Geochemical mapping based on regularly spaced composite stream sediment samples produced from stored aliquots - State of Paraná pre-Cambrian Shield, Brazil

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RESUMO

Uma coleção de 6.587 amostras de sedimentos fluviais ativos cobrindo cerca de 4.800 km² no Escudo do Paraná, no sul do Brasil, foi usada para produzir 75 amostras compostas, cada uma representando uma célula de 5' x 5'. As amostras originais foram recuperadas dos arquivos do Serviço Geológico do Paraná - MINEROPAR e do Serviço Geológico do Brasil - SGB / CPRM. As amostras compostas foram submetidas a quatro procedimentos analíticos com a determinação de 66 elementos. Os mapas geoquímicos dos elementos isolados, bem como a análise de correlação bivariada, mostraram seis associações entre elementos, cada uma refletindo a herança geoquímica de litologias específicas e pelo menos uma área com alto potencial exploratório, anteriormente desconhecida dada a pequena quantidade de elementos analisados nas amostras originais. Os mapas geoquímicos foram produzidos pela classificação das células (mapas de pixels) ou pela aplicação de interpolação com a mínima curvatura, considerada como o melhor interpolador para a geração dos mapas de isógradas (mapas vetoriais). A comparação entre amostras compostas e originais mostrou que, mesmo com diferentes técnicas analíticas, o teor dos elementos nas amostras compostas é semelhante à média do teor nas amostras originais em cada célula. Os resultados obtidos nos permitem recomendar a adoção deste conjunto de procedimentos em coletas de amostras de sedimentos fluviais cobrindo grandes áreas, com pelo menos três vantagens: (a) eliminar custos de campo recuperando amostras já coletadas e arquivadas, (b) reduzir a quantidade de amostras a serem analisadas e (c) minimizar quaisquer erros de posicionamento das estações de amostragem, coletadas antes do advento do equipamento GPS. A verificação e detalhamento das áreas de interesse evidenciadas por este procedimento podem ser feitas facilmente com a análise das amostras originais ainda armazenadas nas coleções.

Palavras-chave: mapeamento geoquímico, geoquímica multipropósito, amostras compostas

ABSTRACT

A collection of 6,587 active stream sediment samples covering about 4,800 km² in the Paraná Shield, southern Brazil was used to produce 75 composite samples each representing a 5' x 5' cell. The original samples were retrieved from the archives of the Geological Service of Paraná - MINEROPAR and the Geological Service of Brazil - SGB / CPRM. The composite samples were submitted to four analytical methods with the determination of 66 elements. Geochemical maps of the isolated elements along with bivariate correlation analysis showed six associations between elements, each representing specific lithologies and at least one area with high exploratory potential, which was previously unknown given the small amount of elements analyzed in the original samples. The geochemical maps were produced either by cell classification (pixel maps) or by the application of the minimum

curvature interpolation method, considered as the best interpolator for the generation of the isograd maps (vector maps). The comparison between composite and original samples showed that, even with different analytical techniques, the element contents of the composite samples are similar to the average of the contents in the original samples on each cell. The results obtained allow us to recommend the adoption of this set of procedures in stream sediment sample collections covering large areas, with at least three advantages of: (a) eliminating field costs by retrieving already collected and archived samples, (b) reducing the amount of samples to be analyzed and (c) minimize any positioning errors of sampling sites collected before the advent of GPS equipment. The verification and detailing of the areas of interest evidenced by this procedure can be done easily with the analysis of the original samples still stored in the collections.

Keywords: geochemical mapping, multi-purpose geochemistry, composite samples

1. INTRODUCTION

In the State of Paraná, mainly in the pre-Cambrian Shield, mineral exploration surveys were carried out in the 1970s, 1980s and the beginning of the 1990s by many state owned organizations like Departamento Nacional da Produção Mineral (National Department of Mineral Production) DNPM, Serviço Geológico do Brasil (Brazil Geological Survey) CPRM, Petrobrás Mineração S.A. (Petrobras Mining) PETROMISA, Companhia Nacional de Energia Nuclear (Brazilian Nuclear Company) NUCLEBRÁS and Serviço Geológico do Paraná (State of Paraná Geological Survey) MINEROPAR

Despite the large amount of data produced by these surveys at the time, almost all stream sediments samples were analyzed only for Cu, Pb, Zn, Ni, Co, Fe and Mn mostly due to limited analytical techniques. In very restricted areas, Au, F, Mo, Sn and W were also analyzed. After the analytical procedures, the dry pulps (<80 #) were carefully stored. It is important to emphasize that under sub-tropical climate with wet season concentrated on the hot summer, as in the case of the study area, the geochemical processes of mobilization and transport are mainly hydromorphic, making it is quite impossible to find sulfide grains released by exploratory targets in stream sediment samples. Under this regime, the highest contents of almost all elements, are found in the finer grain fractions.

Using this area as a test, Licht and Tarvainen (1996) showed how the integration of old exploration geochemistry data sets may be used to produce maps with multipurpose applications, e.g., mineral exploration, regional planning, identification and management of environmental liabilities and public health risk areas.

According to an international effort to establish global geochemical baselines, the International Union of Geological Sciences (IUGS) constituted the International Geological Correlation Program's (IGCP) Project 259, and published the final report "A Global Geochemical Database for Environmental and Resource Management" containing all field and laboratory protocols to be followed by all countries which wish to adhere to the project. One of the protocols determines that stream sediments samples should represent catchment basins which must be contained on 1°30' square cells composing a global grid (Darnley et al. 1995; Smith et al. 2018).

By applying this general concept, the present research used the retrieval of ordinary stream sediments samples collected by previous surveys and appropriately stored, to produce composite samples representative of 5' side sub-cells which were analyzed for 66 elements. This regular grid covers a large portion of the State of Paraná pre-Cambrian Shield also known as Paraná 1st Plateau (Figure 1).

It is assumed that the analytical results are representative of the whole cell. The results of such new procedures and multi-element analytical techniques which had been applied to the composite samples will be tested and compared to verify its feasibility and reliability.
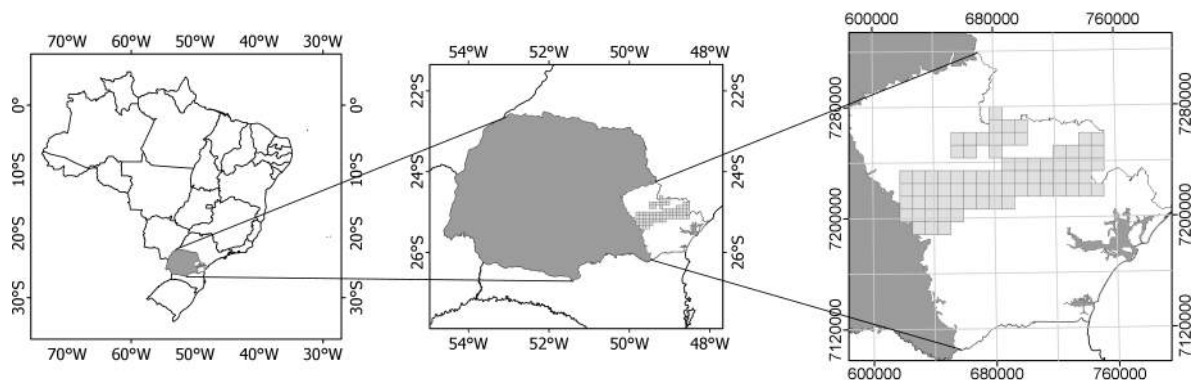
1.1. A BRIEF GEOLOGICAL OVERVIEW

The State of Paraná pre-Cambrian Shield is formed by igneous and metamorphic rocks ranging from Archean to Cambrian, locally covered with volcano-sedimentary sequences, sedimentary rocks and unconsolidated sediments (Figure 2). High grade metamorphic rocks, outcrop in the southeastern portion, and the low grade metamorphic, in the north-northwest portion. In the Proterozoic, Cambrian, and in the early Paleozoic terrains, magmatic events gave rise to granitic intrusions. In the Mesozoic many intrusions of carbonatite, alkaline and basic rocks occurred. In the area covered by the present research, at least five ore types or models are known, (1) Zn-Pb-Cu-Ag-Cd sulfides; (2) REE and F hosted by alkaline rocks and carbonatites; (3) Fluorspar disseminations or veins in

metamorphic limestone *roof-pendants* hosted by the *Três Córregos* granite; (4) Sulfide Au and (5) Pt-Pd in meta-basic or meta-ultrabasic rocks.

In the region there are large tectonic lineaments extending hundreds of kilometers of Brazilian Cycle and even younger, since they affect the granites intruded in this period. The main faults are Northeast transcurrent, typically anastomosed, with movements of the order of hundreds of kilometers that would have been responsible for the development of cataclasites and lenticularization of geological units and the narrow and elongated forms of the sin- and late-tectonic granites which are present in this region (Fiori *et al*. 1984; Fiori 1985).

1.2. THE FORMER GEOCHEMICAL DATABASE

As presented by Licht and Tarvainen (1996), the data base covering the Paraná pre-Cambrian Shield was composed by the integration of geochemical data from 42 surveys. Almost all samples were sieved at <80 mesh (<0.162 mm) and analyzed by atomic absorption after aqua regia digestion. The number of samples and the analyzed elements

in each survey are presented in Tables 1 and 2 and their spatial distribution is shown in Figure 6. A summary of this research may be found in Licht (2018). Even considering these discrepancies it was possible to compare the results and geochemical maps produced with this old geochemical data set with the new multi-element database.

1.3 HYPOTHESIS

The working hypothesis for this research was: would the concept proposed by the IGCP-259 Project for geochemical mapping on a

global scale, be applicable on a much more detailed scale with reliable results?

1.3.1 OBJECTIVES

The main objectives of this research were: (1) to produce a multielement geochemical database of the Pre-Cambrian Shield of Paraná,

applying the concept of the Global Geochemical Reference Network (GGRN) proposed by the IGCP-259. (2) To test the

feasibility of producing a reliable geochemical database using composite samples according to a regular grid, retrieving old stream sediment samples appropriately stored and (3) Is it feasible to apply these procedures in other regions aiming the optimization of financial resources ?

2. MATERIALS AND METHODS

To improve the spatial resolution of the results and the accuracy of their application, the Global Geochemical Reference Network (DARNLEY *et al.* 1995) was divided in 5' ($\approx$ 8 km) side sub-cells. The geographic reference of the original samples and sub-cells was converted to UTM SAD69. Thus geochemical maps are also referred to this coordinate system and datum.

2.1. PREPARATION OF THE COMPOSITE SAMPLES

The selected stream sediments samples, previously collected and stored by MINEROPAR (Figure 3) and SGB/CPRM, had already been disaggregated and sieved to minus 0,162 mm (< 80 mesh) before analysis.

Table 1 - Summary of analytical procedures for integrated stream sediment surveys. Analytical procedures: (1) aqua regia digestion atomic absorption; (2) HNO₃ concentrate and hot digestion/atomic absorption; (3) colorimetry; (4) hydride generation/atomic absorption; (-) not analysed. After Licht & Tarvainen (1996).

Company	Survey	Elements / analytical procedures							
		Cu	**Pb**	**Zn**	**Ni**	**Co**	**Fe**	**Mn**	**As**
Mineropar	Paraiso	(1)	(1)	-	-	-	-	-	-
	Marquês de Abrantes	-	(1)	-	-	-	-	-	-
	Nagib Silva	(1)	(1)	(1)	-	(1)	-	-	-
	Tigre-Betara-Açungui	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(4)
	Formação Agua Clara	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)
	Caçador Jacui	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)
	Barra do Itapirapuã	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(4)
	São Silvestre	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)
	Volta Grande	(1)	(1)	(1)	-	-	(1)	(1)	(4)
	Castro	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(4)
	Antinha	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(4)
	Capivari-Pardo (fill-in)	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(4)
	Canha-Carumbé	-	(1)	-	-	-	-	-	-
	Guaratubinha	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(4)
	Anhangava	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(4)
	Capivara	(1)	(1)	(1)	-	-	(1)	(1)	-
	Santana	(1)	(1)	(1)	-	-	(1)	(1)	-
	Granitos	(1)	(1)	(1)	-	(1)	-	-	(4)
	Capivari-Pardo (regional)	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(4)
DNPM-CPRM	Vale do Ribeira	(2)	(2)	(2)	(2)	(2)	(2)	(2)	-
	Guaratubinha-Piên	(2)	(2)	(2)	(2)	(2)	-	-	(3)
	Castro-Piraí	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(3)
Petromisa	Furnas-Ponta Grossa	(2)	(1)	(1)	(1)	(1)	(1)	(1)	-
	Furnas-Ponta Grossa (fill in)	(2)	(2)	(2)	-	-	-	-	(2)
Total amount in the integrated database		**14,746**	**15,267**	**14,694**	**9,117**	**9,026**	**7,831**	**7,876**	**7,351**

Table 2 - Summary of integrated fluorine stream sediment and pan concentrate surveys. All samples were analysed by alkali fusion/specific ion electrode. After Licht & Tarvainen (1996)

Company	Survey	Type of sample
Mineropar	Paraíso	Pan concentrate
	Cantagalo	Pan concentrate
	Nagib Silva	Stream sediment
	Barra do Itapirapuã	Stream sediment
	Volta Grande	Pan concentrate
	Volta Grande	Stream sediment
	Capivari-Pardo (fill-in)	Pan concentrate
	Canha-Carumbé	Pan concentrate
	Anhangava	Pan concentrate
	Granitos	Pan concentrate
	Capivari Pardo	Pan concentrate
Data in the integrated database		**2,270**

Thus the <80# pulps of the original samples contained in each sub-cell were retrieved from the archives (Figure 3) and an almost similar portion of each put into a numbered plastic container, thus setting the composite sample of each sub-cell (Figure 4). During preparation of the composite samples, proper procedures were adopted to minimize sample contamination such as having the exhaust fan turned on and carefully cleaning the workbench (Figure 5).

