

## **RARE EARTH ELEMENTS IN A URANIUM DEPOSIT IN PEDRA, PERNAMBUCO, BRAZIL**

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### **ABSTRACT**

Rare Earth Elements (REEs) are similar in the physical and chemical properties of their compounds and are most commonly found in nature associated with terrestrial radionuclides. The high interest in conducting research on REEs is due to their multiple applications and high economic value. In this light, the present study analyzed samples of soil and rocks from an anomalous area replete with uranium and thorium, in the town of Pedra, Pernambuco, Brazil, in an attempt to identify the occurrence and concentrations of these elements. For these analyses, neutron activation, followed by high-resolution gamma spectrometry, was used to define the REEs. The following REEs were identified in the study area: La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, and Sc. The most abundant elements in the region, within samples of soil and rock, respectively, were: Ce (63-503 mg.kg<sup>-1</sup> / 19.6 to 2243.5 mg.kg<sup>-1</sup>), Nd (25.0 to 249.0 mg.kg<sup>-1</sup> / 3.8 to 1951.0 mg.kg<sup>-1</sup>), and La (30.6 to 253.0 mg.kg<sup>-1</sup> / 12.1 to 517.0 mg.kg<sup>-1</sup>). The other REEs presented concentrations of between the detection limit and 46.0 mg.kg<sup>-1</sup>. The results indicate that the Ce, La, and Nd concentrations appeared in up to 12 times the average occurrences in the earth's crust and up to 4.6 times higher than the averages reported in studies worldwide, including Brazil. Therefore, further studies are warranted to examine the economic viability of REEs in the area and to confirm the occurrence of these anomalous elements in the studied region.

### **1. INTRODUCTION**

Rare Earth Elements (REEs), over the years, have been treated as strategic issues and even as “national sovereignty” by some federal governments. The explanation for this is that these elements contain a multiplicity of uses in a wide range of areas, especially in the petroleum industry, whose catalyzers used in the refining of petroleum contain some of these elements, as well as in high tech industries, where these elements are considered essential inputs in the production of equipment, such as high definition TV's, smartphones, tablets, computers, among other products.

Today, the global demand for these elements is of approximately 150,000 tons per year, with a projection for future growth. Around 97.5% of the global production of REEs is concentrated in China, which places this country as one of the dominating competitors in the market, with the advantage of interfering directly in the price of REEs in the international market, as logged in 2010, when some of these elements underwent significant increases in prices after China's restriction on exports. In an attempt to reduce this dependence, many countries, including Brazil, have invested in research aimed at the analysis and discovery of new areas with the potential for the exploration of REEs.

In Brazil, as of 2010, the Federal Government, through the Brazilian Ministries of Mines and Energy (MME) and Science, Technology, and Innovation (MCTI), has been developing studies that will serve as the foundation for the drafting of a policy for the production and exploration of REEs in Brazil. Some of these studies indicate that the occurrences of REEs in Brazil are associated with radioactive minerals [1], such as in the case of monazite, composed of a rare-earth orthophosphate, which presents a thorium (Th) content of between 0.1% and 30% and up to 1.5% of uranium (U) [2].

This association of REEs with radioactive minerals was one of the aspects that motivated, not only the present study, but also the choice of the area to be studied. The town of Pedra, located in the semiarid agreste region of the state of Pernambuco, is recognized for the occurrence of a considerable radioactive anomaly of U and Th in calcium silicate and granite rocks, respectively [3,4,5]. Another aspect which inspired the present study was the absence of specific publications that define the existence of these elements in the study area and that indicate their respective concentrations, in turn opening the door for studies to be conducted aimed at evaluating the technical and economic viability of the extraction of REEs in the future, which could lead to economic development for the region.

Innumerable techniques are capable of determining the presence and concentration of REEs in the environment. In the specific case of this study, which used environmental samples, Neutron Activation Analysis, followed by High-Resolution Gamma Spectrometry, was used to define the REEs. This methodological sequence was chosen, as it uses non-destructive

techniques with high sensitivity and is capable of identifying a large quantity of elements present in the sample [6].

