Geochemical fingerprint of siliceous, amphibolitic and magnetitic itabirite types of the region of Serra Azul – Quadrilátero Ferrífero, MG

Caracterização geoquímica dos itabiritos silicoso, anfibolítico e magnetítico da região de Serra Azul - QF, MG

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Abstract

Banded iron formations are important providers of information about the evolution of the hydrosphere, atmosphere, biosphere and lithosphere of the Earth. This study gathers data from the geochemical investigation of major, minor and trace elements (including rare earth elements) of the siliceous, amphibolitic and magnetitic types of itabirite from the Cauê Formation, sampled in the Serra Azul region (Quadrilátero Ferrífero).

Observing the trace elements described as tracers of detrital contamination can be inferred that the magnetitic itabirite has the highest contamination and that the siliceous type has the lowest one.

Although there are differences in the total sum of REE in the three itabirite types of Serra Azul, there are no discrepancies in the REE spectrum of each type. The itabirite types have as common characteristics in their REE spectrum: i) positive Eu anomalies (Planavsky *et al*., 2010); ii) HREE enrichment in relation to the LREE; iii) ratios of $(Sm/Yb)_{SN}<1$ and $(Eu/Sm)_{SN}>1$ (Bau & Möller, 1993). The magnetitic and the siliceous itabirites had positive Y anomalies, a common characteristic that appeared in some amphibolitic samples. On the other hand, the other amphibolitic samples had negative Y anomalies.

Keywords: Cauê Formation, Itabirite, geochemistry, REE, BIF.

Resumo

Formações ferríferas são importantes fontes de informações sobre a evolução da hidrosfera, atmosfera, biosfera e litosfera da Terra. Esse trabalho reúne dados geoquímicos de elementos maiores, menores e traços (incluindo os elementos terras raras) dos itabiritos silicoso, anfibolítico e magnetítico da Formação Cauê provenientes da região de Serra Azul (QF).

Em se tratando das concentrações de elementos-traço, considerados traçadores de contaminação detrital, pode-se inferir que o tipo magnetítico é o que possui uma maior contaminação e que o silicoso, a menor.

Embora existam diferenças no somatório total de ETR nos três diferentes tipos de itabiritos estudados, na região de Serra Azul, não foi possível verificar discrepâncias muito significativas no espectro de ETR dos três diferentes tipos estudados. São características comuns aos três tipos de itabiritos: i) anomalias positivas de Eu (Pla-

navsky et al., 2010); ii) enriquecimento em ETR pesados em relação aos leves; iii) razões $(Sm/Yb)_{SN}$<1 e $(Eu/Sm)_{SN}$>1 (Bau & Möller, 1993). Os itabiritos magnetítico e o silicoso possuem ainda em comum anomalias positivas de Y, uma característica que aparece em algumas amostras do tipo anfibolítico também. As outras amostras de itabirito anfibolítico possuem anomalias negativas de Y.

Palavra-chave: Formação Cauê, itabiritos, geoquímica, FFB, ETR.

1. Introduction

The mineral province of Quadrilátero Ferrífero (QF) is known by its gold deposits and high world quality iron ores deposits. It is located in the southeastern border of the São Francisco Craton, a block relatively stable of Archean and Paleoproterozoic rocks surrounded by Neoproterozoic orogenic belts (Almeida, 1977; Alkmim & Marshak, 1998).

Besides its economic importance, banded iron formations are important providers of data about the evolution of the hydrosphere, atmosphere, biosphere and lithosphere of the Earth (e.g. Dismukes *et al*., 2001; Liang *et al*., 2006; Pufahl, 2010).

The Cauê Iron Formation hosts the iron deposits of the QF province and has apparently the same age as other Paleoproterozoic iron formations around the world. The main lithotype of the Cauê Formation is the Itabirite (metamorphic banded iron formation), and in the QF, there can be distinguished five types: siliceous, amphibolitic, magnetitic, dolomitic and manganesiferous (Pires, 1995; Rosière & Chemale Jr., 2000; Amorim & Alkmim, 2011).

