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APPLICATION OF pXRF (FIELD PORTABLE X-RAY FLUORESCENCE) TECHNIQUE IN FLUVIAL SEDIMENTS GEOCHEMICAL ANALYSIS – BULE STREAM, MINAS GERAIS STATE, BRAZIL

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Abstract

A new methodology based on a portable X-ray fluorescence (pXRF) was applied in this work to analyze the geochemical dispersion halo of a sulfide mineralization along the Bule Stream sediments (Ouro Branco, Minas Gerais State, Brazil). The study area, located in the Iron Quadrangle (QF), has an important sulfide occurrence of antimony and zinc, which was explored between 1920s and 1930s. Stream sediment samples were collected along the Bule Stream and from some of its tributaries. Aluminum, Fe, Ca, Mg, Mn and Ti contents were obtained by the pXRF "mining mode" and quantified in percentage (%), while the results for Cu, Zn, Pb, As, Cr, Ag, Sb and Sr were carried out by the pXRF "soil mode", quantified in parts per million (ppm). The statistical treatment of data by Spearman correlation based on geochemical data and some sediment features were discussed, such as the geochemical affinities between the analyzed elements and supergene processes which control the elemental dispersion. Aluminum, Ca and Mg contents were compared with that of the Upper Continental Crust (UCC), since the composition of the Bule Stream sediments should be related to the composition of the source rocks. The results indicate that the Al contents reflect the surrounding soil maturity. The concentrations of Ca and Mg increase in weathered resistant mineral phases, mainly dolomite. The Fe enrichment is associated with geological units containing this element, such as dolomite/ferruginous itabirites (BIF). The high Mn content is related to the QF unity with larger dolomite occurrence (Gandarela Formation). Secondary environmental characteristics can justify the enrichment of Zn and Cu in the study area. All types of rocks have significant concentration of Cr. The comparison of the elemental concentrations of Bule Stream sediments with the average concentration of the elements in the Earth's upper crust (UCC) reveals intense weathering rate of the parent rocks characterized by high maturity of the geological material, enrichment of Fe and Mn and most of the analyzed trace metals. The results of an enrichment factor with three different normalizers (Al representing clay minerals; Fe + Mn representing oxides/hydroxides and; Ca + Mg representing carbonates) indicate that the carbonate phase is the main conveyor of trace elements.

Keywords: Geochemistry. Iron Quadrangle. Sediments. Portable X-Ray Fluorescence. Metals. Enrichment Factors.

1. Introduction

The region of the Iron Quadrangle (QF) is known as one of the main metallogenetic provinces of the planet and has great importance for the Brazilian mineral production, putting the state of Minas Gerais in the first ranking of CFEM (Financial Compensation for the Exploitation of Mineral Resources) between 2008 and 2014, accounting approximately for US $ 1.047.000.000 (DNPM, 2016). The main commodities in this region are the well-known deposits of Fe, Au and Mn. Regarding the Au deposits, they have several sulfide mineral phases containing large metal content, mainly Cu, Pb, Sb and Zn, which have not economic importance (Pereira and Santos, 1983; Taufen and Marchetto, 1989; Ribeiro-Kwitko and de Oliveira, 2004; Vial et al., 2007). Nevertheless, in the southern part of the QF, characterized by the Dom Bosco synclinal structure, there are relevant sulfide occurrences, such as Bico de Pedra, showing Cu, Pb and Hg sulfides (chalcopyrite, galena and cinnabar, respectively; Borba, 1998), as well as Au occurrences and Bule Hill, which has Sb and Zn sulfide phases (stibnite and sphalerite, respectively). Such mineral occurrences may come from the same hydrothermal event (Guimarães, 1934; Fraga, 1992).

The occurrence of sulfides has not been studied yet in the Bule Hill region, located at Ouro Branco municipality, due to its low Au concentration, which is however more prominent in Bico de Pedra. The works performed by Guimarães (1934) and Fraga (1992) are the only studies that describe the sulfide mineralization in Bule Hill. This sulfide occurrence, which acquired a mining status in the 1930s with the stibnite and sphalerite exploration, is now completely buried since the mining site was affected by erosion processes and was covered by sediment deposition. There are no records of waste deposits around the mined deposit. Nowadays, the Bule Hill sulfide occurrence is located at an environmental protection area (characterized mainly by an important ecological corridor), which has been untouched by human activities since 2002. This feature is important for understanding the actual dispersion of the major and trace elements provided by natural sources. The Bule Stream is strategic for the region as it feeds the Soledade dam that supplies water to the Gerdau/Açominas industrial plant in the iron processing and steel production. In addition, there is dolomite extraction downstream of the river basin, on its right bank.

The main goal of this work is to characterize the behavior and dispersion of major and trace elements of the Bule Stream sediments. In addition, it aims to analyze the geochemical dispersion halo of a sulfide mineralization, using a new methodology, widely used in projects of mineral exploration, facilitating the generation of quantitative results. This study utilized a portable X-ray fluorescence (pXRF) to test parameters that easily meet potential customer goals, saving time and financial resources with sample preparation and laboratory analysis.

2 Study Area

The study region is located in the southeast of most of the QF, occupying an area of approximately 7.200 km^2 (Fig. 1). It is inserted on the southern edge of the São Francisco Craton and is the result of the reworking of a stable area of Early Transamazonian age (Almeida, 1977). The QF is composed by four stratigraphic units, namely 1) a granite-gneiss metamorphic complex; 2) an Archaean greenstone belt sequence (Rio das Velhas); 3) metasediments and; 4) Proterozoic metavolcanic (Minas Supergroup) and metasediment rocks (Itacolomi Group) (Dorr, 1969; Chemale Jr et al., 1994; Zucchetti and Baltazar, 1996, Noce, 2000; Baltazar and Zucchetti, 2007).

The geology of the study area (surrounding the sampling stations) is essentially composed by Minas Supergroup and Itacolomi Group (Fig. 2). The Minas Supergroup is composed by Caraça, Itabira and Piracicaba Groups (Dorr 1969; Rosière and Chemale Jr, 2000). The Caraça Group is predominantly composed of quartzites and phyllites. The Itabira Group comprises the Lake Superior-type banded iron formation (BIF), capped by dolomitic carbonates. The Piracicaba Group is characterized by interbedded quartzite and phyllite containing carbonate lenses. The Itacolomi Group is mostly formed by phyllitic and ferruginous quartzites and conglomerates (Dorr, 1969; Borba, 1998; Noce, 2000).

At the headwaters of Bule Stream, there is sulfide occurrence with Sb and Zn mineral phases, which was explored in the 1920s and 1930s. Nowadays, it is completely buried by gullies. Antimony is an important element for the manufacture of accumulator plates, which is also one of the main alloy components used to produce ammunition and batteries (Reimann et al., 2010). Its oxide species are used in the production of different types of glasses, glazes and porcelain ware. Moreover, the component can also be found in the production trioxide Sb (Sb_2O_3), which catalyzes polyethylene terephthalate (PET) as a flame retardant in the production of plastics, textiles, rubber, pigments, paints, ceramic coatings and crystal glass (Reimann et al., 2010).

Guimarães (1934) explains the genesis of this mineral deposit as a dolomite composed of Pb and Sb in the contact zones between the mineralized zone and host rocks. There was a change mainly in the Pb and Sb-rich mineral phases under oxidizing conditions (stibnite→valentinite) and mineral formation of oxidized compounds such as bindheimite (Pb and Sb), malachite (Cu), Fe oxides and Sb concentrated in the presence of calcite and aragonite. Afterwards, Borba (1998) described the Bico de Pedra deposit, which is located next to Bule Hill deposit and presents similar mineralogy. This author suggests a primary source for the sulfide minerals, derived from shallow plutonic and/or volcanic rocks, which could be the same source of Bule Hill mineralization.

The secondary minerals in this deposit reveal the hydrothermal action through a change "in situ" of the mineralization, with the formation of sulfide minerals and recrystallization of dolomite. The last stage of the formation of this axis supports the existence of previous stibnite-tetrahedrite, pyrite and sulfide phase, where the hydrothermal solutions caused the formation of jamesonita (Sb, Pb and Fe sulfide) by the reaction of alkali sulfides on the bindheimita (Sb and Pb oxides; Guimarães 1934).

