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Elemental Compositional Analysis of Local Pakistani Building Materials Using Instrumental Neutron Activation Analysis

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ABSTRACT

In the present study, elemental composition of local Pakistani building materials (marble, granite, stones and pottery) were determined using Instrumental Neutron Activation Analysis (INAA) technique. On the average, higher numbers of elements were quantified in marble samples followed by stone and pottery samples. The elemental data were subjected to principal component analysis (PCA) which showed that all marble samples have similar composition. In addition, stones show the same chemical content and the pottery samples resemble each other. Therefore, PCA can be successfully used to differentiate between diverse types of building material samples from their elemental composition.

1. Introduction

Construction is one of the main sectors of private and public investment in the world and contributes greatly in the socio-economic development of a nation. Various building materials including bricks, cement, ceramics, concrete, sand, stone, etc. are widely used in construction.

Determination of elemental composition of building materials is essential for determining the chemical origin of these materials. Moreover, knowledge of chemical composition of these building materials is vital to assess and monitor their impact on the environment [1]. Furthermore, such studies can help to compile a database which is of interest to geochemists, geologists and archaeologists [2-4].

Among various analytical techniques, good sensitivity, high accuracy, very low blank contributions and negligible interferences makes instrumental neutron activation analysis (INAA) one of the most reliable compositional characterization techniques for the determination of major, minor and trace elements in all types of geological and biological samples [5, 6]. In the present study, the elemental composition of common building materials including marbles, granite, stones and pottery samples has been determined using INAA. Although pottery is not directly used for construction but clay, which is a basic ingredient of pottery, along with other components is used in the manufacture of ceramic tiles [7]. These samples were selected due to their different geological origin; marbles belong to metamorphic rocks, granite is an igneous rock in nature while stones have sedimentary origin and clay is formed from the weathering of rocks. The main objective of the present study is to carry out the compositional analysis of these materials and find, if possible, a correlation between the elemental profiles with their geological origin. In the current study, the elemental data obtained using INAA has been analyzed to discover the differences and similarities between these samples. Since, sufficient information is not available on the elemental composition of Pakistani building materials; this study will serve as a database for further investigations regarding applications of these samples.

2. Experimental

2.1 Sampling and Sample Preparation

Eleven marble, one granite, six stone and two pottery samples were collected from different locations of the Rawalpindi and Islamabad area as listed in Table 1. The samples were properly catalogue, washed and dried in the sun. They were crushed and sieved through 0.125 mm (120 meshes ASTM) stainless steel sieve to obtain homogenized sample with particle size of less than 125 μm. The samples were stored in labeled polythene containers till analysis.

2.2 Instrumentation and Irradiations

Approximately 100 mg of each sample in duplicate along with two reference materials (RMs) from the International Atomic Energy Agency (IAEA), i.e., IAEA SL-1 (Lake Sediment) and IAEA Marine sediment (SDM2/TM) were packed in clean labeled polyethylene capsules. Multiple batches of the collected samples were then packed and sealed in polyethylene rabbits for different irradiation protocols. These protocols have been devised for the study of different isotopes in accordance with the half-life of the isotope of the desired element and are given in Table 2 [8-10]. The sealed targets were irradiated using the 27 kW, Miniature Neutron Source Reactor (MNSR) with a thermal neutron flux of 1×10^{12} $ncm^{-2}s^{-1}$, housed at the Pakistan Research Reactor II

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Table 1: Details of marble, granite, stone and pottery samples collected from Rawalpindi and Islamabad.

No.	Sample	Sample name	Sample code	Colour
1.	Marbles	Parlino	MPL	Off White
2.		Red & White	MRW	Red
3.		Fancy	MFA	Cream
4.		Sunny White	MSW	White
5.		Nowshera Pink	MNP	Pink & White
6.		Tavera	MTA	Off White
7.		Silky Black	MSB	Gray
8.		Oceanic	MOC	Gray
9.		Flower	MFL	Light Brown
10.		Sunny Gray	MSG	Gray
11.		Ziarat White	MZW	White
12.	Granite	Granite	MGR	Black
13.	Stones	Tote Onyx	STO	White
14.		Indus Gold	SGO	Yellow
15.		Lasbel Green	SLG	Brown
16.		Black & Gold	SGB	Golden black
17.		Barmatic	SBA	Cream
18.		Chocolate	SCH	Dark Brown
19.	Pottery	Pottery 1	P-1	Brown
20.		Pottery 2	P-2	Brown

Table 2: Irradiation conditions for investigated samples.

