

Geochemistry of hematite and itabirite, Quadrilátero Ferrífero, Brazil

(Geoquímica de hematitito e itabirito,
Quadrilátero Ferrífero, Brasil)

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Resumo

Foram coletadas 21 amostras de hematitito e 12 amostras de itabirito em diferentes depósitos do Quadrilátero Ferrífero (QF) e a partir de análises geoquímicas foram obtidos dados referentes aos elementos-traço e elementos terras-raras (ETR). O objetivo é entender a distribuição dos elementos analisados no QF em comparação com formações ferríferas (FF) ao redor do mundo. O conteúdo de elementos-traço é relativamente baixo com considerável variabilidade e é inferior aos das FF de Algoma, Anamikie, Maru na Nigéria e Orissa na Índia. A abundância de ETR é relativamente baixa, porém superior à de Hamersley na Austrália Ocidental, Surgur na Índia e inferior à de Kuruman na África do Sul. O padrão normalizado por condrito mostra um leve grau de fracionamento de ETR leves em relação aos ETR pesados, fracas anomalias positivas de Eu, além de altos valores para a relação $(La/Yb)_{CN}$ e $(La/Sm)_{CN}$.

Palavras-chave: Geoquímica, formações ferríferas, Quadrilátero Ferrífero, hematitito, itabirito.

Abstract

Twenty-one samples of hematite and twelve samples of itabirite were collected from different deposits of the Quadrilátero Ferrífero (QF) area and were analyzed for trace and rare earth elements. The purpose of the study is to understand the element distribution in the QF in comparison with other iron formations (IF) around the world. Trace element contents are relatively low with considerable variability, being lower than the contents in the Algoma IF, Anamikie IF, Maru IF in Nigeria and Orissa IF in India. REE's abundance is relatively low, but higher than REE's of Hamersley IF of Western Australia, Surgur belt in India and lower than Kuruman IF in South Africa. Chondrite normalized patterns show slight degrees of fractionation for LREE to HREE and slightly positive Eu anomalies coupled with positive values of $(La/Yb)_{CN}$ and $(La/Sm)_{CN}$ ratios.

Keywords: Geochemistry, iron formations, Quadrilátero Ferrífero, hematite, itabirite.

1. Introduction

The Quadrilátero Ferrífero (QF) is comprised of an approximately square area of ca. 7.000 km² and hosts one of the largest iron ore deposits in the world (Figure 1).

Researchers have focused on trace and rare earth elements to reveal the origin of classical iron formations (IFs) around the world, such as in the Algoma district and Lake superior region in Canada (Animikie IF) (Gross and Macleod, 1980), the Hamersley IF in Western Australia (Alibert and McCulloch, 1993), the Kuruman formation from the Transvaal Supergroup in South Africa (Bau and Dulski, 1996), the Maru IF in Nigeria (Adekoya, 1998) and the iron formations in the Sargur Belt in India (Kato et al., 1996). Geochemical studies on IFs in Brazil, however, are very scarce. Klein and Ladeira (2000) studied samples of the Cauê Formation from the western Quadrilátero Ferrífero (QF) region, regionally known as itabirite, which are similar to some metamorphosed banded iron formations from the Lake Superior region in North America. Based on trace and rare-earth element analyses, itabirite formed by precipitation from mixed Paleoproterozoic seawater and hydrothermal fluids. The chemistry of the dolomitic variety of this rock was investigated by Spier et al. (2007). These authors proposed a similar origin for the dolomitic itabirite. In the QF two main iron rich rocks occur and they are the main iron ore types exploited in the mines. With the purpose of contributing to the understanding of the geochemical characteristics of the itabirite, whole-rock analyses of representative samples collected from different deposits were performed. The samples were separated in two distinct types: hematite and itabirite depending on their chemical composition. The term itabirite is defined as a laminated, metamorphosed iron formation of iron oxides (hematite, magnetite, martite), abundant in quartz, but very rarely containing mica and other accessory minerals (Dorr and Barbosa, 1963). Hematite is a high grade iron ore

containing more than 90% of hematite in the modal proportion. Trace and rare earth elements were analyzed in terms of its spatial distribution and variation in samples of the same or different types. The resulting values were then compared values from other banded iron formations around the world.

2. Geological setting

The samples analyzed in this study belong to the hematite-magnetite lithofacies of iron formation (IF) in the Quadrilátero Ferrífero region which is located in southern part of the São Francisco Craton (Dorr, 1969) (Fig.1). Two broad compositional types of iron formation occur in the QF area: quartzitic and dolomitic itabirite. IFs of amphibolitic composition can also be found in the QF area, although in much less proportions

and restricted to thin horizons in some locations (Dorr, 1969). In this paper only samples of iron oxide lithofacies were analyzed. The Cauê Formation (age between 6 and 2.4 Ga.) and the overlying Gandarela Formation of the Itabira Group were deposited over an Archean sialic substrate (Cordani et al., 1980; Marshak and Alkmim, 1989) in a continental platform of a passive margin (Marshak and Alkmim, 1989).

The tectonic and metamorphic history of the QF region is controversial. At least two main tectonic events occurred in the area during the Proterozoic. The first is the Transamazonian event (ca 2.1 Ga, Alkmim and Marshak 1998) that generated large northeast-trending regional-scale folds in the QF area (Fig. 1). The second is the Brasiliano Orogeny (ca 600 Ma) generating a series of western-verged