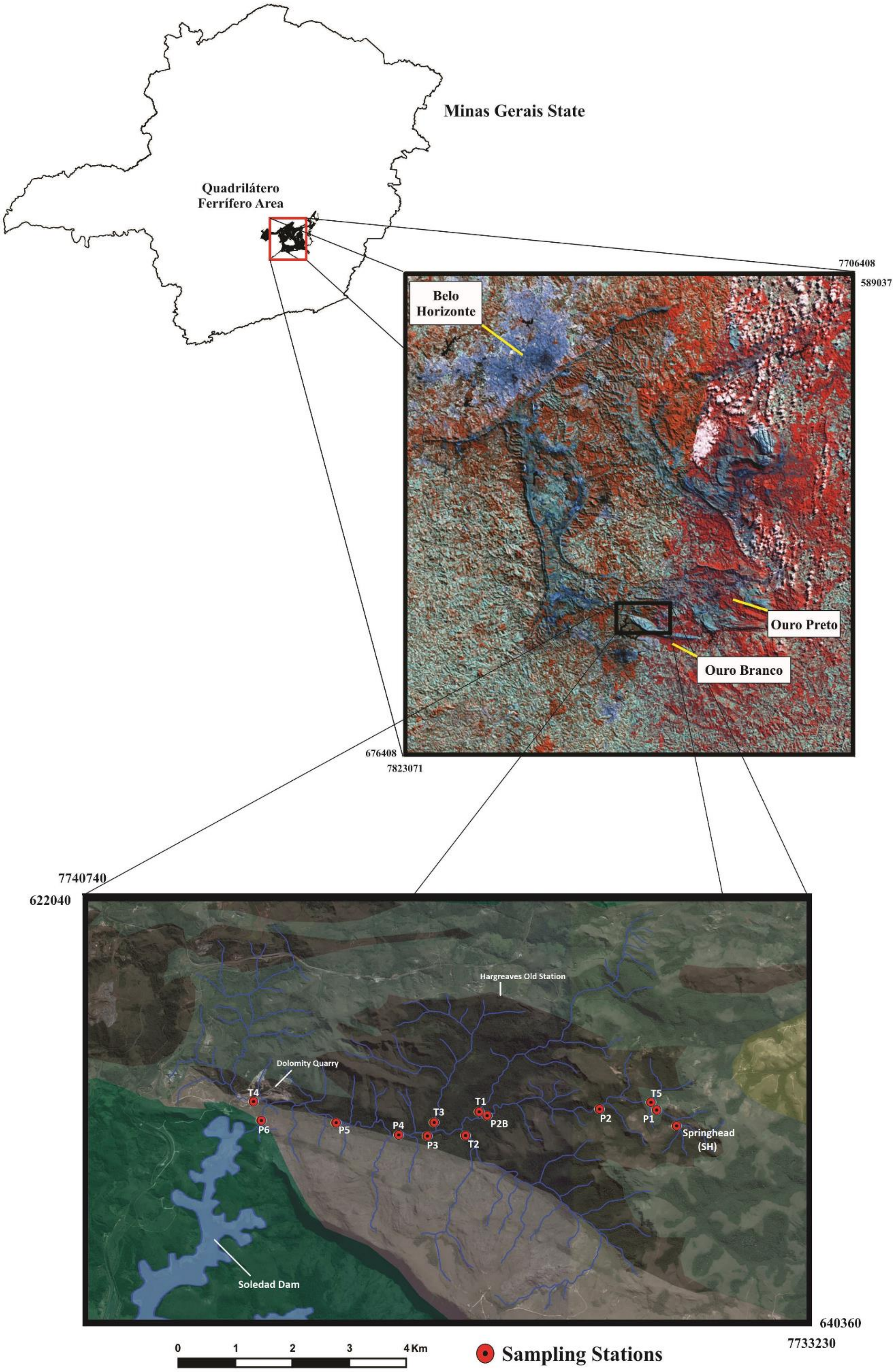

Fig. 1. Study area and sampling stations location.

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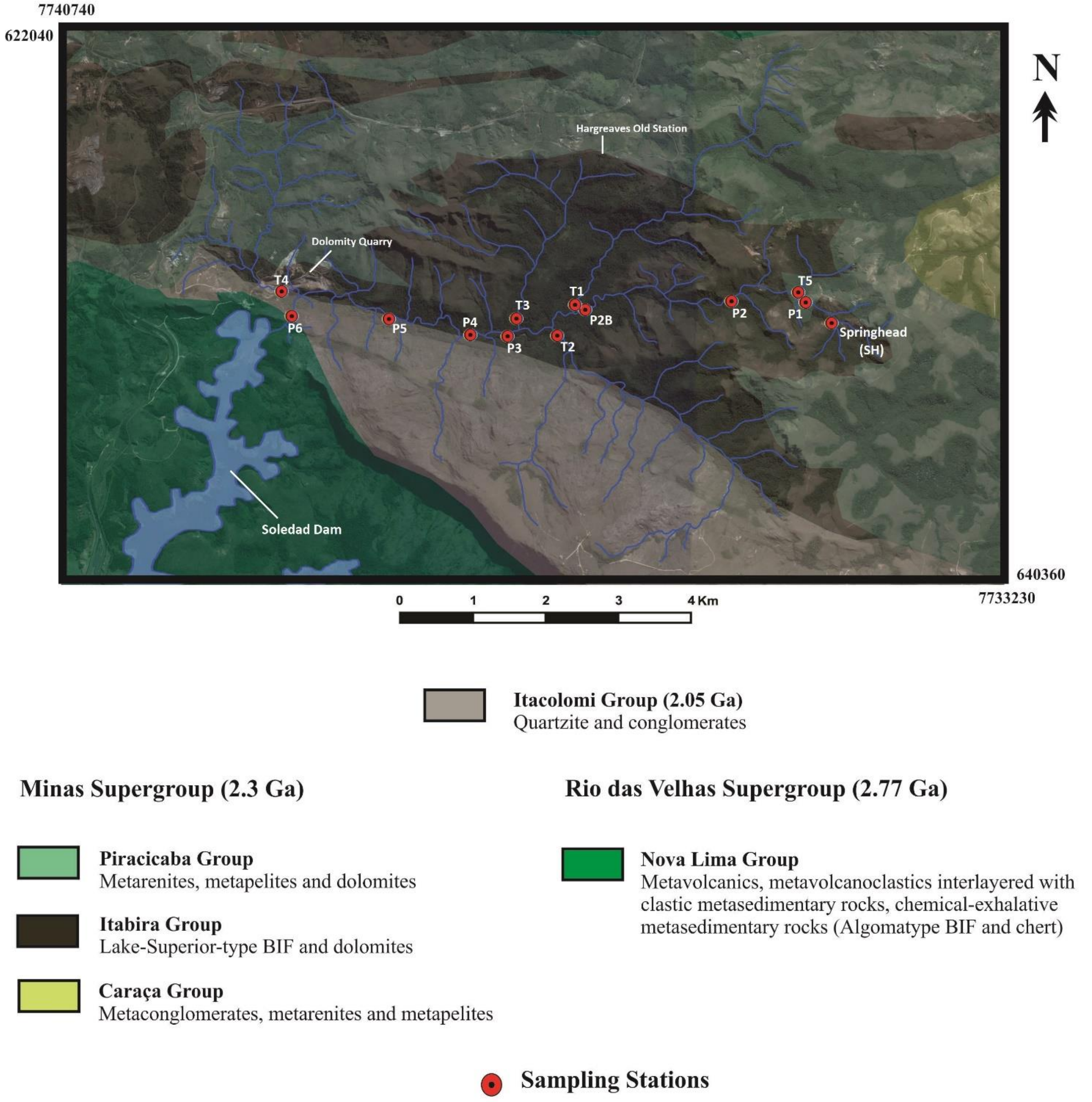

Fig. 2. Geology of the study area and sampling stations location.

The regional climate is classified as tropical of altitude, with seasonal variation in rainfall, having a dry period from May to August and a heavy rainfall period between November and February. These conditions may explain the weathering processes observed in the study area, such as weathering of rocks and regolith lixiviation, since the rainwater is slightly acidic (Drever, 1997). In periods of high precipitation, such as in December and January, the average precipitation is about 300 mm per month. The annual average rainfall and temperature is ≈1190 mm and ≈20.9 °C, respectively (INMET - www.inmet.gov.br: accessed on 18/05/2019).

3. Materials and Methods

3.1 Sampling and samples treatment

Stream sediment samples were collected along the Bule Stream and from some of its tributaries. In total, 13 samples were collected from the springhead to downstream in Soledade Dam, namely, Springhead (SH), sampling points along the main channel of the stream P1, P2, P2B, P3, P4, P5, P6, and tributaries T1, T2, T3, T4, T5 (Figs. 1 and 2).

The sediment sampling was composite and followed standard procedure aiming to collect the fine fraction of

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the active sediment. The surficial sediment samples were collected manually using plastic shovel in rectilinear tracks, from 5 to 10 portions within a radius of 50 meters. These multiple collection points involved an extensive scanning in drainages to obtain a more representative sampling. The sampled volume ranged between 1.0 and 2.0 liters was stored in identified sturdy plastic bags and sealed with clamps. During the sampling, coarser materials, lithoclasts and vegetation were removed with the objective of not influencing the analyses. The pH values of stream water were measured in each sampling point using pH-indicator strips (Merck Millipore).

In the laboratory, the samples were dried at room temperature in plastic pots and, to avoid losses of certain chemicals by high temperatures, taking care to protect the exposed samples to avoid contamination. The drying process lasted about four days and after this procedure, the samples were homogenized, sieved and weighed using a high precision analytical balance, Sartorius model CP124S.

The samples sieving was done on a sieve adjuster, first passing through an 18-mesh sieve (1 mm), followed by a sieve of 0.595 mm and down a sieve 0.177 mm. This fraction (< 0.177 m; < 80 #) was chosen because it produces a better contrast between the background and the anomalies (Levinson, 1974; Rose et al., 1979) and, for that reason, it is widely used in geochemical prospecting programs of stream sediments and soils. In this fraction, some metals of greatest economic interest are associated with oxides/hydroxides (with high Fe and Mn contents), clay minerals (with high Al contents) and organic matter, which are found mainly in the composition of fine fraction (adsorption process). Thus, this fraction (< 0.177mm) was chosen since it allows a more efficient detection of any chemical change that is indicative of potential mineralization. Smaller and lighter bags were used for the storage of samples, to avoid potential interference in the analysis. After sieving, the samples were weighed again.

3.2 X-Ray Fluorescence (XRF)

The X-ray fluorescence is a non-destructive instrumental technique, which allows the identification and estimation of the elemental composition without any kind of sample preparation or chemical pre-treatment, making the analysis fast, allowing the analysis of several elements simultaneously, being non-destructive, with low operational cost and very versatile, being applied in several types of samples (Nagata et al., 2001; Skoog et al., 2009).

This is a semi-quantitative method which produce and detect high frequency electromagnetic radiation emitted by the elements that make up the irradiated sample (Jenkins, 1988). The incident electromagnetic radiation interacts with the sample, and three types of phenomena can occur: emission, absorption and scattering of electromagnetic radiation (Boumans, 1991; Skoog et al., 2009).

X-ray fluorescence analysis consists of three phases: excitation of the sample elements, dispersion of X-rays emitted by the sample and detection of these X-rays. The incident X-rays excite the constituent atoms of the sample. With the excess energy released in the process, each atom emits spectral lines with fluorescent energies and wavelengths characteristic of the element and intensities related to its concentration (Jenkins, 1998; IAEA, 1999; Bleicher and Sasaki, 2000; Weltje and Tjallingii, 2008).

Portable X-ray fluorescence (pXRF) has been commonly used for mineral prospecting and environmental issues for about two decades (eg. Bernick et al., 1995; Kalnicky and Singhvi, 2001; Radu and Diamond, 2009). This portable device is similar to a pistol, with trigger, viewfinder and an X-ray beam exit point (Fig. 3A). This device produces qualitative and semi-quantitative analyzes for studies of soil, rock, sediments, among other materials.

The positive points of using the pXRF are the cost reductions with laboratories specialized in chemical analysis, the easy handling and transport in the field and the immediate result, but it is not advisable to replace the laboratory analysis with the portable device. The pXRF is seen as a primary analysis or as complementary analysis, while laboratory analyzes are required for more detailed geochemical studies.

