Radiological hazard indices and elemental composition of Brazilian and Swiss ornamental rocks

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ABSTRACT

The objective of this paper was to evaluate the radiological risk index of ornamental rocks sold both in Brazil and Europe and to correlate their radioactive content with their chemical composition. The ^{238}U, ^{232}Th and ^{40}K mean values were 62 ± 65, 122 ± 111, 1126 ± 516 Bq kg^{-1} for Brazilian and 93 ± 59, 70 ± 67 and 1005 ± 780 Bq kg^{-1} for Swiss samples, respectively. The radiological index: radium equivalent, external hazard index, absorbed dose rate in air, annual gonadal equivalent dose, annual effective dose equivalent, and excess lifetime cancer risk for Brazilian and Swiss samples were calculated. The main contribution for the radiological indices observed was the radionuclide ^{232}Th, which is associated with REE, Br, Hf, Na, Rb, Sb and Zr in the rock matrix.

Keywords: Ornamental rocks, radiological risk index, granite, elemental composition.

1. INTRODUCTION

In Brazil, approximately 80 percent of the exported dimension stones are commercially named granites [1]. This category includes not only the materials meeting the concept of felsic rocks, but also any mafic fine-grained rocks, or other igneous or metamorphic rocks that possess qualities similar to granite's grainy and interlocking texture [2]. In general, rocks generated in the Earth's crust are more enriched in radioelements, e.g. uranium, thorium and radium, relative to those formed in the mantle. This phenomenon is a consequence of magma partial fusion and fractioned crystallization processes that concentrated them in the silica-enhanced liquid phase [3].

The natural radioactivity of the rocks used as building materials has been increasingly studied due to the rising number of homes coated with ornamental rocks. Such aspect has been causing health concerns as an elevation of toxicity risk in these places may occur [3]. The European Union, for example, has a proper legislation regarding natural radioactivity in building materials, which establishes the gamma activity concentration index as an assessment tool [4]. Thus, this paper aims to evaluate the radiological risk index of dimension stones collected both in Brazil and in Switzerland as well as to correlate their radioactive content with their chemical composition based on the concentration of the stable elements.

2. MATERIALS AND METHODS

2.1 Sampling and sample preparation

The analyzed samples include magmatic and metamorphic rocks of different lithologic types used for decorative purposes that are best sellers in Brazil (20 samples) and Switzerland (14 samples), i.e. diorite, syenite, monzogranite, granitic pegmatites, gneisses, etc. The selected rocks list from Brazil can be found in Fig. 1, and were named according to the Brazilian state acronym where they were collected. Switzerland samples (named CH-sample) are not necessarily mined in this country, but they are easily found for sale in the market and their real provenance was not known for this study. The geographic diversity of the samples is expected to influence the results on the natural radioactivity. The samples preparation included comminution with two different types of crushers, a

jaw crusher and a roll crusher, and pulverization in a pan to attain a product finer than 0.1 mm. The mass reduction stages were carefully conducted so the final 1 g sample was not biased.

Figure 1: *Brazilian samples provenance identification*

2.2 Neutron activation analysis measurement

For the determination of the elemental concentrations, approximately 150 mg of each granite sample were weighed and packed in plastic polyethylene bags. Each batch of samples was irradiated together with two reference materials (RM), USGS STM-2 and NIST SRM 1646a, and a paper filter pipetted with a standard solution of the elements of interest. Each sample was calculated related to each reference material and the final report of the results is the mean value related to each RM. All samples and RM were irradiated for 8 hours in the IEA-R1 research reactor, at IPEN (Instituto de Pesquisas Energéticas e Nucleares) under a thermal neutron flux of 10^{12} cm^{-2} s^{-1}. The cooling time for the elements Na, K, As, Br, Sb, La, Nd, Sm, Tb and U counting varied from 5 to 7 days and for the elements Ca, Sc, Cr, Fe, Co, Zn, Se, Rb, Zr, Cs, Ba, Ce, Eu, Yb, Lu, Hf, Ta and Th was about 15 days.

The counting time was 1 h for each sample and for the reference material. Gamma spectrometry was performed by using an EG&G Ortec Ge high pure Gamma Spectrometer detector (AMETEK Inc., USA) and associated electronics, with a resolution of 0.88 and 1.90 keV for ^{57}Co (122 keV)

and [60]Co (1332 keV), respectively [5]. An analysis of the data was carried out by using an in-house gamma ray software, VISPECT program, to identify the gamma-ray peaks. The methodology evaluation was done by cross-checking the reference materials and synthetic standards.

2.3 Radiological hazard indices

For the activity concentration of natural uranium, thorium and potassium, their specific activity of 12.437 Bq kg^{-1}, 4.057 Bq kg^{-1} and 262 Bq kg^{-1}, respectively, was used considering an isotopic abundance of 99.2742% for [238]U, 100% for [232]Th and 0.0117% for [40]K [6].

Radium equivalent activity (Raeq) was defined as the weighted sum of [238]U, [232]Th and [40]K activities, based on the assumption that 370 Bq kg^{-1} of [238]U, 259 Bq kg^{-1} of [232]Th and 4810 Bq kg^{-1} of [40]K gives an effective dose of 1.5 mGy per year, equal to 1 mSv annual effective dose [7]. Raeq was calculated from the following relation (Eq. 1) suggested by Beretka and Mathew [8]:

$$Raeq = CU + 1.43CTh + 0.077CK \qquad (1)$$

where CU, CTh and CK are the activity concentrations of [238]U, [232Th] and [40]K, in Bq kg^{-1}, respectively.

The external hazard index (Hex), proposed by Hewamanna et al. [9], is applied for a house with walls of finite thickness, windows and doors, and can be calculated as Eq. (2):

$$Hex = CU/740 + CTh/520 + CK/9620 \qquad (2)$$

The radiation hazard due to Hex will be negligible if its value was less than the unity. Additionally, the internal hazard index (Hin), proposed by Krieger [10], takes into consideration the internal exposure due to radon and its short-lived decay products as a threaten to the respiratory system. It is calculated as Eq. (3):

$$Hin = CU/185 + CTh/259 + CK/4810 \qquad (3)$$

The absorbed dose rate (D) is related to the risk due to the amount of radiation deposited in a body per unit of time that arises from terrestrial gamma emitters. D can be derived (nGy h^{-1}) from the measured activity concentrations and the following conversion factors, as given by UNSCEAR [11] and shown in Eq. (4):

$$D = 0.462CU + 0.604CTh + 0.0417CK \qquad (4)$$

The annual gonadal dose equivalent (AGDE) is a measure of the genetic significance of the dose equivalent received by the population's reproductive organs per year [12]. Within this context, the

activity bone marrow and the bone surface cells were also included by UNSCEAR [13] as organs of interest. The AGDE for the rock samples here analyzed were determined by Eq. (5) [14,15].

$$AGDE \ (\mu Sv/y) = 3.09CU + 4.18CTh + 0.314CK \tag{5}$$

The annual effective dose equivalent (AEDE) takes into consideration the adsorbed dose rate and also the time spent in contact with the radioactive source – occupancy factor, according to the formula given by Eq. (6):

$$AEDE \ (\mu Sv/y) = D \ (nGy/h) \ x \ 8760h \ x \ 0.8 \ x \ 0.7 \ Sv/Gy \ x \ 10^{-3} \tag{6}$$

An occupancy factor of 0.8, calculated for building materials, is used considering that a person spends 80% of his time indoors. The conversion factor of 0.7 Sv/Gy converts absorbed dose rate (nGy/h) to annual effective dose equivalent in mSv/y [16].

Excess life time cancer risk (ELCR) represents the risk of fatal cancer during a life time (DL) of 70 years taking into consideration AEDE and a risk factor (RF in Sv^{-1}) established as 0.05 by the ICRP 60 for stochastic effects for the public [17,18] according to Eq. (7):

$$ELCR = AEDE \ x \ DL \ x \ RF \tag{7}$$

2.4 Statistical analysis

Univariate and multivariate statistical analyses were applied to the results for data interpretation. Pearson Correlation Coefficient, in which the correlation coefficient (r) is used to measure association strengths, was used to verify the relationship between the natural radionuclide activity concentrations and stable elements [19,20]. Hierarchical cluster analyses were applied with the purpose of assembling objects based on their similarities. This goal is achieved by sorting cases into groups, or clusters, resulting in a strong association between members of the same cluster, and a weak association between members of different clusters [21]. Principal component analysis was used to quantify the significant variation in the data set and to reduce the number of variables to a small number of indices. These indices retain the maximum amount of the variance and result in the retention of only the important characteristics of the original data [22,23].

3. RESULTS AND DISCUSSION

3.1 Radiological and elemental characterization

For quality control of the results, Table 1 shows the certified values of elements present in the reference materials USGS-STM-2, SRM 1642a and the limit of detection. It can be seen that a good agreement was found between the certified values and the measured values for all the determined elements.

Table 1: Certified values (CV) and measured values (MV) obtained in reference materials for quality control of the results and limit of detection (LD). Values in mg kg^{-1}, except where indicated (%).