Known as the Serra Azul region (Figure 1), the western segment of the Curral Ridge is a region that experienced low deformation and metamorphism (Pires, 1995; Amorim & Alkmim, 2011). Because of this, the geochemical composition of the itabirites of this region approaches the composition of the original sedimentary protoliths of the Cauê Formation.

This study gathers data of major, minor and trace elements (including rare earth elements-REE) of the siliceous, amphibolitic and magnetitic types of itabirite from the Cauê Formation sampled in the Serra Azul region (QF).

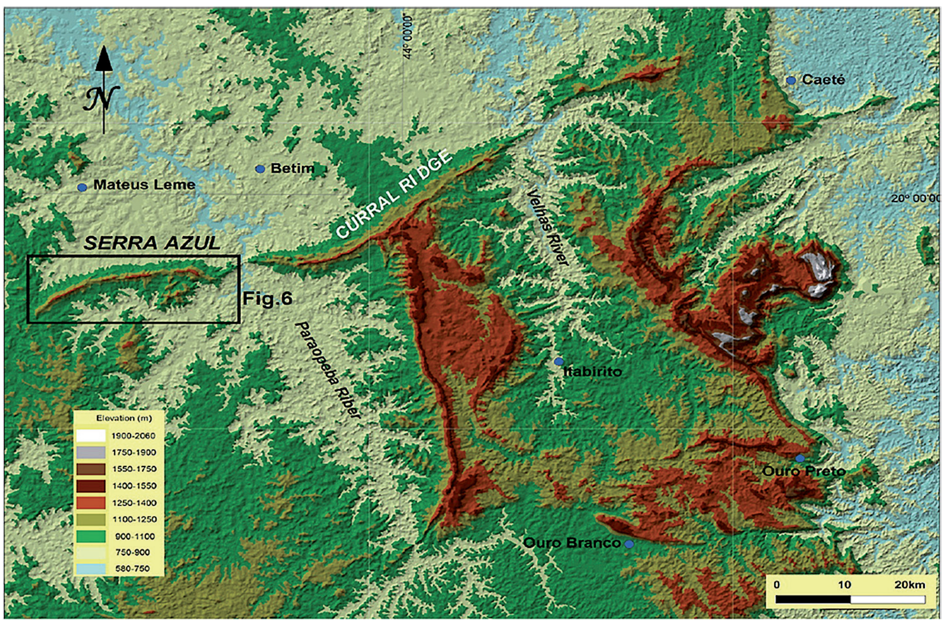

Figure 1
Digital topographic model of the QF region locating the Serra Azul in Amorim e Alkmim (2011)

2. Materials and methods

For this study, samples of the siliceous, amphibolitic and magnetitic types of the Cauê Itabirites collected at USIMINAS Mineração were selected. These samples were crushed, homogenized, pulverized and dried for one hour at a temperature of 100°C.

Major and minor elements were determined through inductively coupled plasma optical emission spectrometry (ICP-OES) and the total iron and ferrous iron content was determined through the titulometric method. The results were validated using the certificated reference material IPT-21A and the quality control material proposed by Sampaio (2012), duplicated samples and blank solutions.

Trace elements, including REE (Rare Earth Elements), were determined by inductively coupled plasma mass spectrometry (ICP-MS). The lanthanides and Yttrium will be called REE herein and were analyzed after acidic dissolution using PFA Savillex® tubes described by Sampaio (2012). The reference material used for the quality control of this method was GIT-IWG (France). In addition, duplicated sample dissolution and blank solutions were performed.

As suggested by Bolhar et al. (2004) and Spier *et al*. (2007), the results of the REE concentrations were normalized by PAAS (Post Archean Australian Shale - SN) (McLennan, 1989).

3. Results

Geochemically, the magnetitic itabirite has low concentrations of SiO_2 (38.67%), P_2O_5 (0.06%) and Fe_2O_3 (23.86%), if compared with the other types of itabirites from Serra Azul.