The set of original samples of each sub-cell was then homogenized, passing four times on a stainless-steel Jones riffle splitter, being one fourth of it sent to the laboratory. Following this procedure, 9,030 original samples were handled, giving rise to 93 composite samples (Figure 6). In order to present geochemical maps with geographic continuity allowing correlations and cause-effect conclusions related to the geological landscape, the isolated cells were disregarded, being selected only 75 sub-cells which were produced using 7,428 original samples (Figure 6 right). Thus, this is the set of geochemical data with which all data treatments, correlations, maps and conclusions will be made in this article.

Figure 3
The Mineropar storage site of the stream sediment samples collected by old geochemical surveys (left); one box containing the envelopes into which the pulps (< 80#) of the original samples are stored, and which were used to produce the composite samples (right).
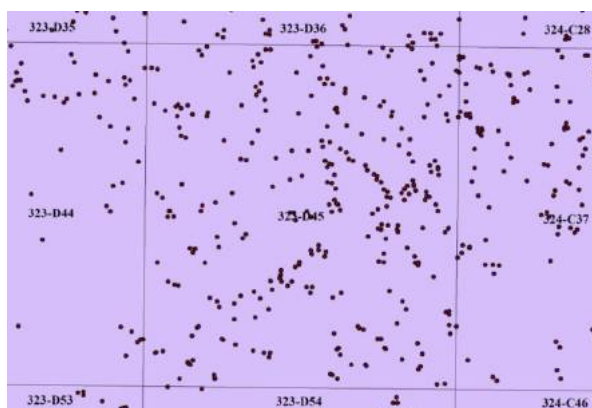
Figure 4
Position of the original stream sediment samples contained on the sub-cell 323-045.

Figure 5
Preparation of composite samples by mixing together a portion of the stream sediment samples contained on each sub-cell (Mineropar laboratory).

2.2 Analytical procedures

All chemical analyses were made at a Brazilian commercial laboratory under contract with SGB-CPRM. There, the composite samples were sieved to <150#, and analyzed for the elements presented in Table 3. Even considering the analytical package composed by four specific techniques, combined in order to obtain the great amount of valid values as possible, some elements as Ag, B, Pd, Re and Se have had all values below the lower detection limit and were disregarded. For the other elements, except Ge, the results below the lower detection limit were multiplied by 0.5 and those above the higher detection limit by 1.5, as used by SGB/CPRM and MINEROPAR since the 1980's and suggested by Reimann *et al.* (2005).

Figure 6
The original 9,030 stream sediments samples and the 93 5' x 5' sub-cells (ca. 8 x 8 km) (left); the selected 75 sub-cells (composite samples) containing 7,428 original samples, to be used in the present article (right)

Table 3 - Summary of the analytical techniques and respective lower detection limits for each element, applied to the composite samples.

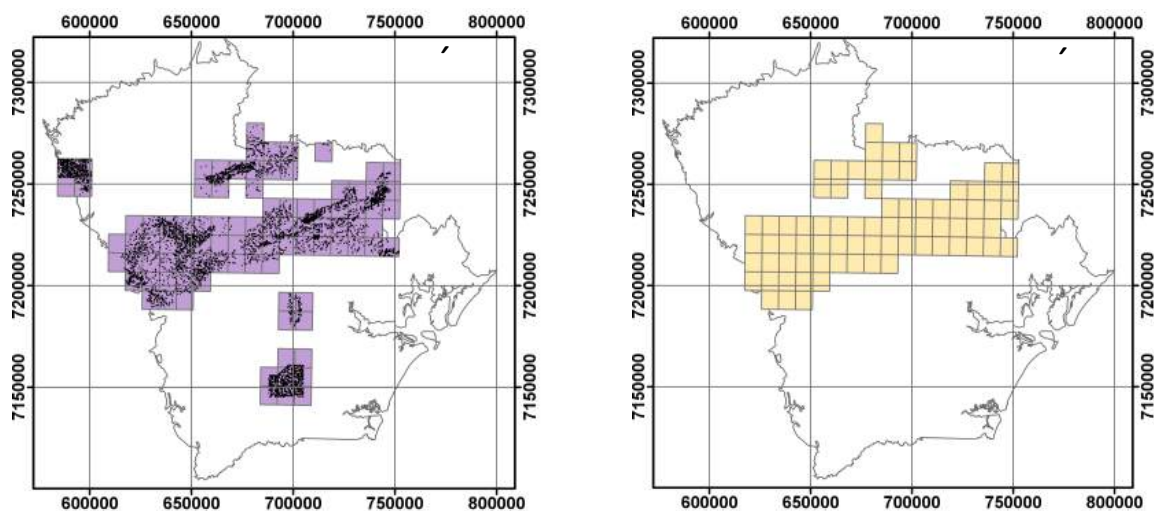| Element (unit)	Analytical package	Lower Detection Limit	Valid values	Element (unit)	Analytical package	Lower Detection Limit	Valid values
Al (%)	ICM14B	0.01	75 (100%)	Sc (ppm)	ICM14B	0.1	75 (100%)
Ba (ppm)	IMS95A	5	75 (100%)	Sm (ppm)	IMS95A	0.1	75 (100%)
Be (ppm)	IMS95A	0.1	75 (100%)	Sn (ppm)	IMS95A	0.3	75 (100%)
Bi (ppm)	ICM14B	0.02	75 (100%)	Sr (ppm)	IMS95A	0.5	75 (100%)
Ca (%)	ICM14B	0.01	75 (100%)	Tb (ppm)	IMS95A	0.05	75 (100%)
Cd (ppm)	ICM14B	0.01	75 (100%)	Th (ppm)	IMS95A	0.1	75 (100%)
Ce (ppm)	IMS95A	0.1	75 (100%)	Ti (%)	ICM14B	0.01	75 (100%)
Co (ppm)	IMS95A	0.5	75 (100%)	Tl (ppm)	ICM14B	0.02	75 (100%)
Cr (ppm)	ICM14B	1	75 (100%)	Tm (ppm)	IMS95A	0.05	75 (100%)
Cs (ppm)	IMS95A	0.05	75 (100%)	U (ppm)	IMS95A	0.05	75 (100%)
Cu (ppm)	IMS95A	5	75 (100%)	V (ppm)	ICM14B	1	75 (100%)
Dy (ppm)	IMS95A	0.05	75 (100%)	Y (ppm)	IMS95A	0.05	75 (100%)
Er (ppm)	IMS95A	0.05	75 (100%)	Yb (ppm)	IMS95A	0.1	75 (100%)
Eu (ppm)	IMS95A	0.05	75 (100%)	Zn (ppm)	ICM14B	1	75 (100%)
F (ppm)	ISE03A	30	75 (100%)	Zr (ppm)	IMS95A	0.5	75 (100%)
Fe (%)	ICM14B	0.01	75 (100%)	P (ppm)	ICM14B	50	74 (98.67%)
Ga (ppm)	IMS95A	0.1	75 (100%)	Mo (ppm)	ICM14B	0.05	69 (92.00%)
Gd (ppm)	IMS95A	0.05	75 (100%)	In (ppm)	ICM14B	0.02	67 (89.33%)
Hf (ppm)	IMS95A	0.05	75 (100%)	Sb (ppm)	ICM14B	0.05	66 (88.00%)
Hg (ppm)	ICM14B	0.01	75 (100%)	S (%)	ICM14B	0.01	58 (77.33%)
Ho (ppm)	IMS95A	0.05	75 (100%)	Ta (ppm)	IMS95A	0.05	56 (74.76%)
K (%)	ICM14B	0.01	75 (100%)	W (ppm)	IMS95A	0.1	55 (73.33%)
La (ppm)	IMS95A	0.1	75 (100%)	As (ppm)	ICM14B	1	50 (66.67%)
Li (ppm)	ICM14B	1	75 (100%)	Na (%)	ICM14B	0.01	39 (52.00%)
Lu (ppm)	IMS95A	0.05	75 (100%)	Pt (ppb)	FAI515	5	19 (25.33%)
Mg (%)	ICM14B	0.01	75 (100%)	Te (ppm)	ICM14B	0.05	19 (25.33%)
Mn (ppm)	ICM14B	5	75 (100%)	Au (ppb)	FAI515	5	13 (17.33%)
Nb (ppm)	IMS95A	0.05	75 (100%)	Ge (ppm)	ICM14B	0.1	2 (2.67%)
Nd (ppm)	IMS95A	0.1	75 (100%)	Pd (ppb)	FAI515	5	0 (0%)
Ni (ppm)	IMS95A	5	75 (100%)	Re (ppm)	ICM14B	0.1	0 (0%)
Pb (ppm)	ICM14B	0.2	75 (100%)	Se (ppm)	ICM14B	1	0 (0%)
Pr (ppm)	IMS95A	0.05	75 (100%)	Ag (ppm)	ICM14B	0.01	0 (0%)
Rb (ppm)	IMS95A	0.2	75 (100%)	B (ppm)	ICM14B	110	0 (0%)

Key for the analytical techniques: ICM14B = Aqua regia digestion + ICP-MS; IMS95A = LiBO$_2$ fusion + ICP-MS; ISE03A = Alkaline fusion, dissolution and determination by Specific Ion Electrode; FAI515 = fire assay + ICP-OES.

2.3 QUALITY CONTROL

The analyses of the 75 composite samples were monitored by the internal quality control of the contracted laboratory, which comprises the use of analytical blanks, duplicate and certified standard samples. Furthermore, the analyses of original vs. composite samples, and also composite vs. duplicate samples were evaluated. To verify the analytical reprodu-

cibility and also to test the homogeneity of the composite samples, portions of eight randomly selected composite samples (323-D/45, 323-D/51, 323-D/63, 324-C/05, 324-C/34, 324-C/40, 324-D/11 and 324-D/38) were sent to the laboratory as a new sample, thus composing a replicate sample.

2.4 STATISTICAL DATA TREATMENT

The results were submitted to statistical analyses to obtain either univariate or bivariate information. The classical and robust statistical estimates for each of the variables were calculated: minimum value, first quartile, median, mean, third quartile and maximum value as well the percentiles not only to evaluate the statistical behavior of the variables (Appendix 2), but also as a support to the construction of the geochemical maps.

The authors are aware that a geochemical database with such complexity would be a very adequate dataset to the application of a statistical approach of Compositional Data (CoDa). Nonetheless, a conventional statistical treatment was adopted, which is supported by

the following observation by Reinmann *et al.* (2012): "... *the very aim of a regional geochemical mapping project is to study and predict the distribution (concentration) of a chemical element in two-dimensional space. Such maps have been successfully used to aid geological mapping, for mineral exploration, for documenting contamination, and for detecting a multitude of additional processes that determine the distribution of chemical elements at the Earth's surface. It will be hard to convince a regional geochemist that all these maps are "wrong" and that dimensionless ratio maps (which ratio?) are the only correct maps.*"

2.4.1 BIVARIATE CORRELATION PROCEDURES

The Pearson correlation coefficient (r) is an usual technique to measure the similarity of behavior between pairs of variables. To be considered valid, a correlation coefficient should be checked against significance tables containing the critical values for the correlation coefficients, considering the degrees of freedom of each pair of variables (number of pairs – 2) and a probability level, either 0.05 or 0.01. Otherwise, the Spearman rank correlation, is more applicable to highly skewed data sets, since it is not linear and thus not affected by the presence of outliers. To be

statistically valid under these premises, a correlation coefficient should be higher than the critical index found in the table. The validated correlation coefficients are thus highlighted on the correlation matrix to be correctly considered on further analysis.

Correlation diagrams are useful tools to graphically synthesize a correlation matrix (KRUMBEIN; GRAYBILL 1965 *APUD* SINCLAIR; BLACKWELL 2006). They were drawn using only positive correlation coefficients higher than 0.65, and using the application EZCorrGraph (CAMPOS 2018).