	USGS – STM-2				NIST SRM 1646a				LD
	CV		MV		CV		MV		
As					6.23	±0.21	6.1	±0.7	2.1
K(%)	3.38	±0.17	3.1	±0.8	0.864	±0.016	0.9	±0.4	0.11
La	154	±11	148.1	±6.7	17		18.7	±0.9	0.56
Na(%)	6.61	±0.38	6.4	±0.2	0.741	±0.017	0.74	±0.03	0.021
Nd	81	±4.8	84	±19	15		14	±3	3.02
Sb					0.3		0.32	±0.06	0.12
Sm	12	±0.9	8.6	±0.8					0.066
U	7.6		7	±1	2		2.2	±0.5	0.26
Ba	639	±61	648	±74	210		230	±36	56
Ca(%)	0.78	±0.03	0.7	±0.2	0.519	±0.02	0.6	±0.1	0.26
Ce	253	±23	231	±14	34		35	±2	0.67
Co					5		4.9	±0.2	0.17
Cr					40.9	±1.9	43	±2	1.56
Cs	1.52	±0.06	1.6	±0.5					0.42
Eu	3.45	±0.25	3.4	±0.3					0.072
Fe(%)	3.77	±0.09	3.7	±0.1	2.008	±0.039	2.03	±0.06	0.011
Hf	27	±0.8	28.0	±0.9					0.18
Lu	0.6	±0.04	0.60	±0.05					0.029
Rb	114	±11	117	±14	38		38	±5	6.43
Sc					5		4.85	±0.06	0.023
Se					0.193	±0.028	0.3	±0.2	0.32
Ta	16	±1.1	17	±1					0.15
Tb	1.33		1.3	±0.2					0.21
Th	27	±5	29	±3	5.8		5.8	±0.6	0.14
Yb	4.2	±0.8	4.3	±0.7					0.22
Zn	223	±19	216	±16					2.50
Zr	1280	±62	1257	±147					130

Table 2 shows the commercial name, provenance, sample code, petrographic classification and activity concentrations (AC) for ^{232}Th, ^{238}U and ^{40}K, in Bq kg^{-1}. The uncertainty of the results was obtained by means of error propagation for 95% of confidence. Considering all the samples, thorium, uranium and potassium AC showed a range from 2.5 to 2966 Bq kg^{-1}, 3.9 to 214 Bq kg^{-1} and 25 to 2372 Bq kg^{-1}, respectively. The highest values of activity concentrations were found for Th in sample CH7, from Switzerland; for U, in the sample RJ1 from Rio de Janeiro, Brazil; and for ^{40}K, in the sample MG2, from Minas Gerais, Brazil.

A comparison of the AC according to the samples' place of origin is shown in Fig. 2. Among the Brazilian samples, the ones from Minas Gerais (MG) presented the highest ^{40}K value. Despite the fact that only one sample from Rio de Janeiro (RJ) was analyzed, it showed the highest ^{238}U content and presented almost the same value as the mean concentration of São Paulo (SP) samples for ^{232}Th. The mean AC and standard deviation for all Brazilian and Swiss samples were: 62 ± 55 Bq kg^{-1} and 93 ± 60 Bq kg^{-1} for ^{238}U; 1126 ± 516 Bq kg^{-1} and 1005 ± 778 Bq kg^{-1} for ^{40}K; 122 ± 111 Bq kg^{-1} and 293 ± 806 Bq kg^{-1} for ^{232}Th, respectively. These values indicate that a wide range of radionuclides AC can be found in the analyzed ornamental rocks. The high mean and standard deviation for ^{232}Th in the Swiss samples were due to the value found in sample CH7. If not taking this sample in consideration, the mean value and standard deviation become 70 ± 67 Bq kg^{-1} for this radionuclide, lower than the Brazilian mean AC.

The differences observed in the activity concentrations are not just related to the provenance of the rocks, but mainly to their mineralogical composition. Elements with a lithophile behavior such as U, Th and K concentrate in the Earth`s crust during the melting in the mantle and basalt differentiation being accumulated in felsic igneous melts [24]. Higher concentrations of U are generally found in acid igneous or granitic rocks while basaltic rocks contain lower concentration [25]. Thorium is 3 to 4 times more abundant than uranium in the rocks of the lithosphere [26] and sedimentary rocks generally contain only few μg g^{-1} of this element. On the other hand, its concentration can be up to 10 times higher in acid igneous rocks, where it can substitute the rare earth elements [27].

Fig. 3 shows the Th/U ratio in the samples. It can be seen that the ornamental rocks from Brazil tend to be enriched in Th compared to the Swiss samples. This ratio is closer to the global average (3 to 4) in the CH samples while most of the Brazilian ones present this ratio in the range of 5 to 15.

The high values of Th/U ratio in the São Paulo samples are probably due to an enrichment in Th as their concentrations are generally higher than mean values found in granites [28].

Table 2: Activity concentration of ^{232}Th, ^{238}U and ^{40}K, in Bq kg^{-1}, of the analyzed samples, their commercial names and petrographic classification.

Sample ID	Commercial name	Petrographic classification	^{232}Th Bq/kg		^{238}U Bq/kg		^{40}K Bq/kg	
CH1	Rosso Lucido	SGR	80	±4	64	±4	1674	±493
CH2	Iragna	GRN	97	±5	101	±7	1551	±463
CH3	Basaltito	BST	240	±14	169	±9	1797	±86
CH4	Branco Suiça	BGM	34.9	±2.1	19	±2	558	±31
CH5	Flor di Pesco	MRB	37.0	±2.2	144	±7	31	±7
CH6	Bianco Cristal	MGR	85	±5	181	±17	1306	±229
CH7	Sodalita	NSY	2966	±174	<LD		<LD	
CH8	Piettra Lavica	ADT	19.3	±1.1	86	±6	447	±43
CH9	Pietra Lavica (1)	ADT	3.87	±0.25	<LD		<LD	
CH10	Pietra de Jerusalem	MRB	2.47	±0.15	32	±2	25	±18
CH11	Onsernone Lucido	GRN	53.9	±3.0	65	±5	201	±116
CH12	Mônaco Light	MRB	49.5	±3.0	16	±1	2213	±671
CH13	Lusera Fiammata	MGC	143	±9	146	±3	1250	±368
SP1	Capão Bonito Grãos Maior	MGR	356	±20	46	±3	599	±177
SP2	Capão Bonito	MGR	387	±21	131	±8	1182	±348
SP3	Vermelho Bragança	MGR	169	±10	94	±5	1186	±65
SP4	Maracujá	MGR	282	±16	24	±6	1125	±73
SP5	Vermelho Jacarandá	SGR	147	±8	47	±5	223	±106
SP6	Marrom São Paulo	SGR	122	±7	73	±5	1385	±80
SP7	Blinder Vermelho Claro	MGR	131	±8	52	±3	1246	±65
ES1	Blinder Cinza Escuro	QMZ	14.4	±0.9	4	±2	1041	±191
ES2	Branco Siena	SGR	44.1	±2.5	10	±2	871	±60
ES3	Cinza Corumbá	MGR	66.0	±3.8	83	±4	1326	±84
ES4	Cinza Castelo	MGR	82	±4	18	±3	962	±51
ES5	Branco Marfim	SGR	73	±4	25	±3	1365	±76
ES6	Verde Pavão	QMZ	11.2	±0.6			1275	±75
ES7	Cinza Novo Mundo	SGR	104	±5	19	±2	1333	±66
ES8	Verde Ubatuba	QMZ	17.9	±1.0	22	±3	549	±33
BA1	Azul Bahia	FMZ	22.6	±1.3	146	±9	1694	±515
BA2	Azul Bahia Escuro	FMZ	80	±5	100	±6	772	±53
MG1	Café Imperial	AFS	49.3	±3.0	65	±13	1797	±342
MG2	Café Imperial Claro	AFS	51.5	±3.2	16	±1	2372	±703
RJ1	Rosa Capri	SGR	230	±13	214	±16	1384	±81

SGR: Syenogranite; MGR: monzogranite; FMZ: foid-monzodiorite; GRN: granodiorite; BST: basaltite; BGM: biotite gneiss with muscovite; MRB: marble; QMZ: quartz monzodiorite; NSY:

nepheline syenite; AFS: alkali feldspar syenite; ADT: andesite; MGC: mylonitic gneiss with chlorite and muscovite.

Figure 2: *Mean activity concentration according to the sample origin: CH: Switzerland, BR: Brazil. SP, ES, BA, MG and RJ stands for the Brazilian states of São Paulo, Espírito Santo, Bahia, Minas Gerais and Rio de Janeiro, respectively*
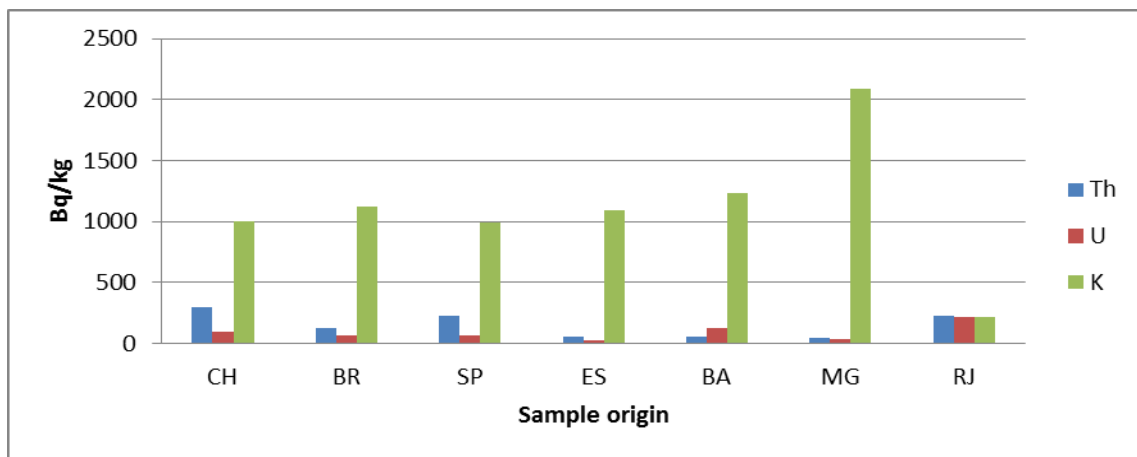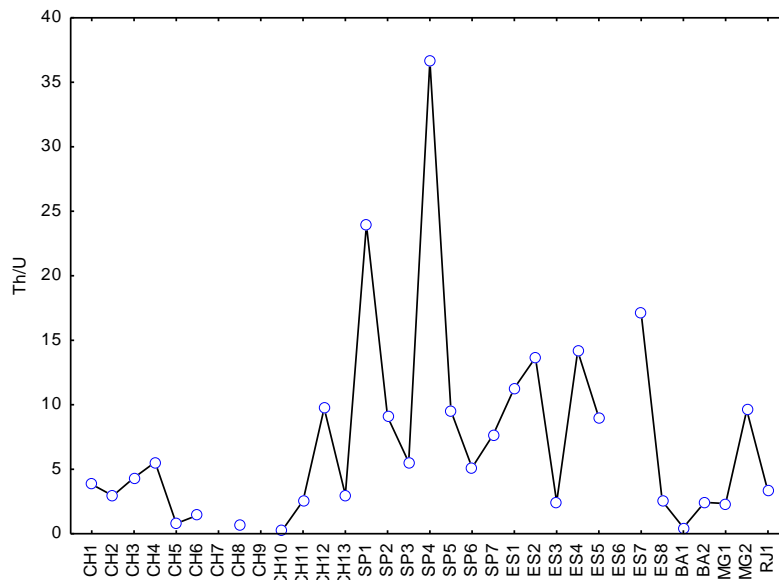