Protocol	Irradiation time/ decay time/ counting time	Isotopes quantified
Sequential	30 s/2 m/100 s	^{28}Al, ^{49}Ca, ^{27}Mg, ^{51}Ti, ^{52}V
Short	30 s/2 h/300 s	^{42}K, ^{56}Mn, ^{24}Na
Intermediate	1 h/2 d/900 s	^{76}As, ^{82}Br, ^{42}K, ^{140}La, ^{24}Na, ^{122}Sb, ^{153}Sm, ^{175}Yb
Long	5 h/2–3 w/7200 s	^{131}Ba, ^{141}Ce, ^{60}Co, ^{51}Cr, ^{134}Cs, ^{152}Eu, ^{59}Fe, ^{181}Hf, ^{203}Hg, ^{177}Lu, ^{147}Nd, ^{86}Rb, ^{122}Sb, ^{46}Sc, ^{85}Sr, ^{153}Sm, ^{117m}Sn, ^{182}Ta, ^{160}Tb, ^{233}Th, ^{65}Zn

Where s = seconds, m = minutes, h = hours, d = days, w = weeks

(PARR-II) at Pakistan Institute of Nuclear Science and Technology (PINSTECH). After irradiation, the targets were cooled for the appropriate cooling periods, and then transferred to pre-cleaned, pre-weighed polyethylene capsules for counting.

The activated samples were counted using a high purity germanium detector (Canberra Model AL-30) attached to a PC-based multi-channel analyzer (Inter Technique model pro-286e) through a sensitive spectroscopy amplifier (Ortec model 2010). The resolution of the system is 1.9 keV for the 1332.5 keV peak of ^{60}Co with peak-to-Compton ratio of 40:1. GammaVision software (Ametek, Inc version 6.0.1.0) was used for recording the gamma spectra while ANGES software (IAEA version1.0.0.2) was used for data acquisition. The data files, containing information on peak energy, peak area, etc., along with the indigenously developed computer program "GammaCal'' were used to obtain elemental concentrations. All necessary corrections (background subtraction, etc.) were done and the final results were obtained on dry weight basis.

3. Results and Discussion

3.1 Quality Assurance (QA)

Quality assurance was performed using two standard materials, IAEA Lake Sediment (IAEA SL-1) and IAEA Marine sediment (SD-M-2/TM). The results of the present study are presented in Table 3 and show that 24 elements were quantified within 5% error of certified values in case of SL-1. Only 3 elements Hg, Lu and Sn have concentration values with more than 20% error, which may be due to their lower concentrations in SL-1 standard. In case of SDM-2, about 70% of the quantified elements have less than 20% error with respect to the certified values. Therefore, the results obtained are reliable and provide confidence in the experimental procedures. Limits of detection (LOD) of the quantified elements are also tabulated in Table 3.

3.2 Elemental Composition of Local Building Materials

3.2.1 Elemental composition of marble and granite samples

The elemental compositions of marble samples studied in the present work are given in Tables 4a and 4b. From these tables it can be seen that maximum numbers of elements up to 29 were determined in MPL, while only 10 elements were measured in MZW. Moreover, variations in concentrations of the same element were observed among different marble samples. Some of the elements, like As, Ce, Cr, Fe, Mn, Na, Sm, Sn and Zn were found in all the samples but at different concentration levels. Additionally, the variations in the concentrations of elements, in µg/g, is quite large in case of Al (105-4390), K (106-2013), Mg (217-2691), Sr (30-178), Mn (2-188) and Na (18-201). Furthermore, Ti is observed to be found in higher concentration which is in line with the published data [11, 12]. Concentrations between 1 to 10 µg/g were observed for As, Br, Ce, Co, Cr, Hf, La, Rb, Sc and Sm while Sn, V and Zn concentrations were found in the 10 to 30 µg/g range. The elements with less than <1 µg/g concentrations include Eu, Lu, Sb, Ta, Th and Yb. Such large variations may be due to differences in the geological locality, from where each sample is collected.

Elemental data of granite sample is also given in Table 4b. Granite differs from marble both in physical properties as well as in the geological origin [13] and this difference is also manifested in the tabulated data where the concentrations of majority of the quantified elements in granite are much higher (>10-100 times) than the marble samples.