2.4.2 GEOCHEMICAL MAPPING

Due to the large dimension of the sub-cells (ca. 8 km side) the geochemical maps showing the cells classified by its elemental content display a rough aspect of a matrix of pixels (Figure 7).

In order to produce better structured geochemical maps with smoothest contours, it was applied the minimum curvature interpolation method, with an unitary isotropic

search radius, maximum residual value of 1.5, 100,000 maximum interactions and an unitary relaxation value (SURFER 2002). In order to restrict the interpolated maps to the limits of the studied area, a geographic filter (polygon mask) was applied to cut out the outer sub-cells. So, the elemental contents become represented by isograd curves (isovalues), highlighting the geochemical structures.
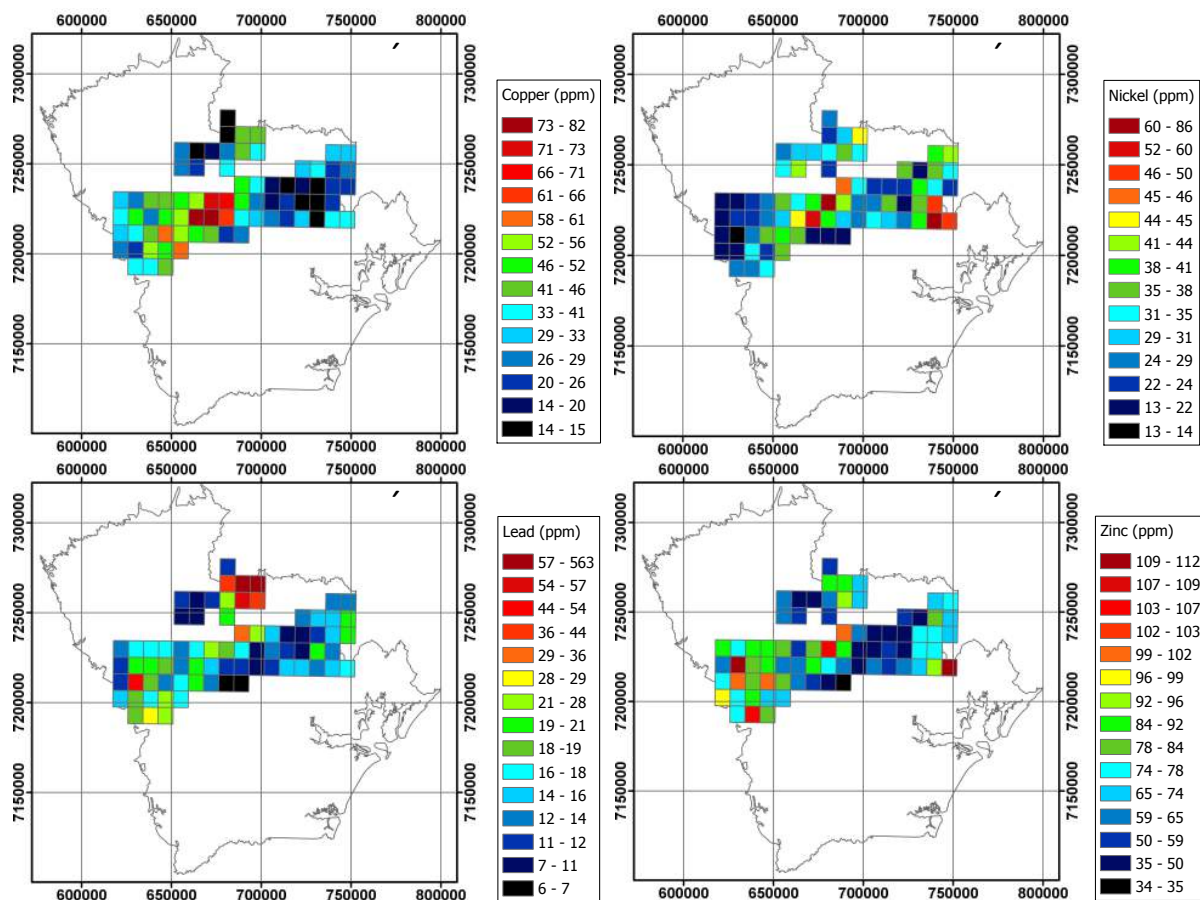
Figure 7

Geochemical maps showing the 75 sub-cells classified (raster style) by its Cu (upper left), Ni (upper right), Pb (lower left) and Zn (lower right) contents in the stream sediment composite samples.

2.4.3 NUMERIC-CHROMATIC SCALE USED ON THE GEOCHEMICAL MAPS

To better distinguish and also to enhance those areas with higher concentration in the geochemical map and attenuating the lower ones, was adopted a scale composed by selected percentile, i.e., 5, 15, 25, 40, 50, 65, 75, 85, 90, 91, 93, 95, 97, 98, along the lowest and maximum values of the chosen element. Weaver *et al.* (1983), Bølviken *et al.* (1986) and Björklund and Gustavsson (1987), justify the usage of this scale also to minimize outlier's influence.

To compose a numerical value expressing the association of element obtained from the correlation analysis (see item 3.5), the content of the elements must be converted to a common measure scale, since each element has a specific unit and range of measure. The standard unit or Z score (Formula 1) reduces all variables to a similar and dimensionless measure scale, preserving their distribution curves and statistical behavior.

$$z_i = \frac{x_i - \bar{x}}{s} \qquad \text{Formula 1}$$

Thus, the associations of elements will become expressed as the algebraic grand sum of the standard unit of each element, which compose a specific association, as exemplified by the Formula 2.

$$Association\ 2 = z_{Ba} + z_{Na} + z_{Sr} \quad \text{Formula 2}$$

3. RESULTS

3.1. CONTENTS IN THE ORIGINAL VS. COMPOSITE SAMPLES

When comparing the contents of the same element in both data sets – original and composite samples – different magnitudes of measure were obtained. There are two main reasons to explain this discrepancy: (1) *sample density*: the original samples contained in each cell represent small catchment basins and the composite samples represent a mix of all them, thus the lowest and highest contents in each cell, as well as the highest standard deviations, will appear on the analyses of the original samples; (b) *analytical procedures*: the original samples were sieved to < 80# fraction and digested with concentrate and hot HNO_3;

the elements were determined by atomic absorption spectrometry. On the other hand, the composite samples, which were constituted by small portions of < 80# pulps, were sieved again to <150#, digested by aqua regia and then analysed by ICP-MS. Thus it is clear that the analytical procedure applied on the composite samples was able to release a higher amount of the elements, which will reflect on higher values for the 1st quartile, median, average and 3rd quartile.

The differences in the statistic estimates for the same elements in both set of samples are shown in Table 4.

Table 4 – Summary of the statistical estimates comparing the element contents on the original samples and on the composite samples

Element	Type of sample	N	Lowest content	1st quartile	Median	Average	3rd quartile	Highest content	Standard Deviation
As (ppm)	Original	4,170	0.05	1	2	3.28	4	186	6.0652
	Composite	75	0.55	0.55	2	4.477	5.5	34	6.3677
Co (ppm)	Original	4,971	1	10	16	18.68	24	121	12.1554
	Composite	75	8.2	14.65	18.1	18.92	21.95	35.7	6.3811
Cu (ppm)	Original	6,876	1	10	18	23.13	29	700	23.1453
	Composite	75	14	25.5	33	36.72	46	82	15.2958
F (ppm)	Original	1,093	73	349	564	645.73	830	8,450	556.9180
	Composite	75	91	187	262	345.1	360.5	5,308	594.1555
Fe (%)	Original	1,833	0.05	1.5	2.4	2.79	3.4	15	1.9049
	Composite	75	1.68	3.495	4.37	4.457	5.315	8.84	1.4626
Mn (ppm)	Original	5,254	10	390	700	1340.33	1500	55,000	2080.2110
	Composite	75	346	693.5	1053	1365	1676	4403	920.3308
Ni (ppm)	Original	4,519	1	11	16	19.46	24	251	14.3580
	Composite	75	13	24	31	32.43	38	86	11.5854
Pb (ppm)	Original	7,428	1	12	16	22.46	22	12,000	145.3671
	Composite	75	6.9	11.85	15.6	25.11	19.45	563	63.7022
Zn (ppm)	Original	6,816	1	41	61	68.12	85	1,300	44.6322
	Composite	75	34	59	74	71.35	84	112	19.3959

3.2. COMPOSITE SAMPLES - ORIGINAL VS. REPLICATE ANALYSIS

Ideally, the results obtained from the original and its replicate sample, should have equal values, so in the quality control charts a line with a slope of 45° in relation to the abscissa would be generated. However, due to natural sample heterogeneity and the steps of homogenization and splitting in the Jones riffle splitter during the process of producing composite samples, this ideal scenario does not occur, and for some elements the analytical error surpassed ±10%. Since an error of ±10% between original and duplicate analysis is generally acceptable for the exploration

geochemistry purposes (THOMPSON; HOWARTH 1973, 1976*a*, 1976*b*), the quality control charts were established considering a channel of ±10% centered in the 45° line. For almost all elements with errors worse than ±10%, the major discrepancies are found in the region of lowest contents, a very common situation in analytical databases. On the other hand, for some elements such as Sn and W, whose dispersion is based on the clastic form producing a random and almost high analytical variability, an error worse than ±10% is comprehensible and acceptable (Table 5).

Table 5 – Reproducibility of analytical results on the quality control pairs of composite samples (original vs replicate)

Better than ± 10% (all samples inside the confidence channel)	Worse than ± 10%		
	Lower contents	**Higher contents**	**Randomly distributed**
As, Be, Ca, Ce, Co, Cr, Cs, Eu, Gd, Ge, Mg, Pb, Pt, Sr, Th, V	Al (1), Ba (2), Bi (2), Cd (2), Cu (1), Dy (1), Er (1), Fe (1), F (4), Ga (1), Hf (3), Hg (2), Ho (2), In (3), K (1), La (1), Li (4), Lu (1), Mn (1), Mo (4), Na (1), Nb (2), Nd (1), Ni (3), P (2), Pr (1), Rb (1), S (2), Sb (2), Sc (2), Sm (1), Sr (1), Tb (2), Ti (1), Tm (2), U (1), Y (1), Yb (1), Zn (1), Zr (4)	Au (1), In (1), Lu (1), Mo (1), Na (1), P (1), S (1), Te (2), Tl (1), Tm (1), Y(1), Yb (1)	Sn (8), Ta (7), W (5)

Note: the figure between parenthesis is the number of pairs falling out the confidence channel of ± 10%

From the Table 6 it becomes clear that quality control pairs 6 and 7, are those which concentrate the analytical error for several elements. This seems to indicate that the composite samples should be produced with more than four homogenization steps on the Jones riffle splitter. Some representative cases of quality control charts are shown in Figure 8.

Table 6 – Elements out of the ± 10% confidence channel in each quality control pair (original vs. replicate composite sample)

Quality control pair (composite sample code)	Elements
1 (323-D/45)	F, Hf, Hg, La, Mo, P, Sn, Sr, Ta, W, Zr
2 (324-C/05)	Al, Au, In, K, Li, Mo, Ni, S, Sn, Ta, Te, Zr
3 (324-D/11)	In, Na, Nb, S, Sb, Sn, Ta, Tm, W
4 (324-C/40)	In, Na, P, Sn, Ta, W, Zr
5 (323-D/63)	Cd, Li, Mo, Ni, P, Sn, Ta
6 (324-C/34)	Ba, Bi, Cu, Cd, Dy, Er, F, Fe, Hf, Ho, Li, Lu, Mn, Mo, Nb, S, Sc, Sn, Tb, Ti, Tl, Tm, W, Y, Yb, Zn, Zr
7 (323-D/51)	Ba, Bi, Er, F, Ga, Hf, Ho, In, Lu, Mo, Nd, Ni, Pr, Rb, Sb, Sc, Sm, Sn, Ta, Tb, Te, Tm, U, Y, Yb, W
8 (324-D/38)	F, Hg, Li, Sn, Ta

3.3 COMPARISON BETWEEN ORIGINAL VS. COMPOSITE SAMPLES

The concentration of the elements determined in the composite samples were compared to the mean and to the median concentration of the original samples contained in the respective cells (see Appendix 1). This comparison could only be made for As, Co, Cu, F, Fe, Mn, Ni, Pb and Zn, which compose the former geochemical database (LICHT; TARVAINEN 1996). As emphasized before (item 3.1), it is necessary to take into account that this correlation analysis was performed between contents obtained with two different analytical techniques in the original and in the composite samples.

Table 7 - Correlation coefficient (r) between the contents of the composite samples and the median and the average of contents of the original samples contained in the same cell.

	As	**Co**	**Cu**	**F**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
Median	0,75	0,79	0,88	0,16	0,81	0,78	0,55	0,27	0,47
Average	0,64	0,72	0,86	0,49	0,81	0,88	0,59	0,99	0,62

Notes: N = 75, degrees of freedom = 73; critical $r_{0.01}$ = 0.31. Correlation coefficient lower than the critical r, are underscored.