With high concentrations of the oxides: Mn (0.37%), Ca (4.20%), Ti (0.004%), Mg (4.96%) and Fe II (13.95%), these green rocks are rich in the trace elements, such as: Cr (4.765 µg/g), Cs (0.905 µg/g), Sc (0.158 µg/g), Ga (0.253 µg/g), Rb (1.242 µg/g), Sr (15.238 µg/g), Zr (1.110 µg/g), Hf (0.024 µg/g), Th (0.222 µg/g) and Bi (0.021 µg/g) and have low concentrations of Ni (4.126 µg/g), Cu (2.902 µg/g), Nb (0.054 µg/g), In (0.0049 µg/g) and Ba (15.273 µg/g).

Containing a total concentration of REE between 5.466 µg/g and 42.663 µg/g, the magnetitic itabirite has in general an REE spectrum (Figure 2) characterized by the presence of positive anomalies of Eu (Planavsky, 2010) and Y, negative anomalies of Ce (Bau & Dulski, 1996), enrichment in HREE (heavy REE) in relation to the LREE (light REE) and Y/Ho ratios near 38.67. Studying the criteria suggested by Bau & Möller (1993) for iron formations, the magnetitic itabirite shows ratios of $(Sm/Yb)_{SN}<1$ and $(Eu/Sm)_{SN}>1$. Deeply studying the Ce anomalies as suggested by Planavsky (2010) and Bau & Dulski (1996), the proposed ratios $(Ce/Ce^*)_{SN}$ e $(Pr/Pr^*)_{SN}$ were respectively less or near one, leading to indicate that the Ce negative anomalies were in fact positive anomalies of La in the samples.

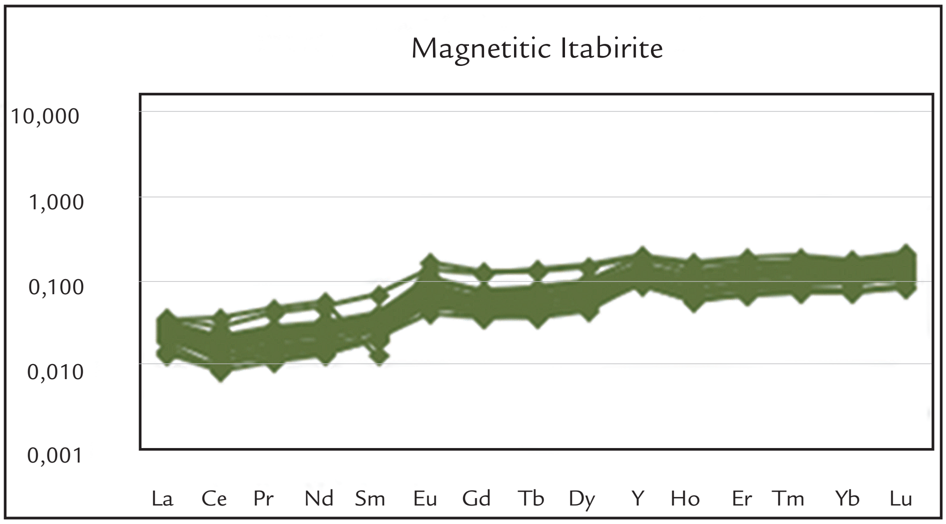

Figure 2
REE spectrum of the magnetitic itabirite from Serra Azul, PASS normalized (McLennan, 1989).

The siliceous itabirite possesses a medium composition of SiO_2 (43.76%), Fe_2O_3 (50.54%), and FeO (1.94%), with low contents of $Al2O_3$ (0.034%), MnO (0.100%), and TiO_2 (0.001%) when compared with the other two types of itabirite studied. Rich in trace elements, such as Nb (0.093 µg/g), In (0.007 µg/g) and Sn (0.207 µg/g), the siliceous itabirite have low concentrations of Ni (2.737 µg/g), Ga (0.172 µg/g), Rb (0.172 µg/g), Sr (0.973 µg/g), Zr (0.686 µg/g) Cs (0.033 µg/g), Ba (10.567 µg/g), Hf (0.012 µg/g) and U (0.099 µg/g).