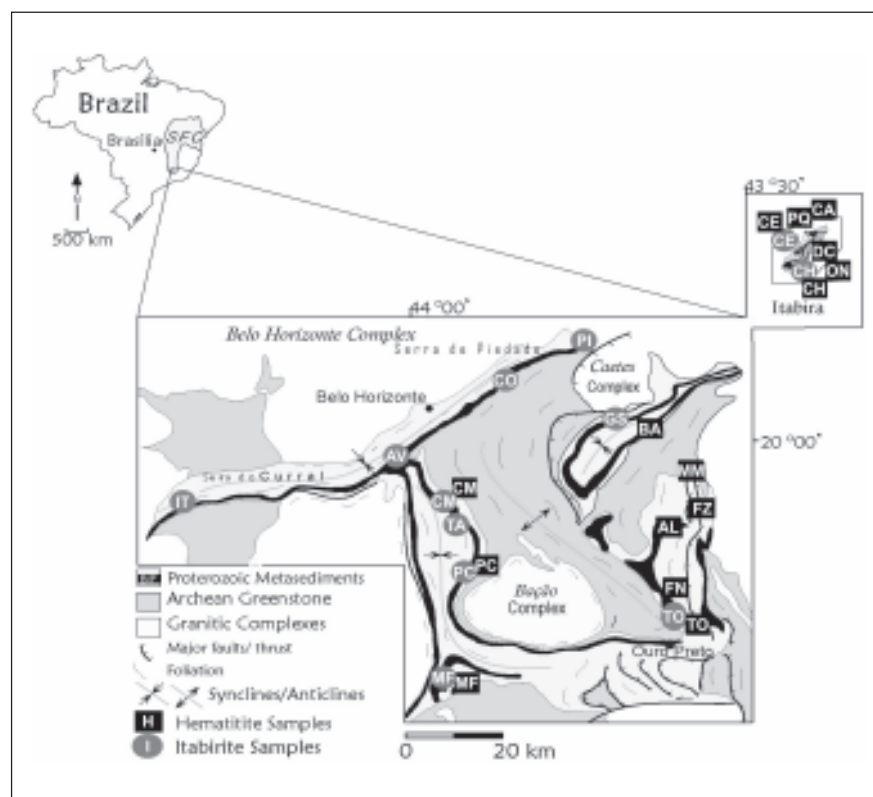


Figure 1 - Simplified geological map of the Quadrilátero Ferrífero (after Dorr, 1969), (SFC) São Francisco Cráton. Sampled iron ore deposits: IT-Itatiaiuçu, AV- AVG Mineração, CO-Córrego do Meio, PI-Piedade, CM-Capitão do Mato, TA-Tamanduá, PC-Pico do Itabirito, MF-Mina de Fábrica, GS-Gongo Soco, BA-Baú, MM-Morro da Mina, FZ-Fazendão, AL-Alegria, FN-Fábrica Nova, TO-Timbopeba, CE-Mina de Conceição, PQ-Mina do Periquito, DC-Mina de Dois Córregos, ON-Mina do Onça, CH-Mina da Chacrinha, CA-Mina de Cauê.

thrust-and- fault structures associated with the development of pervasive tectonic fabrics (schistosity, mylonitic foliations, crenulation cleavage and mineral stretching lineations) (Chemale et al., 1994).

The QF region has been usually divided into two major tectonic domains (Rosière et al., 2001). The eastern region is considered as a high strain domain with a widespread shear zone development and pervasive structures. By contrast, the deformation in the western portions is typically low. Synclines are preserved and primary structures can be recognized.

The metamorphic grade also increases from the west (lower greenschist facies) to the east (lower amphibolite facies) (Herz, 1978; Pires, 1995). The mineral assemblage indicates temperatures ranging from 300°C in the west region to 600°C in the east (Pires, 1995).

3. Mineralogy and petrography

The analyzed iron-rich rocks are comprised of hematite and itabirite (Fig. 2). The difference between them is the proportion of iron oxide to quartz. The mineral composition of both sample types is characteristically simple. By far the major constituent minerals are hematite, magnetite and quartz. Occasionally, minor to trace amounts of minerals such as tourmaline, apatite and few other silicates, such as amphiboles, may be present, particularly in IFs of the western domain of the QF region. The hematite is composed basically of hematite (Fig. 2a, b). Magnetite is also present in varied amounts depending on the location of the sampling. It is most commonly found in the western domain of the QF area. The magnetite grains progressively become rare in the iron formation towards the eastern domain as they are progressively transformed to hematite. They are only observed as relict grains immersed in a matrix of

hematite crystals. There, magnetite crystals are mostly euhedral and in a large extent oxidized to hematite (Fig. 2c). By contrast, the hematite grains occur in a great variety of shapes. They can be granular (Fig. 2d) with irregular or straight boundaries. Hematite grains of tabular or platy shape (Fig. 2e) are more often observed in the high-strain domains of the QF, particularly in the eastern domain. Hematite grains in these rocks show a strong shape and crystallographic preferred orientation (Morales et al. 2008).

On the other hand, itabirite (Fig. 2f) has remarkable compositional banding

with alternating layers of iron oxide and quartz of variable thicknesses. The proportion of iron oxides and quartz in each layer may vary in wide proportions. However pure oxide layers are essentially composed of hematite in granular, tabular or platy shapes. The microstructures of hematite grains in these layers may vary from aggregates of randomly oriented crystals to those where basal planes of hematite are preferred-oriented, usually defining a plane of foliation similar to that of micas (Fig. 2g). In general grain sizes tend to be smaller in the iron formation of the western domain than in their counterparts of the eastern domain.