Table 3: Concentration of elements (in µg/g, on dry weight basis at 95% confidence interval) in IAEA certified reference materials used for QA.

Element	IAEA SL-1 lake sediment		IAEA marine sediment (SD-M-2/TM)		Limit of detection (LOD) in µg/g
	Present results	IAEA values [14]	Present results	IAEA values [15]	
Al	89040±3730	(89000)	34570±6610	(32000)	30
As	27.70±4.90	27.50±1.45	13.02±1.62	18.30±0.95	0.2
Br	7.50±4.40	6.82±0.87	49.17±2.29	65.70±10.30	0.2
Ce	102±16.90	117±8.50	54.69±2.06	54.30±4.30	0.55
Co	19.80±1.30	19.80±0.75	13.74±0.48	13.60±0.55	0.10
Cr	99.10±2.70	104±4.50	82.54±3.38	77.20±9.40	1.80
Cs	7.01±0.07	7.01±0.44	10.12±1.43	8.05±1.29	0.20
Eu	1.60±0.01	(1.60)	0.81±0.04	0.85±0.20	0.01
Fe	64470±3620	67400±850	29250±1520	27100±1750	80
Hf	4.14±0.14	4.16±0.29	2.78±0.02	2.83±0.48	0.05
Hg	0.09±0.02	(0.13)	0.07±0.04	0.05±0.01	0.03
K	15000±500	(15000)	19350±1690	17600±2100	80
La	50.50±1.30	52.60±1.55	28.96±2.98	26.20±2.20	0.40
Lu	0.34±0.15	(0.54)	0.29±0.17	0.24±0.07	0.01
Mg	29000±356	(29000)	BDL	BDL	200
Mn	3460±100	3460±80.00	BDL	BDL	2.20
Na	1720±150	1720±60.00	12960±950	13500±1250	15
Nd	44.50±11.30	43.80±1.40	38.80±8.90	24.60±10.25	1.20
Rb	110±5.64	113±5.50	105±12	99.70±14.50	1.20
Sb	1.32±0.22	1.31±0.06	1.24±0.25	0.99±0.17	0.02
Sc	17.30±1.80	17.30±0.55	10.48±0.26	10.30±0.75	0.05
Sm	9.25±0.30	9.25±0.26	4.58±0.11	4.27±0.81	0.10
Sn	2.10±0.50	(4.00)	7.31±5.30	8.00±7.90	1.80
Sr	88.30±52.88	(80.00)	BDL	BDL	30
Ta	1.43±0.12	(1.58)	1.08±0.29	0.84±0.20	0.05
Tb	1.40±0.30	(1.40)	1.00±0.36	0.52±0.05	0.05
Th	13.40±1.10	14.00±0.50	8.47±0.49	8.15±0.95	0.03
Ti	5260±1380	5170±185	BDL	BDL	250
V	170±27.30	170±7.50	87.67±11.47	91.20±12.65	2.5
Yb	3.40±0.20	3.42±0.32	1.60±0.07	1.62±0.26	0.02
Zn	223±5.70	223±5.00	96.30±4.25	74.80±3.15	0.50

Data in parenthesis represents information values.

3.2.2 Elemental Composition of Stone Samples

The results of elemental composition of stones samples as determined by INAA are presented in Table 5. Again the values are average of at least 6 determinations. The data in Table 5 shows that SCH has comparatively higher concentrations of elements as compared to other samples. The elements Cs, Lu and Eu were found below 1 µg/g level, while Sc, Sm, Sn, Th and Hf were determined to be between 1-5 µg/g and Br and Co were found to be ~10 µg/g. However, the variation in the concentration of elements (in µg/g) is considerable in case of Al (746-19883), Fe (7242-30174), Mg (5237-28255), Cr (3.36-103.31), Sb (1.52-53.55), Mn (457-2373), Na (123-10480) and Zn (1.91-52.47). The concentrations of Al, Hf, Lu, Nd, Th and V were below the detection limits in STO and SLG, while Eu, Hf and K were found below their limits of detection in SGB.

3.2.3 Elemental Composition of Pottery Samples

Table 6 shows the elemental composition of pottery samples determined via INAA. All concentrations have been duly corrected for moisture content and are reported on dry weight basis. From these results it can be seen that 24 elements were determined in both samples with quite similar values. In fact, the values vary <5% for all except Sb. The elements Eu, Hf, Lu, Sb and Sn were found at less than 5 µg/g concentration level; while As, Co, Cs, Sc and Th were determined at less than 25 µg/g.