3.3 Application of pXRF in this study

The analyses of the Bule Stream sediment samples were carried out at the Belo Horizonte Regional Office of Geological Survey of Brazil (Companhia de Pesquisa de Recursos Minerais, CPRM), Minas Gerais State, using a Portable X-ray Fluorescence (pXRF), coupled to a desk device (X-ray protection chamber) and connected to a computer (Fig. 3). The device is manufactured by Innov-X Olympus System Inc. Company and the specific model is the Delta Premium model 511590 (Fig. 3A). Qualitative analyses are related to the magnitude of the element concentration and to the probability of these concentrations to occur.

From the software coupled to the pXRF device is possible to track the results obtained for each chemical element in real time. The device has four types of configuration: 1) the Power mode (Alloy Mode); 2) Ore mode (Mining Mode); 3) Soil Mode and; 4) Consumer Goods mode. In this study, the soil and ore modes were chosen because it is the one that best applies to the work proposal and for present in better analysis resolution for stream sediments (Sarala, 2009; Bowell et al., 2012; Sarala and Mäkikyrö, 2012; Plourde et al., 2013).

Quality control was assessed by analysis of blank reagents, 06 blind duplicates and 06 replicate samples of the standard sediment reference material G01W019. Analytical results agree with the certified values for all the studied elements and the accuracy varied between 4 and 8%.

Analytical precision was assessed using 04 samples prepared in duplicate and analyzed at random positions within a batch and the analytical precision ranged approximately between 2% for Al and 8% for Pb. Additionally, the Standard Reference Material® 2710a (Montana I Soil) was used to verify the accuracy of the pXRF method. The recovery rates for elements ranged from 92% for Ti to 98.3% for Fe. The analytical results for the elements Al, Fe, Ca, Mg, Mn and Ti were obtained by the Mining mode, quantified in percentage (%), while the results for Cu, Zn, Pb, As, Cr, Sb and Sr were carried out in the Soil mode, quantified in parts per million (ppm).

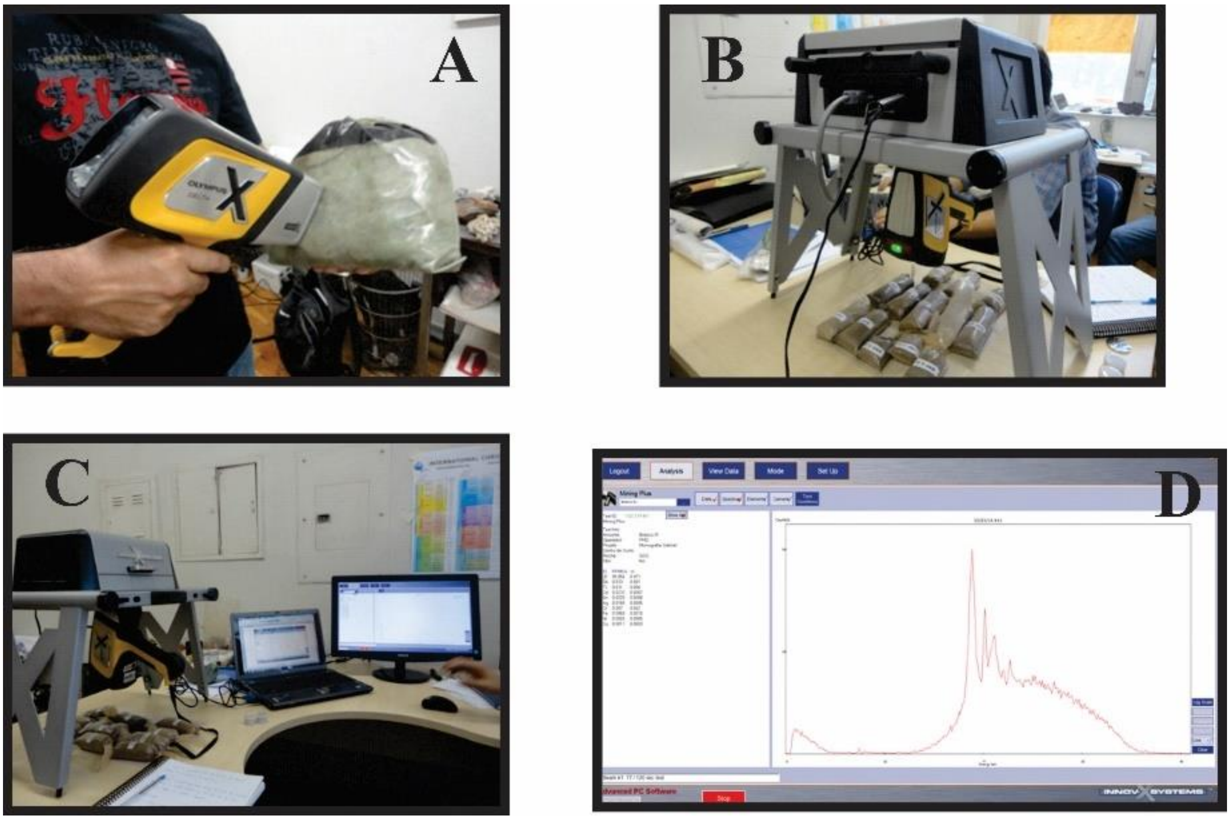

Fig. 3. A: portable X-ray fluorescence (pXRF); B: desk device (X-ray protection chamber); C: pXRF connected to the computer; D: Results obtained from pXRF software in the computer.

3.4 Statistical Analyzes

In order to better understand the relationships between elemental concentrations to corroborate some hypothesis some previously discussed hypotheses, the data were submitted to correlation analysis. In addition, an enrichment factor was determined. Since all the variables (analyzed elements) do not have normal distribution, the Spearman correlation test (from non-parametric statistics) was used. This analysis does not consider the use of assumptions about the distribution of the variable frequency, that is, it does not require that the relation between the variables be linear. This statistical analysis may consider sampling with n< 30. It should be mentioned that the data concentration of the elements was log-normalized to this analysis, in order to reduce the influence of outliers (Reimann et al., 2008; Grunsky, 2010). So, it was considered that the correlation coefficient values > 0.80 are highly significant (at $p < 0.01$); between 0.79 and 0.60 significant (at $p < 0.05$); and below 0.59 insignificant (at $p < 0.1$).

The enrichment factor (EF) is commonly used to indicate possible contamination or anthropogenic contributions, measuring the extent of pollution by metals (Kerstern and Förstner, 1995; Audry et al., 2004). However, in this work, the EF will be considered a tool to indicate the enrichment of metals in sediments according to a supergene natural process, since the study area has a sulfide mineralization and is not polluted.

The calculation of EF considers the concentration of the element to be assessed by the concentration of a common element in the study region, namely, normalizer. It is adopted as normalizer element a chemical species with low mobility, naturally present in the area and good affinity for trace elements or a conservative element.

In the present study, the elements considered as normalizers were: Al, representing the clay minerals; the

Fe + Mn, representing the oxides and hydroxides and; Ca + Mg representing the carbonates in the region. Although Ca and Fe are moving elements, their use as reference is due to their presence in high concentrations in the local lithology.

The use of this methodology was proposed in order to identify the main metals transporters in the study area. The normalization factor was calculated from the average proportion of the sample's levels (Yongming et al., 2006; Silva-Filho et al., 2014). It should also be noted that all the elements involved in these calculations were converted to the same concentration unit, in this case, in parts per million (ppm). Thus, for this study, the used reference ratio is the mean ratio of all the analyzed samples and the EF is given by:

$$EF = (Me/N \text{ sediment sample}) / (Me/N \text{ sediment samples average})$$

where Me is the metal to be normalized and N is the chosen normalizer.

4 Results and Discussion

4.1 Results of pXRF and pH

The results of pXRF and pH water in each sampling station and some statistical parameters are shown in Table 1. The average concentration of the elements in the Earth's upper crust (UCC; Wedepohl 1995) was added to compare and identify enrichment or depletion of a given element.

Figures 4 and 5 show the concentration of the analyzed elements along Bule Stream and its tributaries. The red line in each graph indicates the UCC of that element. The comparison of the average concentrations of the elements present in Bule Stream (Table 1) with the UCC (Wedepohl, 1995) reveals the general depletion of the major elements such as Al, Ca and Mg and trace elements, Pb, and Sr while there is an enrichment of Fe and Mn, and the trace elements Cu, Zn, and Cr. Sb was detected only in the sampling station (P4) with an enrichment of 74 times above the average concentration of his element in UCC.

The enrichment verified for Fe is preferably associated to the dolomite and ferruginous itabirites (BIF) geological units. In the Gandarela Formation, the predominant geological unit in Bule Stream, occurs significant itabirite levels associated with dolomite (DNPM, 1986). There is also the presence of ferruginous dolomite Cauê Formation, which is basically composed of dolomite, maghemite and tremolite (Neri et al., 2013).

The high Mn content in the analyzed samples compared to UCC should be related to the presence of this element in high concentrations in dolomites and in some iron formations of the QF. The Gandarela Formation presents high Mn content associated with ferruginous dolomites (Monteiro, 2005; Carvalho Filho et al., 2011).

In Bule River sediments, the average Ti concentration is almost the same estimated for the UCC with an only point enrichment in a tributary of the main stream (T1). Titanium is a chalcophile element, which is associated with Cu and Zn sulfides (Krauskopf and Bird, 1995). Its behavior could be linked to the Fe behavior, which also has low chemical mobility in tropical environments (Cornu et al., 1999). These features may also explain the Ti behavior in the study area. Titanium reaches high concentrations when BIFs are present and should be related to secondary minerals formation (weathering).

Some geochemical characteristics of secondary environment can justify the enrichment of Zn and Cu in the study area. Considering the overall environmental conditions of Brazilian soils, trace elements, such as Cu and Zn, are associated directly with Fe, especially in the itabirites and their weathering products. This fact could be due to the high reactivity of itabirites to intense hydrothermal process observed in the QF region, generating sulfide minerals (sphalerite for Zn and chalcopyrite for Cu) as product (Ferreira et al., 1994; Oliveira et al., 2000; Rosière and Chemale Jr, 2013). Consequently, the weathering products have significant Zn and Cu content. Several authors point out that the Fe oxides/hydroxides present in the soil are direct sources of those trace elements (Tardy, 1997; Oliveira et al., 2000).

Lead bioavailability in secondary environment is closely linked to mineral species: it is high in the carbonates, medium in oxides/hydroxides and low in sulfides (Bosso and Enzweiler, 2008). Lead has low mobility and also displays the ability to form complexes with organic matter, oxides and clay minerals (Wedepohl, 1978; Costa, 2001). Such as Zn and Cu, Pb may also be related to Fe in the study area, since it is found in the itabirites composition (hydrothermal process), in some volcanic/plutonic rocks or adsorbed in oxides/hydroxides as well. These characteristics may explain the abrupt decrease of the Pb concentration in P5.