Figure 3: *Th/U ratio in the analyzed samples*

For chemical characterization of the ornamental rock samples, trace elements were also determined and their concentrations are shown in Table 3. Table 4 shows the Pearson correlation coefficients obtained for these results. According to the results, Th showed a good correlation with rare earth elements (REE), Br, Hf, Na, Rb, Sb and Zr; uranium was well correlated only with Cs; and K presented good correlations with Ba, REE, Zr and a negative correlation with Ca. The good correlation among Th, Zr, and REE may indicate that these elements are probably associated with minerals such as zircon and apatite [29,30]. The elevated value of Th, REE and Zr found in sample CH7 matches with the nepheline syenite mineralogy, probably due to the presence of apatite-like minerals, monazite and zirconosilicates [31].

Cluster analysis (CA) applied to the variables, Fig. 4, also shows the Th association with REE, Hf and Zr, also indicating a common origin for these elements, e. g., present in the same minerals constituents of the rocks. Potassium and U, on the other hand, are associated with elements such as Ca, Co, Zn and Fe. Fig. 5 shows the loading factors, obtained by factor analysis for the determined elements. The result agreed with the one obtained by CA and shows a high loading factor for Th and REE in the first factor, while U and K, present low loading factors for both, factor 1 and 2, being negative for U. This results indicates that the mineral bearing Th must be distinct from that bearing U and K. In addition to the uranium-bearing minerals, this element can be present in rocks by isomorphic substitution of calcium [32], what could cause the weak inverse loading factor for these elements in factor 2.

The influence of elemental composition of the analyzed rocks is highlighted in Fig. 6 in which clusters formed according to the rock type can be seen. Generally, rocks of the same petrographic classification are grouped together independently of their provenance.

3.2 Radiological risk assessment

The radiological hazard index radium equivalent activity (Raeq), external hazard index (Hex), internal hazard index (Hin), absorbed dose rate (D), annual gonadal dose equivalent (AGDE), annual effective dose equivalent (AEDE) and excess life time cancer risk (ELCR) obtained for the samples analyzed in this study are shown in Table 5.

Table 3: Concentrations and uncertainties of trace elements, in mg kg^{-1}, except where indicated %, determined in the analyzed samples.

	As	±	Ba	±	Br	±	Ca %	±	Ce	±	Co	±	Cr	±	Cs	±	Eu	±	Fe %	±	Hf	±	La	±	Lu	±
CH1	7.6	0.4	776	38	8.5	0.3	0.23	0.03	57	2	0.38	0.03	69	2	5.1	0.2	0.77	0.02	0.778	0.008	5.90	0.08	27.1	0.5	0.78	0.03
CH2			2638	138	5.5	0.3	1.13	0.09	90	3	4.65	0.07	495	13	4.1	0.2	0.72	0.02	2.75	0.03	6.24	0.09	25.3	0.4	8.0	0.3
CH3	7.6	0.4	1124	57	<LD		2.5	0.2	177	6	8.1	0.1	83	2	37	3	2.46	0.07	3.61	0.03	9.3	0.1	109	2	0.39	0.02
CH4	<LD		417	22	<LD		1.3	0.1	47	2	3.76	0.06	159	4	1.7	0.1	0.94	0.03	1.75	0.02	4.04	0.06	26.8	0.5	0.16	0.01
CH5	0.5	0.2	70	7	4.1	0.3	27	2	36	1	0.44	0.03	20.9	0.6	<LD		0.15	0.01	0.165	0.003	0.23	0.02	22.9	0.4	0.061	0.004
CH6	1.8	0.3	188	20	3.5	0.3	0.7	0.1	29	1	1.60	0.09	185	6	17	2	0.33	0.02	0.79	0.01	3.83	0.08	12.3	0.2	0.65	0.03
CH7	<LD		1401	101	227	2	4.4	0.6	609	21	4.3	0.2	113	4	<LD		29.0	0.9	4.08	0.06	<LD		302	5	<LD	
CH8	53	2	820	57	<LD		9.1	0.3	64	2	46.0	0.9	231	7	<LD		2.18	0.07	7.97	0.08	5.23	0.08	35.1	0.7	0.25	0.02
CH9	<LD		181	27	<LD		3.6	0.2	24	1	30.2	0.3	254	7	<LD		1.74	0.04	5.64	0.05	0.92	0.06	17.4	0.1	0.17	0.02
CH10	<LD		24	9	1.7	0.2	32	2	5.6	0.3	5.78	0.06	319	9	0.09	0.06	0.076	0.005	0.540	0.006	0.16	0.03	3.74	0.08	0.027	0.003
CH11	<LD		1221	95	10.0	0.4	2.9	0.2	77	4	5.2	0.1	639	17	1.6	0.2	1.28	0.05	3.57	0.03	6.69	0.08	63.8	0.4	0.27	0.01
CH12	1.6	0.3	4773	189	<LD		0.17	0.03	338	11	17.3	0.2	155	4	2.7	0.2	6.4	0.2	3.92	0.03	7.19	0.09	162	3	0.26	0.01
CH13	3.1	0.2	174	14	<LD		0.61	0.02	85	3	1.46	0.06	289	8	9.3	0.3	0.205	0.008	1.25	0.01	6.78	0.08	37.6	0.7	1.20	0.05
SP1	0.4	0.1	2769	140	4.9	0.2	0.78	0.06	318	10	3.12	0.06	692	17	3.9	0.2	0.69	0.02	2.76	0.02	12.9	0.2	73	1	16.6	0.6
SP2	0.27	0.06	2320	124	7.7	0.1	0.74	0.06	295	10	2.73	0.05	594	15	6.9	0.3	0.98	0.03	2.87	0.03	12.9	0.2	76	1	15.3	0.5
SP3	<LD		517	27	1.9	0.5	0.85	0.08	156	6	2.53	0.06	154	4	4.1	0.3	0.78	0.03	1.51	0.01	7.31	0.09	90	2	0.39	0.02
SP4	1.7	0.1	1289	88	<LD		1.54	0.08	286	9	9.2	0.2	222	7	0.5	0.2	1.69	0.06	2.18	0.02	10.2	0.1	168	3	0.33	0.02
SP5	<LD		584	47	39.4	0.4	0.84	0.05	110	5	4.39	0.06	496	13	3.4	0.2	1.46	0.04	1.69	0.02	5.87	0.07	52.4	0.4	0.222	0.009
SP6	1.0	0.3	875	68	<LD		0.68	0.05	154	8	3.18	0.05	353	9	2.5	0.2	1.36	0.06	2.06	0.02	10.1	0.1	83.8	0.5	0.99	0.03
SP7	<LD		726	38	3.0	0.5	0.76	0.07	119	4	3.27	0.08	294	8	2.1	0.2	0.93	0.03	1.70	0.02	7.3	0.1	74	1	0.58	0.02
ES1	<LD		3358	225	<LD		2.9	0.4	123	4	17.7	0.3	51	2	2.9	0.5	2.83	0.09	6.41	0.07	4.7	0.1	62	1	0.25	0.02
ES2	<LD		623	47	<LD		1.72	0.08	65	2	3.5	0.1	365	11	<LD		0.99	0.04	1.42	0.02	4.21	0.06	33.8	0.7	0.095	0.009
ES3	5.5	0.4	1193	84	<LD		2.29	0.10	116	4	7.1	0.2	245	8	7.3	0.3	1.55	0.05	3.13	0.03	8.27	0.09	59	1	0.42	0.02
ES4	<LD		2914	257	136	2	3.0	0.1	291	9	365	3	13.6	0.6	1.4	0.1	3.5	0.1	4.14	0.03	15.0	0.2	151	3	0.31	0.02
ES5	21	1	413	41	<LD		1.10	0.07	56	2	474	4	10.4	0.5	1.9	0.1	0.82	0.03	1.67	0.01	4.88	0.06	24.3	0.4	0.32	0.02
ES6	<LD		3180	284	<LD		3.1	0.2	156	5	93.6	0.8	13.5	0.5	<LD		4.0	0.1	4.71	0.04	16.5	0.2	77	1	0.34	0.02
ES7	<LD		815	81	<LD		1.34	0.07	117	3	151	1	11.0	0.4	1.4	0.2	0.97	0.03	2.32	0.02	11.8	0.1	53.8	0.9	0.40	0.02
ES8	<LD		1828	162	1.6	0.7	4.6	0.2	142	4	23.4	0.2	423	11	0.23	0.06	2.80	0.07	5.32	0.04	5.97	0.07	78	1	0.178	0.008
BA1	3.4	0.3	138	9	91.9	0.8	0.56	0.04	28.4	0.9	0.75	0.03	99	3	5.0	0.2	0.12	0.01	1.44	0.01	11.9	0.1	14.2	0.3	0.26	0.01
BA2	8.7	0.5	222	22	103	2	0.51	0.05	47	2	3.2	0.1	55	2	7.0	0.3	0.34	0.01	2.09	0.02	20.2	0.2	25.5	0.5	0.27	0.01
MG1	3.8	0.8	5874	392	<LD		2.3	0.3	287	10	15.2	0.3	133	4	3.4	0.6	8.2	0.2	4.11	0.06	7.4	0.2	144	3	0.42	0.03
MG2	1.7	0.3	4981	197	<LD		0.18	0.03	352	12	18.0	0.2	161	4	2.8	0.2	6.6	0.2	4.09	0.04	7.49	0.09	173	3	0.27	0.01
RJ1	3.3	0.7	1074	72	<LD		1.37	0.08	198	7	5.4	0.2	150	5	1.30	0.07	1.40	0.04	2.10	0.02	8.14	0.09	113	2	0.33	0.01