From the correlation coefficient (Table 7) and also from the correlation graphs (Figures 9 to 11), it becomes clear that, apart from As, Co and Cu, the concentrations of the composite samples behave much more similarly to the average value of the original samples contained in the respective sub-cell than to it median.

Figure 8

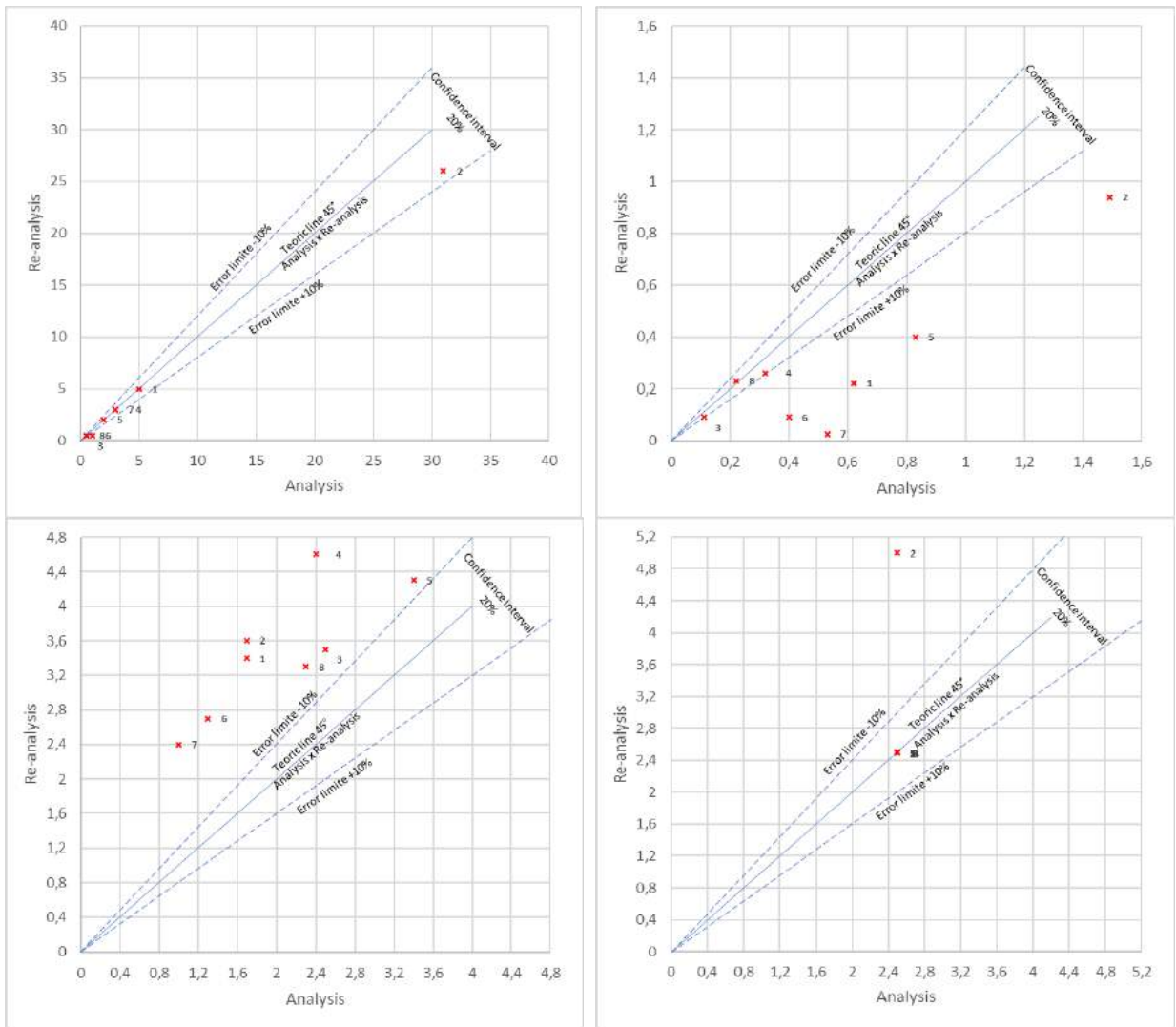Composite samples vs. duplicates. Quality control charts of selected elements: As (upper left), Mo (upper right), Au (lower left) and Sn (lower right).

Figure 9

Correlation graph for As (ppm) content in the composite samples vs the median of the original samples (r = 0.75) (left) and the average of the original samples (r = 0.64) (right). The confidence channel represents the significance level of 0.05.
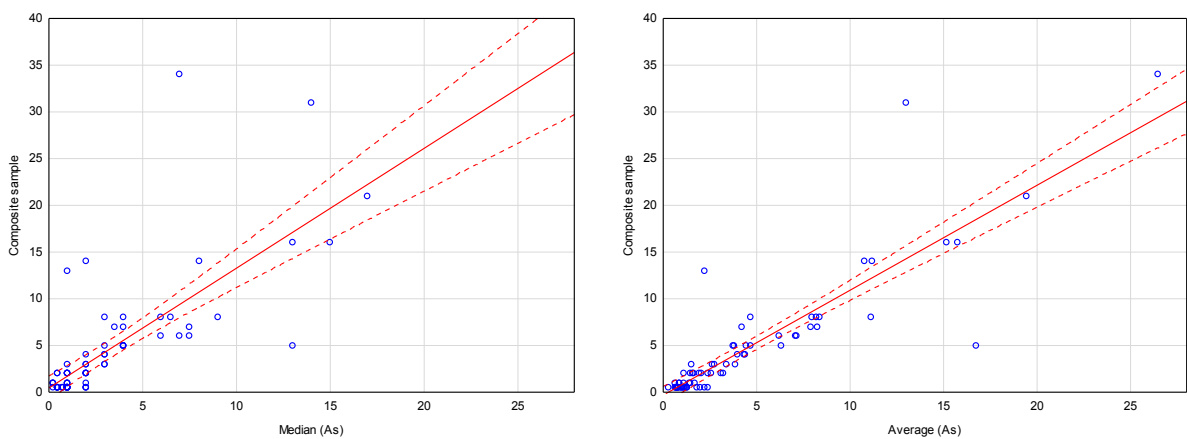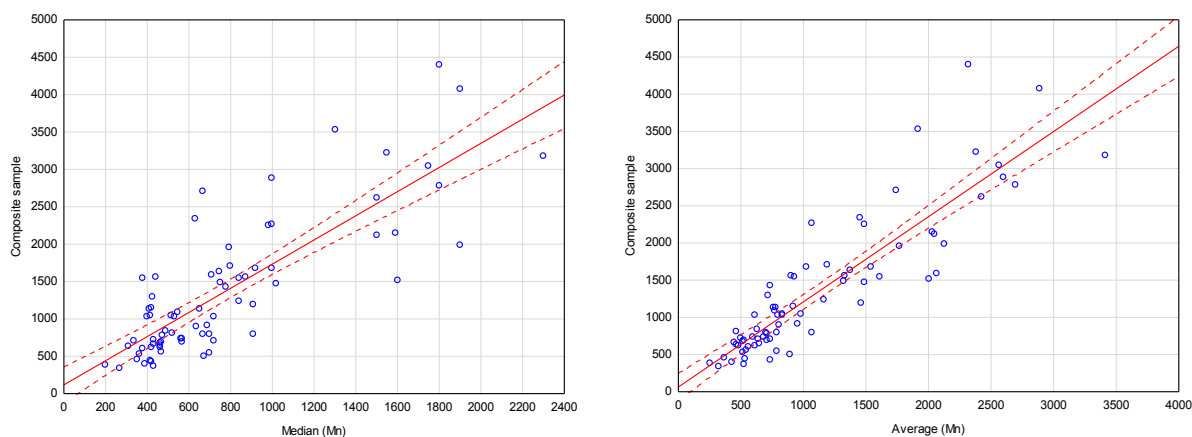
Figure 10

Correlation graph for Mn (ppm) content in the composite samples vs the median of the original samples (r = 0.78) (left) and the average of the original samples (r = 0.88) (right). The confidence channel represents the significance level of 0.05
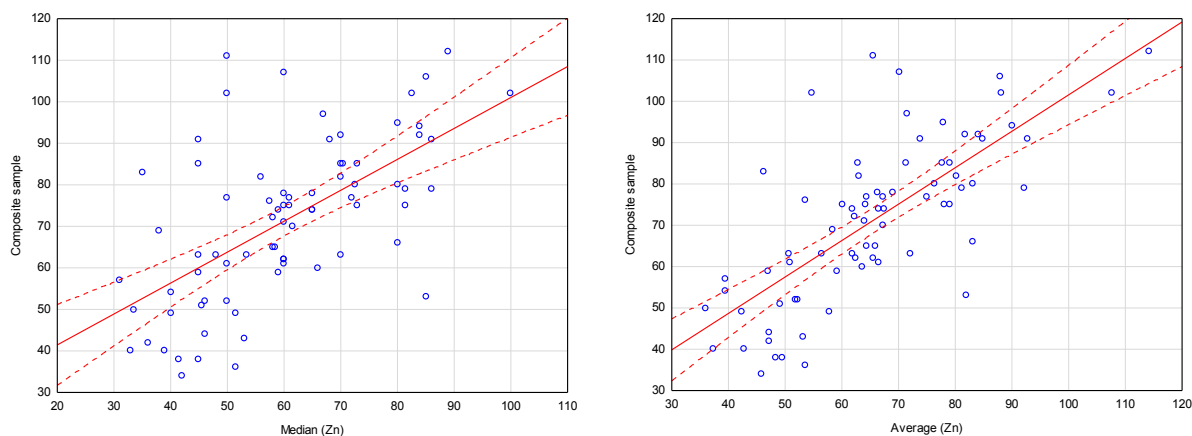

Figure 11

Correlation graph for the Zn (ppm) content in the composite samples vs the median of the original samples (r = 0.47) (left) and the average of the original samples (r = 0.62) (right). The confidence channel represents the significance level of 0.05.

It is possible to explain this fact making a parallel with some statistical concepts. For a data set which contains *outlier* values, they will display an important role on the calculation of the average, increasing its value, but will display a minor importance in the calculation of the median, reducing its value. Following this line of thought, it is clear that original samples with outlier contents were included and influenced the composite samples increasing its content, which made the final content of the composite sample more similar to the average than to the median.

Thus, except for As, Co and Cu, the angle of the correlation lines for the means of the original samples vs. the contents of the composite samples are closer to 45°, the confidence channels become narrower and the correlation indexes are higher. All of these indicators are evidence for similar behaviors.

On the other hand, two single cases of non-significant correlation indices, i.e., less than critical r, are those of the median of F and of Pb.

With these results it can be stated that except for three exceptions (As, Co and Cu), for the data set here considered, the content of the composite samples works as the arithmetic mean of the contents of the original samples of the respective cell.

3.4 GEOCHEMICAL MAPPING OF THE FORMER VS. THE NEW GEOCHEMICAL DATABASES

When the general arrangement of the geochemical structures in the maps produced with the contents of composite samples are compared to those produced with the mean contents of the original samples (Figure 12 to Figure 20), it is surprising that maps drawn with such different datasets are so similar.

Figure 12

Arsenic (ppm) in stream sediments: 6,587 original samples (left) and 75 composite samples (right)

Figure 13

Cobalt (ppm) in stream sediments: 6,587 original samples (left) and 75 composite samples (right)

Figure 14

Copper (ppm) in stream sediments: 6,587 original samples (left) and 75 composite samples (right)

Figure 15

Fluorine (ppm) in stream sediments: 6,587 original samples (left) and 75 composite samples (right). Only few, and very geographically concentrated, original samples were analyzed for F and the resulting map (left) became incomplete and shows a strange display.