Table 4a: Concentrations (in µg/g unless specified) of some major, minor and trace elements of marble samples and granite at 95% confidence interval on dry weight basis.

Element	MPL Mean ±Unc	MRW Mean ±Unc	MFA Mean ±Unc	MSW Mean ±Unc	MNP Mean ±Unc	MZW Mean ±Unc
Al	206±40	0.45±0.05*	740±80	105±20	545±25	BDL
As	0.50±0.10	1.80±0.10	1.90±0.40	0.40±0.10	2.90±0.70	0.211±0.003
Br	0.60±0.20	BDL	0.20±0.10	0.30±0.20	1.10±0.30	BDL
Ce	4.02±0.60	9.50±2.50	2.60±0.40	1.80±0.50	4.20±0.50	0.60±0.03
Cr	3.40±0.30	4.25±0.20	4.30±0.30	2.45±0.10	1.90±0.60	1.90±0.10
Cs	BDL	BDL	BDL	BDL	BDL	BDL
Co	0.10±0.02	1.80±0.20	2.50±0.20	0.10±0.01	0.70±0.10	BDL
Eu	0.05±0.01	0.30±0.01	0.034±0.004	0.009±0.001	0.10±0.01	BDL
Fe	254±1	0.46±0.01*	870±50	380±50	1050±50	94±4
Hf	0.20±0.10	1.06±0.03	0.073±0.002	0.05±0.03	0.24±0.03	BDL
Hg	0.03±0.02	0.03±0.01	0.03±0.01	0.03±0.01	BDL	BDL
K	220±15	0.20±0.02*	BDL	203±14	820±60	BDL
La	3.40±0.10	6.30±0.30	1.30±0.05	0.40±0.03	3.60±0.10	0.60±0.03
Lu	0.04±0.01	0.06±0.01	0.020±0.003	0.020±0.004	0.02±0.02	BDL
Mg	536±96	0.23±0.05*	0.16±0.01*	483±37	0.23±0.05 *	BDL
Mn	54.05±1.40	122±19	187±3	29.93±3.16	179±36	2.25±0.60
Na	72.20±2.70	200±10	73.00±2.70	42.3±2.2	81.50±3.00	18.10±0.40
Nd	BDL	BDL	BDL	BDL	BDL	BDL
Rb	2.30±0.20	6.10±0.80	3.80±1.20	2.10±1.10	1.20±0.30	BDL
Sc	0.15±0.01	1.30±0.06	0.34±0.01	0.07±0.01	0.29±0.02	BDL
Sb	0.020±0.002	0.30±0.02	0.30±0.10	0.13±0.04	0.30±0.02	BDL
Sm	0.55±0.03	1.17±0.06	0.33±0.02	0.14±0.01	0.57±0.03	0.20±0.01
Sn	25.20±7.60	22.20±6.75	21.30±9.00	19.90±8.30	13.20±4.10	8.10±2.30
Sr	91.90±24.50	54.80±14.06	153±39	60.46±17.08	34.19±10.19	BDL
Ta	0.06±0.02	0.25±0.02	0.096±0.003	BDL	0.07±0.02	BDL
Tb	0.06±0.01	0.40±0.04	0.09±0.04	BDL	0.08±0.02	BDL
Th	0.115±0.004	0.780±0.008	0.120±0.008	0.04±0.01	0.30±0.02	BDL
Ti	425±56	0.10±0.01*	294±36	BDL	BDL	BDL
V	2.99±0.20	12.25±3.70	4.35±1.40	BDL	BDL	BDL
Yb	0.20±0.01	0.50±0.02	0.070±0.003	0.020±0.001	0.12±0.01	BDL
Zn	6.20±0.20	18.60±0.99	4.10±0.70	3.80±1.40	7.00±1.10	0.40±0.04

BDL = Below detection limit *Conc. in %

3.3 Rare earth Geochemistry of Investigated Building Materials

On the basis of charge and ionic radius, the rare earth elements (REE) are subdivided into two groups; light rare earth elements (LREEs) including La, Ce, Nd, Sm and Eu and heavy rare earth elements (HREEs) comprising Tb, Lu and Yb. REEs are generally present in a wide range of rock-forming minerals at trace levels. The concentrations of REE in different geological samples are generally given in the form of chondrite normalized values which helps in petrogenetic interpretation [16]. In the present study, the REE values are normalized using average chondrite values [17]. Furthermore, the chondrite-normalized REE values for Post-Archaean