	Na	±	Nd	±	Rb	±	Sb	±	Sc	±	Se	±	Sm	±	Ta	±	Tb	±	Yb	±	Zn	±	Zr	±
	%																							
CH1	1.67	0.04	19	1	235	11	1.01	0.08	11.66	0.06	0.7	0.2	0.13	0.01	1.64	0.06	1.51	0.08	4.7	0.4	6393	302	217	19
CH2	2.5	0.1	16	1	612	28	0.13	0.02	7.28	0.04	1.1	0.3	0.24	0.01	1.66	0.06	0.98	0.07	4.2	0.3	84	5	361	25
CH3	1.99	0.05	81	5	434	22	1.2	0.1	4.87	0.03	<LD		21	1	1.32	0.08	1.10	0.08	2.5	0.2	81	5	573	28
CH4	3.29	0.08	21	2	68	4	0.20	0.04	4.66	0.03	<LD		1.41	0.07	0.65	0.04	0.34	0.04	0.87	0.08	71	4	193	15
CH5	0.051	0.002	10	2	5.1	0.9	<LD		0.55	0.01	31.2	0.4	3.7	0.2	41	1	0.33	0.04	<LD		26	2	<LD	
CH6	2.24	0.05	19	3	228	14	<LD		3.45	0.03	2.1	0.6	6.6	0.3	2.2	0.1	1.4	0.1	3.2	0.2	44	4	166	26
CH7	12.2	0.3	318	37	<LD		3	1	11.47	0.08	<LD		98	4	2.7	0.2	12	1	5.3	0.5	906	52	1733	103
CH8	2.93	0.07	27	4	27	2	0.18	0.03	19.8	0.1	23	1	6.3	0.2	24.7	0.8	1.9	0.4	1.8	0.3	105	6	156	73
CH9	2.39	0.06	12	2	1	1	<LD		14.49	0.07	0.3	0.7	4.4	0.2	1.0	0.1	0.4	0.1	1.3	0.2	162	7	61	48
CH10	0.023	0.001	3	2	<LD		0.15	0.02	0.432	0.007	21.5	0.6	0.57	0.02	18.1	0.4	0.25	0.04	0.8	0.1	244	10	7	9
CH11	2.84	0.07	28	9	80	3	0.73	0.09	10.71	0.05	45	1	9.1	0.3	51	1	0.3	0.1	3.0	0.4	148	6	295	40
CH12	2.36	0.05	150	6	178	10	0.24	0.02	8.99	0.04	0.0	0.3	26	1	1.93	0.09	1.62	0.06	1.8	0.2	102	4	533	17
CH13	2.66	0.06	42	2	336	18	0.35	0.02	2.35	0.01	2.7	0.2	11.7	0.4	3.9	0.1	2.23	0.06	8.1	0.9	64	2	214	10
SP1	1.15	0.02	104	6	724	32	<LD		4.03	0.02	2.7	0.6	8.5	0.3	4.9	0.1	2.0	0.1	8.6	0.7	85	5	373	21
SP2	1.64	0.04	113	6	969	43	0.20	0.02	4.40	0.02	3.6	0.8	11.43	0.41	8.0	0.2	2.1	0.1	5.4	0.4	89	5	475	25
SP3	2.24	0.05	75	9	298	15	<LD		4.00	0.02	<LD		17.8	0.9	1.01	0.06	1.05	0.07	2.1	0.2	52	3	271	17
SP4	2.21	0.05	118	15	220	10	0.06	0.01	4.66	0.03	7.8	0.3	14.2	0.5	8.8	0.3	1.4	0.5	2.0	0.3	53	3	403	36
SP5	1.71	0.04	49	7	350	12	0.38	0.07	3.90	0.02	9.6	0.8	5.7	0.2	8.6	0.2	0.62	0.07	1.3	0.2	48	2	230	19
SP6	2.92	0.07	70	4	298	11	0.20	0.02	5.21	0.03	3.5	0.4	14.3	0.5	4.0	0.1	1.68	0.08	5.8	0.6	84	4	387	16
SP7	2.39	0.05	53	7	212	11	0.28	0.05	3.57	0.02	2.0	0.3	11.6	0.6	2.7	0.1	0.91	0.07	3.3	0.3	48	3	266	20
ES1	2.84	0.06	48	7	113	8	<LD		11.50	0.08	1.6	0.7	11.6	0.5	1.0	0.1	0.8	0.1	1.5	0.2	177	12	338	70
ES2	2.34	0.05	29	3	105	5	0.03	0.05	5.53	0.04	1.0	0.5	5.2	0.2	1.02	0.05	1.1	0.3	0.67	0.09	33	2	170	14
ES3	2.49	0.06	48	3	203	9	0.6	0.2	7.37	0.05	1.0	0.6	8.8	0.3	1.27	0.06	1.2	0.3	2.4	0.3	79	4	363	31
ES4	2.00	0.05	142	18	136	5	0.2	0.1	9.54	0.05	3	2	18.6	0.6	3.3	0.1	1.6	0.1	1.9	0.2	206	7	666	44
ES5	1.70	0.04	38	5	218	8	0.04	0.02	5.33	0.03	3	2	5.7	0.2	2.13	0.08	1.6	0.1	2.3	0.2	121	4	134	55
ES6	2.31	0.05	84	10	75	3	<LD		14.33	0.07	<LD		12.6	0.4	0.88	0.05	1.2	0.1	1.8	0.2	209	7	832	40
ES7	1.85	0.04	72	10	266	10	0.31	0.05	5.71	0.03	3	2	9.7	0.3	4.2	0.1	1.9	0.1	2.8	0.3	87	3	517	39
ES8	2.06	0.05	72	3	41	2	1.4	0.5	11.28	0.05	0.9	0.6	11.2	0.4	1.50	0.05	0.8	0.1	1.3	0.1	144	5	346	36
BA1	8.6	0.2	3.8	0.9	246	11	0.13	0.02	0.21	0.004	7	2	5.2	0.2	13.4	0.3	0.17	0.03	2.9	0.3	66	4	593	19
BA2	9.0	0.2	19	2	278	12	0.59	0.05	0.49	0.01	16.6	0.2	2.28	0.09	19.3	0.6	0.32	0.08	1.6	0.2	115	6	938	25
MG1	2.39	0.05	105	14	225	17	1.2	0.5	9.92	0.07	103	2	31	1	132	4	2.0	0.2	3.3	0.2	263	17	460	62
MG2	2.61	0.06	157	6	185	10	0.26	0.02	9.36	0.05	0.0	0.3	28	1	2.01	0.09	1.68	0.06	1.8	0.2	106	4	554	17
RJ1	2.41	0.05	77	13	257	11	0.4	0.1	4.55	0.03	27.3	0.5	11.8	0.4	30.3	0.9	1.0	0.3	2.4	0.3	41	3	363	38

Table 4: Pearson correlation coefficient obtained using the whole data set of elemental concentrations. Marked correlations are significant at $p < .050$.