Studying the contents of REE, the general sum of concentration of the siliceous itabirite remains between 4.410 µg/g and 12.519 µg/g. The general REE spectrum of this type of rock (Figure 3) presents positive anomalies of Eu (Planavsky, 2010) and Y, negative anomalies of Ce (Bau & Dulski, 1996), enrichment in HREE in relation to LREE and Y/Ho ratios near 35.59. Analyzing the Bau & Möller (1993) criteria, the siliceous itabirite has ratios of $(Sm/Yb)_{SN}<1$ and $(Eu/Sm)_{SN}>1$. Wanting to verify the veracity of the Ce anomalies, the ratios $(Ce/Ce^*)_{SN}<1$ and $(Pr/Pr^*)_{SN}\approx1$ (Planavsky, 2010; Bau & Dulski, 1996), were observed and possibly indicate that the Ce negative anomalies were generated in some samples from anomalous La concentration used in the math calculation. Only five samples had true negative Ce anomalies.

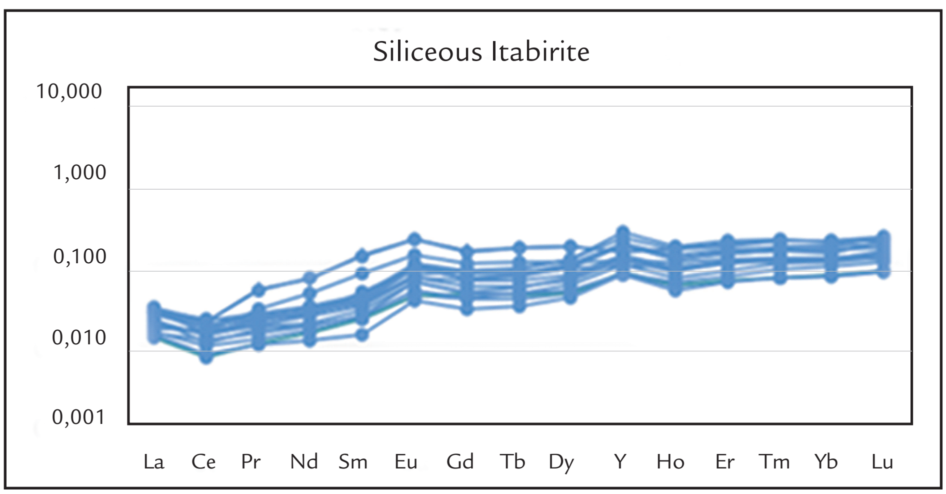

Figure 3
REE spectrum of the siliceous itabirite from Serra Azul, PASS normalized (McLennan, 1989).

The amphibolitic itabirite, geochemically, has high concentrations of Fe_2O_3 (51.36%), Al_2O_3 (0.183%) and P_2O_5 (0.148%), medium of SiO_2 (42.47%), TiO_2 (0.002%), MgO (0.100%) and low f FeO (1.31%) and CaO (0.04%). Rich in trace elements, such as Ni (4.895 μg/g), Cu (4.260 μg/g), Cs (0.100 μg/g), Ba (98.781 μg/g) and U (0.296 μg/g), this type of μg/g), Sr (7.397 μg/g), Zr (0.870 μg/g), Hf (0.017 μg/g), Th (0.125 μg/g), Ga (0.243 μg/g), Rb (0.531 μg/g), Cr (1.060 μg/g), and Sn (0.157 μg/g).

Containing a total concentration of REE between 8.517 μg/g and 21.132 μg/, the amphibolitic itabirite has a REE spectrum (Figure 4) characterized by positive Eu anomalies (Planavsky, 2010), positive 1996) anomalies, enrichment in HREE in relation to the LREE and Y/Ho ratios near 28.82. Analyzing the ratios described by Bau & Möller (1993), the samples have $(Sm/Yb)_{SN}<1$ and $(Eu/Sm)_{SN}>1$. Deeply studying the Ce anomalies as suggested by Planavsky *et al.* (2010) and Bau & Dulski (1996), the proposed ratios $(Ce/Ce^*)_{SN}$ and $(Pr/Pr^*)_{SN}$ indicate that all the samples have truly negative Ce anomalies.