Figure 16

Iron (ppm) in stream sediments: 6,587 original samples (left) and 75 composite samples (right)

Figure 17

Lead (ppm) in stream sediments: 6,587 original samples (left) and 75 composite samples (right)
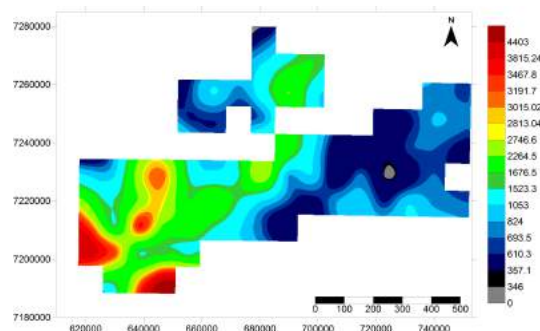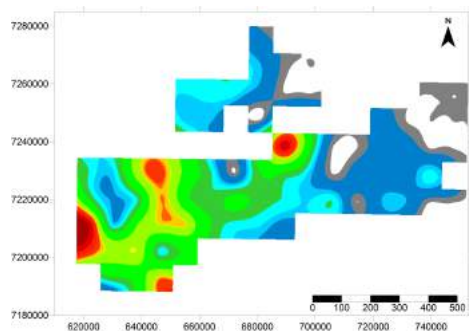
Figure 18

Manganese (ppm) in stream sediments: 6,587 original samples (left) and 75 composite samples (right)
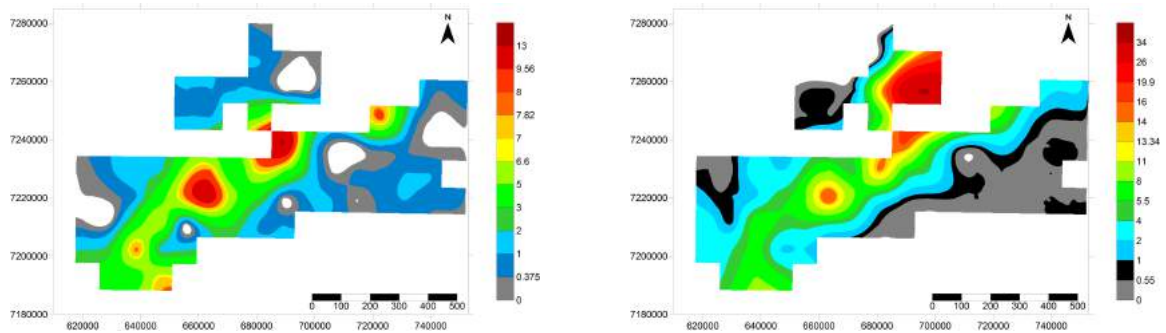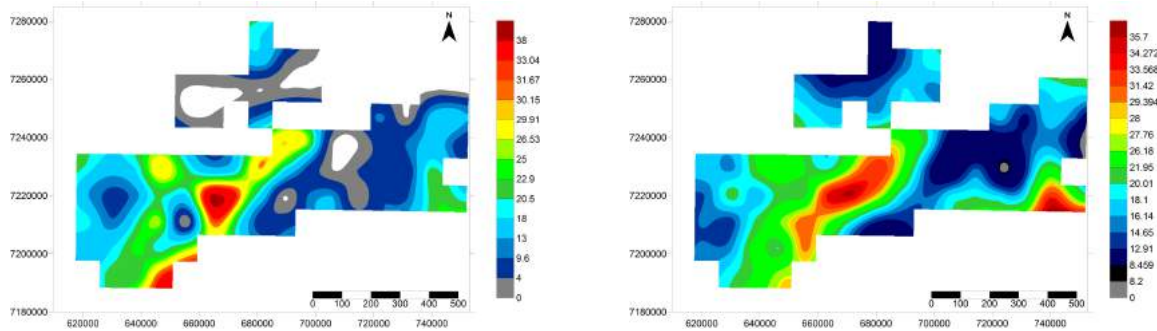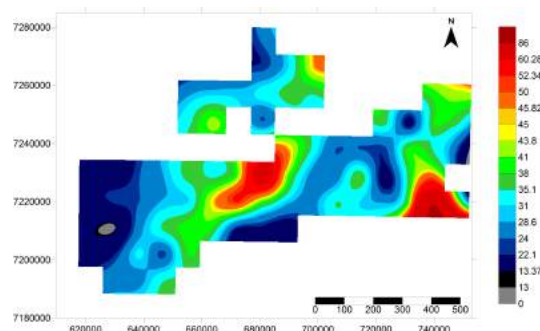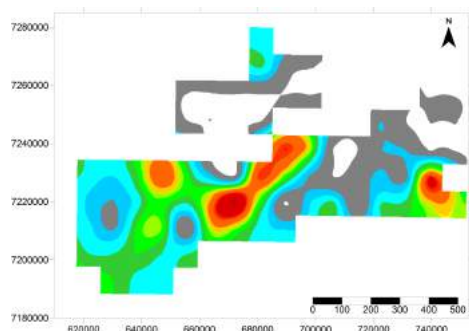

Figure 19

Nickel (ppm) in stream sediments: 6,587 original samples (left) and 75 composite samples (right)
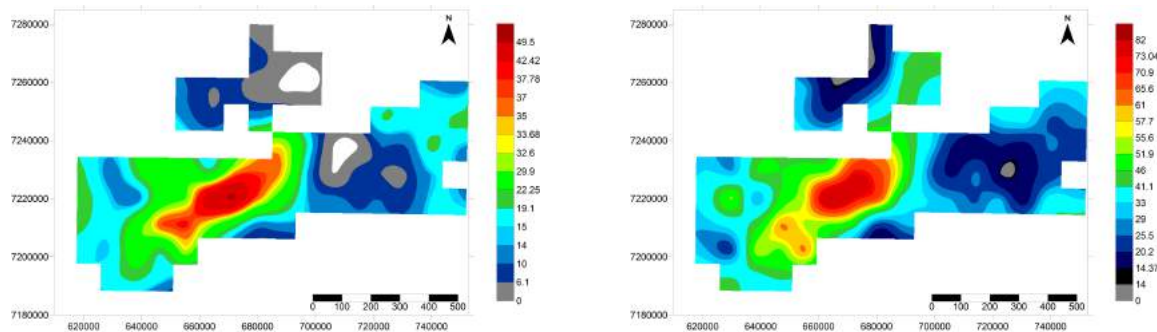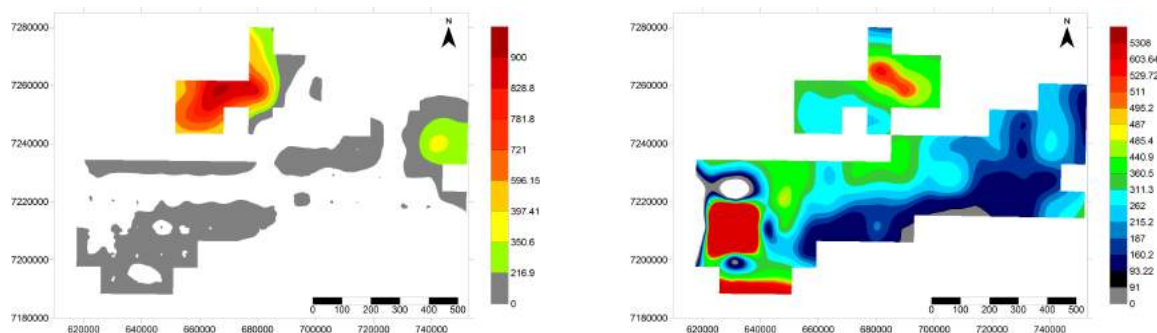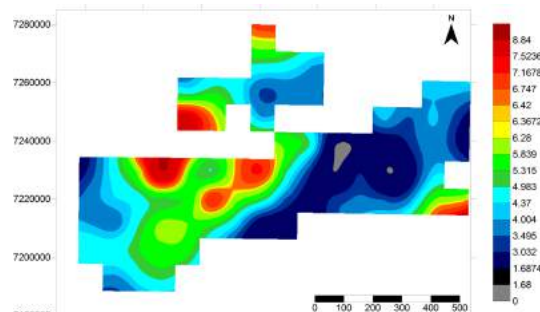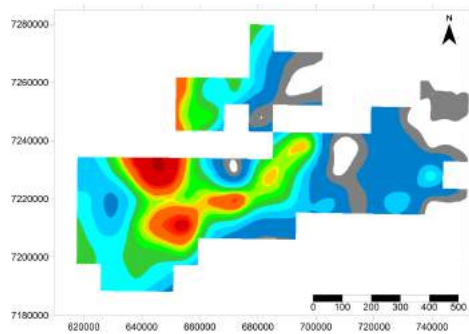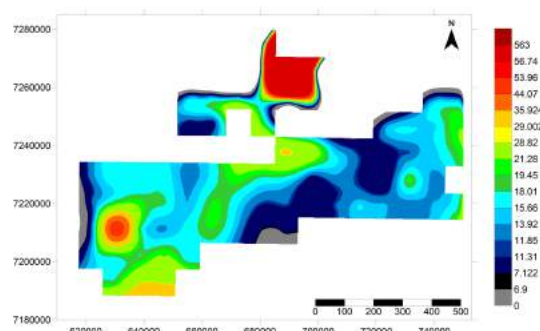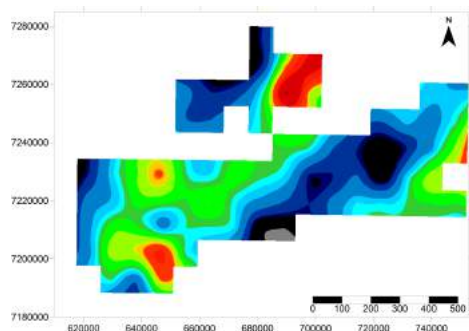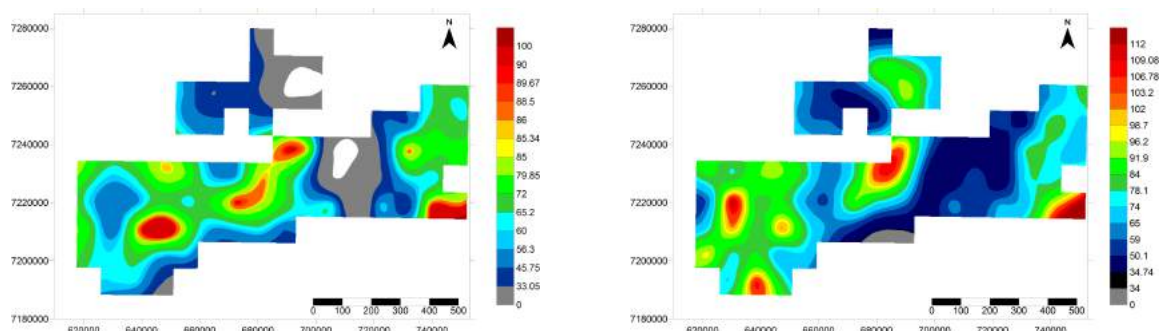
Figure 20
Zinc (ppm) in stream sediments: 6,587 original samples (left) and 75 composite samples (right)

As it can be seen on Figures 12 to 20, the geochemical maps showing the distribution of the results of composite samples lost some detail and spatial resolution. However, it is also possible to observe the clear concordance between the main geochemical structures shown in both maps for each element. This fact was expected and has been reported by Fordyce *et al.* (1993) and Darnley *et al.* (1995). These authors state that the geochemical patterns follow a fractal pattern, in which forms are similar and reproduce themselves regardless the observation scale.

3.5 STATISTICAL BEHAVIOR AND DISTRIBUTION OF THE ELEMENTS

The studied area is represented by a very complex geological background (item 1.1), thus a statistical appraisal of the multi-element database produced by the geochemical analysis of the composite samples is presented only as a reference (Appendix 2).

Almost all the histograms are clearly log-normal, showing a strong and positive asymmetry, with the median positioned in the first three class intervals. Some elements like Co and Cu are uni-modal, others like Cr, Dy and Er are bi-modal and still others are polymodal like Ca, Cd, Ce and Eu.

Such modal variations express the heterogeneity of the chemical composition of the samples, which in turn reflect the complexity of the geological background of the study area.

3.6 BI-VARIATE CORRELATION ANALYSES AND ASSOCIATION OF ELEMENTS

Using the Pearson linear correlation technique, only those pairs of variables with correlation coefficients higher than the critical value of 0.575 ($\alpha = 0.01$) were retained. The exception is Au, whose critical value is 0.684. Due to the large number of variables, to draw the correlation diagrams, it was necessary to adopt a cut-off value for the correlation coefficient, thus being considered only the pairs of elements with $r \geq 0.65$.

The correlation diagrams constructed from these selected pairs have grouped 49 elements into seven associations that are presented in Figure 21 and summarized in Table 8.

All pairs in which Al, Au, Ca, Cr, Ga, Ge, Hg, In, Li, Nb, Pt, S, Sn, Sr, Te, Tl and W participate, had correlation coefficient lower than 0.65, thus these elements were not included in any of the seven associations.

The maps showing the distribution of these geochemical associations (Figure 22 to 27) were drawn with the algebraic grand sum of the standard unit (Z_i) of the elements composing each association.

It is important to note that the main direction of the geological and structural framework of the researched region are well delineated in the maps of the elemental associations, since all show main geochemical trends according to NE-SW.