	Th	U	K	As	Ba	Br	Ca	Ce	Co	Cr	Cs	Eu	Fe	Hf	La	Lu	Na	Nd	Rb	Sb	Sc	Se	Sm	Ta	Tb	Yb	Zn	Zr
Th	1.00																											
U	0.31	1.00																										
K	0.08	0.11	1.00																									
As	-0.32	-0.10	-0.31	1.00																								
Ba	-0.01	-0.34	**0.49**	-0.21	1.00																							
Br	**0.73**	-0.07	0.14	0.59	0.10	1.00																						
Ca	-0.04	0.02	**-0.57**	0.16	-0.24	-0.16	1.00																					
Ce	**0.69**	-0.21	**0.45**	-0.35	**0.60**	**0.63**	-0.24	1.00																				
Co	-0.09	-0.30	0.05	0.35	0.03	0.38	-0.07	0.00	1.00																			
Cr	-0.03	-0.04	-0.35	-0.17	0.00	-0.46	-0.07	0.03	**-0.37**	1.00																		
Cs	0.26	**0.57**	0.27	0.09	-0.15	-0.04	-0.13	-0.07	-0.16	-0.14	1.00																	
Eu	**0.89**	-0.33	**0.50**	-0.04	0.33	**0.78**	-0.05	**0.77**	-0.03	-0.18	-0.06	1.00																
Fe	0.08	-0.27	0.08	**0.67**	**0.49**	0.38	-0.16	0.29	0.08	-0.01	-0.02	0.32	1.00															
Hf	**0.37**	0.07	0.25	-0.18	0.23	**0.70**	**-0.47**	0.41	0.15	-0.08	0.07	0.10	0.09	1.00														
La	**0.68**	-0.22	**0.48**	-0.29	**0.53**	**0.74**	-0.22	**0.94**	0.01	-0.14	-0.05	**0.81**	0.31	0.33	1.00													
Lu	**0.69**	0.11	-0.04	-0.20	0.21	-0.25	-0.14	**0.38**	-0.12	**0.62**	0.02	-0.17	-0.02	0.27	-0.02	1.00												
Na	**0.65**	0.18	0.19	0.06	-0.10	**0.82**	-0.26	0.32	-0.14	-0.22	0.04	**0.62**	0.11	**0.51**	0.37	-0.16	1.00											
Nd	**0.76**	-0.27	**0.48**	-0.32	**0.50**	**0.71**	-0.22	**0.97**	0.08	-0.09	-0.06	**0.85**	0.29	**0.43**	**0.96**	0.22	**0.39**	1.00										
Rb	**0.81**	0.28	0.18	-0.34	0.12	-0.19	-0.35	**0.37**	-0.13	**0.50**	0.25	-0.21	-0.24	**0.38**	0.05	**0.85**	-0.06	0.24	1.00									
Sb	**0.78**	0.16	0.06	-0.14	0.12	0.57	-0.01	**0.55**	-0.21	-0.12	0.40	**0.81**	0.29	0.01	**0.59**	-0.17	**0.54**	**0.61**	-0.11	1.00								
Sc	0.11	-0.34	0.12	**0.69**	**0.40**	0.22	-0.16	0.21	0.12	-0.06	-0.18	**0.36**	**0.84**	-0.08	0.26	-0.13	0.01	0.24	**-0.39**	0.35	1.00							
Se	-0.13	0.16	-0.12	0.07	0.31	-0.07	0.23	0.08	-0.12	-0.05	-0.14	**0.41**	0.08	-0.08	0.18	-0.15	-0.01	0.00	-0.15	**0.45**	0.08	1.00						
Sm	**0.90**	-0.11	**0.67**	-0.26	0.33	**0.75**	-0.12	**0.83**	-0.05	-0.18	0.14	**0.97**	0.24	0.22	**0.87**	-0.07	**0.58**	**0.90**	0.06	**0.80**	0.27	0.31	1.00					
Ta	-0.09	0.13	-0.07	0.02	0.34	-0.13	0.20	0.05	-0.11	0.00	-0.12	0.09	0.07	-0.07	0.09	-0.09	-0.04	-0.03	-0.11	0.17	0.06	**0.99**	0.07	1.00				
Tb	**0.96**	-0.06	**0.46**	0.13	0.12	**0.72**	-0.09	**0.73**	0.01	-0.09	0.07	**0.92**	0.17	0.26	**0.71**	0.37	**0.59**	**0.81**	0.41	**0.75**	0.24	-0.04	**0.93**	-0.06	1.00			
Yb	0.32	0.33	0.15	-0.31	0.03	0.01	-0.26	0.31	-0.15	**0.37**	0.12	0.12	-0.21	0.24	0.12	**0.65**	0.09	0.23	**0.65**	0.24	-0.17	-0.05	0.24	0.01	**0.38**	1.00		
Zn	0.08	-0.05	0.17	0.02	-0.06	-0.03	-0.07	-0.05	-0.06	-0.17	-0.01	0.06	-0.17	-0.07	-0.05	-0.04	0.00	-0.04	-0.02	0.26	0.23	-0.08	0.08	-0.06	0.12	0.18	1.00	
Zr	**0.76**	0.10	**0.37**	-0.35	0.26	**0.92**	-0.19	**0.70**	0.00	-0.30	0.17	**0.79**	0.20	**0.90**	0.71	0.06	**0.77**	**0.76**	0.15	**0.70**	0.11	0.06	**0.79**	-0.01	**0.74**	0.17	-0.01	1.00

Figure 4: *Dendrogram for the variables measured in the analyzed ornamental rocks*
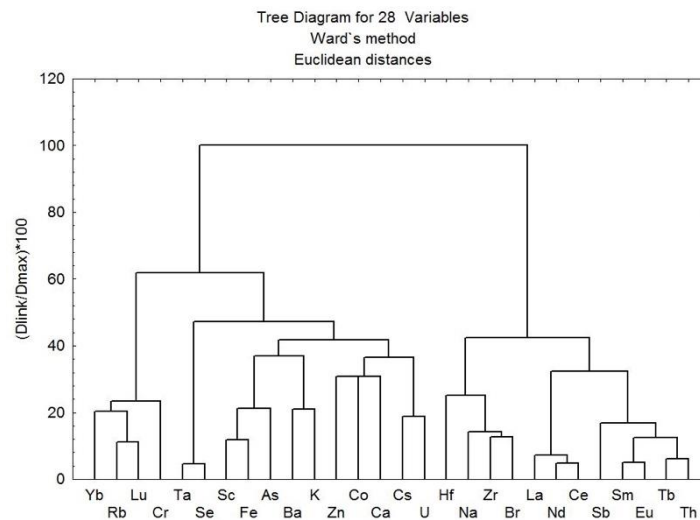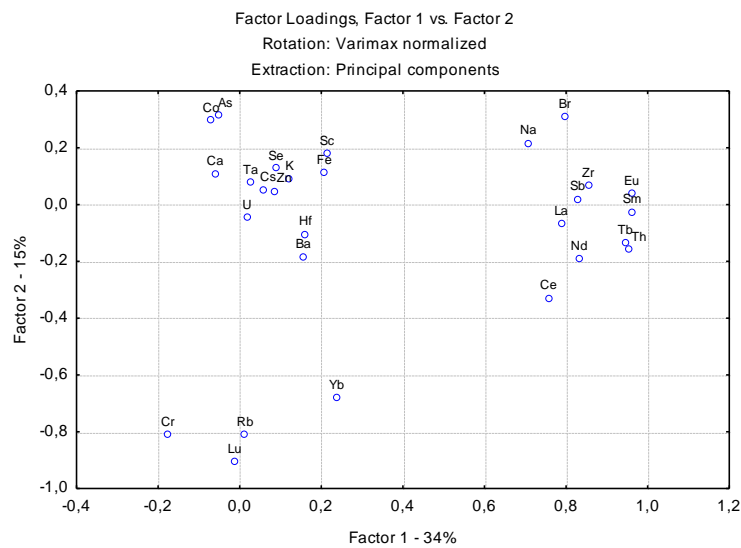

Figure 5: *Factor analysis graph with the loading factors for factor 1 and 2, with the explained variance of each factor*

As sample CH7 showed the highest values for all radiological hazard indices determined, it will be discussed separately. Thus, citation to all samples means that CH7 is not included.

The range of Raeq varied from 5.5 to 775 Bq kg^{-1} in the samples CH9 and SP2, respectively, with a mean value of 299 Bq kg^{-1}. Fig. 7 shows the mean values for samples from Switzerland and Brazil and also for Brazilian states. The mean value (and standard deviation) of Raeq in Swiss samples was 257 ± 187 Bq kg^{-1} and for the Brazilian samples 325 ± 175 Bq kg^{-1}. Samples from Espírito

Santo state (ES) were the ones with the lowest Raeq mean value. The recommended value of 370 Bq kg^{-1} was exceeded in samples from São Paulo (SP), Rio de Janeiro (RJ) and Switzerland (CH). Sample CH7 exceeded this value 11.5 times. For a comparison purpose, Fig. 7 shows mean Raeq obtained in samples from Pakistan, PK, [33]; Egypt, EG, [34]; Jordan, JO, [35]; and with two other Brazilian assessments, BR2 [3] and BR3 [36]. As can be observed, Brazilian samples tend to present higher Raeq average values than those observed abroad. There was a good agreement in the mean values obtained in this study with the ones reported for other Brazilian samples.

Figure 6: *Dendrogram obtained in the cluster analysis according to the rock classification*
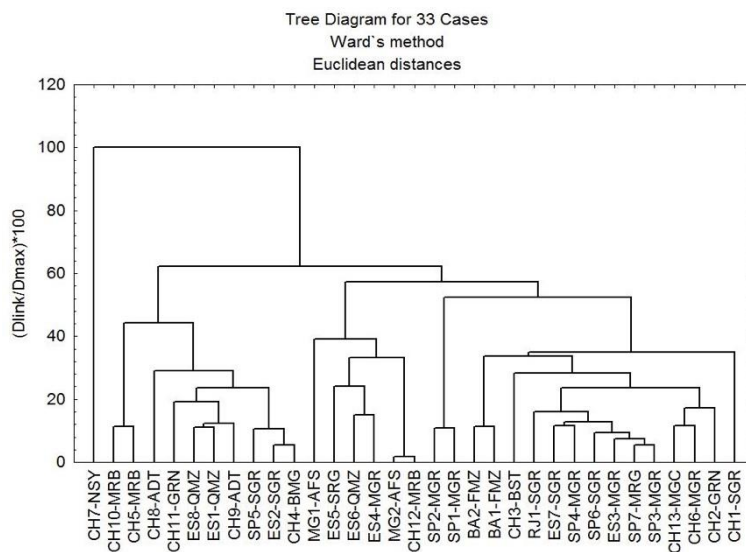
Figure 7: *Radium equivalent, in Bq kg-1, according to the samples origin (this study: CH, BR1, SP, ES, BA, MG and RJ) and literature values (PK, EG, BR2, JO and BR3)*
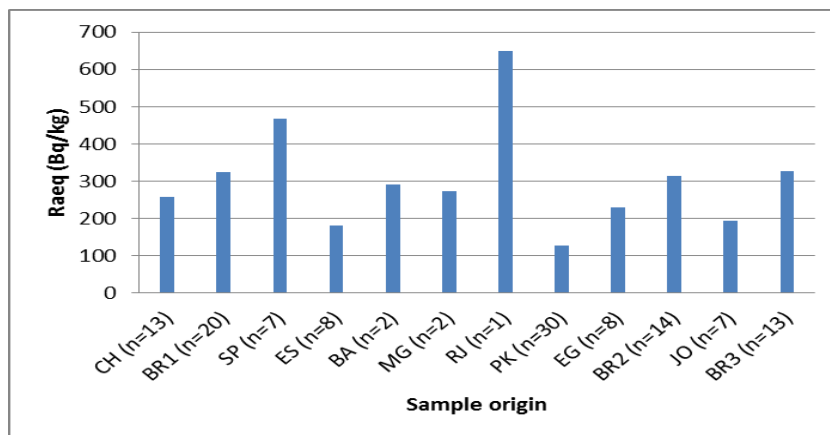
Table 5: Radiological hazard indices radium equivalent activity (Raeq), external hazard index (Hex), internal hazard index (Hin), absorbed dose rate (D), annual gonadal dose equivalent (AGDE), annual effective dose equivalent (AEDE) and excess life time cancer risk (ELCR).