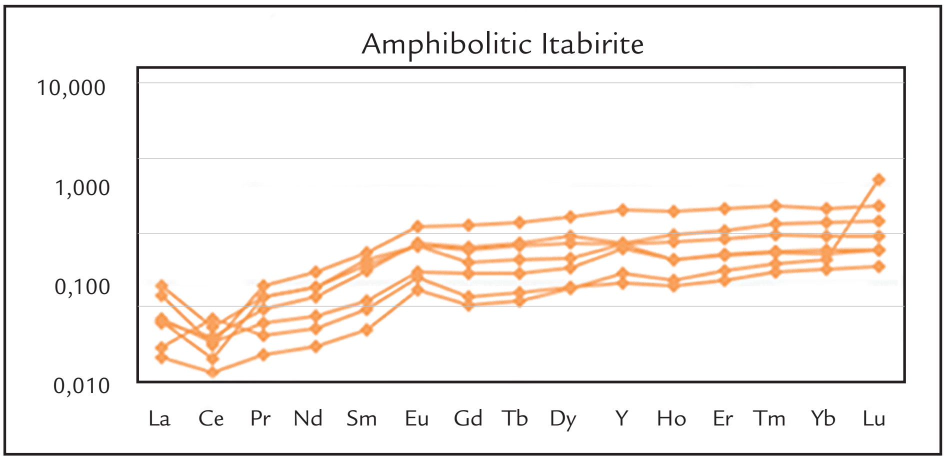

Figure 4
REE spectrum of the amphibolitic itabirite from Serra Azul,
PASS normalized (McLennan, 1989).

4. Discussions

The main general characteristics of the magnetitic itabirite are: low concentrations of the major oxides of Si, P, Fe III and the trace elements of Ni, Cu, Nb, In, and Ba, along with the highest concentrations of the oxides of Mn, Ca, Ti, Mg, Fe II and the trace elements of Cr, Sc, Rb, Sr, Zr, Th, Hf and Bi, if compared with the siliceous and amphibolitic itabirites. The siliceous itabirite is chemically composed of the lowest concentrations of Al, Mn and Ti oxides and trace elements when compared with the other types of itabirites studied, excluding Cs and U that are found in low concentrations. The amphibolitic itabirite is characterized by the highest concentrations of Al, P and Fe III oxides and trace elements as compared to other types of studied itabirites, excluding Nb, In and Sn that are found in higher concentrations.

Analyzing the trace elements Sc, Sr, Zr, Hf and Th that are tracers of detrital contamination (Bolhar *et al.*, 2004; Bau & Möller, 1993, Bau & Alexander, 2009), the same trend can be seen. The highest concentration of these trace elements is present in the magnetitic type of itabirite. The medium concentrations can be seen in the amphibolitic type and are followed by the ones observed in the siliceous itabirite. It can be inferred that the itabirite type that has the highest detrital contamination amount is the magnetitic being followed by the amphibolitic and finally by the siliceous type.

The average Y/Ho ratios observed in the three different types of itabirites are close ratios (38.67 for the magnetitic, 35.59 for the siliceous and 28.82 for the amphibolitic), which are similar to the average ratio (42) determined by Alexander *et al.* (2008) and (39) for early Archean and early Paleoproterozoic iron formations (Planavsky *et al.*, 2010).

The different types of itabirites of Serra Azul have varied total REE sums. The siliceous type has the lowest sum of these elements, followed by the magnetitic type and, finally, the amphibolitic type, the richer REE lithology. Although there is a difference in the REE sums of the three types of itabirites, when the spectrum of the REE is observed, there are no discrepant differences between them (fig. 5).