Considering the present-day reality in Brazil, where the search for new areas that contain REEs has been increasing considerably, it is believed that this study, conducted with the aim of qualifying and quantifying these REEs in soil and rock samples collected in the town of Pedra, Pernambuco, Brazil, will divulge the existence of this region, which had previously been disregarded from the viewpoint of mineral extraction, in turn presenting a potential for production that can result in economic development for the region.

## **2. MATERIALS AND METHODS**

### **2.1. Collection and treatment of samples**

The collection procedure was carried out in an area of approximately 2 km<sup>2</sup>, which included granite and amphibolite calcium-silicate outcrops. In this region, 115 soil samples were collected from 23 different points and 55 rock samples from 11 outcrops. Considering this information, this study analyzed samples collected from 34 different sampling points in the study area.

Each collection point was demarcated in 5 m x 5 m plots and subdivided into quadrants, where 5 samples were collected from each point. These 5 samples, after being homogenized, corresponding to a sampling point. Before collection, the points were first cleared, extracting about 5.0 kg from each point, at a depth of between 30 and 50 cm, corresponding to the C horizon.

In the collection of rock samples, the granite and amphibolite calcium-silicate outcrops that existed throughout the region were given priority. Of the 11 rock outcrops, six corresponded to the granite outcrops, whereas 5 corresponded to the amphibolite calcium-silicate outcrop. Approximately 10 kg was collected from each outcrop, discarding the intemperized surfaces.

The procedure for sample collection also took the topography of the region into consideration. However, in some locations, the sample collection proved impossible due to specific limitations, including the existence of dams, residences, corrals, and closed plantations of forage palm and tall grass.

After collection, the soil samples underwent pre-treatment that respected the following stages: drying in a greenhouse at 60 °C; breaking up of the soil sample; sifting, homogenization, quartering, and reduction of the granulometry of the soil sample to pass through a 63 µm sieve. The rock samples were ground and pulverized to reach the same granulometry of the soil samples (63 µm). All of these actions were carried out in partnership with the Mineral Technology Laboratory of the Department of Mining Engineering from Universidade Federal de Pernambuco (UFPE).

After having been treated, approximately 1.5 g from each sample was added to a polyethylene recipient, which was later sent to the Neutron Activation Analysis Laboratory (NAAL), located in the Nuclear Reactor Center for Research (CRPq) from the Energy and Nuclear Research Institute (IPEN) from the National Nuclear Research Commission (CNEN), located in the state of São Paulo, where the samples underwent neutron activation and later analysis by gamma spectrometry. The mass was enough to perform the analysis of each sample in triplicate, given that the mass necessary for neutron activation did not exceed 100 mg.

## **2.2. Neutron Activation Analysis and Gamma Spectrometry**

Approximately 100 mg of each sample was irradiated for a period of 8 hours in an IEA-R1 research reactor from IPEN/CNEN-SP, at an average neutron flux of  $4.5 \times 10^{12} \text{ n.cm}^{-2}.\text{s}^{-1}$ , together with the following reference materials: GS-N (ANRT) granite and BE-N (IWG-GIT) basalt.

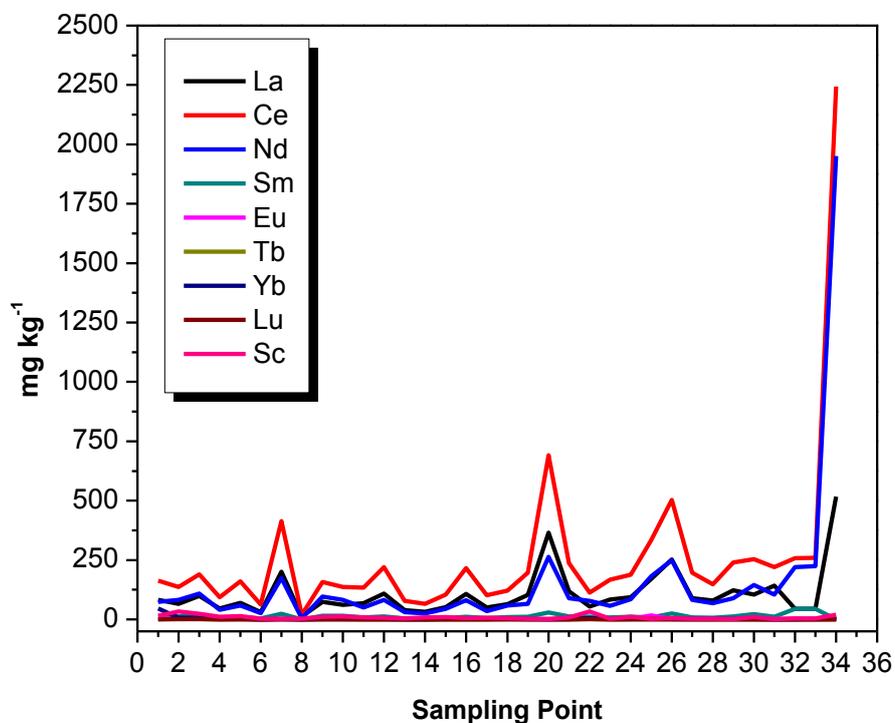
After irradiation, the samples were measured in a high resolution gamma spectrometry system. These measures were taken at two different times, with the first count carried out 7 days after irradiation and the second count 15 days after irradiation. This was deemed necessary so that the sample activities, as well as the reference materials, could decline, in