	Ra eq		H_{ex}		H_{in}		D		AGDE		AEDE		ELCR	
	Bq/kg						nGy/h		mSv/y		mSv/y		x10^{-3}	
CH1	308	±49	0,41	±0,02	1.0	±0.1	148	±25	1.1	±0.2	0.7	±0.1	2.5	±0.4
CH2	359	±50	0,48	±0,03	1.2	±0.2	170	±26	1.2	±0.2	0.8	±0.1	2.9	±0.4
CH3	651	±36	0,88	±0,05	2.2	±0.1	298	±16	2.1	±0.1	1.46	±0.08	5.1	±0.3
CH4	112	±7	0,15	±0,01	0.35	±0.02	53	±3	0.38	±0.02	0.26	±0.02	0.91	±0.06
CH5	199	±11	0,27	±0,02	0.93	±0.05	90	±5	0.61	±0.03	0.44	±0.02	1.55	±0.08
CH6	403	±42	0,54	±0,04	1.6	±0.2	189	±20	1.3	±0.1	0.9	±0.1	3.2	±0.3
CH7	4241	±249	5,70	±0,48	11.5	±0.7	1791	±105	12.4	±0.7	8.8	±0.5	30.8	±1.8
CH8	148	±11	0,20	±0,01	0.63	±0.04	70	±5	0.49	±0.04	0.34	±0.02	1.20	±0.09
CH9	5.5	±0.4	0,0074	±0,0007	0.015	±0.001	2.3	±0.1	0.016	±0.001	0.011	±0.001	0.040	±0.003
CH10	37	±4	0,050	±0,004	0.19	±0.02	17	±2	0.12	±0.01	0.08	±0.01	0.29	±0.03
CH11	157	±18	0,21	±0,02	0.60	±0.06	71	±9	0.49	±0.06	0.35	±0.04	1.2	±0.2
CH12	257	±57	0,35	±0,02	0.7	±0.2	129	±30	0.9	±0.2	0.6	±0.1	2.2	±0.5
CH13	446	±44	0,60	±0,03	1.6	±0.1	206	±22	1.4	±0.2	1.0	±0.1	3.5	±0.4
SP1	600	±45	0,81	±0,06	1.7	±0.1	261	±21	1.8	±0.1	1.3	±0.1	4.5	±0.4
SP2	775	±65	1,04	±0,07	2.4	±0.2	344	±31	2.4	±0.2	1.7	±0.2	5.9	±0.5
SP3	427	±24	0,58	±0,03	1.41	±0.08	195	±11	1.37	±0.08	0.96	±0.05	3.3	±0.2
SP4	514	±35	0,69	±0,05	1.5	±0.1	228	±16	1.6	±0.1	1.12	±0.08	3.9	±0.3
SP5	276	±24	0,37	±0,03	0.87	±0.08	120	±11	0.83	±0.08	0.59	±0.06	2.1	±0.2
SP6	354	±20	0,48	±0,03	1.15	±0.07	165	±9	1.17	±0.07	0.81	±0.05	2.8	±0.2
SP7	336	±19	0,45	±0,03	1.05	±0.06	156	±9	1.10	±0.06	0.76	±0.04	2.7	±0.2
ES1	105	±18	0,141	±0,007	0.29	±0.06	54	±10	0.40	±0.07	0.26	±0.05	0.9	±0.2
ES2	140	±10	0,19	±0,01	0.40	±0.03	68	±5	0.49	±0.04	0.33	±0.02	1.16	±0.09
ES3	279	±16	0,38	±0,02	0.98	±0.06	133	±8	0.95	±0.06	0.65	±0.04	2.3	±0.1
ES4	209	±13	0,28	±0,02	0.61	±0.04	98	±6	0.70	±0.04	0.48	±0.03	1.7	±0.1
ES5	235	±14	0,32	±0,01	0.70	±0.04	113	±7	0.81	±0.05	0.55	±0.03	1.9	±0.1
ES6	114	±7	0,154	±0,002	0.31	±0.02	60	±3	0.45	±0.03	0.29	±0.02	1.03	±0.06
ES7	270	±15	0,36	±0,02	0.78	±0.04	127	±7	0.91	±0.05	0.62	±0.03	2.2	±0.1
ES8	89	±6	0,121	±0,006	0.30	±0.02	44	±3	0.31	±0.02	0.21	±0.02	0.75	±0.05
BA1	308	±50	0,42	±0,02	1.2	±0.2	152	±26	1.1	±0.2	0.7	±0.1	2.6	±0.5
BA2	274	±17	0,37	±0,02	1.01	±0.06	127	±8	0.89	±0.05	0.62	±0.04	2.2	±0.1
MG1	273	±43	0,37	±0,03	0.9	±0.2	135	±22	1.0	±0.2	0.7	±0.1	2.3	±0.4
MG2	273	±60	0,37	±0,02	0.8	±0.2	138	±32	1.0	±0.2	0.7	±0.2	2.4	±0.5
RJ1	649	±41	0,87	±0,06	2.3	±0.2	295	±19	2.1	±0.1	1.45	±0.09	5.1	±0.3
RV or WM[a]	370		<1		<1		84		0.36		0.46		1.16	

[a]RV or WV: recommended value or worldwide average value.

The external (Hex) and internal (Hin) hazard indices presented mean values of 0.38 and 0.995, respectively considering all samples. The values ranged from 0.011 to 1.25 for Hex, in samples CH9 and SP2, respectively, and from 0.015 to 2.45 for Hin, in the same samples. Fig. 8 shows that the average values of both of these indices were slightly higher for the Brazilian samples than for the Swiss ones. Among the Brazilian states, the samples from São Paulo (SP), Espírito Santo (ES) and Bahia (BA) presented very close average values while Minas Gerais (MG) samples presented the lowest ones. Comparing with values in the literature, only the samples from MG present lower values than those observed in samples from abroad. Good agreement for this parameter was also found among the Brazilian samples analyzed in this study and the values (BR2) reported by Moura et al. [3]. Brazilian samples presented Hin average values higher than those from all other countries shown in Fig 8. Nevertheless high values of Hin were also found in building material by Bello et al. [37], whose measures varied from 0.23 to 3.99 for rocks, sediment and building samples in Southwestern Nigeria and by Alharbi et al. [38] who found values varying from 0.14 to 2.12 in granite rocks of Kingdom of Saudi Arabia.

**Figure 8**: *External (Hex) and internal (Hin) hazard indices, according to the samples origin (this study: CH, BR1, SP, ES, BA, MG and RJ) and literature values (PK, EG, BR2 and JO)*
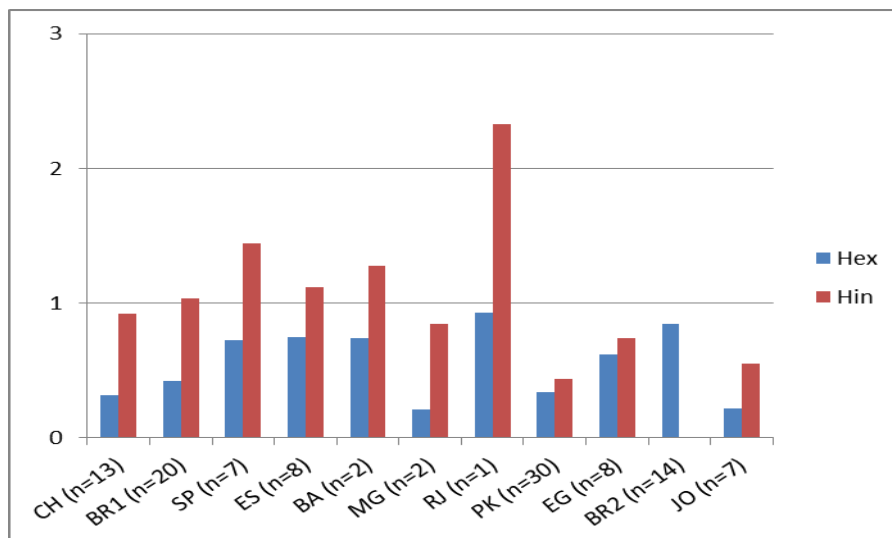
Considering the limit of 1 for Hex and Hin, the former was exceeded in two SP samples while the latter was exceeded in all SP samples but SP5, in BA and RJ samples, among the Brazilian ones. Among the Swiss samples Hex was not exceeded while Hin was higher than 1 in 5 samples. CH7

presented values for external and internal hazard index 5.7 and 11.5 times higher than the recommended value, respectively.