The application of Spearman rank correlation was not so effective in separating associations of chemical elements, and for this reason only the results from the Pearson correlation was considered to establish the element associations, in the geochemical mapping and in the correlation with the geological background.
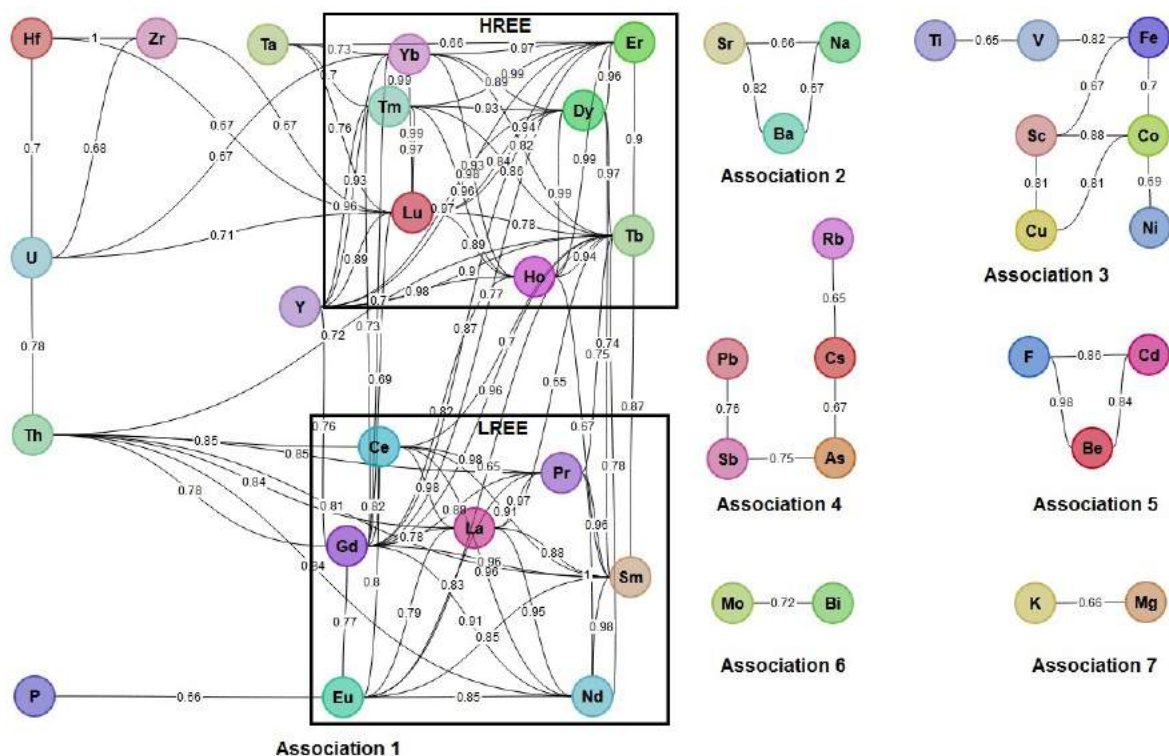
Table 8 – Summary of the associations of elements produced by bi-variate correlation analysis in the stream sediment composite samples (see Figure 21).

Association	Elements
1	Hf-Zr-U-Ta-Y-Tb-Dy-Ho-Er-Tm-Yb-Lu-Th-La-Ce-Pr-Nd-Sm-Eu-Gd-(P)
2	Ba-Na-Sr
3	Fe-Sc-Co-Cu-Ni-Ti-V
4	As-Cs-Sb-Pb-Rb
5	Cd-Be-F
6	Bi-Mo
7	K-Mg

3.7 GEOCHEMICAL ASSOCIATIONS AND GEOLOGICAL BACKGROUND – A CAUSE-EFFECT RELATIONSHIP

The geological inheritance is clearly presented in all maps either for the isolated elements or for their associations. We attribute this main relationship to the fact that the original stream sediment samples were collected in the 1970s and 1980s, when human occupation in the studied area was still incipient. Examples of human influence on geochemical survey data in part of this researched area are found in Licht (2018).

Association 1 - related to the granitic bodies of Alto Turvo, Graciosa, Rio Salto, Banhado and Morro Grande. The lowest values predominate in the meta sedimentary rocks which belongs to the Açungui Group and over the Três Córregos Granite (Figure 22).

Association 2 - emphasizes the northern portion of the Três Córregos Granite. The lower values predominate in the Açungui Group meta-sedimentary rocks (Figure 23).
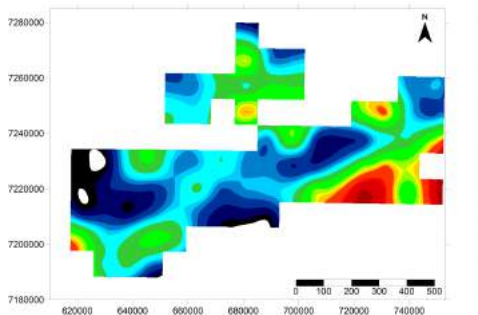
Figure 22
Geochemical map of the association 1
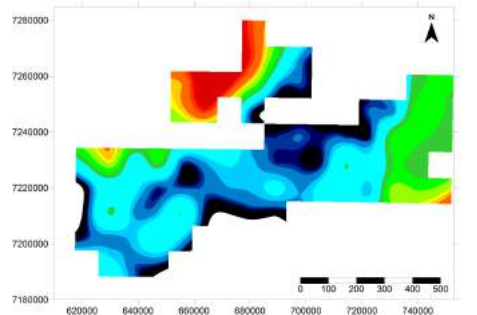
Figure 23
Geochemical map of association 2

Both associations 1 and 2 reflect the presence of granitic intrusions, but are also strongly influenced by intrusions of alkaline bodies, some associated with carbonatites as is the case of that known as 'Barra do Itapirapuã'.

Association 3 – mostly associated to the Votuverava Formation, which belongs to the Açungui Group. The lowest values, apparently

coincides with the transcurrent Lancinha Fault zone (Figure 24).

Association 4 - has a similar behavior to Association 3 and fits to the Votuverava Formation, but there is a geographic coincidence between the main Pb occurrences and mines located in the Ribeira river valley and the highest values of the Association 4. The lowest values occur mainly over the Três Córregos Granite (Figure 25).
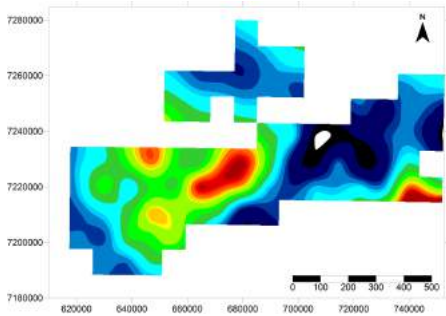
Figure 24
Geochemical map of the association 3
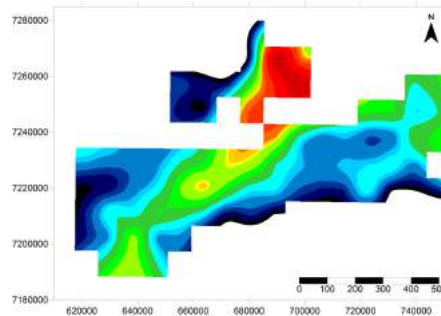
Figure 25
Geochemical map of the association 4

Association 5 - mark those cells where meta-sedimentary rocks of the Votuverava Formation predominate. In this region, some fluorspar occurrences are known, being the active F mine in the Mato Preto carbonatite the most important. In addition to F, W is associated to the Nagib Silva and Areia Branca granites. Its lowest values predominate on the Gneiss-migmatite Complex. In the south-

western border, an extremely high value for this association is related to southern portion of the Três Córregos granite (Figure 26).

Association 6 - has high values in the cells to the north, but especially in that cell located on the Banhado Granite. As occur with association 5, the lowest values predominate in the gneiss-migmatite complex (Figure 27).
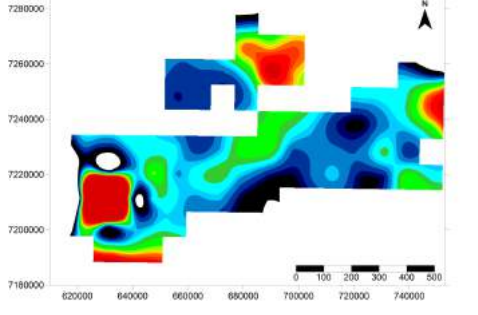
Figure 26
Geochemical map of the association 5
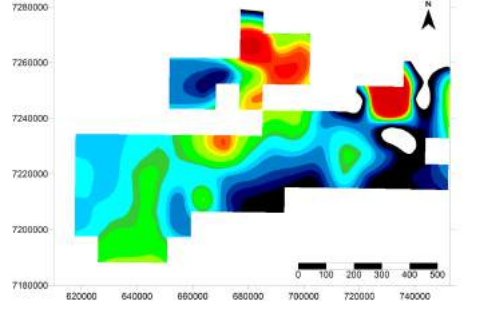
Figure 27
Geochemical map of the association 6

Association 7 – based on the available geological knowledge, the authors do not reach any causal relationship for the Association 7 composed by K – Mg in the studied area.

3.8 FAVORABILITY TO MINERAL EXPLORATION

An extremely valuable result of this research was to point-out a special location, geographically coincident to southern portion of the Três Córregos Granite. This is the case of the sub-cell 323-D / 52 which shows high values of the Association 5 (Figure 26) followed by some indicator and pathfinder elements, e.g, Au, Cd, Tl and Hg (Figure 28) as well as F (Figure 15), which do not participate in any of the associations.

The database of mineral occurrences does not indicates any mineral showing which would justify this multielement geochemical anomaly. Therefore, this sub-cell constitutes an area of great potential and favorability for mineral exploration of Au, F and other associated elements mentioned above.
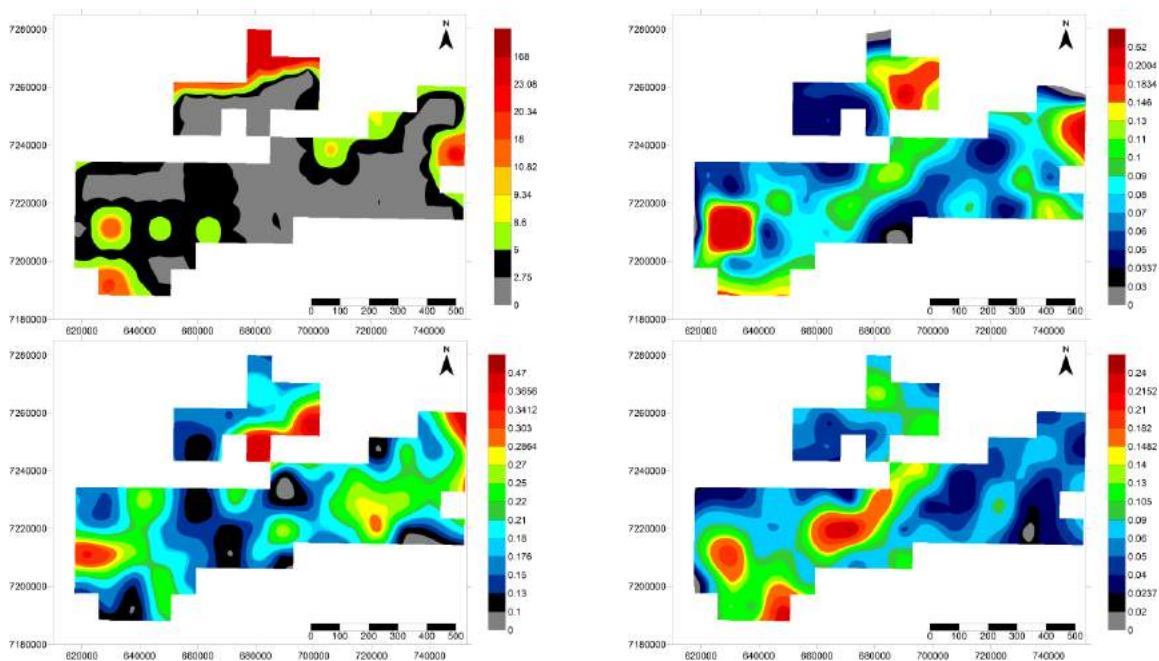
Figure 28
Geochemical map of Au (ppb) (upper left), Cd (pm) (upper right), Tl (ppm) (lower left) and Hg (ppm) (lower right) in the 75 stream sediments composite samples. In the western border of the studied area and in all of these maps a geochemical high is clearly marked, corresponding to the southern portion of the Três Córregos Granite.

The follow-up of this mineral exploration target could be easily made, by retrieving the original samples from the sample storage site and sending it to be analyzed by the same analytical techniques. The Figure 28 shows the original stream sediments sampling sites displayed over the hydrographic network of the sub-cell 323-D / 52 and the geologic background. Some sampling sites are slightly displaced from the hydrographic network because they were collected in the 1980's when aerial photos were the main technique for orientation in the field, causing some errors in the coordinates attributed to the samples.

4. CONCLUSIONS

Composite samples representing a regular cell grid which has been composed from old stream sediment samples adequately stored constitute an useful and low cost technique to quickly evaluate large areas with no additional field costs. At a relatively low cost, these composite samples may be submitted to multielement analysis, producing reliable geochemical maps and revealing new geochemical structures and associations of elements, some of them pointing to unknown exploratory targets.

From the elements which has been directly compared (As, Co, Cu, F, Fe, Mn, Ni, Pb and Zn) the present research showed that the contents of the composite samples are statistically valid and equivalent to the arithmetic mean of the previous analytical results of the original samples used to composed it.