Some elements display punctual enrichment, such as Ca, enriched in downstream of the Bule Stream (P6 sampling point) if compared to the concentration of UCC, possibly due to the dolomite exploitation in that part of the stream. Titanium (T1 and T2) and Zn (T2) also have enrichment peaks, but with low difference in concentrations compared to UCC.

The comparison of Ca and Mg contents with the respective UCC concentrations allows understanding some geochemical characteristics of the Bule Stream sediments. Calcium and Mg are present in weathering resistant mineralogical phases, mainly dolomite. These elements depletion is given by other more susceptible weathering mineral phases, like other carbonates and silicates, where those elements are easily dissolved by the water.

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Tab. 1. Results obtained by pXRF from the sediment samples and some statistical parameters of the data set. Legend: UCC = average concentration of the element in the Earth's upper crust (Wedepohl, 1995); SH – springhead; T – tributary and; P - sampling point on the principal river channel.

	Coordenates		**Major elements (%)**						**Trace elements (mg kg^{-1})**						
Sampling Stations	**(UTM)**	**pH**	**Al**	**Fe**	**Ca**	**Mg**	**Mn**	**Ti**	**Cu**	**Zn**	**Pb**	**As**	**Cr**	**Sb**	**Sr**
SH	637639 / 7736694	6.0	2.21	4.46	0.69	0	0.32	0.34	25.9	33.1	5.9	7.4	28.1	0	10.1
P1	637331 / 7736933	5.5	1.75	4.34	0.7	0	0.2	0.34	13.8	26.7	9.1	4.2	23.5	0	29.5
T5	637163 / 7737044	5.2	1.68	14.75	0.76	0	1.01	0.13	15.5	46.1	12.1	0	64.3	0	16.3
P2	636421 / 7737041	5.5	1.15	14.63	0.76	1.34	0.56	0.13	34.3	55.3	11.9	10.8	106.2	0	31.8
P2B	634159 / 7736765	5.7	2.28	20.14	0.75	0	0.79	0.2	32.3	51.9	13.2	9.6	95.7	0	31.7
T1	634090 / 7736795	5.7	3.26	13.39	0.83	0	0.59	0.59	26.5	49.6	14.4	12.7	112.4	0	35.2
T2	633898 / 7736597	5.3	3.89	6.36	0.73	0	0.42	0.39	44.1	68.2	13.8	14.2	102.2	0	23.6
T3	633469 / 7736594	6	1.64	15.4	0.78	0	1.36	0.15	19.2	40.1	15.2	4.6	59.1	0	16.5
P3	633605 / 7736595	5.7	3	11.6	0.75	0	0.87	0.35	14.4	36.1	14.4	8.2	39.5	0	12.4
P4	632943 / 7736503	5.7	3.07	17.05	0.75	0	1.07	0.27	11.8	34.4	17.1	11.6	63.3	23.2	8.9
P5	631884 / 7736731	5.5	2.3	24.86	0.79	0	1.03	0.17	17.1	32.1	10.6	11.9	54.7	0	8.6
T4	630437 / 7737095	6.5	1.72	6.3	2.15	0	0.45	0.23	11.1	27.4	0	5.5	38.2	0	10.5
P6	630487 / 7736927	6.0	0.85	8.82	10.24	1.34	0.61	0.11	8.2	28.6	0	0	35.1	0	12.5
UCC		**-**	**2.21**	**4.46**	**0.69**	**0**	**0.32**	**0.34**	**25.9**	**33.1**	**5.9**	**7.4**	**28.1**	**0**	**10.1**

		Major elements (%)						**Trace elements (mg kg^{-1})**						
Statistical parameters	**pH**	**Al**	**Fe**	**Ca**	**Mg**	**Mn**	**Ti**	**Cu**	**Zn**	**Pb**	**As**	**Cr**	**Sb**	**Sr**
Mean	5.7	2.22	12.47	1.59	0.21	0.71	0.26	20.93	40.68	10.57	7.75	62.92	1.77	19.05
Median	5.7	2.21	13.39	0.76	0.00	0.61	0.23	17.1	36.1	12.2	8.20	59.3	0.00	16.3
Minimum	5.2	0.85	4.34	0.69	0.00	0.2	0.11	8.1	26.7	0.00	0.00	23.1	0.00	8.6
Maximum	6.5	3.89	24.86	10.24	1.34	1.36	0.59	44.2	68.2	17.1	14.2	112.1	23.2	35.2

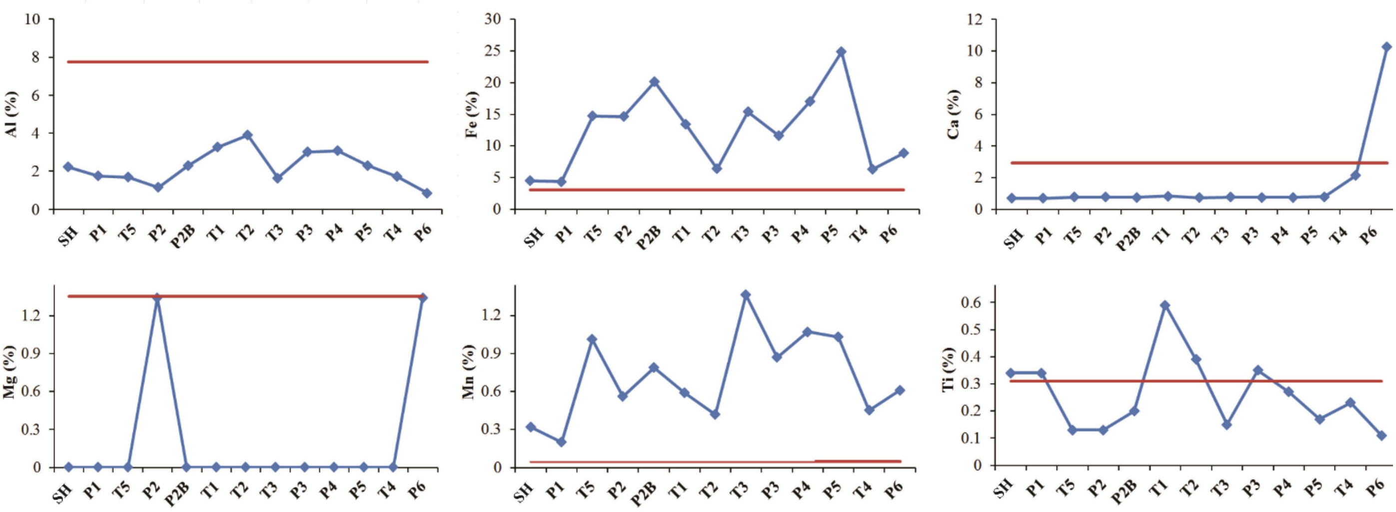

Fig. 4. Major elements distribution along the Bule Stream and its tributaries. The red line represents UCC = average concentration of the element in the Earth's upper crust (Wedepohl, 1995) and the blue line represents the concentration of the element at the sampling point. Legend: SH – springhead; T - tributary and; P - sampling point on the principal river channel.

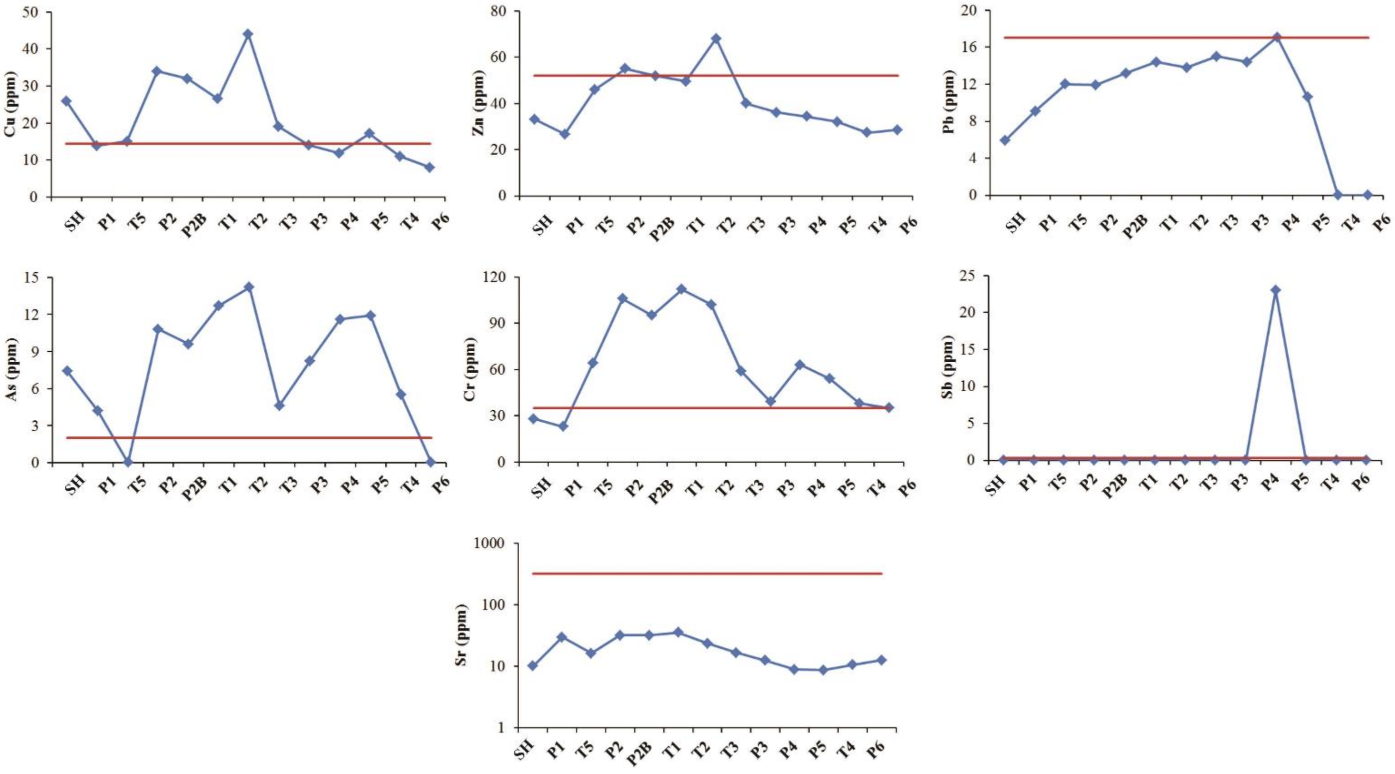

Fig. 5. Trace metals concentrations along the Bule Stream and its tributaries. The red line represents UCC = average concentration of the element in the Earth's upper crust (Wedepohl, 1995) while the blue line prepresents the concentration of the element at the sampling point. Lagend: SH - springhead, T - tributary and; P - sampling point on the principal river channel.