The absorbed dose rate (D) ranged from 2.3 to 344 nGy h^{-1}, with a mean value of 139 nGy h^{-1} considering all samples. The lowest value was measured in sample CH9 and the highest one in sample SP2. Fig 9 shows the comparison among the D values obtained in the samples analyzed in this study and also values reported in the literature. Among the Brazilian samples, the ones from São Paulo (SP) and Rio de Janeiro (RJ) showed the highest values, and the lowest ones were found in Espírito Santo (ES) samples. Brazilian average was higher than the one observed in Swiss samples and also higher than that reported for PK, JO and EG. The absorbed dose rate measured is quite similar to that found in granites analyzed by Anjos et al. [39]. Compared with the world average value of 58 nGy h^{-1} [11], only three Swiss and three Brazilian samples were below it, indicating that the majority of the analyzed samples are up to six times greater than the world average value. In the case of sample CH7 with a D of 1791 nGy h^{-1}, the worldwide average value is exceeded by 31 times.

Figure 9: *Absorbed dose rate, in nGy h-1, according to the samples origin (this study: CH, BR1, SP, ES, BA, MG and RJ) and literature values (PK, EG, JO and BR4)*
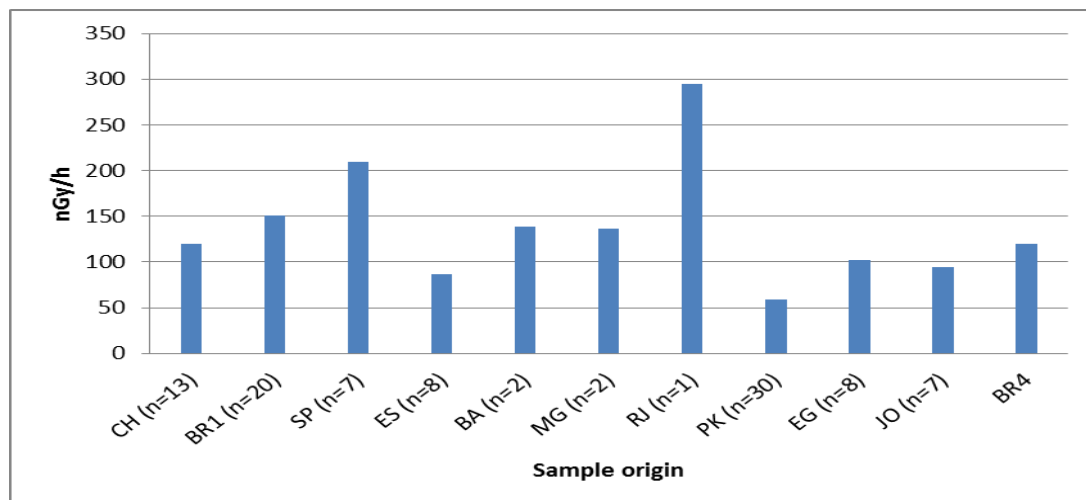
The annual gonadal dose equivalent (AGDE), annual effective dose equivalent (AEDE) and excess life time cancer risk (ELCR) indices presented mean values of 0.983 mSv y^{-1}, 0.683 mSv y^{-1} and

2.389, respectively, for all samples. AGDE varied from 0.016 to 2.393 mSv y^{-1}; AEDE varied from 0.011 to 1.685 mSv y^{-1} and ELCR varied from 0.040 to 5.899, all in samples CH9 and SP2, respectively. Fig 10 shows mean values for these parameters according to their origin and compared with the same values for literature in construction materials from Iraq (IQ) [40] and from Egypt (EG). The mean value of AGDE is higher for the Brazilian samples than that collected in Switzerland and those reported for Iraq and Egypt. Among the Brazilian samples the highest values were found in São Paulo (SP) and Rio de Janeiro (RJ) samples. Considering the average world value of 0.36 mSv y^{-1} for AGDE [12] (UNSCEAR, 1998) only two samples from Switzerland and three samples from Brazil have values below it. The values found in this study are up to 6.6 times higher than the world average, and sample CH7 exceeded this value by 34 times. Of the total, fifteen samples are greater than the established limit of 1 mSv y^{-1} [41].

Figure 10: *Annual gonadal dose equivalent (AGDE), annual effective dose equivalent (AEDE) and excess life time cancer risk (ELCR) according to the samples origin (this study: CH, BR1, SP, ES, BA, MG and RJ) and literature values (IQ and EG)*
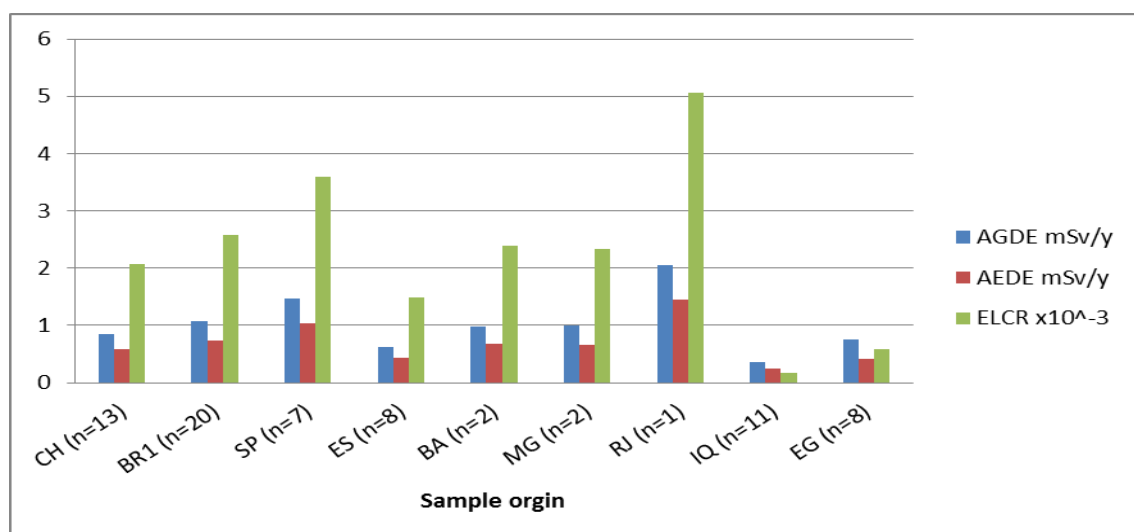
The results of AEDE were lower than the average annual indoor effective dose from terrestrial radionuclides of 0.41 mSv y^{-1} [42] in six samples from Switzerland and in five samples from Brazil. The measured values were up to 3.6 times higher than the worldwide average value and sample CH7 was 19 times greater than this average value. Six samples exceeded the limit of 1 mSv y^{-1}.

The results of ELCR were lower than the average global value in only three Swiss samples and in three samples from Brazil. The values above the average were up to five times higher and for sample CH7, 26 times higher.

3.3 Multivariate statistics of the radiological risk indices

Cluster analysis was applied to evaluate the radiological indices among the analyzed samples considering the activity concentrations of ^{232}Th, ^{238}U and ^{40}K, and the radiological indices determined in this study. The result is showed in Fig. 11. From the CA result it is obvious that sample CH7 is highlighted, being the one with the highest values for all radiological risk indices determined among the analyzed samples.

Figure 11: *Dendrogram obtained in cluster analysis considering the activity concentrations of the radionuclides and radiological risk indices*
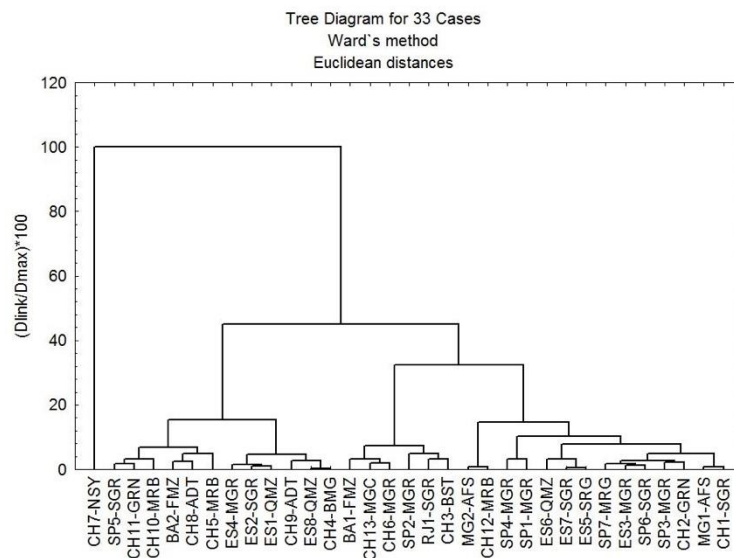
Cutting the dendrogram at a level of 20% of the 100*Dlink/Dmax, three main groups (excluding sample CH7) were observed (Fig. 11). The basic statistics for each group is summarized in Table 6.

Table 6: Basic statistics of the obtained groups using cluster analysis, considering the activity concentrations of the radionuclides and radiological indices.