turn diminishing the occurrence of interferences and guaranteeing a more efficient qualification and quantification of the REEs

After activation, respecting the times specified above, the samples were measured using the experimental arrangement, composed of a Canberra<sup>®</sup>, model GX2020, HPGe detector, with a resolution of 2.0 keV for the <sup>60</sup>Co energy of 1,332, attached to a multichannel analyzer (MCA) with 8,196 channels. The treatment and manipulation of the spectra, as well as the data analysis, were performed using the Canberra<sup>®</sup>, Genie-2000<sup>®</sup> software. In an attempt to correct the dead time, the measures were taken at a geometry of 12 cm from the face of the detector.

### 3. RESULTS

The obtained results demonstrate that, among the 17 existing REEs, 9 could be identified in the study area, specifically: La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, and Sc. In figure 1, the concentrations of each REE could be observed within all analyzed samples, regardless of the matrix. It was also possible to observe that, in the majority of the samples, the REE concentrations did not surpass 300 mg kg<sup>-1</sup>.



**Figure 1: REE concentrations for all of the studied environmental matrixes**

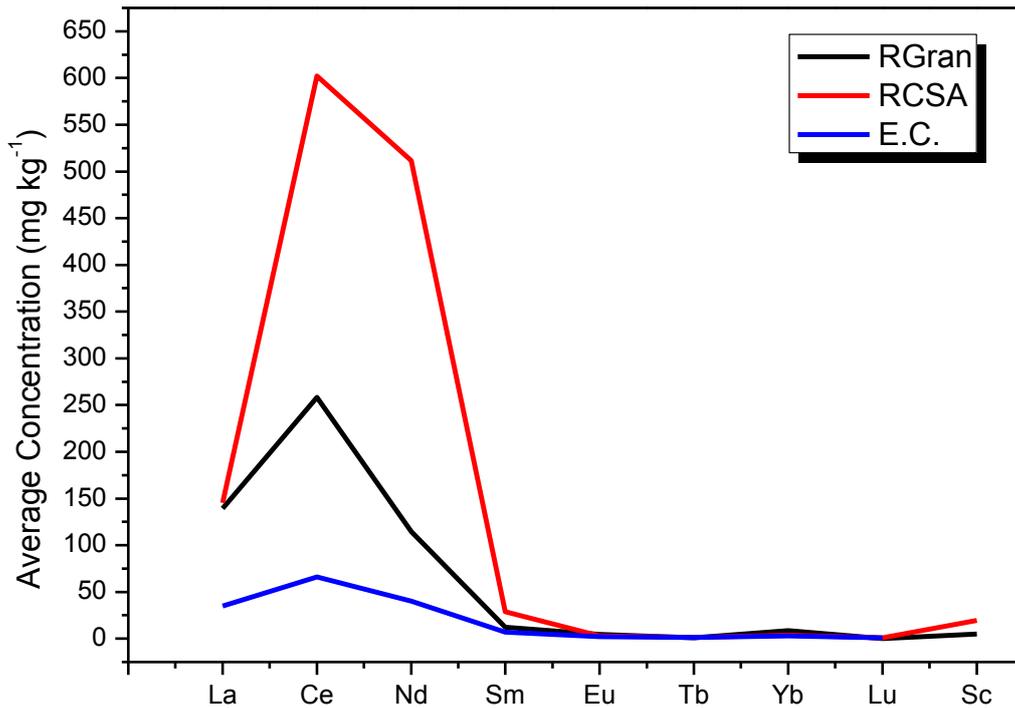
### 3.1. Rock samples

Evaluating the results obtained for the different types of rocks present in the study area, specifically granite and amphibolite calcium-silicate rocks, from which different REE concentrations could be identified, it could be observed that, in comparison to the granite rocks, the amphibolite calcium-silicate rocks present greater concentrations in 7 of the 9 elements (La, Ce, Nd, Sm, Tb, Lu, and Sc), highlighting Nd and Ce, whose averages were 4.5 and 2.3 times higher than that found in the granite rocks (Table 1).

**Table 1. Data referent to the REEs present in the analyzed rocks.**

Parameters	Granite Rocks (mg kg <sup>-1</sup> )								
	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Sc
<b>Outcrops</b>	6	6	6	6	6	6	6	6	6
<b>Minimum</b>	12,1	19,6	3,8	0,8	0,9	< 0,1	0,1	< 0,1	1,8
<b>Maximum</b>	365,0	692,0	264,0	29,0	17,0	1,4	46,0	0,6	14,9