All types of rocks, mainly mafic and ultramafic rocks have significant Cr concentrations. This element has low mobility in the secondary environment since its mineral species (chromite) is resistant to weathering, and to be easily absorbed by Fe and Al oxides/hydroxides in acidic to neutral conditions (Singh and Gilkes, 1991; McLean et al., 1992; Warren and Haak, 2001). Therefore, these attributes make Cr concentrations higher than UCC, in most of the sampling stations (T5, P2, T1, T2, T3, P3, P4, P5 and T4).

Regarding the pH range of the Bule Stream, it could be inferred that the As enrichment in the sediments originated from the solubilized sulfide minerals in the weathered rocks and soils. The enrichment of As may also have resulted from ion exchange, from Fe and Mn oxides/hydroxides, clay minerals and organic matter (Raiswell and Canfield, 1998; Carvalho, 1995; Borba and Figueiredo, 2004). In addition, significant As concentrations are found in common minerals from the study region, like magnetite, ilmenite and also arsenopyrite (Costa, 2001).

Due to the sulfide occurrence in the springhead area of the Bule Hill stream, with Sb in its mineralogical composition, it was expected to found high concentrations of Sb in the sediment. Nevertheless, Sb was above the detection limit of the pXRF only in one station (P4), where its concentration was higher than the UCC (23 ppm).

Sr is an element that has high mobility in all geological environments and sometimes is associated with Ca, especially in carbonate rocks. Due to the equal ionic radii, Sr can replace Ca in carbonate minerals and Ba in apatite (Faure, 1986; Carvalho, 1995), common minerals found in the geological units of the study area (accessory minerals, mainly of itabirites). Comparing the concentrations of Sr in the study area with UCC, this element presents the highest value among the depleted analyzed elements (16 times smaller than UCC). This basically reflects its relative solubility and allows to deduce that the study region has maturity of weathering processes (Lapworth et al., 2012).

Indeed, the occurrence of metals could be related to the proximity of an ore sulfide deposit: trace metal content should decrease downstream from a mine or an ore deposit due to the "dilution effect" in the sediment (Bradley and Lewin, 1982; Jain et. al., 2005). It is believed that the occurrence of the sulfide deposit would be upstream of the watershed due to the concentrations found in the analyzes.

Finally, considering that the study area has a sulfide mineralization, it could be possible that the pH in the Bule Stream may be connected to pyrite oxidation process in the supergene environment. This process releases hydrogen ions in surface water and groundwater, causing pH decrease (Hem, 1985; Eary, 1999). Figure 6 presents the pH along the Bule Stream and its tributaries where the pH values ranged from 5.2 to 6.5, revealing the occurrence of weakly acid water. The sampling stations T5 and T2 have the lowest pH values, 5.2 and 5.3, respectively. By contrast the T4 has the highest value (6.5).

The slightly acidic pH of the study area does not have such a high potential for leaching geological materials, such as acid mine drainage (pH as low as 3.2; Campaner et al., 2014), originating from sulfide deposits (Christensen et al., 1996; Skousen et al., 1998; Shu et al., 2001). The pH seems to exert influence on trace metals behavior in the water-sediment system along the Bule Stream, as it is possible to observe in Figure 7. The trace metals show slight tendency of lower concentrations in higher pH values and higher concentrations in lower pH values. This observation reinforces the hypothesis that some processes triggered by pH variations, as hydrolysis and adsorption reactions are important for trace metals availability in that environment (Krauskopf and Bird, 1995; Drever, 1997).

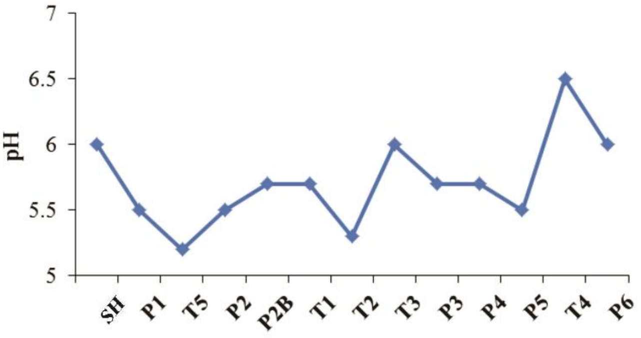

Fig. 6. pH values distribution along the sampling points in Bule Stream and its tributaries. Legend: Springhead (SH), T - tributary (or T) and P - sampling point on the principal river channel.

4.2 Correlation analysis of geochemical data

The highly significant correlations ($p < 0.01$) were obtained between: Al and Ti; Al and As, Fe and Mn; Mn and Pb; Cu and Zn; Cu and As; Cu and Cr; Zn and Cr and; As and Cr (Table 2; Fig. 8). Some of these trends are shown in Fig. 8.

The correlation between Al and Ti may reflect supergene processes, like weathering of regional rocks, mainly laterization processes. These elements, together with Fe and Mn, are responsible for > 90 % of laterites composition (Tardy, 1997). The correlation between Al and As can be also explained by supergene processes, but in this case, for the adsorption process of the As by clay minerals.

Arsenic, depending on the pH and Eh conditions of the aqueous environment, can form complexes, especially As^{5+}, and this specie can form inner sphere connection with clay minerals (Raiswell and Canfield, 1998; Vasconcelos et al., 2012). This may justify the correlation between Al and As.

The correlation between Fe and Mn is noticeable since these elements form large part of the sediments in the region: Fe from the itabirites and Mn related to hydrothermal processes on the rocks of the studied area. As mentioned before, the itabirites are reactive lithotypes to hydrothermal fluids, then, Fe and Mn can occur together in the endogenous environment, which explains the presence of these elements in weathering products (soil and sediment) on the geological units of the region (Rosiere and Chemale Jr, 2000; Robb, 2005).

The correlation between Mn and Pb should be also related to supergene processes. In addition, Mn can form oxide/hydroxides which can adsorb or co-precipitate with

Pb and other metals in its amorphous structure. Furthermore, according to Guimarães (1934), Mn and Pb are part, even if small, of the mineralization composition, as major phases of oxide and sulfide, respectively.

The correlation between Cu and Zn and between Cu and As should be due to its affinity for the sulfide phases, the main components of the mineralized zone (sphalerite for Zn, chalcopyrite and covellite for Cu and arsenopyrite for As; Guimarães, 1934). Nevertheless, this correlation should also represent the presence of those elements in exchange sites available in the catchment oxides/hydroxides, clay minerals and organic matter (Yariv and Cross, 1979; Raiswell and Canfield, 1998).

The good correlations of Cr with Zn and As represent an atypical case among the elements correlations. However, the relationship of Cr with chalcophile elements may reflect the influence of hydrothermal processes in shear zones between the units of the Rio das Velhas Supergroup, which have ultramafic rocks with significant Cr content (Nova Lima Group) (Fernandes et al., 2018), and units of the Minas Supergroup (supracrustal sequences).

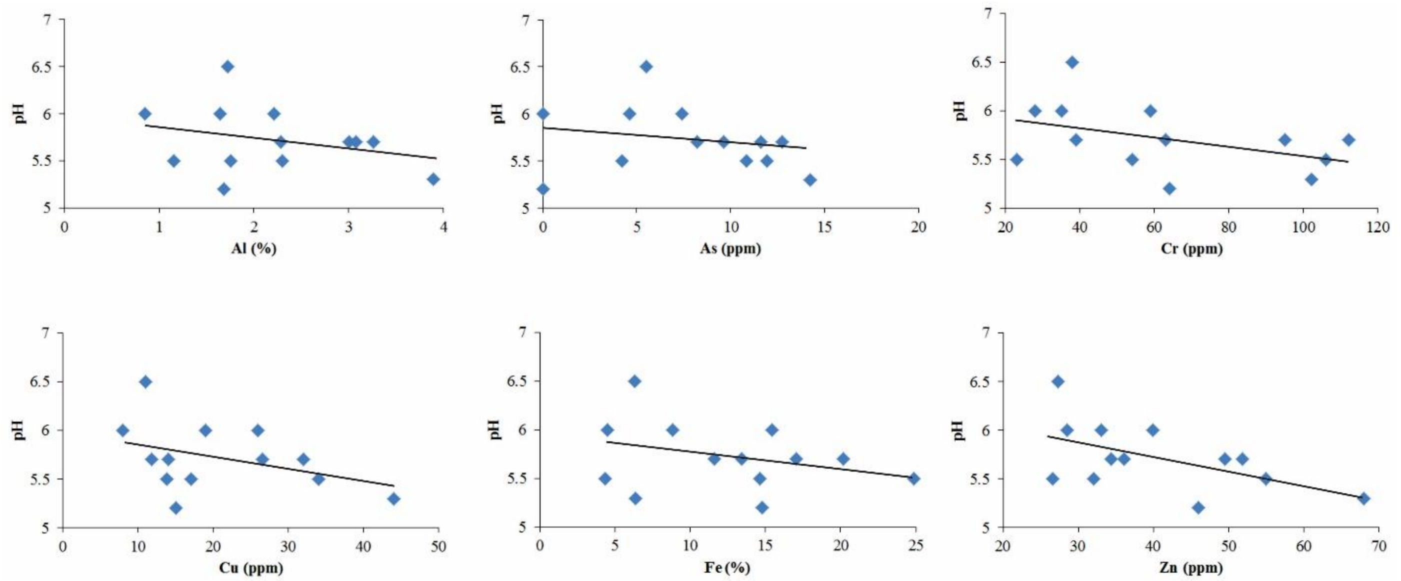

Fig. 7. Trace element concentrations distribution according to pH along the sampling stations in Bule Stream and its tributaries.

Tab. 2. Results obtained from Spearman's correlations between the analyzed elements ($p < 0.01$).

