bedrock (Table 1). Keasler and Loveland [7] have suggested that pH exerts an important control on REE concentrations by promoting higher concentrations at low pH.

All 14 REEs (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and 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 [5]. Investigation of the REE speciation in the groundwaters using the theoretical Eh-pH diagrams of Brookins [8] showed that all the REEs present in waters in this study existed in the free X^{3+} ionic forms under the prevailing Eh and pH conditions (Tables 1 and 2).

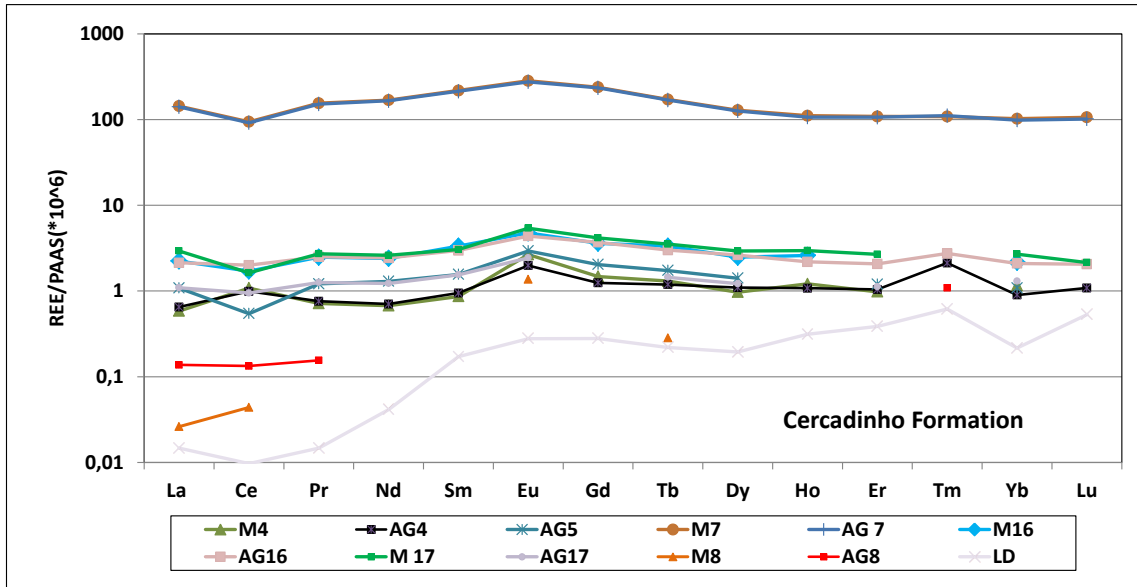
3.2. REE Patterns in Spring Water Samples

Fig. 2 and 3 present the normalized (PAAS) patterns of the REE concentrations for the spring water samples collected in the aquifers Cercadinho, Moeda and Cauê, respectively. The REE values of the reference material Post Archaean Australian Shales (PAAS) are described in Table 2.

The plot of the normalized REE data (Fig. 2 and 3) reveal a middle (MREE) enrichment relative to the LREE and HREE. These patterns have been observed in some natural acid waters and leachates from rocks and have been described as humped-shaped patterns [9]. This behavior is also verified through the (MREE/LREE) and (MREE/HREE) ratios, whose values are all higher than 1, except AG4 [Tab. 3]. Leybourne et al., [10] suggested that MREE enrichment is a result of the fact they are either more easily leached from the source rocks or more soluble under the local Eh and pH conditions. Enriched MREE in groundwater has also been attributed to water-rock interactions such as ion exchange and/or adsorption/desorption on mineral surfaces including Fe-Mn coatings on sedimentary particles, aluminosilicate detritus-rich carbonate rocks, and secondary minerals in fractures and vugs within carbonate rocks [11].