Even in this area, which was already submitted to many previous mineral exploration surveys, the procedure of retrieval stream sediment samples collected by old surveys and analyzing them by modern analytical techniques was able to delineate a very interesting geochemical target, located on the southern portion of the Três Córregos Granite.

The usage of modern data processing procedures and statistical approaches such as Compositional Data (CoDa) and Geostatistics, on such multielement database, may enable more advanced interpretations with great economy of financial resources.

Lastly, the authors believe that one of the most important contributions of the present research is to proof the viability of the application of this cell grid technique based on composite stream sediments samples in other Brazilian regions and even other countries, which have large sample storage facilities representing large and relatively unexplored regions.

5. ACKNOWLEDGEMENTS

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APPENDIX 1

Element contents in each sub-cell of the regular grid. Composite refer to the element content achieved by analyzing the composite samples (see item 2.2).

Original, ẋ and Md refer respectively to the arithmetic mean and to the median values of the previous analyses (see item 1.2) of the original samples (N) contained in each sub-cell.

Sub-cell	Type of sample		N	As (ppm)	Co (ppm)	Cu (ppm)	F (ppm)	Fe (%)	Mn (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
323-D/33	Composite		1	0.5	17.4	33	216	3.25	900	20	13.4	85
	Original	ẋ	12	0.27	22.00	23.00			807.50	14.17	12.08	71.33
		Md		0.25	19.5	18			635	14	12	73
323-D/34	Composite		1	0.5	15.6	29	162	4.78	1046	18	17.2	78
	Original	ẋ	76	1.22	16.22	16.24			976.91	12.29	17.89	66.26
		Md		1	15.5	13			515	11.5	18	60
323-D/35	Composite		1	3	21.9	46	238	6.19	2623	24	16.5	91
	Original	ẋ	19	2.74	19.68	27.62			2428.75	19.21	23.59	73.78
		Md		2	19	22			1500	18	22	68
323-D/36	Composite		1	2	25	46	403	8.84	3044	29	17.6	92
	Original	ẋ	88	2.06	31.03	32.15			2563.86	31.90	24.64	84.15
		Md		2	29.5	29			1750	30	25	84
323-D/42	Composite		1	1	15	38	186	3.79	1952	21	11.4	62
	Original	ẋ	94	0.65	14.77	22.04			1768.83	11.23	15.88	62.50
		Md		0.25	13	20			795	10	15	60
323-D/43	Composite		1	1	21.1	52	166	4.37	1544	23	19.6	111
	Original	ẋ	63	0.89	11.97	18.29			927.14	9.70	18.37	65.63
		Md		0.25	8	14			380	7	17	50
323-D/44	Composite		1	2	16.3	29	317	4.72	2339	24	20.4	82
	Original	ẋ	72	1.61	13.41	15.07			1457.38	13.58	20.32	63.11
		Md		1	12	12			630	13	21	56
323-D/45	Composite		1	5	20.9	48	487	5.27	2777	29	18.4	85
	Original	ẋ	286	3.82	23.15	34.38			2700.03	21.12	22.18	78.99
		Md		4	21	25			1800	20	21	70
323-D/51	Composite		1	3	14.9	31	353	3.98	3177	14	11.7	75
	Original	ẋ	140	1.53	20.20	23.35			3415.36	11.86	18.27	78.16
		Md		1	19	19			2300	12	16	73
323-D/52	Composite		1	1	14.1	37	5308	3.76	1564	13	52.4	102
	Original	ẋ	37	0.87	11.73	16.49			903.05	9.49	22.27	54.73
		Md		0.25	10	16			440	6	21	50
323-D/53	Composite		1	7	20.4	44	667	5.02	3536	27	18.9	79
	Original	ẋ	63	4.22	22.75	33.02			1913.02	19.71	23.51	92.27
		Md		4	20	27			1300	19	20	86
323-D/54	Composite		1	5	26.2	61	352	6.1	2123	36	13.8	102
	Original	ẋ	137	4.71	27.38	43.19			2044.92	22.35	17.10	107.65
		Md		4	25	35.5			1500	20	16	100
323-D/60	Composite		1	3	14.9	29	511	4.95	4073	18	14.1	97
	Original	ẋ	185	2.61	14.76	20.06			2892.23	15.62	16.72	71.50
		Md		2	14	16			1900	15	16	67
323-D/61	Composite		1	4	15.8	25	384	4.81	3226	22	18.5	77
	Original	ẋ	64	4.36	18.64	17.63			2381.72	16.88	23.38	67.23
		Md		3	18	16			1550	15	23.5	61
323-D/62	Composite		1	6	23.5	54	464	5.31	1521	32	18	85
	Original	ẋ	38	7.11	25.22	31.50			2001.21	20.70	22.94	77.75
		Md		7.5	22.5	27.5			1600	18	23	70.5
323-D/63	Composite		1	2	20.1	51	255	5.59	1592	23	21.3	70
	Original	ẋ	71	2.58	24.79	26.53			2063.57	19.00	29.50	67.32
		Md		2	19	20			710	17.5	27	61.5
323-D/70	Composite		1	5	19.4	41	483	3.87	1713	27	18.8	75
	Original	ẋ	81	4.47	23.70	25.96			1194.63	17.59	19.59	64.19
		Md		4	21.5	18			800	18	19	61
323-D/71	Composite		1	8	22.4	38	497	4.63	2883	27	28.9	107
	Original	ẋ	64	4.70	23.70	24.14			2602.19	16.30	15.59	70.10
		Md		4	21	20			1000	14	14	60
323-D/72	Composite		1	6	27.1	42	487	5.03	4403	35	28.7	83
	Original	ẋ	13	6.23	30.46	21.92			2316.67	18.83	25.85	46.31
		Md		7	32	16			1800	14.5	25	35

Sample	Stat	n									
324-A/67	Composite	1	0.5	11	18	292	6.42	629	25	11.8	54
	Original x̄	25	0.72	14.08	7.99	388.24	4.90	465.60	14.60	16.98	39.43
	Md		0.5	11	5.4	350	5	311	14	13	40
324-A/76	Composite	1	2	10.5	17	535	4.92	1133	23	40.5	91
	Original x̄	98	1.56	15.35	11.20	728.75	3.60	761.75	15.69	50.75	92.79
	Md		1	15	8	487.5	2.72	410	15	14	45
324-A/77	Composite	1	14	14.8	42	442	4.72	1635	31	563	85
	Original x̄	62	11.18	16.65	34.99	529.36	2.95	1371.53	18.43	225.06	62.75
	Md		2	13	27	450	2.96	746	17	30	45
324-A/78	Composite	1	21	18.9	45	397	4.03	1681	45	58.9	74
	Original x̄	88	19.44	15.20	32.06		3.16	1020.04	27.02	45.33	61.87
	Md		17	14	30		3.05	1000	27.5	28	65
324-C/01	Composite	1	0.5	15.8	29	309	4.57	651	28	11.7	63
	Original x̄	38	0.82	6.99	13.14	696.15	2.36	648.45	10.82	14.29	50.74
	Md		0.75	7.5	10	620	2.32	460	10	14	48
324-C/02	Composite	1	0.5	12.9	15	328	5.18	1086	30	10.8	50
	Original x̄	124	1.01	7.12	7.51	935.48	2.59	768.82	12.33	12.47	36.09
	Md		1	7	6	900	2.55	545	11.4	11	33.5
324-C/03	Composite	1	1	13.8	19	314	4.67	737	30	11.3	49
	Original x̄	196	1.09	9.09	10.36	949.29	2.76	678.61	14.68	13.38	42.44
	Md		1	8.5	7	860	2.35	560	14.65	12.3	40
324-C/04	Composite	1	13	14.6	28	431	3.41	1302	33	24.3	63
	Original x̄	137	2.22	21.00	15.93	1044.71	4.94	719.17	29.37	30.65	56.52
	Md		1	17.5	7	940	4.015	425	26	19	45
324-C/05	Composite	1	31	18.1	44	511	3.72	2266	37	54.4	95
	Original x̄	77	13.00	11.87	34.77		3.43	1067.05	25.57	52.91	77.96
	Md		14	11.5	32.4		3.3	1000	24	32.5	80
324-C/06	Composite	1	34	15.7	37	449	3.56	1239	35	37.4	74
	Original x̄	56	26.45	17.98	36.87		3.83	1163.45	32.58	35.87	66.57
	Md		7	16.8	29.5		3.635	840	23.8	24	65
324-C/10	Composite	1	0.5	19.2	29	289	7.85	613	34	10.7	61
	Original x̄	55	0.78	11.48	17.41	1096.25	3.80	612.86	16.60	12.42	50.84
	Md		0.5	11.7	15	715	3.6	460	16	13	50
324-C/11	Composite	1	0.5	17.2	22	277	6.42	618	42	10.9	59
	Original x̄	81	0.84	7.86	10.80	825.15	2.66	477.29	13.48	14.09	47.07
	Md		1	7.2	8	735	2.635	420	14	14	45
324-C/13	Composite	1	7	16.6	41	262	4.1	793	24	19.7	52
	Original x̄	18	7.94	10.93	18.25		5.37	1069.77	15.30	19.23	52.27
	Md		3.5	10	16		4.56	911	11.55	17	50
324-C/18	Composite	1	7	16.8	33	219	4.02	506	36	12.8	53
	Original x̄	50	8.28	23.99	36.93		5.25	896.66	30.11	13.23	81.91
	Md		7.5	20	27		3.8	670	28	13	85
324-C/23	Composite	1	16	26	48	379	5.66	1982	46	29.2	102
	Original x̄	41	15.19	29.51	33.67		5.38	2124.82	33.18	28.76	88.05
	Md		13	27	31		4.7	1900	32	22.5	82.5
324-C/24	Composite	1	8	20	35	267	4.85	1191	35	24.8	62
	Original x̄	55	8.21	22.35	20.33		3.78	1462.41	24.74	21.45	65.59
	Md		3	20	18		3.03	910	21	16	60
324-C/25	Composite	1	2	10.1	20	211	1.68	435	24	14.6	38
	Original x̄	99	1.46	13.40	19.80		2.78	734.93	17.02	16.59	49.59
	Md		1	10	13		2.45	420	12	13	45
324-C/26	Composite	1	1	8.9	17	194	1.9	437	24	10.6	42
	Original x̄	154	1.43	9.41	10.64		1.77	535.23	12.29	12.71	47.28
	Md		1	8	9		1.64	415	11	11	36
324-C/27	Composite	1	2	10.9	20	214	2.25	393	23	9	38
	Original x̄	114	1.91	10.53	13.09		1.86	432.90	12.50	11.15	48.37
	Md		1	10	10.5		1.65	390	10	10	41.5
324-C/28	Composite	1	5	22	50	388	5.84	1479	37	13.5	80
	Original x̄	78	3.75	21.24	29.91		4.74	1488.99	22.60	19.50	76.31
	Md		3	19.5	28		4.5	1020	18	18	72.5
324-C/29	Composite	1	8	19.9	53	241	5.01	1139	34	17.4	59
	Original x̄	25	7.95	15.07	29.76		4.82	781.20	13.39	21.42	59.11
	Md		6.5	13	23		4.9	650	10	18	59
324-C/30	Composite	1	5	28	72	365	6.57	1433	41	21.1	79
	Original x̄	5	16.76	13.94	37.33		5.79	739.58	16.50	23.78	81.17
	Md		16.76	13.94	37.33		5.79	739.58	16.50	23.78	81.17