Australian Shale (PAAS), Upper Continental Crust (UCC) and North American Shale Composite (NASC) are also calculated and plotted in Fig. 1 and are compared with marble, granite, stone and pottery samples investigated in the present study. These results show a general downward trend from left to right with enrichment of LREEs and depletion of HREEs. Usually, the enrichment of rare earth elements (REE) in geological samples is closely related to insoluble materials in rocks while REE content also depends on quartz, clay, mica, silicate and other minerals. Figs. 1a, 1c and 1d show a slight negative Eu anomaly, which is probably due to the crystallization of plagioclase; this is not the case for granite as seen from Fig. 1b. It can be seen that both marble and stone samples exhibit lower normalized REE values than UCC, NASC, and PAAS. In the case of granite sample, the normalized values of both La and Ce are slightly close to UCC while Sm, Eu and Tb are higher and Lu is much lower than the chondrite normalized values of UCC, NASC and PAAS. In the case of pottery samples, all the REEs exhibit much higher concentrations than that of UCC, NASC and PAAS except for Eu.

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Table 4b: Concentrations (in µg/g unless specified) of some major, minor and trace elements of marble samples and granite at 95% confidence interval on dry weight basis.

Element	MTA Mean ± Unc	MSB Mean ± Unc	MOC Mean ± Unc	MFL Mean ± Unc	MSG Mean ± Unc	MGR Mean ± Unc
Al	380±70	140.±41	420±86	332±17	455±236	5.80±0.10 *
As	0.60±0.24	0.230±0.003	0.90±0.07	0.50±0.10	0.96±0.02	BDL
Br	0.80±0.10	0.30±0.06	1.14±0.30	1.03±0.30	1.50±0.30	7.30±3.60
Ce	3.10±1.90	2.50±0.20	1.70±0.10	1.60±0.06	2.70±0.30	63.40±3.70
Cr	6.40±0.10	6.80±0.09	6.10±0.10	7.00±0.20	5.30±0.97	164±11
Cs	BDL	BDL	BDL	BDL	0.217±0.001	BDL
Co	1.10±0.10	0.120±0.003	0.90±0.10	0.50±0.03	0.30±0.03	59.40±3.40
Eu	0.03±0.01	0.040±0.004	0.040±0.003	0.030±0.002	0.05±0.02	2.57±0.16
Fe	818±120	105±18	980±55	428±51	1241±114	10.70±0.45*
Hf	BDL	BDL	0.09±0.01	0.06±0.01	BDL	7.40±0.20
Hg	BDL	BDL	BDL	BDL	BDL	0.08±0.04
K	389±4	BDL	282±26	175±15	259±16	0.53±0.06*
La	0.80±0.15	2.30±0.07	0.60±0.25	0.70±0.30	1.30±0.50	28.80±3.20
Lu	0.02±0.01	0.018±0.002	BDL	0.008±0.001	0.02±0.01	0.09±0.01
Mg	485±160	217±40	534±112	BDL	BDL	1.30±0.05*
Mn	59±12	24.40±5.50	63.60±12.50	21.30±4.20	33.70±7.70	0.136±0.001*
Na	82.20±1.90	48.90±4.60	165±3	91.10±1.70	73.30±3.40	1.65±0.06*
Nd	BDL	BDL	BDL	BDL	1.40±0.15	BDL
Rb	1.80±0.50	BDL	1.95±0.07	BDL	BDL	19.60±2.40
Sc	0.25±0.01	0.20±0.01	0.30±0.01	0.20±0.01	0.25±0.03	31.05±1.50
Sb	0.20±0.01	0.10±0.09	0.20±0.01	0.20±0.03	BDL	BDL
Sm	0.30±0.01	0.40±0.02	0.43±0.02	0.40±0.05	0.30±0.01	9.43±0.50
Sn	15.20±5.30	14.80±5.80	14.20±4.90	13±5	8.10±3.10	8.90±5.60
Sr	108±33	30.40±10.00	178±53	106±31	BDL	212±59
Ta	0.090±0.005	BDL	0.11±0.01	0.090±0.005	BDL	3.20±0.40
Tb	BDL	0.05±0.01	BDL	BDL	BDL	1.24±0.43
Th	0.60±0.60	0.20±0.02	0.10±0.03	0.10±0.01	0.10±0.01	2.60±0.07
Ti	BDL	BDL	BDL	BDL	BDL	2.26±0.25*
V	16.60±5.90	BDL	9.30±0.09	10.50±0.10	BDL	404±30
Yb	0.030±0.001	0.20±0.09	BDL	BDL	BDL	1.90±0.40
Zn	4.60±0.54	6.02±2.30	8.80±5.70	5.0±1.7	3.40±0.40	170±30