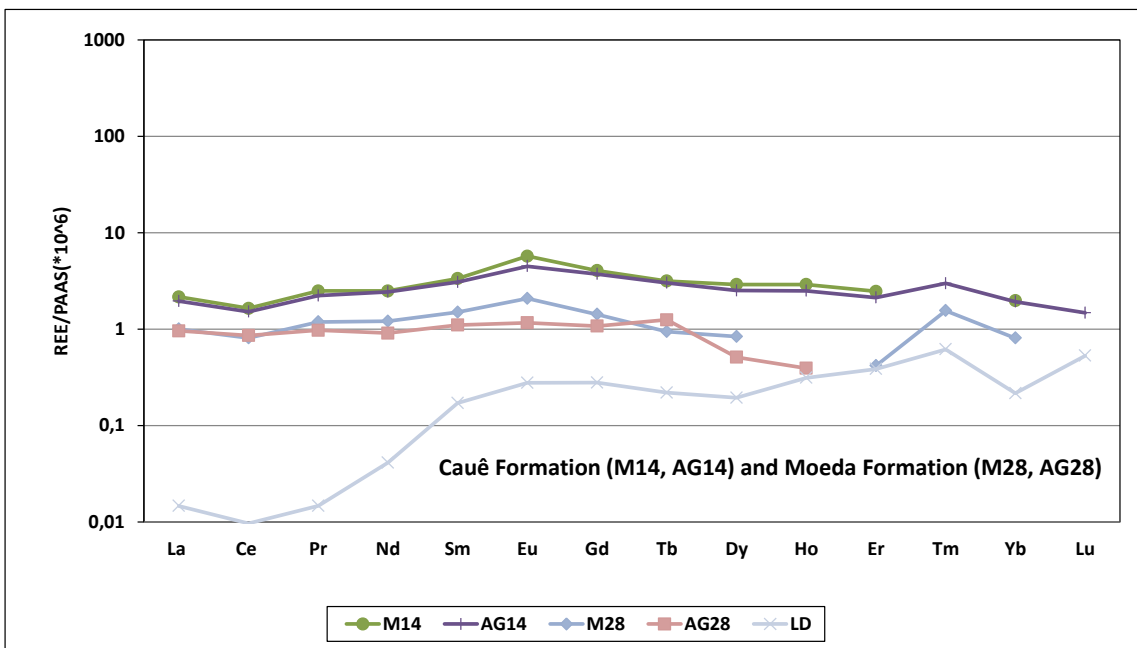
The plot of the normalized REE data (Fig. 2 and 3) also reveal a smooth negative Ce anomaly (except M4 and AG4) and a smooth positive Eu anomaly. These patterns were also verified through the (Ce/Ce), (Eu/Eu) ratios (Tab. 3), whose values can indicate anomalies in Ce and Eu with respect to neighboring REE [12]. As can be seen in table 3, all values of (Ce/Ce) ratios are <1 , indicating a negative anomaly of Ce in all the samples, except for M4 and AG4. On the other hand, all values of the (Eu/Eu) ratios are >1 , indicating a positive anomaly of Eu (Tab. 2).

The negative Ce anomalies is 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, whereas positive Eu anomalies are probably related to the redox conditions.



LD- Detection Limit of the technique (ICP-MS) for REE determination.

Figure 2: REE diagram normalized to Post Archaean Australian Shales (PAAS) for water samples from the Cercadinho aquifer.



LD- Detection Limit of the technique (ICP-MS) for REE determination

Figure 3: REE diagram normalized to Post Archaean Australian Shales (PAAS) for water samples from the Cauê and Moeda aquifers.

Table 3: Rare earth element (REE) concentrations (ng L⁻¹) and major parameters of water samples from Cercadinho, Moeda and Cauê aquifers after normalization of data to PAAS

Aquifers	Water samples	ΣREE _n	ΣMREE _n / ΣLREE _n	ΣMREE _n / ΣHREE _n	Ce/Ce ^a	Eu/Eu ^b
Cercadinho	M4	14	2.1	1.5	1.7	2.4
	AG4	16	1.7	0.7	1.4	1.8
	AG5	16	2.0	2.2	0.5	1.6
	M7	2140	1.6	1.4	0.6	1.2
	AG7	2095	1.6	1.4	0.6	1.2
	M16	31	1.7	2.1	0.7	1.4
	AG16	37	1.5	1.0	0.9	1.3
	M17	39	1.6	1.2	0.6	1.5
	AG17	14	1.2	1.5	0.8	
Cauê	M14	35	1.9	1.6	0.7	1.6
	AG14	36	1.8	1.1	0.7	1.3
Moeda	M28	14	1.4	1.6	0.7	1.4
	AG28	9	1.2	5.1	0.9	1.1

ΣREE represents the total concentration of 14 rare earth elements from La to Lu;

^a Ce/Ce=Ce_n/(La_n × Pr_n)^{1/2}, ^b Eu/Eu=Eu_n/(Sm_n × Gd_n)^{1/2};

Subscript *n* indicates that data were normalized to the the Post-Archean Australian Shales (PAAS).

4. CONCLUSIONS

This study showed that groundwater samples from different Iron Quadrangle aquifers presented pH values ranging from 3.8 to 7.0, indicating an acid nature of most of these spring waters. The investigation of REE speciation showed that all the REEs exist in the free X³⁺ ionic forms, under the prevailing Eh and pH conditions.

In the studied samples the uranium concentrations (<2.3–1176 ng L⁻¹) were below the guideline level set by Brazilian legislation (Ministry of Health 518- 03/2004). Thorium concentrations ranged from <0.39-11.0 ng L⁻¹ and the sum of the REEs ranged from 6.0 to 37657 ng L⁻¹. As there are no permissible limits related for the REEs and thorium for different water quality standards in Brazil, more attention must be paid to the local residents' health risk caused by spring waters (REEs were > 1000 ng L⁻¹) originating from aquifers located in Sabará, Barão de Cocais, Santa Bárbara, Mário Campos, Congonhas and Lavras Novas.

The REE patterns in the spring waters from the Cercadinho, Cauê and Moeda aquifers are characterized by middle REE (MREE) enrichment compared to the light REE (LREE) and heavy REE (HREE), negative Ce anomalies (except for one sample) and positive Eu anomalies in all three aquifers studied.

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