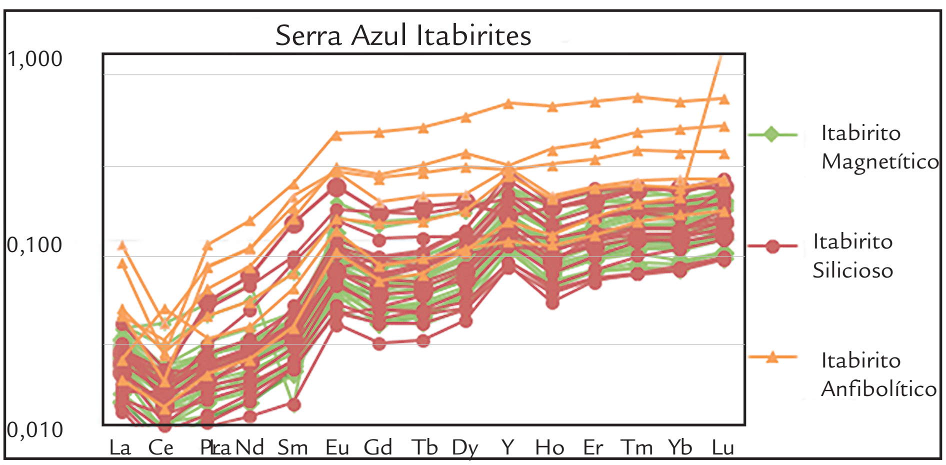

Figure 5
REE spectrum of all the itabirite studied types from Serra Azul,
PASS normalized (McLennan, 1989).

All the three itabirites types studied had as common characteristics: positive Eu anomalies (Planavsky *et al.*, 2010), enrichment in HREE in relation to the LREE, ratios of $(Sm/Yb)_{SN}$<1 and $(Eu/Sm)_{SN}$>1. The magnetitic and siliceous type still had the positive Y anomaly in common, a characteristic that was also present in some samples of the amphibolitic type but there were others that had showed negative Y anomalies. Positive anomalies of La were characterized in the magnetitic itabirite and in some samples of the siliceous type that also had samples with true negative Ce anomalies. The amphibolitic itabirite was characterized as having only true negative Ce anomalies.

5. Conclusions

Geochemically, the magnetitic itabirite is characterized by: the highest concentrations of MnO, CaO, TiO_2, MgO, FeO and trace elements as Cr, Sc, Rb, Sr, Zr, Hf, Th and Bi. The siliceous itabirite is composed of the lowest concentrations of Al_2O_3, MnO, TiO_2 and trace elements, if compared with the other two types of studied itabirites. Characterized by the highest concentrations of Al_2O_3, P_2O_5 and Fe_2O_3, the amphibolitic itabirite contains the highest concentrations of trace elements in the studied samples.

Observing the trace elements described as tracers of detrital contamination (Bolhar *et al.*, 2004; Bau & Möller, 1993, Bau & Alexander, 2009), it can be inferred that the magnetitic itabirite has the highest contamination and that the siliceous type has the lowest one.

The three itabirite types studied have average Y/Ho ratios that are similar to the average proposed for Archean and early Paleoproterozoic iron formations in literature (e.g. Alexander *et al.*, 2008; Planavsky *et al.*, 2010).

Although there are differences in the total sum of REE in the studied itabirite types of Serra Azul, there are no discrepancies in the REE spectrum of each type. The three types had common characteristics in their REE spectrum:

i) positive Eu anomalies (Planavsky *et al.*, 2010);

ii) HREE enrichment in relation to the LREE; ratios of $(Sm/Yb)_{SN}$<1 and $(Eu/Sm)_{SN}$>1 (Bau & Möller, 1993). The magnetitic and the siliceous itabirites had positive Y anomalies, a common characteristic that appeared in some amphibolitic samples; on the other hand, the other ones had negative Y anomalies. Positive anomalies of La were characterized in the magnetitic itabirite and in some samples of the siliceous type that also had samples with true negative Ce anomalies. The amphibolitic itabirite was characterized as having only true negative Ce anomalies.

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