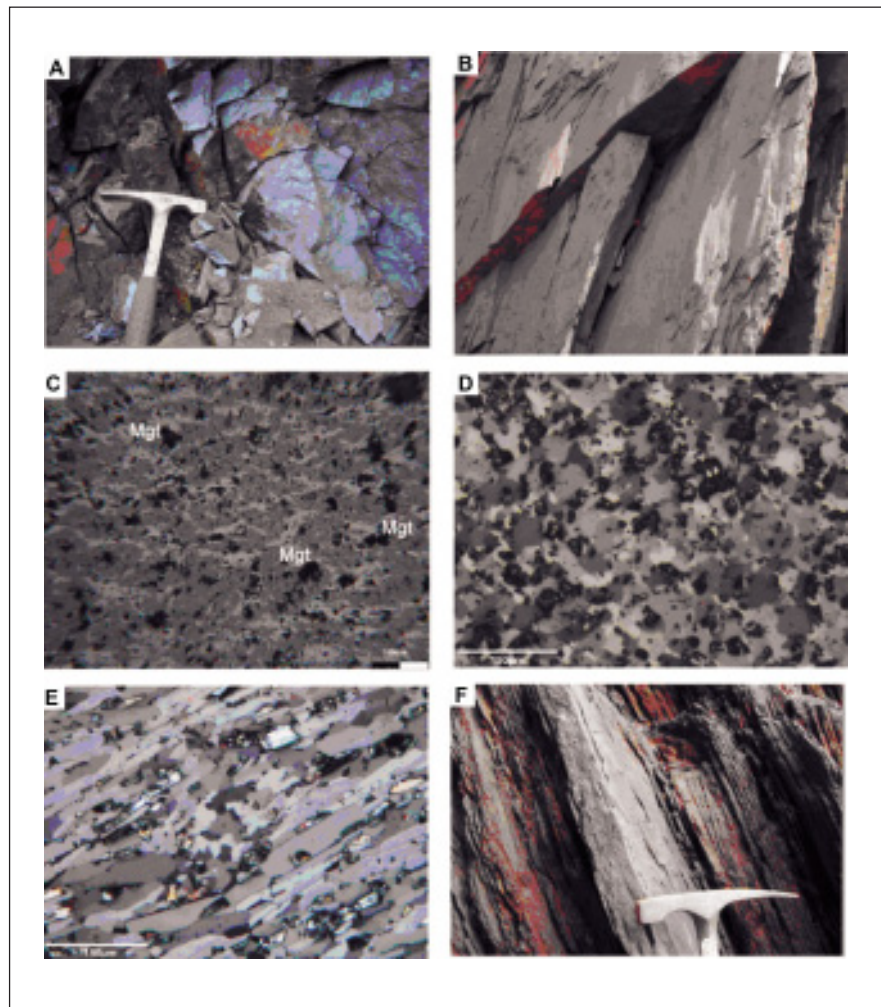


Figure 2 - Features of the analyzed samples. (A) Hematite with characteristic metallic luster and massive aspect. (B) Foliated type of hematite. (C) Relicts of martitized crystal of magnetite immersed in euhedral crystals of tabular hematite, polished section. Crossed polarized light. (D) Aggregate of granular hematite crystals in polished section taken from sample (A) under crossed polarized light. (E) Foliated hematite showing a strong preferred orientation of tabular crystals. (F) Outcrop with foliated itabirite.

4. Methodology

Twenty-one samples of hematitite (high grade hematite ores) and twelve of itabirite were analyzed for trace and rare earth elements. We have analyzed only cohesive and fresh samples, e.g. those without any sign of weathering collected from a deep open pit mine. Hematitite samples are chemically more homogeneous even though in some specimens a contrasting arrangement of hematite crystals disposed in alternating bands gives rise to a planar anisotropy similar to those of the itabirite. The samples were cleaned and dried and then crushed to 150 mesh size in a tungsten carbide ringmill. The fine fraction pulverized samples were sent to the ACME Analytical Laboratories Ltd. (Vancouver, BC, Canada) for geochemical analyses. Major and trace elements Zr and Y were determined by wavelength dispersive, sequential X-ray fluorescence spectrometer. Selected trace (V, Co, Ni, Cu, Zn, Rb, Sr, Ba, Hf and Ta) and rare-earth elements were determined by inductively coupled plasma mass spectrometry (ICP-MS) at ACME Lab. The limit of detection of trace elements is > 0.5 ppm for the group (Hf, Nb, Rb, Sr, V, Co), the limit is > 0.1 for the group (Y, Ta) and 1ppm for Sn, whereas, the limit of detection of Rare earth elements is > 0.05 ppm for (Eu, Gd, Tb, Dy, Yb, Tm, Er, Ho, Lu), while the limit is > 0.1 ppm for Sm and > 0.4 ppm for Nd.

5. Results

5.1 Trace Elements (TE)

Thirteen trace elements (V, Co, Ni, Cu, Zn, Rb, Sr, Y, Zr, Nb, Ba, Hf and Ta) were determined in the hematitite and itabirite samples (Table 1.). In both ores the trace element contents present a wide range of concentrations similar to the other IFs around the world (Cole, 1981; Adekoya, 1998). Both hematitite and itabirite show similar concentration all over the QF region (Fig. 3).

In the hematitite samples the abundance of the trace elements varies between ca. 23.6 - 262 ppm. Most

individual trace elements show wide concentrations. V is the most abundant with an average of 39 ppm. The Co (9 ppm), Ni (5.5ppm), and Y contents (8.2 ppm) also present a wide range of values (1-45.8 ppm). In the lower range of the values appear Rb (0.3-6ppm), Sr (0.3-22.7 ppm), Zr (1.7-25.1 ppm), Nb (0.3-11.3 ppm), Hf (0.3-0.6 ppm) and Ta (0.1-0.3 ppm). Ba is an important trace element with concentration relatively higher than the last group of trace elements (Rb-Ta), but with a large scattering of values (0.3-35.2 ppm). Sample HA12 has high values of some trace elements such as V, Co, Y, Sr, Ba and Zr.

The concentration of trace elements in the itabirite samples is in average 87.8 ppm, and, just as the hematitite, also shows a wide range of values (Table 1). V and Co are the most abundant. The V values vary from 2.5 to 55ppm averaging 20.6 ppm (Table 1). The Co concentrations have an average value of around 21.6 ppm. The Ba content averages 13.3ppm within a wide range of values (0.3 - 66.1ppm). Hf and Ta present very low concentrations with an average of 0.3 ppm similar to the Rb content. The average concentration of the other trace elements is very low with high variability: Cu (min. and max.: 0.1-19.8 ppm), Zn (0.1-8 ppm), Sr (0.5-21.8 ppm), Y (1.2-14.1 ppm), Zr (0.7-13.5 ppm) and Nb (0.3-4.7 ppm).

Similar to the hematitite, the values of some trace elements, such as V, Ni, Co, Y and Ba from samples collected in the eastern domain, are very distinct from the values from the western domain.

5.2 Rare Earth Elements (REEs)

In hematitite samples, the sum of REE contents average 26.85 ppm. The values for light REE (LREE; La to Eu) in all samples vary between 2.39 and 200.34 ppm and are 4 times higher than the heavy REE (HREE; Gd to Lu) which values range from 0.41 to 8.74 ppm. In itabirite samples the total content of REE is in average of around 16.91 ppm

(Table 1). The abundance of LREE is approx. 15.23 ppm, ranging from 1.71 to 63.83 ppm, whereas, the total content of HREE sums up to 1.68 ppm (0.34-5.01 ppm). All samples show an increase in the LREE content relative to the HREE content, which is more pronounced in the hematitite samples. To evaluate the degree of fractionation of LREE to HREE, REE's were normalized to chondrites (CN) (Evensen et al., 1978). The shape of the distribution of (REEs)_{CN} shows nearly horizontal patterns with relatively slight high fractionation of LREE to HREE and this was similar for both hematitite and itabirite (Fig.4). LREE fractionation was determined by the ratio (La/Sm)_{CN} and HREE fractionation was obtained by the ratio (Gd/Yb)_{CN}. In the hematitite LREE fractionation ratio (La/Sm)_{CN} presents an average of 5.3 (Table 1), whereas, the ratios (Gd/Yb)_{CN} and (Sm/Yb)_{CN} have an average value of 1.4 and 1.6 respectively. For the itabirite, the (La/Sm)_{CN} ratio presents an average of 5.8, whereas, the (Sm/Yb)_{CN}, (Gd/Yb)_{CN} ratios have an average of 2.1 and 1.9, respectively (Table 1). The bulk fractionation degree of LREE to HREE was determined for the hematitite and itabirite samples by the ratio of (La/Yb)_{CN} which gave averages of 7.7 and 7.3, respectively. Their ratio reaches higher values in some samples, mostly those located in the eastern domain of QF region. The values for the Eu anomaly (Eu/Eu*) are slightly positive and variable in all the samples collected in QF mines.