<b>Average</b>	139,45	258,3	114,6	12,1	4,4	0,9	8,7	0,2	5,0
<b>Amplitude</b>	352,9	672,4	260,2	28,2	16,1	1,4	45,9	0,5	13,1
	Amphibolite Calcium - Silicate Rocks (mg kg <sup>-1</sup> )								
<b>Outcrops</b>	5	5	5	5	5	5	5	5	5
<b>Minimum</b>	45,1	113,0	78,0	< 0,5	0,12	< 0,1	0,8	< 0,1	4,7
<b>Maximum</b>	517,0	2243,5	1951	44,8	5,9	2	7,6	1	34
<b>Average</b>	145,3	602,3	511,6	22,9	2,8	0,9	3,7	0,4	19,3
<b>Amplitude</b>	471,9	2130,5	1873,0	44,8	5,78	2	6,81	1	29,3

Figure 2 shows a comparative analysis of the results obtained in this study for the rock samples as regards the average concentrations of REE in the earth's crust [7]. The majority of the elements detected in the area presented the same magnitude in terms of concentration. La, Ce, and Nd presented a differential behavior, with average concentrations of much higher than the average found in the earth's crust. In granite rocks, the averages of such elements were, respectively, 4.0, 3.9, and 2.9 fold higher than the average of the earth's crust. As regards the amphibolite calcium-silicate rocks, the averages of concentrations were 4.2, 9.0, 12.0 fold higher, respectively.



**Legend:** RGran – Granite Rock; RCSA – Amphibolite Calcium - Silicate Rock; E. C. – Earth's Crust

**Figure 2: Comparative Analysis of the average REE concentrations in the rock samples in Pedra, Pernambuco, Brazil**

The rocks analyzed in the present study present considerably high contents of Th in the granite rocks (average of 40.2 mg.kg<sup>-1</sup>) and of U in the amphibolite calcium-silicate rocks (average of 3.132 mg.kg<sup>-1</sup>), the latter considered an anomaly [5]. The relevant association among the REEs and these radionuclides [2] may well justify the high levels of these elements in the rocks, which are considered to be anomalous in U and Th.

### 3.2. Soil Samples

Table 2 presents the results from the descriptive statistics of the soil samples, in which one can observe the existence of a behavior that is identical to that found in the rock samples. The group of data proved to be less heterogeneous than in the rock samples, but still presented points with high concentrations that were relatively similar to the anomalous areas.