	Al	Fe	Ca	Mg	Mn	Ti	Cu	Zn	Pb	As	Cr	Sb
Al												
Fe	0.08											
Ca	-0.37	0.27										
Mg	-0.63	-0.06	0.37									
Mn	-0.03	**0.85**	0.36	-0.11								
Ti	**0.84**	-0.39	-0.47	-0.55	-0.40							
Cu	0.31	0.19	-0.34	-0.06	-0.17	0.25						
Zn	0.27	0.36	-0.16	0.06	0.13	0.10	**0.84**					
Pb	0.51	0.51	-0.18	-0.37	**0.61**	0.33	0.31	0.56				
As	**0.78**	0.29	-0.14	-0.20	0.00	0.55	**0.60**	0.52	0.45			
Cr	0.32	0.51	0.14	0.06	0.24	0.07	**0.68**	**0.89**	0.55	**0.62**		
Sb	0.31	0.31	-0.16	-0.12	0.39	0.08	-0.31	-0.08	0.46	0.23	0.08	
Sr	-0.07	-0.09	-0.02	0.23	-0.31	0.10	0.55	0.57	0.18	0.10	0.55	-0.39

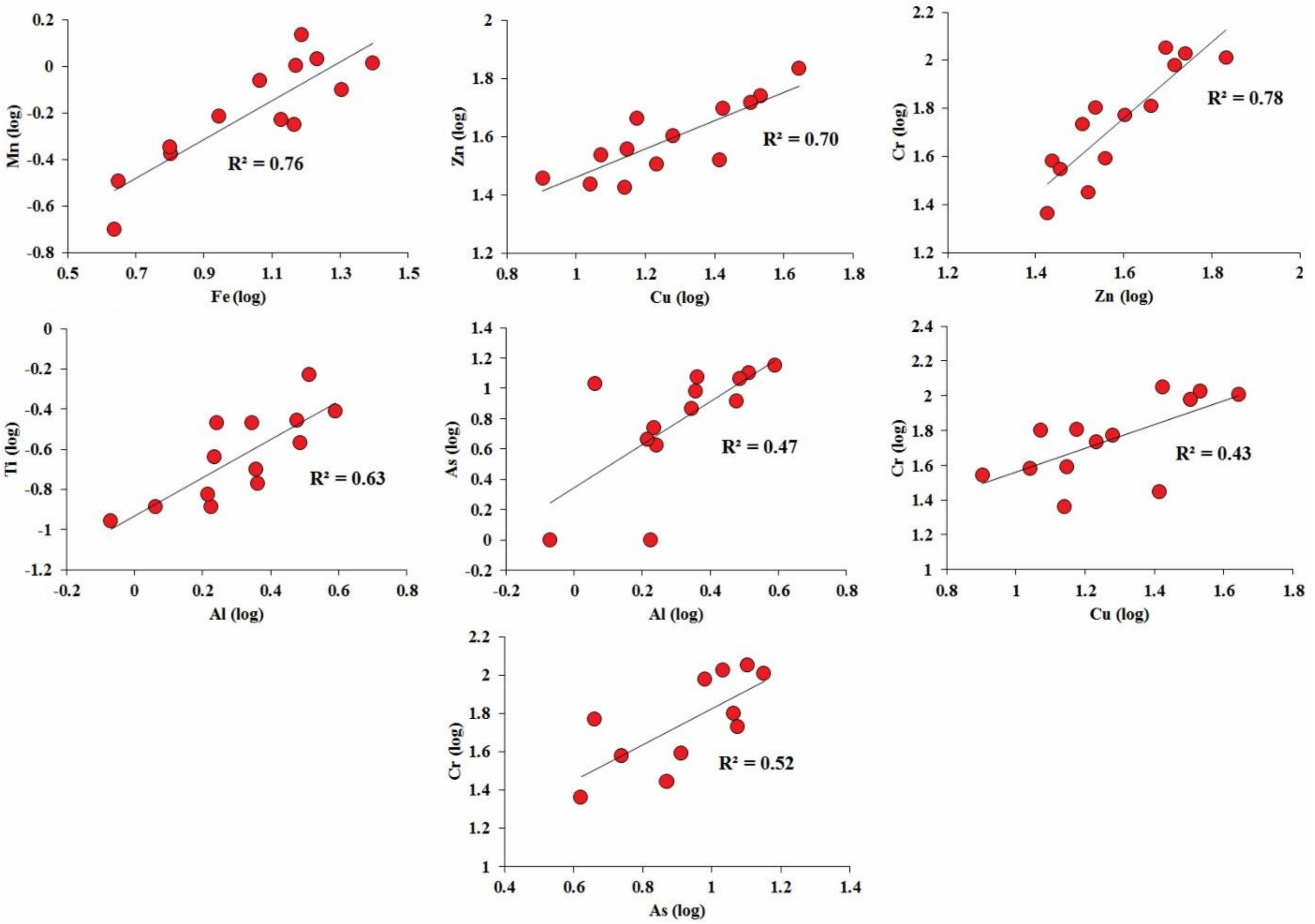

Fig. 8. Biplots representing the best correlations between the elements, for the analyzed sediment samples. Values are logarithmic.

4.3 Enrichment Factor

The enrichment factor equation was applied to identify the main metal conveyor in each sampling station (Fig. 9).

It may be noted that the metals carriers considered in this study predominate according to the sampling stations. Then, Al, representing clay minerals, is the most representative metal carrier on P2 and P6, highlighting its EF values in P2 for Zn, Sr, Cu, As and Cr, reaching the 3 value, which is considered a moderate enrichment. The predominance of Al as the main carrier in P2 may be due to the presence of waterfalls where the high energy increases the erosion of aluminous metasediments near the mineralized zone, which justifies the significant values of EF for this sampling station. On the other hand, the predominance of Al in P6 should be due to the influence of the debouchment area of the Bule Stream to Soledade dam, which has great accumulation of aluminous sediments.

The normalizer Fe + Mn, representing the oxides and hydroxides, is seen as the main carrier in the springhead part of the stream (SH and P1) and one of its tributaries (T4), with moderate enrichment (EF > 2) to As, Cu and Zn. For the SH sample station, the carbonate matrix (Ca + Mg) has EF values close to Fe + Mn values, especially for As, Cu, Pb and Cr. These values can be due to either the mineralization, which has dolomite as host rock, and Fe and Mn oxides/hydroxides, which can be hydrothermal products or have as source the itabirite present in the same area. In contrast, Zn, which has great affinity to carbonate rocks, displays in the SH sample station the highest value of EF for Fe + Mn (the highest one among all the sampled points; EF > 4). Which could be explained by the affinity of this metal also for Fe and Mn oxides/hydroxides (Rose et al., 1979; Yariv and Cross, 1979). This information suggests that Zn has greater dispersion in secondary environment compared to other analyzed metals.

In the other sampling stations, namely, T5, P2B, T1, T2, T3, P3, P4 and P5, the main trace metals carrier is the carbonate matrix (Ca + Mg).

The enrichment factor for Sb was only calculated for the station P4, where the concentration of this element was above the detection limit of the method. The carbonate phase (Ca + Mg) is the main carrier of Sb, getting the highest EF value of the study area among all normalizers (> 30). The EF values for Fe + Mn and Al for Sb also have their highest values for the P4, showing significant enrichment (> 9). Such EF values can corroborate future studies to characterize a new exploration target for Bule hill and surroundings.

Carbonates also remain as the predominant carrier matrix when mean FE values are analyzed in all sampling stations for each normalizer (Fig. 10). The EF average values found in the region for both Al and Fe + Mn are all less than 2, which does not characterize enrichment. Considering Ca + Mg for As, the results showed more significant EF values, but little above 2, which can be considered a moderate enrichment.

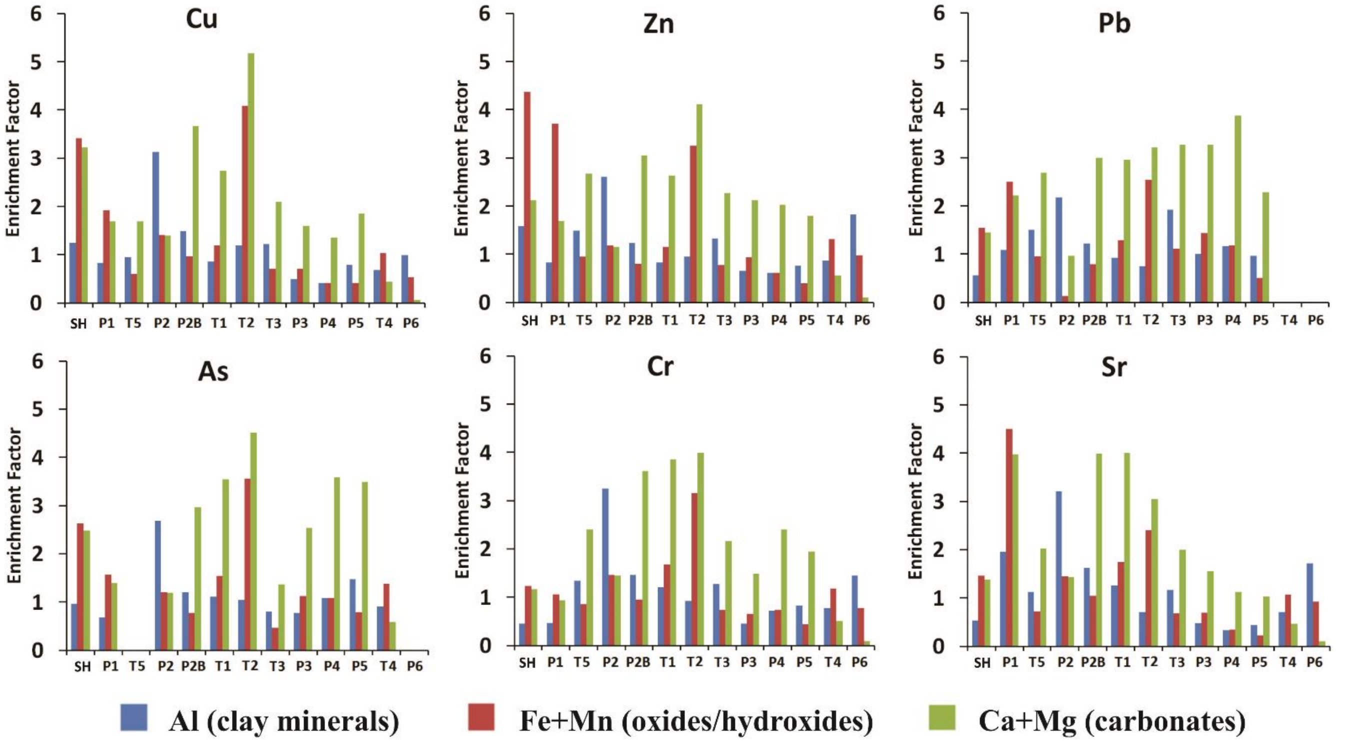

Fig. 9. Enrichment factor of trace metals for each chosen normalizer along the Bule stream and its tributaries. Legend: SH – Springhead; T - tributary and; P - sampling point on the principal river channel.