6. Discussion

The amount of iron and silica in this rock is larger than 99 weight %. In the hematitite type, silica is less than 1% in weight, making these rocks a nearly pure hematite iron ore.

This study indicates that the iron formation from the QF region shares some characteristics with other known IFs around the world. The banding of the itabirite in the QF shares some characteristics similar to the Hamersley Basin in Australia, the Orissa region of India and those of South Africa (James, 1954; Cole, 1981).

Table 1 - Trace and rare earth elements (in ppm) of hematite and itabirite samples (H) hematite, (I) itabirite, the rest of sample names refer to the mines listed in Figure 1.

TRACE ELEMENTS - HEMATITITE																								
ppm	HMF	HPC	HCM	HBA	HFN ₁	HFN ₂	HAL ₁	HAL ₂	HMM	HMM ₂	HFZ ₁	HFZ ₂	HTO	HCE	HPQ ₁	HPQ ₂	HDC ₁	HDC ₂	HCH	HCA	HON	MIN	MAX	AVG
V	37	18	57	69	17	2.5	42	67.0	10	8.0	96	56.0	37	48	43	37.0	74	37.0	22	25	18.0	2.5	96	39
Co	4.7	14.3	3.8	6.6	14.2	5.8	11.3	20.9	6.0	4.5	5.6	18.6	6.3	20.3	6.6	2.3	5.2	9.2	11.3	6.6	4.8	2.3	20.9	9.0
Ni	37.3	6.3	30.7	1.7	4.0	0.9	2.6	13.8	1.5	4.2	1.4	3.0	1.8	0.9	1.0	1.0	0.9	0.4	1.1	0.3	0.2	0.2	37.3	5.5
Cu	8.2	0.9	7.8	2.0	0.6	0.5	2.9	3.5	0.5	1.9	0.1	6.0	2.3	0.3	4.6	10.5	1.9	2.4	3.4	1.8	1.6	0.1	10.5	2.9
Zn	5.0	3.0	6.0	3.0	2.0	1.0	2.0	50.0	2.0	3.0	1.0	6.0	1.0	1.0	1.0	1.0	2.0	1.0	1.0	0.5	0.1	0.1	50.0	4.4
Rb	0.3	0.7	0.6	0.3	0.3	0.3	0.3	0.3	0.3	0.7	0.3	6.0	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	6.0	0.6
Sr	5.8	1.6	10.2	8.1	1.0	0.3	3.7	22.7	0.3	0.9	3.7	3.6	2.8	1.4	1.3	1.9	2.7	1.0	3.8	0.5	0.3	0.3	22.7	3.7
Y	9.2	2.8	10.6	3.1	3.4	8.6	13.5	45.8	7.4	6.0	16.8	7.5	4.7	7.9	4.4	1.1	9.3	2.7	2.1	4.3	1.0	1.0	45.8	8.2
Zr	2.0	4.1	4.4	3.4	9.5	3.6	1.7	25.1	4.4	3.7	4.0	15.3	2.7	11.4	2.3	3.9	18.8	12.7	6.2	4.7	3.3	1.7	25.1	7.0
Nb	11.3	0.3	9.2	0.3	0.6	0.3	0.3	1.8	0.3	0.3	0.3	0.5	0.3	0.3	0.3	0.3	0.9	0.3	0.3	0.3	0.3	0.3	11.3	1.4
Ba	2.9	2.2	28.3	32.3	7.8	1.9	5.8	11.0	8.2	7.3	4.2	10.2	2.8	35.2	12.1	12.3	7.7	28.5	4.2	0.3	0.9	0.3	35.2	10.8
Hf	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.6	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.6	0.3
Ta	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.3	0.3	0.1	0.1	0.2	0.1	0.1	0.1	0.1	0.3	0.1
ΣTE	122	168.0	168.0	130	60.8	23.6	86.6	262	41.3	32.9	133.8	133	62.4	128	77.5	72	124	96	56.1	45.0	31.2	23.6	262	92.6
TRACE ELEMENTS - ITABIRITE																								
ppm	IT	IAV	ICO	IFI	ICM	ITA	IPC	IMF	ITO	IGS	ICE	ICH	MIN	MAX	AVG									
V	16.0	9.0	18.0	9.0	10.0	47.0	12.0	55.0	2.5	7.0	21.0	41.0	2.5	55.0	20.6									
Co	2.3	43.9	29.7	34.3	34.9	2.1	1.1	1.7	20.5	25.6	31.9	31.3	1.1	43.9	21.8									
Ni	22.3	3.2	3.3	3.6	6.6	42.1	17.4	33.4	1.3	0.8	1.2	0.4	0.4	42.1	11.3									
Cu	3.8	0.7	0.1	0.4	19.8	8.0	3.6	6.6	0.7	0.7	0.4	2.0	0.1	19.8	3.9									
Zn	2.0	2.0	1.0	1.0	8.0	3.0	2.0	3.0	1.0	0.1	1.0	0.1	0.1	8.0	2.0									
Rb	0.3	0.3	0.6	0.3	0.3	1.2	0.3	1.1	0.3	0.3	0.3	0.3	0.3	1.2	0.5									
Sr	0.8	10.3	2.8	0.9	21.8	3.9	1.7	4.5	0.5	3.1	2.8	2.1	0.5	21.8	4.6									
Y	2.6	7.9	4.0	2.5	8.4	5.8	1.2	4.2	3.3	14.1	1.8	3.9	1.2	14.1	5.0									
Zr	1.7	1.4	2.2	0.9	13.5	1.5	1.2	8.1	1.4	0.7	1.4	2.5	0.7	13.5	3.0									
Nb	2.5	0.3	0.3	0.3	0.7	4.7	2.0	3.8	0.3	0.3	0.3	0.3	0.3	4.7	1.3									
Ba	2.3	3.5	19.2	0.3	3.6	17.1	5.6	66.1	5.7	13.3	1.3	21.7	0.3	66.1	13.3									
Hf	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3									
Ta	0.1	0.5	0.5	0.4	0.3	0.1	0.1	0.1	0.3	0.3	0.5	0.4	0.1	0.5	0.3									
ΣTE	57	83.3	82	54.2	128.4	136.8	48.5	187.9	38.1	66.8	64.2	106.3	38.1	187.9	87.8									
RARE EARTH ELEMENTS - HEMATITITE																								
ppm	HMF	HPC	HCM	HBA	HFN ₁	HFN ₂	HAL ₁	HAL ₂	HMM	HMM ₂	HFZ ₁	HFZ ₂	HTO	HCE	HPQ ₁	HPQ ₂	HDC ₁	HDC ₂	HCH	HCA	HON	MIN	MAX	AVG