**Table 2. Data referent to the REEs present in the analyzed soil samples.**

Statistical Results	Concentration (mg kg <sup>-1</sup> )								
	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Sc
<b>Number of Points</b>	23	23	23	23	23	23	23	23	23
<b>Minimum</b>	30,6	63,0	25,0	3,8	0,6	< 0,1	0,4	< 0,1	1,9
<b>Maximum</b>	253,0	503,0	249,0	24,9	4,0	1,6	6,8	0,9	23,2
<b>Average</b>	90,9	185,4	81,3	11,5	1,4	0,7	1,7	0,2	7,7
<b>1<sup>st</sup> Quartile</b>	56,8	119,3	48,0	7,2	1,1	0,5	1,03	0,2	3,5
<b>2<sup>nd</sup> Quartile</b>	84,0	167,0	80,5	10,7	1,35	0,6	1,3	0,2	7,1
<b>3<sup>rd</sup> Quartile</b>	106,3	217,8	89,5	14,1	1,6	0,9	2,1	0,25	10,2
<b>Standard Deviation</b>	51,5	103,7	51,5	6,1	0,7	0,4	1,3	0,2	5,0
<b>Coeff. of Variation (%)</b>	56,6	55,9	63,4	53,1	45,9	52,7	77,9	78,3	64,5
<b>Asymmetry</b>	1,8	1,7	1,8	1,0	2,7	0,8	3,0	2,5	1,4

The majority of studies conducted worldwide that treat the theme of REEs is mainly geared toward the exclusive analysis of one element or another, attempting to evaluate their application in a specific activity, such as the investigation of the structural, magnetic, and optical properties of REEs when substituting other elements. Studies that analyze the presence of these elements and their respective concentrations in nature do in fact exist, but are rare and have mainly been published in China.

Table 3 shows a comparison of the results from this study with results from studies in prior literature, using, in addition to the average concentrations of REEs found in the earth's crust, those elements identified in some studies conducted using soil samples.

**Table 3. Comparison among the average data from REEs: present study x world studies**

Regions	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Sc
	mg kg <sup>-1</sup>								
<b>This Study</b>	<b>90,9</b>	<b>185,4</b>	<b>81,3</b>	<b>11,5</b>	<b>1,4</b>	<b>0,8</b>	<b>1,7</b>	<b>0,2</b>	<b>7,7</b>
Earth's Crust	35	66	40	7	2,1	1,2	3,1	0,8	-
Japan*	18	40	18	3,7	1	0,6	2,0	0,3	-
China**	34,7	74,8	33	5,63	1,11	0,77	2,64	0,45	-
Brazil***	24	53	22	2,6	1,1	0,85	< 1	-	19

Source: [7] / \* [8] / \*\* [9] / \*\*\* [10].

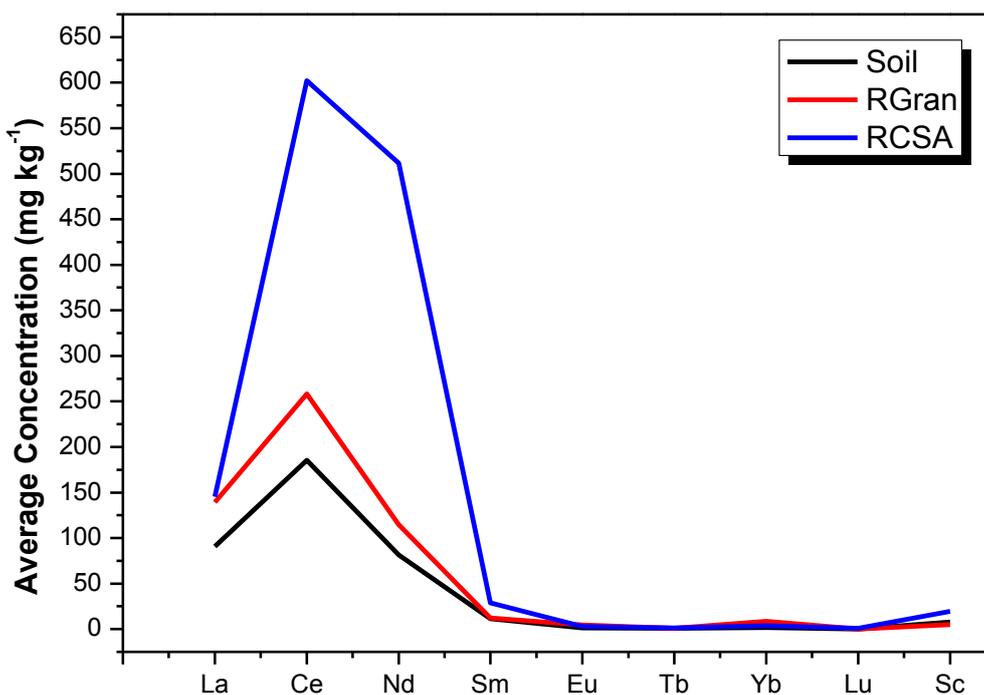
The elements Sm, Nd, La, and Ce presented, respectively, average concentrations of 2.8, 2.6, 2.0, and 1.6 times higher than the average from the earth's crust. However, the other elements, with the exception of Sc, presented average concentrations of between 0.25 and 0.6 times lower than the average of the earth's crust. Sc was considered an exception, as no register of its existence in the earth's crust could be found.