BDL = Below Detection Limit   * Conc. in %

Table 5: Concentrations (in µg/g unless specified) of some major, minor and trace elements of stones at 95% confidence interval on dry weight basis.

Element	STO Mean ±Unc	SGO Mean ±Unc	SLG Mean ±SD	SGB Mean ±Unc	SBA Mean ±Unc	SCH Mean ±Unc
Al	BDL	0.50±0.06*	BDL	746±95	1.25±0.188*	1.98±0.23*
As	36.90±1.03	10.40±0.47	21.70±3.30	4.90±0.10	2.90±0.09	5.24±0.96
Br	5.20±0.20	1.60±0.30	6.40±5.50	11.80±0.60	2.80±0.50	8.40±0.20
Ce	2.60±0.20	18.30±1.30	6.80±0.58	9.70±0.80	10.90±0.70	36.50±2.50
Cr	3.40±0.30	32.10±2.10	29.80±1.70	5.90±0.80	103±5	29.04±2.50
Cs	BDL	0.80±0.01	0.30±0.10	0.90±0.01	0.50±0.05	BDL
Co	9.80±0.60	3.80±0.50	8.30±0.50	7.00±0.50	7.30±0.42	5.80±0.40
Eu	0.05±0.01	0.40±0.06	0.10±0.03	BDL	0.30±0.02	0.70±0.02
Fe*	0.76±0.06	2.18±0.10	2.07±0.10	3.01±0.15	0.72±0.03	1.45±0.09
Hf	BDL	0.30±0.02	0.28±0.07	BDL	0.50±0.06	1.96±0.10
K	180±15	230±40	465±10	BDL	1410±25	0.22±0.04*
La	0.70±0.10	7.70±1.10	BDL	1.10±0.03	9.30±0.80	25.30±0.60
Lu	BDL	0.03±0.01	BDL	0.010±0.002	0.05±0.01	0.12±0.02
Mg*	1.20 ±0.30	13.07±0.20	2.30±0.36	2.80±0.46	0.52±0.11	2.13±0.34
Mn*	0.11±0.02	0.12±0.01	0.20±0.02	0.24±0.03	0.0457±0.0064	0.19±0.02
Na	630±26	460±20	975±40	123±7	530±30	10480±440
Rb	BDL	BDL	27.80±15.40	24.90±6.60	BDL	BDL
Nd	BDL	12.20±0.80	BDL	1.20±0.06	7.90±0.60	12.70±2.20
Sb	12.70±0.30	1.50±0.02	2.70±0.20	53.60±2.66	7.50±0.10	2.10±0.40
Sm	0.30±0.02	2.00±0.10	0.70±0.07	0.10±0.02	1.60±0.07	3.50±0.20
Sn	2.40±0.60	3.04±0.95	2.30±0.50	1.80±0.40	2.10±0.40	3.50±0.70
Sc	0.70±0.02	4.10±0.10	0.70±0.02	0.20±0.02	3.40±0.10	4.05±0.20
Th	BDL	0.40±0.01	BDL	0.60±0.01	1.40±0.08	4.40±0.06
V	BDL	34.40±5.30	BDL	7.90±1.48	31.50±8.86	36.80±7.70
Zn	8.40±0.50	51.70±2.20	3.90±0.20	1.90±0.30	43.20±1.90	52.50±2.90

BDL = Below Detection Limit * Conc in %

Table 6: Concentrations (in µg/g unless specified) of some major, minor and trace elements of pottery samples at 95% confidence interval on dry weight basis.