La	2.4	2	2.7	1	2.8	0.5	3.1	39.9	3.1	4.5	2	5.4	14.3	1.6	5.8	4.2	4.2	2.1	0.7	0.9	0.7	0.5	39.9	6.51
Ce	5	3.7	4.7	1.4	3.1	0.9	6.9	104.3	3.2	3.9	6.6	9	22.8	2.6	3.7	6.7	7.2	3.7	1.2	1.4	1.3	0.9	104.3	13.96
Pr	0.73	0.36	0.5	0.17	0.55	0.13	1.04	9.44	0.56	0.67	0.61	0.9	2.83	0.27	1	0.79	0.91	0.6	0.16	0.16	0.14	0.13	9.44	1.45
Nd	3.2	0.9	2.4	1.4	1.8	0.4	4.2	33.5	2.6	2.5	2.6	3	11.5	1	4.3	3.1	4.1	2.8	0.6	0.4	0.4	0.4	33.5	5.46
Sm	1	0.3	0.6	0.2	0.3	0.2	1.3	6.5	0.4	0.4	1.2	0.8	2	0.3	0.9	0.8	1.1	0.5	0.2	0.2	<0.1	0.2	6.5	1.22
Eu	0.27	0.08	0.23	0.1	0.09	0.08	0.45	1.51	0.12	0.14	0.41	0.4	0.5	0.08	0.14	0.2	0.4	0.1	<0.05	0.06	<0.05	0.06	1.51	0.34
Gd	1.23	0.22	1.02	0.32	0.28	0.24	1.51	4.41	0.4	0.49	1.36	0.8	1.65	0.2	0.71	0.89	1.17	0.4	0.25	0.38	<0.05	0.2	4.41	1.04
Tb	0.2	0.05	0.16	0.06	0.03	0.08	0.24	0.76	0.08	0.09	0.26	0.1	0.26	0.05	0.09	0.08	0.2	0.1	0.05	0.05	0.01	0.01	0.76	0.17
Dy	1.07	0.37	1.14	0.35	0.29	0.58	1.42	4.92	0.67	0.54	1.55	0.9	1.05	0.31	0.56	0.37	1.12	0.5	0.27	0.4	0.09	0.09	4.92	1.04
Ho	0.29	0.07	0.26	0.08	0.06	0.17	0.35	1.09	0.16	0.1	0.38	0.2	0.16	0.1	0.12	0.05	0.25	0.1	<0.05	0.07	<0.05	0.05	1.09	0.25
Er	0.8	0.22	0.77	0.21	0.25	0.55	1.01	3.23	0.63	0.44	1.36	0.9	0.49	0.33	0.36	0.12	0.73	0.2	0.15	0.26	<0.05	0.12	3.23	0.76
Tm	0.12	<0.05	0.15	0.05	<0.05	0.11	0.17	0.58	0.11	0.06	0.22	0.2	0.09	0.06	0.09	<0.05	0.11	0.1	0.15	<0.05	<0.05	0.05	0.58	0.16
Yb	0.87	0.35	0.86	0.24	0.34	0.59	0.91	3.36	0.86	0.44	1.35	1.2	0.34	0.43	0.48	0.17	1.4	0.4	0.16	0.25	<0.05	0.16	3.36	0.48
Lu	0.12	0.16	0.03	0.48	0.08	0.15	0.04	0.05	0.03	0.06	0.07	0.2	0.15	0.16	0.04	0.25	0.05	0.1	0.04	0.02	0.11	0.02	0.48	0.13
ΣLREE	13.63	7.56	12.15	4.65	8.93	2.53	18.74	199.05	10.45	12.69	15.04	20.3	55.58	6.28	16.64	16.56	19.28	10.3	3.16	3.79	2.55	2.39	199.05	23.64
ΣHREE	3.27	1.17	3.21	1.05	0.73	1.57	2.48	14.01	1.79	1.1	3.38	3.6	2.24	1.08	1.65	0.99	2.94	0.9	0.5	0.53	0.2	0.41	14.01	3.21
ΣREE	17.3	8.78	15.52	6.06	9.95	4.68	22.64	213.57	12.91	14.33	19.97	24	58.08	7.67	18.29	17.52	22.94	11.7	3.93	4.57	2.75	2.89	214	26.85
Eu/Eu*	1.1	1.4	1.95	1.8	1.7	1.5	1.5	1.3	1.4	1.5	1.5	2	1.3	1.5	0.8	1.23	1.6	1.3	1	1	3.24	0.8	3.24	1.5
(La/Sm) _H	2.4	6.7	4.5	5	2.5	9.3	2.4	6.1	7.8	11.3	1.7	6.8	7.15	2.3	6.4	5.3	3.8	4.2	3.5	4.5	7	1.7	11.3	5.3
(Gd/Yb) _H	1.4	0.6	1.2	1.3	0.3	0.8	1.7	1.3	0.5	1.3	1	0.7	4.9	1.7	1.5	3.5	0.8	1	1.8	1.5	1	0.3	4.9	1.4
(La/Yb) _H	2.8	5.7	3.1	4.2	0.8	8.2	3.4	11.7	3.8	11.3	1.5	4.5	42.1	3	12.1	21	3	5.3	4.4	3.8	7	0.8	42.1	7.7
(Sm/Yb) _H	1.2	1.0	0.77	0.95	0.6	1.0	1.6	3.3	0.7	1.1	1.8	0.9	4.1	1.5	2.1	5.2	1.0	1.4	1.3	0.96	2.2	0.6	5.2	1.6
RARE EARTH ELEMENTS - ITABIRITE																								
ppm	IT	IAV	ICO	IFI	ICM	ITA	IPC	IMF	ITO	IGS	ICE	ICH	MIN	MAX	AVG									
La	1	1.3	1.6	0.6	4.2	4.5	0.8	2.8	1.5	15.1	0.5	0.8	0.5	15.1	3.75									
Ce	1.7	2.6	2.9	0.8	5.9	7.5	0.8	8.2	1.8	19.8	1.2	1.4	0.8	19.8	5.15									
Pr	0.2	0.36	0.45	0.1	0.73	0.8	0.15	0.95	0.25	4.12	0.16	0.24	0.1	4.12	0.929									
Nd	0.5	1.9	2.1	0.5	2.8	3.6	<0.4	4	0.9	19.8	0.6	1.3	0.5	19.8	4.48									
Sm	0.2	0.5	0.6	0.1	0.7	0.6	0.1	0.9	0.1	3.9	0.3	0.5	0.1	3.9	0.43									
Eu	<0.05	0.17	0.16	<0.05	0.16	0.16	<0.05	0.19	<0.05	1.27	0.13	0.14	0.13	1.27	0.378									
Gd	0.23	0.62	0.58	0.19	0.69	0.57	0.06	0.86	0.28	3.49	0.24	0.8	0.06	3.49	0.86									
Tb	0.03	0.11	0.13	0.03	0.13	0.15	0.03	0.11	0.07	0.52	0.05	0.1	0.03	0.52	0.14									
Dy	0.23	0.53	0.58	0.41	0.92	0.75	<0.05	0.54	0.32	2.45	0.19	0.58	0.19	2.45	0.78									
Ho	0.06	0.16	0.13	0.09	0.21	0.19	<0.05	0.09	0.08	0.41	<0.05	0.12	0.06	0.41	0.16									
Er	0.21	0.47	0.85	0.32	0.71	0.49	0.08	0.31	0.23	1.02	0.2	0.24	0.08	1.02	0.44									
Tm	<0.05	0.08	0.15	0.05	0.1	0.07	<0.05	0.06	0.07	0.16	<0.05	0.05	0.16	0.095										
Yb	0.24	0.53																						