In general, there is a predominance of Ca + Mg (carbonates) as the main trace metal carrier in the study area, as shown by the higher values of EF in most stations for all metals (Fig. 5) and the mean FE values for metals of all the analyzed stations (Fig. 6). In addition, the carbonate matrix itself should be naturally enriched in metals, since the carbonate rocks are reactive to hydrothermal processes, which are profuse in the study area (as evidenced by the sulfide occurrence of the Bule Hill, the occurrences of imperial topaz and gold at Bico de Pedra area, less than 3 km from the study area), as well as the structural features for fluid percolation (Fraga, 1992; Borba, 1998).

5 Conclusion

The sulfide occurrence in Bule Hill is an important record of mineral potential from the QF, even if this is one of the largest and most studied metallogenetic provinces on the planet. In this sense, this study showed that pXRF is a useful tool and has the potential to be a common tool due to its ease of use.

The main feature of pXRF is the portability; the device was easy and effective to reproduce the results, increasing the versatility both in field and laboratory, since its response is given in real time and with good accessibility. The conclusions about the use of pXRF are: 1) reduction of costs with laboratories specialized in chemical analysis; 2) easy handling and transport; 3) the immediate result and; 4) data reliability compared to laboratory analysis (under a good assessment by quality assurance/quality control QA/QC). This tool can be useful mainly in the prospecting projects at their beginning, in order to select mineralizing favorable areas with high metals concentrations. Nevertheless, it is not recommended the full replacement of the laboratory chemical analysis by the pXRF. The pXRF is seen as the primary analysis or a complementary analysis, while laboratory analyses still provide better quality controls, especially regarding precision and accuracy.

Care and proper precautions must to be taken into consideration when handling the pXRF during field-work as the radioactive loads supplied by the tool poses a threat to human health.

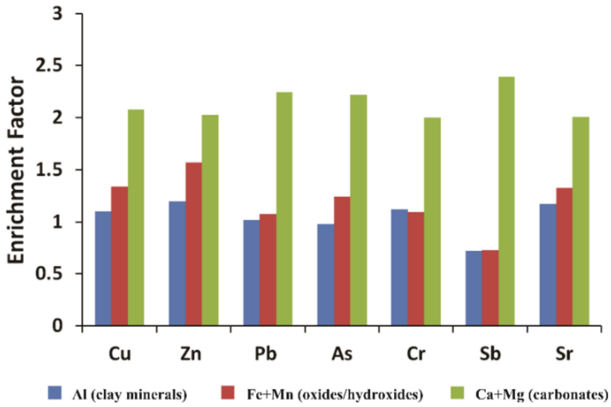

Fig. 10. Average Enrichment Factor values of trace metals in Bule Stream for each chosen normalizer.

Based on the statistical results and the comparison of the obtained data with the average concentration of the elements in the Earth's upper crust (UCC), it can be concluded that the studied region: has an intense weathering process, leaching elements of high mobility, such as Ca, Mg and Sr and; displays developed soils, which justifies the low Al content and high concentrations of Fe and Mn (laterization process) due to the geological context.

Regarding the EF values, Fe + Mn has the most effect in SH, P1 and T2, as these sediments are the most Fe-poor. It is thus normal that EF normalized to the average Fe + Mn is the highest for these samples. The very high amount of Ca in SH (and in a lesser extent in P2) and the very high amount of Mg in T4 strongly drive up the average Ca + Mg value, which in turn explains why the enrichment factors are higher using Ca + Mg as normalizer in all samples except in SH, T4 and P2. The results of this work suggest that the Bule Stream region has main metals carrier the carbonate mineral phase, since this lithotype may have naturally high levels of trace metals, due to its high reactivity with hydrothermal processes.

Acknowledgments

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Reference

Almeida, F.F.M., 1977. O Cráton do São Francisco. Revista Brasileira de Geociências 7(4), 349-364.

Audry, S., Schäfer, J., Blanc G., Jouanneau, J.M., 2004. Fifty-year sedimentary record of heavy-metal pollution (Cd, Zn, Cu, Pb) in Lot River reservoirs (France). Environmental Pollution 132, 413-426. https://doi.org/10.1016/j.envpol.2004.05.025

Baltazar, O.F., Zucchetti, M., 2007. Lithofacies associations and structural evolution of the Archean Rio das Velhas greenstone belt, Quadrilátero Ferrífero, Brazil: A review of the setting of gold deposits. Ore Geology Reviews 32, 471-499. https://doi.org/ 10.1016/j.oregeorev. 2005.03.021

Bernick, M.B., Kalnicky, D.J., Prince, G., Singhvi, R., 1995. Results of field-portable X-ray fluorescence analysis of metal contaminants in soil and sediment. Journal of Hazardous Materials 43(1-2), 101-110. https://doi.org/10.1016/0304-3894(95)00030-X

Bleicher, L., Sasaki, J.M., 2000. Introdução à difração de raios-X em cristais. Universidade Federal do Ceará, Fortaleza, 255 p.

Borba, R.P., Figueiredo, B.R., 2004. A influência das condições geoquímicas na oxidação da arsenopirita e na mobilidade do arsênio em ambientes superficiais tropicais. Brazilian Journal of Geology 34(4), 489-500. https://doi.org/10.25249/0375-7536.2004344489500

Borba, R.P., 1998. O magmatismo ácido e sua relação com a mineralização aurífera de Bico de Pedra, greenstone belt Rio das Velhas, Quadrilátero Ferrífero, Minas Gerais, Brasil. PhD Thesis, Universidade de Campinas, São Paulo, Brazil, 162p.

Bosso, S.T., Enzweiler, J., 2008. Ensaios para determinar a (bio) disponibilidade de chumbo em solos contaminados: revisão. Química Nova 31(2), 394-400.

Boumans, P., 1991. Total reflection X-ray fluorescence spectrometry. Proc. of the Third Workshop on TXRF, Vienna, 15-17 May 1990. Spectrochim. Acta, Oxford, 46B, p. 1313.

Bowell, R.J., Egorova, L., Gurevick, D., Sedov, V., Holwell, D.A., Mikhailov, A., Kordi, P., 2012. Grass roots exploration in remote areas: An example from the Kuene region, Namibia. CIM Journal 3, 33–46.

Bradley, S.B., Lewin, J., 1982. Transport of heavy metals on suspended sediments under high flow conditions in a mineralised region of wales. Environmental Pollution Series B, Chemical and Physical 4(4), 257–267. https://doi.org/10.1016/0143-148X(82)90012-X

Campaner, V.P., Luiz-Silva, W., Machado, W., 2014. Geochemistry of acid mine drainage from a coal mining area and processes controlling metal attenuation in stream waters, southern Brazil. Anais da Academia Brasileira de Ciências 86(2), 539-554. http://dx.doi.org/10.1590/0001-37652014113712

Carvalho Filho, A., Curi, N., Marques, J.J.G.S.M., Shinzato, E., Freitas, D.A.F., Jesus, E.A., Massahud, R.T.R., 2011. Óxidos de manganês em solos do Quadrilátero Ferrífero (MG). Revista Brasileira de Ciências do Solo 35(3), 793-804.

Carvalho, I.G., 1995. Fundamentos da geoquímica dos processos exógenos. Bureau Gráfica, Salvador, 176 p.

Chemale Jr, F., Rosière, C.A., Endo, I., 1994. The tectonic evolution of the QuadriláteroFerrífero, Minas Gerais, Brazil. Precambrian Research 65(1-4), 25-54.

Christensen, B., Laake, M., Lien, T., 1996. Treatment of acid mine water by sulphate-reducing bacteria: Results from a bench scale experiment. Water Research 30(7), 1617-1629.

Cornu, S., Lucas, Y., Lebon, E., Ambrosi, J.P., Luizão, F., Rouiller, J., Bonnay, M., Colin, N., 1999. Evidence of titanium mobility in soil profile Manaus, central Amazonia. Geoderma 91, 281-295.

Costa, A.T., 2001. Geoquímica das águas e dos sedimentos da bacia do rio Gualaxo do Norte, leste-sudeste do Quadrilátero Ferrífero (MG): estudo de uma área afetada por atividades de extração mineral. MsD Thesis, Universidade Federal de Ouro Preto, Minas Gerais, Brazil, 146p.

DNPM - Departamento Nacional de Produção Mineral. 2016. Desenvolvimento Geoeconômico de Minas Gerais. Documento Básico, Publicação Especial nº 5, Ministério de Minas e Energia, DNPM – 3º Distrito Centro-Sul.

DNPM – Departamento Nacional de Produção Mineral. 1986. Principais Depósitos Minerais do Brasil. Brasília.

Dorr, J.V.N., 1969. Physiographic, stratigraphic and structural development of the Quadrilátero Ferrífero, Minas Gerais, Brazil. U.S. Geological Survey Prof. Paper 641-A, 1-110.

Drever, J.I., 1997. The geochemistry of natural waters. Prentice Hall, New Jersey, 275 p.

Eary, L.E., 1999. Geochemical and equilibrium trends in mine pit lakes. Applied Geochemistry 14, 963-987.

Faure, G., 1986. Principles of isotope geology. Wiley, New York. 286 p.

Fernandes, V.M.T., Evangelista, H.J., Queiroga, G.N., 2018. Pedogeochemistry of ultramafic soils from the Córrego dos Boiadeiros Body, Quadrilátero Ferrífero, Minas Gerais, Brazil. REM - International Engineering Journal 71(4), 571-578. http://dx.doi.org/10.1590/0370-44672017710180

Ferreira, S.A.D., Santana, D.P., Fabris, J.D., Curi, N., Nunes Filho, E., Coey, J.M.D., 1994. Relações entre magnetização, elementos traços e litologia de duas sequências de solos do Estado de Minas Gerais. Revista Brasileira de Ciências do Solo 18(2), 167-174.

Fraga, L.M.B., 1992. Estrutura da região do Morro do Bule, Sinclinal Dom Bosco, Quadrilátero Ferrífero - MG. Master's Dissertation, Federal University of Rio de Janeiro, Rio de Janeiro, Brazil, 130 p.