Element	P-1 Mean ±Unc	P-2 Mean ±Unc
Al*	6.51±0.86	6.66±0.93
As	21.96±1.95	21.90±4.10
Ce	103±6	97.50±5.50
Co	20.10±1.75	19.90±0.70
Cr	97.60±6.10	90.10±4.00
Cs	20.50±1.40	20.50±0.40
Eu	1.40±0.12	1.30±0.02
Fe*	4.71±0.26	4.60±0.21
Hf	4.40±0.10	4.60±0.20
K*	3.51±0.11	3.55±0.06
La	48.60±3.30	47.20±2.55
Lu	0.80±0.10	0.80±0.10
Mg*	0.56±0.10	0.54±0.10
Mn	840±190	860±190
Na*	1.05±0.02	1.16±0.01
Nd	74.40±7.90	71.76±7.70
Rb	161.0±26.2	178.0±32.5
Sc	17.16±0.70	16.63±0.06
Sb	2.00±0.90	2.50±0.80
Sm	7.83±0.40	7.74±0.20
Sn	4.39±0.20	4.59±0.10
Th	19.70±1.50	18.70±1.20
V	154±37	168±18
Zn	237.0±23.8	230.0±22.4

*Conc in %

*Conc in %

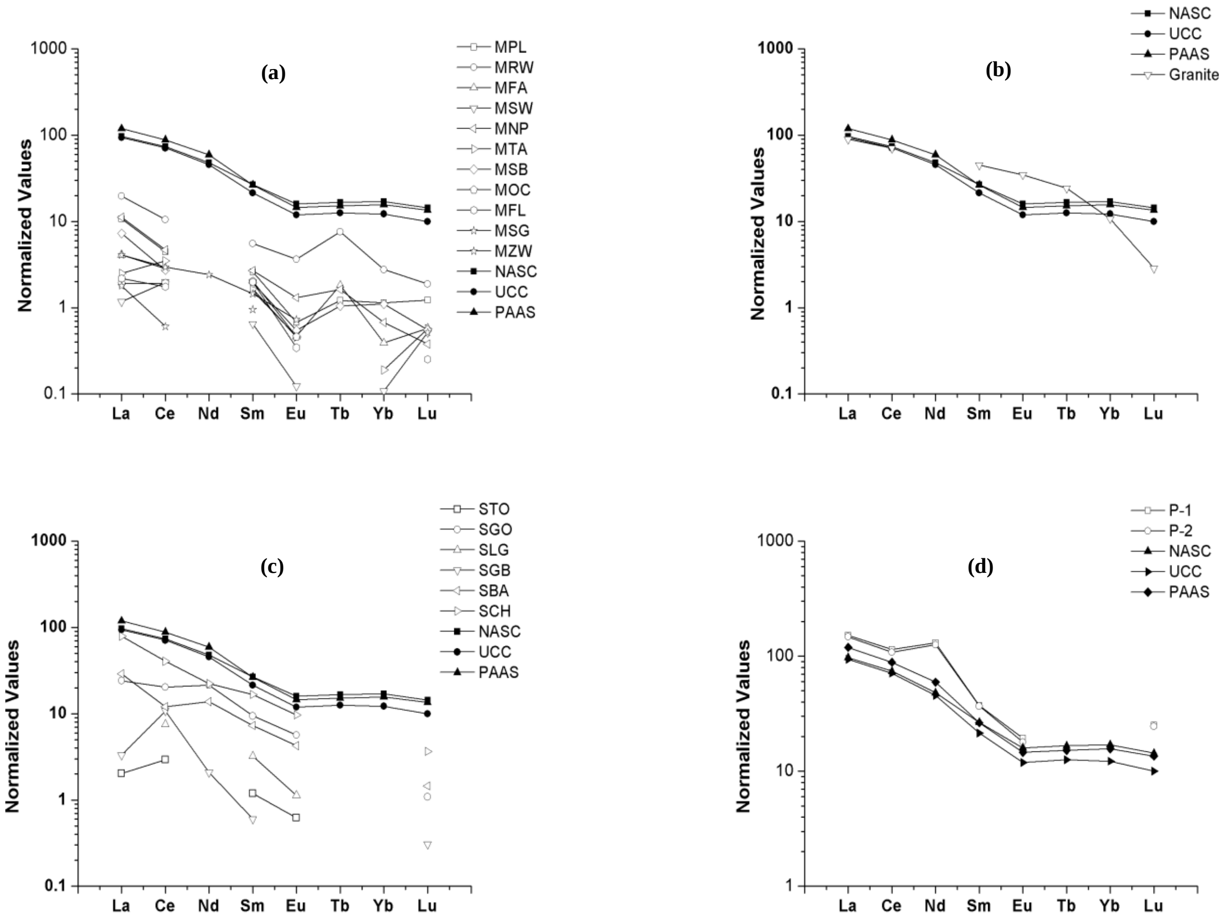

Fig. 1: Chondrite normalized values of investigated building materials (a) Marble, (b) Granite, (c) Stones and (d) Pottery.