The concentrations defined for the elements La, Ce, Nd, Sm, Eu, and Tb proved to be higher than reported in a studied carried out in Japan [8], which analyzed the REEs present in 44 samples of eight types of soil in the country, using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). In this case, such elements presented average concentrations of between 1.3 and 4.6 fold higher. The Yb and Lu were the only elements whose concentrations were lower than the study performed by Ran and Liu (by approximately 0.8 and 0.6 fold, respectively).

Concerning one study carried out in China [9], which analyzed the REEs in 364 collected samples in 19 types of soil from different locations within the country, using Neutron Activation Analysis and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) – the elements La, Ce, Nd, Sm, Eu, and Tb presented average concentrations of between 1.0 and 2.6 fold higher. The elements from this study whose average concentrations presented values of less than the aforementioned study include Yb (approximately 0.6 fold lower) and Lu (approximately 0.4 fold lower).

Compared with the study carried out in Brazil [10], which defined the concentration of a given quantity of elements (among them, REEs) in Belo Horizonte, Minas Gerais, Brazil, using the  $k_0$  method of Neutron Activation Analysis, followed by Gamma Spectrometry with HPGe detector, with 15% efficiency in soil samples, the average concentrations of elements La, Ce, Nd, Sm, Eu, Yb, and Lu were between 1.3 and 1.44 fold higher. The only elements of this work that presented average concentrations of lower than the data obtained by the aforementioned study were Tb and Sc (around 0.9 and 0.4 fold, respectively).

Figure 3 presents a comparison between the soil and rock samples, using the average concentrations of REEs identified in the study area, whose data were presented in Tables 1 and 3.



Legend: RGran – Granite Rock; RCSA – Amphibolite Calcium - Silicate Rock

**Figure 3. Comparative analysis of the average concentrations of REEs between the soil and rock samples in Pedra, Pernambuco, Brazil**

Considering the environmental matrixes, it could be observed that the concentrations present in the rock samples are quite a bit higher than those found in the soil samples, especially when compared to the amphibolite calcium-silicate rock, whose concentration is approximately 3.2 fold higher in the case of Ce. The relevant difference in the contents of the REEs in these environmental matrixes can be explained by considering that the rocks are elements that compose the soil, and the REEs are more concentrated within these, disregarding the anthropic change of these elements within the soil.

In general terms, both in the rock samples as well as in the soil samples analyzed in this study, it could be verified that, among the REEs found in the study area, Ce, Nd, and La were the elements which presented relatively higher concentrations, both in that reported in the literature and in the averages from the earth's crust. Some previously mentioned studies make reference to the high levels of toxicity of the elements La and Nd when coming into contact with human beings. Even with the referent elements presenting differential contents, it was

not possible to draw firm conclusions about the toxicological potential of the region, given that authorized limits have not yet been established for these elements in Brazil.

#### 4. CONCLUSIONS

Among the REEs identified in the study area, Ce, La, and Nd presented the most relevant concentrations, with values of much higher than the averages found for the earth's crust (up to 12 fold) and for the global averages reported in prior literature (up to 4.6 fold). The remaining REEs presented a behavior similar to that found worldwide.

Further studies are warranted to prove the possible anomaly of the elements Ce, La, and Nd in the rocks in the study area, as well as the economic viability of the REEs that exist in the study area, in an attempt to verify whether or not these elements in fact contain a quantity that can make their extraction possible, which could in turn lead to economic development for the region.

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