	Valid N	Mean	Median	Minimum	Maximum	Std.Dev.	Skewness	Kurtosis
				Group 1				
Th	12	44.7	35.9	2.5	147.4	41.7	1.46	2.36
U	11	49.7	31.6	3.9	143.8	44.4	1.07	0.37
K	11	516.3	549.5	24.9	1041.0	365.4	0.01	-1.43
Ra eq	12	145.9	144.1	5.5	275.5	84.0	0.06	-0.51
Hex	12	0.19	0.16	0.011	0.47	0.14	0.69	-0.19
Hin	12	0.52	0.50	0.015	1.01	0.31	0.17	-0.93
D	12	67.8	68.8	2.3	126.6	37.5	-0.09	-0.36
AGDE	12	0.48	0.49	0.016	0.89	0.26	-0.14	-0.27
AEDE	12	0.33	0.34	0.011	0.62	0.18	-0.09	-0.36
ELCR	12	1.16	1.18	0.040	2.17	0.64	-0.09	-0.36
				Group 2				
Th	6	184.5	186.3	22.6	387.1	129.7	0.45	-0.09
U	6	164.4	157.5	130.9	213.7	30.2	0.80	0.05
K	6	1435.8	1345.3	1182.2	1797.4	251.2	0.75	-1.48
Ra eq	6	538.8	547.5	308.4	775.5	179.4	0.02	-1.74
Hex	6	0.741	0.75	0.27	1.25	0.354	0.15	-0.79
Hin	6	1.90	1.91	1.23	2.45	0.497	-0.22	-2.12
D	6	247.3	250.4	151.6	343.6	75.4	-0.005	-1.99
AGDE	6	1.73	1.75	1.08	2.39	0.52	0.006	-2.05
AEDE	6	1.21	1.23	0.74	1.69	0.37	-0.005	-1.99
ELCR	6	4.25	4.30	2.60	5.90	1.29	-0.005	-1.99
				Group 3				
Th	14	117.3	88.5	11.2	355.7	95.4	1.63	2.33
U	13	52.0	52.4	15.6	100.8	30.4	0.20	-1.41
K	14	1460.5	1349.0	598.5	2372.2	449.3	0.51	0.97
Ra eq	14	328.5	293.3	114.2	600.2	121.5	0.79	1.20
Hex	14	0.40	0.32	0.04	1.04	0.27	1.27	1.57
Hin	14	1.02	0.99	0.31	1.74	0.37	0.18	0.34
D	14	154.1	142.8	59.9	260.8	49.6	0.54	1.13
AGDE	14	1.10	1.04	0.45	1.82	0.34	0.48	1.17
AEDE	14	0.76	0.70	0.29	1.28	0.24	0.54	1.13
ELCR	14	2.65	2.45	1.03	4.48	0.85	0.54	1.13

Group 1 was formed by the samples with lower activity concentrations and radiological hazard indices, meaning they are the safest samples among the analyzed ones. The values of Skewness and

Kurtosis, near zero and negative, respectively, indicate that these samples form an homogeneous group with normal distribution for the radiological indices. For these samples the radiological hazard indices are mainly related to ^{232}Th concentrations as can be seen in Fig. 12, with inverse correlation between ^{238}U and ^{40}K.

Group 2 was formed by the samples with the highest activity concentrations and radiological hazard indices. Thus, these are the less safe samples among the analyzed ones considering gamma exposure, indicating that care must be taken in their use. This group contains foid-monzodiorite, mylonitic gneiss with chlorite and muscovite, monzogranite, syenogranite and basaltite rock types from Switzerland, Bahia, São Paulo and Rio de Janeiro. The radiological hazard indices are mainly related to ^{232}Th activity concentration, as can be seen in Fig. 13, with ^{238}U and ^{40}K directly correlated. As group 1, this group is also an homogenous group with normal distribution for the radiological hazard indices.

Figure 12: *Principal component analysis result with the loading factor for the first and second component for the group 1 of the dendrogram shown in Fig 11*
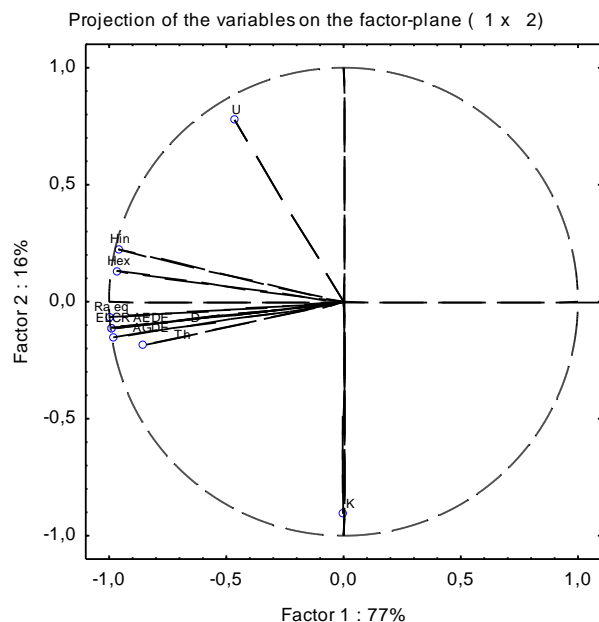

Group 3 presents the samples with intermediate values for the activity concentrations and radiological hazard indices. Nevertheless, only Raeq and Hex are within the limits for gamma external exposure, indicating that care must also be taken in their use. These samples form an

heterogeneous group and the positive values of kurtosis indicate that the distribution is higher and narrower than the normal. Thorium content is also the main responsible for the observed radiological hazard indices, as shown in Fig. 14, also with negative correlation between ^{238}U and ^{40}K.

Figure 13: *Principal component analysis result with the loading factor for the first and second component for the group 2 of the dendrogram shown in Fig. 11*

Projection of the variables on the factor-plane (1 x 2)
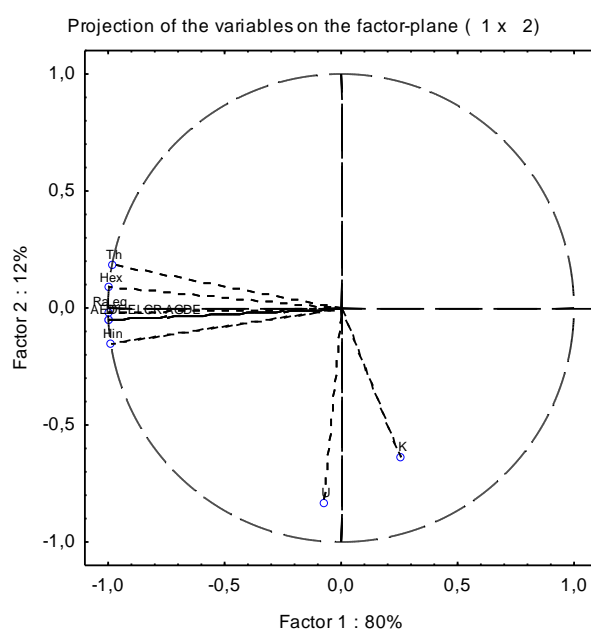
4. CONCLUSION

The analysis of ornamental rocks from Brazil and Switzerland showed that the activity concentrations of thorium, uranium and potassium covered a wide range of values, varying from 2.5 to 2966 Bq kg^{-1}, from 3.9 to 214 Bq kg^{-1} and 25 to 2372 Bq kg^{-1}, respectively. The highest ^{232}Th activity concentration was found for sample CH7, from Switzerland; the highest ^{238}U activity concentration was measured in RJ1 sample from Rio de Janeiro, Brazil; and for ^{40}K, in the sample MG2, from Minas Gerais, Brazil. The mean activity concentration and standard deviation for all

Brazilian and Swiss samples were: 62 ± 55 Bq kg^{-1} and 93 ± 60 Bq kg^{-1} for ^{238}U; 1126 ± 516 Bq kg^{-1} and 1005 ± 778 Bq kg^{-1} for ^{40}K; 122 ± 111 Bq kg^{-1} and 293 ± 806 Bq kg^{-1} for ^{232}Th, respectively.

Figure 14: *Principal component analysis result with the loading factor for the first and second component for the group 3 of the dendrogram showed in Fig. 11*
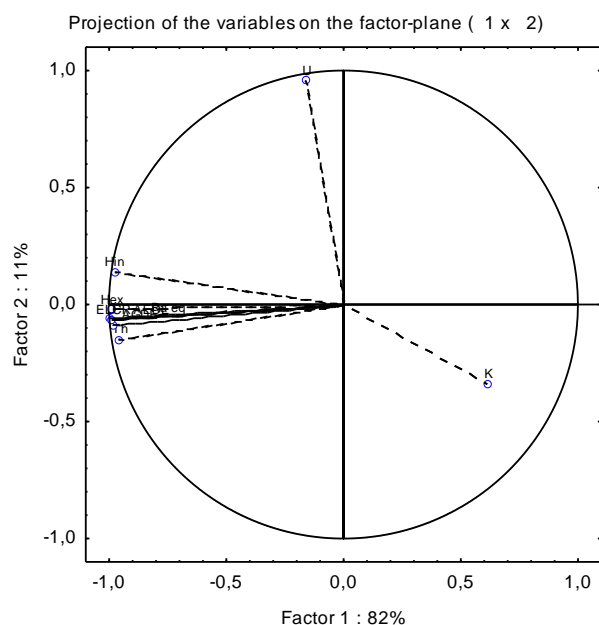
Brazilian ornamental rocks tend to be enriched in Th with a Th/U ratio varying from 5 to 15. Swiss samples possess this ratio closer to the global average, 3 to 4. Thorium was well correlated with rare earth elements (REE), Br, Hf, Na, Rb, Sb and Zr; uranium only with Cs; and K presented good correlations with Ba, REE, Zr and a negative correlation with Ca. These findings indicate that Th, Zr, and REE may probably be associated with minerals such as zircon and apatite. Multivariate statistical analysis indicated that the variance observed in the analyzed rocks is more related to their petrographic classification than their provenance.

The radiological hazard index radium equivalent activity (Ra$_{eq}$), external hazard index (H$_{ex}$), internal hazard index (H$_{in}$), absorbed dose rate (D), annual gonadal dose equivalent (AGDE), annual effective dose equivalent (AEDE) and excess life time cancer risk (ELCR) were exceeded in about two thirds of the Brazilian and Swiss samples. Results indicated that samples CH4, CH5, CH8, CH9, CH10, CH11, SP5, ES1, ES2, ES4, ES8 and BA2 are the safest ones considering gamma

exposure. All the other samples should not be used in large amounts, mainly in the parts of the house where people can stand for long periods such as the rooms.

5. ACKNOWLEDGMENT

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