In relation to trace elements, the mean values for hematite and itabirite are comparable to averages reported by Spier et al. (2007), Lindenmayer et al. (2001), and Klein and Ladeira (2000) (Table. 2). The analyzed data presents lower concentrations in comparison to the data from Klein and Ladeira (2000), but more or less similar to the values found by Spier et al. (2007). However when compared with other IFs in the world, both hematite and itabirite show lower average contents of trace elements (Table 2). Both hematite and itabirite samples have a lower concentration of the Ba element than the data obtained from Klein and Ladeira (2000) and Spier et al. (2007) in the QF region. Also the same result is obtained in comparison to the Ba data of IFs around the world.

The values for the V, Co, Ni elements for the Lake Superior region (Animikie IF) are higher than those of the itabirite of the QF. The V contents in the hematite are higher than in the itabirite, but are not very distinct from the data set from Nigeria (Adekoya, 1998). In comparison to the Canadian Algoma-type IFs data (Gross and Macleod, 1980), some

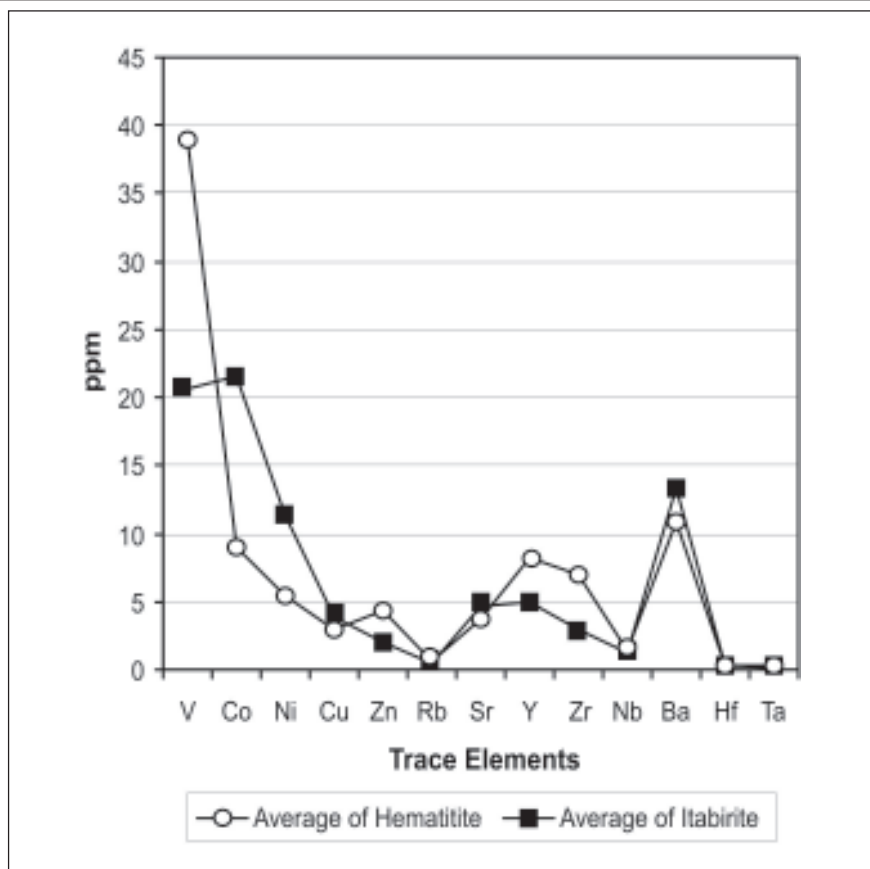


Figure 3 - Plot of the average concentration of trace-elements of the hematite and itabirite samples.