Grunsky, E.C., 2010. The interpretation of geochemical survey data. Geochemistry: Exploration, Environment, Analysis 10, 27-74. https://doi.org/10.1144/1467-7873/09-210

Guimarães D. 1934. Jazida de Minério Sulfurado do Morro do Bule, Hargreaves, Ouro Preto, MG. Serviço Geológico e Mineralógico do Brasil, Technical Report.

Hem, J.D., 1985. Study and interpretation of the chemical characteristics of natural water. U.S Geological Survey Water-Supply Paper 2254.

IAEA - International Atomic Energy Agency. 1999. Industrial and environmental applications of nuclear analytical techniques. Report of a workshop held in Vienna, 7-11 September 1998, IAEA, VIENNA, 1999 IAEA-TECDOC-1121. ISSN 1011-4289.

Jain, C.K., Singhal, D.C., Sharma, M.K., 2005. Metal Pollution Assessment of Sediment and Water in the River Hindon, India. Environmental Monitoring and Assessment 105(1-3), 193–207. https://doi.org/10.1007/s10661-005-3498-z

Jenkins, R., 1988. X-Ray Fluorescence Spectrometry. John Wiley & Sons, New York, 1988. ISBN 0-471-83675-3

Kalnicky, D.J., Singhvi, R., 2001. Field portable XRF analysis of environmental samples. Journal of Hazardous Materials 83(1-2), 93-122.

Kerstern, M., Förstner, U., 1995. Speciation of trace metals in sediments. In: Ure, A (ed) Chemical Speciation in the Environment. Blackie Academic & Professional, London, pp 301-321.

Krauskopf, K.B., Bird, D.K., 1995. Introduction to Geochemistry. WCB McGraw-Hill, Boston, 640p.

Lapworth, D.J., Knights, K.V., Key, R.M., Johnson, C.C., Ayoade, E., Adekanmi, M.A., Arisekola, T.M., Okunlola, O.A., Backman, B., Eklund, M., Everett, P.A., Lister, R.T., Ridgway, J., Watts, M.J., Kemp, S.J., Pitfield, P.E.J., 2012. Geochemical mapping using stream sediments in west-central Nigeria: Implications for environmental studies and mineral exploration in West Africa. Applied Geochemistry 27(6), 1035-1052. https://doi.org/10.1016/j.apgeochem.2012.02.023

Levinson, A.A., 1974. Introduction to exploration geochemistry. Maywood, Applied Publishing, 605p.

McLean, J.E., Bledsoe, B.E., Sourcebook, E.E.A. 1992. Behavior of metals in soils (EPA/540/S-92/018). U.S. Environmental Protection Agency, Washington, D.C.

Monteiro, E.A., 2005. Projeto APA Sul RMBH: Recursos Minerais. In: Silva, S.L. (ed) Projeto APA Sul RMBH: Estudos do meio físico. CEMAD/CPRM, Belo Horizonte, 46-50.

Nagata, N., Bueno, M.I.M.S., Peralta-Zamora, P.G., 2001. Métodos Matemáticos para Correção de Interferências Espectrais e Efeitos Interelementos na Análise Quantitativa por Fluorescência de Raios-X. Química Nova 24(4), 531-539.

Neri, M.E.N.V., Rosière, C.A., Lana, C.C., 2013. Supergrupo Minas na Serra de Bom Sucesso, extremo sudoeste do Quadrilátero Ferrífero-MG: petrografia, geoquímica e isótopos de U-Pb. Geologia USP. Série Científica 13(2), 175-202.

Noce, C.M., 2000. Geochronology of the Quadrilátero Ferrífero: a review. Geonomos 7, 15–23.

Oliveira, T.S., Fontes, M.P., da Costa, L.M., Horn, A.H., 2000. Relationship between magnetization and trace elements content of Brazilian soils from different parent materials. Soil Science 165(10), 825-834.

Pereira, R.M., Santos, R.A., 1983. A ocorrência de scheelita estratiforme de Caeté, MG: base de uma nova interpretação metalogenética para os índices de W, Sb, Hg do Quadrilátero Ferrífero. Mineração e Metalurgia 450, 38-42.

Plourde, A.P., Knight, R.D., Kjarsgaard, B.A., Sharpe, D.R., Lesemann, J.E., 2013. Portable XRF spectrometry of surficial sediments, NTS 75-I, 75-J,75-O, 75-P (Mary Frances Lake – Whitefish Lake – Thelon River area), Northwest Territories. Geological Survey of Canada, Open File 7408.

Radu, T., Diamond, D., 2009. Comparison of soil pollution concentrations determined using AAS and portable XRF techniques. Journal of Hazardous Materials 171(1-3), 1168-1171. https://doi.org/10.1016/j.jhazmat.2009.06.062

Raiswell, R., Canfield, D.E., 1998. Sources of iron for pyrite formation in marine sediments. American Journal of Science 298(3), 219-245. https://doi.org/10.2475/ajs.298.3.219

Reimann, C., Filzmoser, P., Garrett, R.G., Dutter, R., 2008. Statistical Data Analysis Explained. John Wiley & Sons Ltd., Chichester, 322 p.

Reimann, C., MatschullatJ., Birke, M., Salminen, R., 2010. Antimony in the environment: lessons from geochemical mapping. Applied Geochemistry 25(2), 175-198. https://doi.org/10.1016/j.apgeochem.2009.11.011

Ribeiro-Kwitko, R., de Oliveira, C.G., 2004. O depósito aurífero de Antônio Pereira, Quadrilátero ferrífero: condições P-T e natureza dos fluídos mineralizadores. Revista Brasileira de Geociências 34(1),117-126.

Robb, L., 2005. Introduction to Ore-Forming Processes. Blackwell, Oxford, 251p.

Rose, A.W., Hawkes, H.E., Webb, J.S., 1979. Geochemistry in Mineral Exploration. Academic Press, London, 657 p.

Rosière, C. A., Chemale Jr, F., 2013. Itabiritos e minérios de ferro de alto teor do Quadrilátero Ferrífero - uma visão geral e discussão. Geonomos 8(2), 27-43.

Rosière, C.A., Chemale Jr, F., 2000. Brazilian iron formations and their geological setting. Brazilian Journal of Geology 30(2), 274-278. https://doi.org/10.25249/0375-7536.2000302274278

Sarala, P., 2009. New advances in geochemical exploration in glaciated terrain – examples from northern Finland. In: Lentz, D., Thorne, K.G. and Beal, K.-L. (eds.), Proceedings of the 24th International Applied Geochemistry Symposium. Fredericton, New Brunswick, Canada, June 1st-4th, 2009. Volume II. The Association of Applied Geochemistry, 565-567.

Sarala, P., Mäkikyrö, M., 2012. Mobile XRF methods in mineral exploration in glaciated terrain – examples from northern Finland. In: 34th International Geology Congress, Brisbane, Australia, 5-10 Aug 2012. Optical Disc (CD-ROM).

Shu, W.S., Ye, Z.H., Lan, C.Y., Zhang, Z.Q., Wong, M.H., 2001. Acidification of lead/zinc mine tailings and its effect on heavy metal mobility. Environment International 26(5-6), 389-394.

Silva-Filho, E.V., Marques, E.D., Vilaça, M., Gomes, O.V.O., Sanders, C.J., Kutter, V.T., 2014. Distribution of trace metals in stream sediments along the Trans-Amazonian Federal Highway, Pará State, Brazil. Journal of South American Earth Sciences 54, 182-195. https://doi.org/10.1016/j.jsames.2014.04.011

Singh, B., Gilkes, R.J., 1991. Weathering of a chromian muscovite to kaolinite. Clays Clay Minerals Journal 39(6), 571-579. https://doi.org/0.1346/CCMN.1991.0390602

Skoog, D.A., Holler, F.J., Nieman, T.A., 2009. Princípios de Análise Instrumental, 5ª ed. Porto Alegre, Brasil, Bookman. 836p.

Skousen, J., Rose, A., Geidel, G., Foreman, J., Evans, R., Hellier, W., 1998. Handbook of technologies for avoidance and remediation of acid mine drainage. West Virginia University, West Virginia.

Tardy, Y., 1997. Petrology of Laterites and Tropical Soils. Strasbourg, France, 408p.

Taufen, P.M., Marchetto, C.M.L., 1989. Tropical weathering control of Ni, Cu, Co, and platinum group element distributions at the O'Toole Ni-Cu sulphide deposit, Minas Gerais, Brazil. Journal of Geochemical Exploration 32 (1–3), 185-197

Vasconcelos, F.M., Ciminelli, V.S.T., Oliveira, R.P., Silva, R.J., 2012. Determinação da especiação química e potencial de mobilidade do arsênio em sítios de mineração. Geochimica Brasiliensis 18(2), 115-120.

Vial, D.S., Duarte, B.P., Fuzikawa, K., Vieira, M.B.H., 2007. An epigenetic origin for the Passagem de Mariana gold deposit, Quadrilátero Ferrífero, Minas Gerais, Brazil. Ore Geology Reviews, 32(3-4), 469-688. https://doi.org/10.1016/j.oregeorev. 2006.11.006

Warren, L.A., Haack, EA., 2001. Biogeochemical controls on metal behaviour in freshwater environments. Earth-Science Reviews 54, 261-320.

Wedepohl, K.H., 1995. The composition of the continental crust. Geochimica et Cosmochimica Acta 59, 1217–1232.

Wedepohl, K.H., 1978. Handbook of Geochemistry. Springer-Verlag, Berlin.

Weltje, G.J., Tjallingii, R., 2008. Calibration of xrf core scanners for quantitative geochemical logging of sediment cores: Theory and application. Earth and Planetary Science Letters 274(3), 423-438. https://doi.org/10.1016/j.epsl.2008.07.054

Yariv, S., Cross, H., 1979. Geochemistry of Colloids Systems for Earth Scientists. Springer, Berlin.

Yongming, H., Peixuan, D., Junji, C., Posmentier, E., 2006. Multivariate analysis of heavy metal contamination in urban dusts in Xian, central China. Science of Total Environment 355 (1-3), 176-186.

Zucchetti, M., Baltazar, O.F., (Eds.), 1996. Projeto Rio das Velhas - Texto explicativo do mapa geológico integrado, escala 1:100.000. 2ª Ed. Departamento Nacional de Produção Mineral/CPRM - Serviço Geológico do Brasil, Belo Horizonte, Brazil, 121p.