Sample	Type	Stat	n									
324-C/31	Composite		1	14	33.1	67	340	7.16	2701	67	18.1	106
	Original	x̄	34	10.77	26.45	39.10		3.81	1737.77	30.57	19.08	88.00
		Md		10.77	26.45	39.10		3.81	1737.77	30.57	19.08	88.00
324-C/32	Composite		1	6	25.2	51	356	4.98	907	42	17.4	92
	Original	x̄	106	7.16	24.74	37.29		2.91	952.49	26.77	21.08	81.71
		Md		6	23	32		2.925	690	24	18	70
324-C/33	Composite		1	4	13.7	28	264	3.01	1053	27	10.3	44
	Original	x̄	102	4.01	11.94	14.20		1.55	832.90	12.40	12.23	47.23
		Md		2	9	12		1.6	416	9	12	46
324-C/34	Composite		1	1	9.4	19	311	1.7	376	26	13.3	40
	Original	x̄	342	1.71	9.83	10.50		1.92	522.38	9.42	15.20	42.65
		Md		2	9	9		1.6	430	9	12	39
324-C/35	Composite		1	0.5	15.2	26	175	3.03	724	38	11.1	57
	Original	x̄	108	1.20	10.70	10.90		1.78	497.83	12.78	13.57	39.42
		Md		1	7	9		1.5	430	10	13	31
324-C/36	Composite		1	0.5	8.2	14	146	1.78	346	19	9.4	40
	Original	x̄	82	0.71	6.45	6.65		1.61	324.64	9.54	11.45	37.38
		Md		0.5	5.5	5.5		1.15	270	8	10	33
324-C/37	Composite		1	8	21.2	56	287	5.4	1672	31	14	65
	Original	x̄	147	11.14	19.22	34.25		4.59	1538.31	17.41	20.99	65.97
		Md		9	18	28		4.05	920	16	20	58
324-C/38	Composite		1	16	34.8	82	278	7.17	2251	45	19.7	60
	Original	x̄	16	15.78	26.11	40.82		4.70	1487.60	20.69	24.32	63.54
		Md		15	19.5	39		4.85	980	19	21	66
324-C/39	Composite		1	8	35.7	74	212	6.05	1567	53	16	91
	Original	x̄	22	8.38	26.41	50.50		5.78	1328.38	34.91	19.21	84.82
		Md		6	21	49.5		6.2	870	31	18.5	86
324-C/40	Composite		1	3	28	65	193	5.21	1036	40	11.5	75
	Original	x̄	104	3.37	20.72	40.45		2.89	830.24	24.76	16.20	79.07
		Md		3	18	33		2.85	720	22	16	81.5
324-C/41	Composite		1	1	17.6	38	200	3.43	694	30	11.9	63
	Original	x̄	134	1.45	11.83	27.56		2.02	705.25	15.71	16.30	72.06
		Md		1	12	24		2	569	15	14	70
324-C/42	Composite		1	43	43	43	43	43	43	43	43	43
	Original	x̄	45	1.85	11.39	16.35		2.09	519.39	12.39	13.27	53.13
		Md		1	10	13		1.9	361	11	13	53
324-C/43	Composite		1	0.5	18.7	29	119	3.26	798	35	11.7	61
	Original	x̄	55	1.27	16.19	13.98		2.44	786.48	20.74	15.47	66.48
		Md		0.75	13	12		2.15	665	16.5	15	60
324-C/44	Composite		1	0.5	20.1	25	97	3.68	1036	31	15.9	51
	Original	x̄	117	0.75	17.75	13.55		2.77	798.45	17.67	18.82	49.07
		Md		0.5	15	10		2.35	530	15	18	45.5
324-C/45	Composite		1	0.5	18.8	30	123	3.56	610	29	14.5	65
	Original	x̄	29	0.70	14.60	11.00		2.89	557.59	22.00	18.10	64.33
		Md		0.5	12	9.5		2.3	380	20.5	18	58.5
324-C/46	Composite		1	5	30.7	55	188	5.83	2146	40	16.5	80
	Original	x̄	172	6.31	33.38	44.69		5.22	2033.58	30.48	20.71	83.11
		Md		4	30	38		4.95	1592.5	26	19	80
324-C/47	Composite		1	4	26.2	51	142	5.32	1544	38	19.3	63
	Original	x̄	80	4.40	28.50	31.54		3.41	1613.42	28.30	22.07	61.88
		Md		3	25	28		3.05	840	22	18.5	53.5
324-C/48	Composite		1	3	18.9	45	108	4.26	1143	22	13.7	52
	Original	x̄	14	3.86	19.05	23.76		1.60	921.43	19.05	24.00	51.86
		Md		3	16	19		1.7	420	17	16	46
324-C/49	Composite		1	0.5	12.6	23	190	2.36	705	21	6.9	36
	Original	x̄	31	2.01	9.21	12.40		1.52	636.21	11.43	9.76	53.64
		Md		2	6	11.5		1.425	334.5	9	10	51.5
324-C/50	Composite		1	0.5	12.5	28	91	2.3	377	18	7.5	34
	Original	x̄	21	2.41	9.33	21.05		1.91	257.79	10.67	10.44	45.90
		Md		2	6.5	13		1.475	200	9	10	42
324-C/55	Composite		1	2	29.7	61	162	5.46	1484	38	16.1	72
	Original	x̄	93	3.09	30.47	34.47		3.92	1322.91	20.83	20.96	62.18
		Md		2	27	30.5		3.8	750	17	18.5	58
324-D/02	Composite		1	2	18.4	32	231	4.04	789	39	13.2	66
	Original	x̄	45	3.23	17.59	29.68		3.95	700.16	31.13	13.18	83.18
		Md		0.5	16	28		3.4	700	29	13	80

Sample	Type	Stat										
324-D/03	Composite		1	2	19.1	32	170	3.98	680	42	13.3	77
	Original	x̄	37	1.11	15.07	32.75		3.11	518.32	34.77	12.96	64.41
		Md		0.5	14	16.5		2.7	460	26	12	50
324-D/10	Composite		1	2	12.4	34	160	3.4	561	20	15.6	49
	Original	x̄	77	2.40	13.27	19.88		2.81	540.76	12.93	16.06	57.79
		Md		2	14	19		2.65	465	12	15.5	51.5
324-D/11	Composite		1	0.5	17.9	25	254	4.08	836	38	15.2	82
	Original	x̄	374	1.30	18.93	18.45	362.47	3.02	630.14	24.98	19.20	80.22
		Md		1	17	17	329.5	2.75	490	23	15	70
324-D/12	Composite		1	0.5	14.7	27	190	3.19	785	35	20.8	74
	Original	x̄	139	0.84	14.92	20.59	349.09	2.48	713.41	20.43	22.67	67.48
		Md		1	16	19	320	2.34	474	16.8	17	59
324-D/19	Composite		1	0.5	13.5	18	152	2.98	659	40	11.7	78
	Original	x̄	103	2.24	12.01	12.82	255.22	2.03	449.75	20.28	12.51	69.05
		Md		2	11.5	12	256	1.9	430	17	12	65
324-D/20	Composite		1	0.5	15.9	26	269	3.85	693	35	14.5	77
	Original	x̄	196	0.92	15.55	20.26	413.02	2.38	524.19	21.05	16.65	75.03
		Md		1	15	20	396	2.275	470	20	15	72
324-D/21	Composite		1	0.5	10.4	23	190	3.05	541	23	19.2	71
	Original	x̄	16	0.67	14.10	19.03	352.14	4.28	790.45	31.57	14.54	63.91
		Md		0.7	12.1	18	354	3.27	700	26	10.19	60
324-D/28	Composite		1	0.5	13	17	163	2.3	462	37	20.1	75
	Original	x̄	78	1.14	11.89	7.82		1.50	367.66	15.94	20.17	60.10
		Md		1	10	7.5		1.4	350	14	17.5	60
324-D/29	Composite		1	0.5	24.5	23	131	4.28	703	50	13.6	76
	Original	x̄	10	1.00	25.00	15.59		3.49	733.64	31.09	21.71	53.56
		Md		1	15	16		3	720	22	20	57.5
324-D/37	Composite		1	0.5	19.2	18	119	3.78	1033	41	12.4	69
	Original	x̄	37	1.10	15.05	8.35		2.54	614.32	19.27	18.36	58.41
		Md		1	12	6.5		1.8	400	16	18	38
324-D/38	Composite		1	0.5	33.7	36	212	5.81	806	86	14.1	94
	Original	x̄	53	1.07	25.25	18.44		3.56	465.44	42.30	18.74	90.07
		Md		1	27	22		4.2	520	43	17	84
324-D/39	Composite		1	0.5	27.4	35	269	6.34	734	50	17.7	112
	Original	x̄	118	0.73	22.84	16.97		4.96	591.34	27.47	21.50	114.24
		Md		0.5	21	15		4.3	570	23	20	89

APPENDIX 2

Variable	Unit	Lowest	1st quartile	Median	Average	3rd quartile	Highest	Standard deviation
Ag	ppm	0.0055	0.0055	0.0055	0.0055	0.0055	0.0055	0
Al	%	0.59	0.995	1.26	1.319	1.525	3.36	0.509289
As	ppm	0.55	0.55	2	4.477	5.5	34	6.367699
Au	ppb	2.75	2.75	2.75	6.433	2.75	168	19.3889
B	ppm	5.5	5.5	5.5	5.5	5.5	5.5	0
Ba	ppm	229	444.5	595	722	962	1720	362.8094
Be	ppm	0.9	1.9	2.2	4.496	2.5	170	19.38187
Bi	ppm	0.03	0.13	0.18	0.2443	0.265	2.34	0.275599
Ca	%	0.04	0.11	0.14	0.2367	0.235	1.74	0.269831
Cd	ppm	0.03	0.06	0.08	0.09027	0.1	0.52	0.060403
Ce	ppm	34	57.15	73.4	81.08	95.05	248.5	33.82458
Co	ppm	8.2	14.65	18.1	18.92	21.95	35.7	6.381117
Cr	ppm	16	29.5	43	48.36	58.5	178	27.6257
Cs	ppm	0.96	1.92	2.85	3.188	4.19	8.17	1.620473
Cu	ppm	14	25.5	33	36.72	46	82	15.29579
Dy	ppm	1.84	2.985	3.53	3.752	4.27	7.31	1.185838
Er	ppm	0.98	1.8	2.18	2.313	2.73	5.44	0.873055
Eu	ppm	0.54	0.87	0.96	1.042	1.21	2.18	0.311335
F	ppm	91	187	262	345.1	360.5	5308	594.1555
Fe	%	1.68	3.495	4.37	4.457	5.315	8.84	1.462633
Ga	ppm	8.7	14.15	17.3	16.59	19	23.3	3.254609
Gd	ppm	2.38	3.61	4.07	4.426	5.23	8.44	1.293823
Ge	ppm	0.055	0.055	0.055	0.0562	0.055	0.1	0.007299
Hf	ppm	4.37	8.24	12.7	19.29	24.06	98.98	17.95158
Hg	ppm	0.02	0.05	0.06	0.08333	0.105	0.24	0.047713
Ho	ppm	0.34	0.595	0.71	0.7572	0.845	1.6	0.260299
In	ppm	0.011	0.025	0.03	0.04517	0.04	0.37	0.058045
K	%	0.04	0.12	0.15	0.1735	0.21	0.48	0.083577
La	ppm	17.9	28.05	35.7	40.17	46.95	127.7	17.53723
Li	ppm	7	9.5	11	12.19	14	24	3.596896
Lu	ppm	0.17	0.29	0.34	0.3944	0.44	1.25	0.189439
Mg	%	0.09	0.175	0.23	0.2647	0.315	0.76	0.133804
Mn	ppm	346	693.5	1053	1365	1676	4403	920.3308
Mo	ppm	0.0275	0.25	0.48	0.5579	0.635	4.05	0.609189
Na	%	0.0055	0.0055	0.01	0.01077	0.02	0.03	0.006456
Nb	ppm	13.87	19.85	25.38	29.55	33.56	91.04	14.52524
Ni	ppm	13	24	31	32.43	38	86	11.58537
P	ppm	27.5	306	401	441.3	548	1239	219.0937
Pb	ppm	6.9	11.85	15.6	25.11	19.45	563	63.70217
Pd	ppb	2.75	2.75	2.75	2.75	2.75	2.75	0
Pr	ppm	3.67	5.69	7.38	8	9.605	19.58	3.082955
Pt	ppb	2.75	2.75	2.75	3.787	3.875	10	1.89625
Rb	ppm	32.4	67.5	79.6	84.14	100.8	164	26.25101
Re	ppm	0.055	0.055	0.055	0.055	0.055	0.055	0
S	%	0.0055	0.01	0.01	0.01031	0.01	0.02	0.00425
Sb	ppm	0.0275	0.08	0.2	0.4674	0.465	5.35	0.812105
Sc	ppm	1.8	4.35	5.6	6.451	7.95	15	2.88038
Se	ppm	0.55	0.55	0.55	0.55	0.55	0.55	0
Sm	ppm	2.4	3.85	4.9	5.068	6	9.6	1.595023
Sn	ppm	0.7	1.7	2.2	2.943	2.8	30	3.604958
Sr	ppm	24.1	53.75	91	158.5	171.4	792.1	176.7956
Ta	ppm	0.0275	0.1788	1.37	1.566	2.265	6.18	1.449313
Tb	ppm	0.34	0.51	0.62	0.6524	0.79	1.2	0.190574
Te	ppm	0.0275	0.0275	0.0275	0.0424	0.04375	0.18	0.030694
Th	ppm	4.9	8.75	11.4	12.9	15.7	29.8	5.538648
Ti	%	0.02	0.07	0.12	0.1296	0.17	0.33	0.070317
Tl	ppm	0.1	0.15	0.18	0.1941	0.22	0.47	0.06611
Tm	ppm	0.14	0.27	0.32	0.3515	0.4	0.94	0.148358
U	ppm	1.19	2.09	2.59	2.897	3.19	7.92	1.203995
V	ppm	15	46.5	82	91.08	132.5	222	51.29268
W	ppm	0.055	0.055	2.3	2.504	3.6	10.8	2.303345
Y	ppm	9.34	17.14	19.56	20.96	22.83	52.89	7.341863
Yb	ppm	1.1	1.9	2.2	2.485	2.8	7.2	1.102907
Zn	ppm	34	59	74	71.35	84	112	19.39594
Zr	ppm	196.7	329.4	483.9	793	961.8	4215	757.6003