Table 2 - Average of trace element contents in the iron formation of this study compared with some iron formations of the QF region and from other parts of the world.

ppm	QF This Study		QF ^a	QF ^b	Superior ^c	Algoma ^d	Nigeria ^e	Orissa India ^f
	Hematite	Itabirite	Itabirite	Itabirite	BIF	BIF	BIF	BIF
V	39	20.6	22.6	-	30.0	97.0	44.0	30.0
Co	9	21.6	-	249.0	27.0	38.0	100.0	35.0
Ni	5.5	11.3	10.5	20.0	32.0	83.0	<10	15.0
Cu	2.9	3.9	<1.0	33.8	10.0	96.0	<10	10.0
Zn	4.4	2.0	-	42.3	2.0	33.0	26.0	-
Rb	0.6	0.5	<1.0	32.9	-	-	20.0	-
Sr	3.7	4.6	5.0	10.3	42.0	83.0	51.0	15.0
Y	8.2	5	3.9	4.8	41.0	54.0	22.0	-
Zr	7.0	3	12.0	2.5	60.0	84.0	60.0	10.0
Nb	1.4	1.3	0.8	6.4	-	-	5.0	-
Ba	10.8	13.3	15.4	55.4	180.0	170.	293.0	70.0
Hf	0.3	0.3	<0.1	0.1	-	-	-	-
Ta	0.1	0.3	-	0.1	-	-	-	-
ΣTE	92.6	87.9	72.3	457.3	424.0	738.0	621.0	185.0

^a Paleoproterozoic banded iron formation (Itabirite of Caue Fm) (Spier et al., 2007).

^b Itabirite from Caue Fm (Klein and Ladeira, 2000).

^c Lake superior silicate facies iron-formation (Animikie) (Gross and Macleod, 1980, Table 3).

^d Algoma oxide facies iron-formation (Gross and Macleod, 1980, Table 3).

^e Maru iron formation (oxide facies) (Adeloya, 1998).

^f Orissa iron-formation (oxide facies), India (Majumder et al., 1982, Table 3).

trace element values like V, Ba, Ni, Co, Nb, Zr revealed higher values than the data of the studied ore of the QF region.

The trace element values for the Orissa iron formation in India are much higher than the data of the studied ore samples, but the value for the V element is in the same range as our analyzed data.

In the studied area, the values presented for Ni and Cu are much lower in comparison with data for the rest of the QF region, as well as from other banded iron formations (BIFs) around the world (Table 2).

REE systematics in the QF iron formations are in the same range of values found in other similar sequences around the world (Fig. 5). On the average, the total content of REEs is relatively low with a moderate fractionation of light REE (LREE) relative to heavy REE (HREE) (Fig. 4), coupled with slightly positive Eu anomalies (average value of 1.5 and 1.6 for hematitite and itabirite samples, respectively). As with other Ifs of similar age, the majority of the analyzed samples display similar REE systematics and are compatible with the results of Bau and Möller (1993) that indicate that Ifs, independent of their provenance, age, and metamorphic grade, display a similar degree of fractionation of LREE ($(La/Sm)_{CN} > 1$) (Table.1).

The sum of REEs of the analyzed samples of this study is higher than the results obtained by Spier (2007) and from the jaspilites of the Carajás formation (Macambira and Schrank, 2002). In comparison to the other BIFs around the world, the itabirite of this study show values more or less similar to the REEs contents of the Surgur belt (Kato et al., 1996) and lower than the Kuruman BIF oxide facies (Klein and Beukes, 1989) (Table 3).

The ratio $(La/Yb)_{CN}$ of hematitite and itabirite samples show higher values in comparison to other BIFs around the world (Table 3).

The iron ore samples (oxide lithofacies) collected from the QF region consist mainly of hematite, magnetite and quartz. The analyzed samples are of two

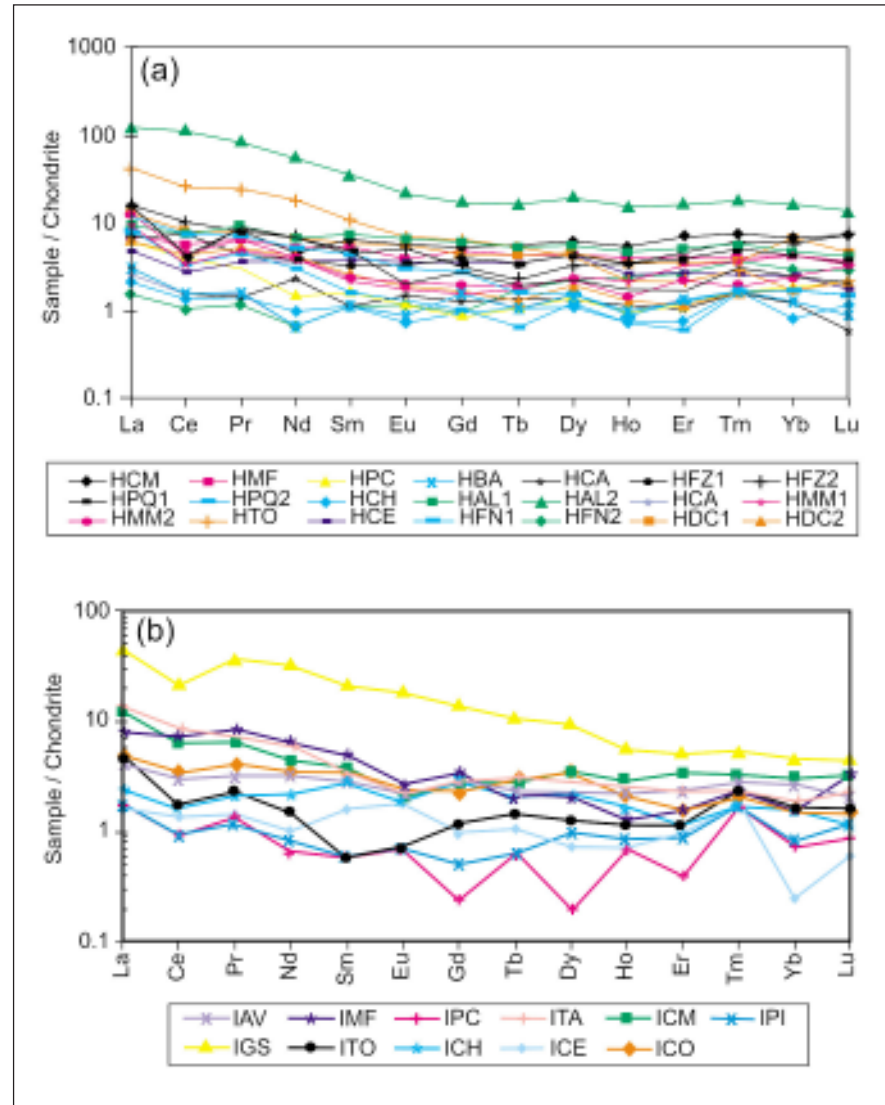


Figure 4 - Chondrite (after Evensen et al., 1978) normalized pattern of rare earth elements (REE) calculated for the hematitite samples (a) and itabirite samples (b).

types: hematitite and itabirite. The hematitite has more than 98% of Fe, whereas, the itabirite has varied contents of iron and silica, on the average higher than 99%.

The concentrations of trace (mainly transition metals) and rare earth elements of the hematitite and itabirite samples show considerable variability and appear in high values, especially in the eastern domain of the QF region. Particularly recorded was data from samples collected from Dois Córregos, Chacrinha, Gongo Soco, Periquito, Conceição and mines from Alegria.

The samples show low REE abundances and a moderate

fractionation ratio of LREE/HREE besides slightly positive Eu anomalies coupled with positive values for the $(La/Yb)_{CN}$, $(La/Sm)_{CN}$ ratios.

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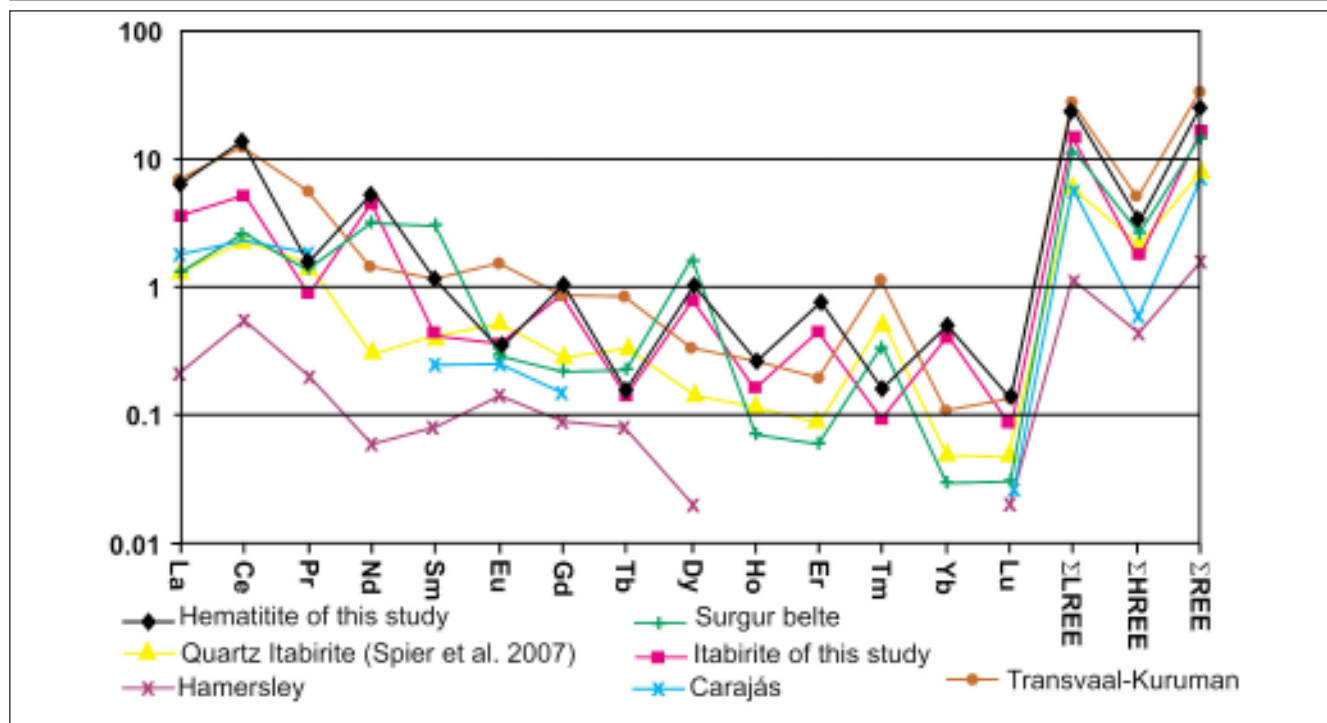


Figure 5 - Graph showing rare earth element content of the analyzed samples compared with some iron formations of the QF region and from other parts of the world (data obtained from Table 3).

Table 3 - Average of rare earth element contents in the iron formation of this study compared with some iron formations of the QF region and from other parts of the world.

ppm	QF This Study		QF ^a Itabirite	QF ^b Itabirite	Superior ^c BIF	Algoma ^d BIF
	Hematite	Itabirite				
La	6.51	3.75	1.4	0.22	7	1.37
Ce	13.96	5.15	2.32	0.54	12.71	2.73
Pr	1.45	0.9	1.59	0.2	5.49	1.46
Nd	5.45	4.48	0.32	0.06	1.47	3.23
Sm	1.22	0.43	0.43	0.08	1.13	3.05
Eu	0.34	0.37	0.54	0.14	1.512	0.3
Gd	1.04	0.86	0.3	0.09	0.85	0.22
Tb	0.17	0.14	0.35	0.08	0.85	0.23
Dy	1.04	0.78	0.15	0.02	0.33	1.65
Ho	0.25	0.16	0.12	ND	0.26	0.07
Er	0.76	0.44	0.09	ND	0.19	0.06
Tm	0.16	0.09	0.56	0.1	1.16	0.34
Yb	0.48	0.43	0.05	ND	0.11	0.03
Lu	0.13	0.08	0.05	0.02	0.13	0.03
ΣLREE	23.64	15.23	6.05	1.1	27.8	11.84
ΣHREE	3.21	1.68	2.21	0.45	5.04	2.93
ΣREE	26.85	16.91	8.26	1.55	32.85	14.78
(La/Yb) _N	7.7	7.3	0.51	0.87	0.88	0.94
(Eu/Eu*) _N	1.5	1.6	1.49	1.33	1.45	2.13

^a Paleoproterozoic banded iron formation (Itabirite of Caue Fm.) (Spier et al., 2007).

^b Hamersley banded iron formation (Glikson et al., 2004).

^c Transversal Supergroup, Kuruman BIF (oxide facies), (Klein and Beukes, 1989).

^d Surgur belt, India (Kato et al., 1996).

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