3.4 Comparison of Different Building Materials

Comparison of the marble, granite, stone and pottery samples studied in the present work shows that the concentrations of all elements present in pottery are much higher than in stones and marble sample, except for Mn, Sb and Sn; while the elemental concentrations in granite are higher than that in pottery with a few exceptions. The elements Hg, Sr, Ta, Tb, Ti and Yb were below the detection limit in pottery samples. The general observed trend is:
Element conc. (granite) > Element conc. (pottery) >
Element conc. (stones) > Element conc. (marble).

A comparison of the quantified elements in marble, stone and pottery has been made with data for several types of building materials from different countries and is presented in Table 7 (a-c). Comparison with other reported studies shows that variations exist between elemental compositions of different materials. In fact, this variation is the result of the differences in the geological origin of the investigated materials.

3.5 Principal Component Analysis (PCA)

Among different multivariate analysis techniques, Principal Component Analysis (PCA) is one of the most frequently used mathematical tools for data reduction, grouping and establishing relationships that may exist between inter-correlated variables. In terms of mathematics, in PCA, the data is transformed to a new coordinate system where each coordinate called "the principal component" is considered to be a linear combination of the observed variables [18, 19]. In simple terms, PCA simplifies the complexity in high-dimensional data while retaining trends and patterns by transforming the data into fewer dimensions considering their similar features. In this way, it can be used to categorize a large data set.

In the present study, PCA was applied to the data set of elemental composition of local building materials after standardization (subtracting mean from each variable and normalizing by dividing by SD) which ensures that each variable contributes equally to the data set variance and carries equal weight in principal component calculation. PCA cannot be applied on a dataset with missing values. Therefore, in the case of the NAA results for building materials for example, Cs, Hg, Nd, Sr, Ta, Tb, Ti, and Yb concentrations were excluded from statistical treatment due to a large number of missing values. Moreover, in the case of elemental data with less than 50% missing values, the missing values were replaced by half of LOD (where LOD is the limit of detection of each element) prior to applying PCA [20]. All the calculations were done using Origin software version 9. The projection of the scores of the investigated building materials onto space of three principal components is given in Fig. 2a. It is evident from these results that all the marble samples fall relatively close to one another in the score plot, which suggests that they have similar characteristics or geology. The granite sample is different from marble; thus it appears separately on the score plot. Similarly, the stone samples resemble one another and pottery samples are almost identical so are grouped together. Rocks and clay are both sedimentary in nature, however clay is produced from erosion of rock samples, therefore it may differ from rock samples. Thus PCA may be used to differentiate between rock samples and group them according to their geology. To further validate the application of PCA for separation of different types of geological samples, elemental data of an ancient Chinese ceramic reference material (IAEA-CU-2006-06 proficiency test) characterized for major, minor and trace elements, by the Institute of High Energy Physics, Chinese Academy of Sciences was used [21]. The results of PCA are shown in the form of 3D score plot in Fig. 2b. It can be seen that the ceramic sample falls close to pottery samples showing that both pottery and ceramic samples share similar chemical characteristics. Therefore, PCA can be used to differentiate between different types of materials.

Table 7a: Global comparison of average composition of marble samples obtained in current study (concentrations in µg/g unless otherwise specified).

Elements	Turkish Marble [22]	Saudi Arabia Marble [23]	Greek Marble [24]	Marble (Ave. Present Study)
Al	30.4	BDL	BDL	0.60*
As	2.0	4.94	0.18	0.99
Br	BDL	BDL	0.84	1.44
Ce	BDL	7.24	10.54	8.13
Co	BDL	0.58	6.76	6.12
Cr	BDL	376	5.72	17.83
Eu	BDL	0.1	0.38	0.29
Fe*	0.32	3.93	3.20	0.98
Hf	BDL	0.37	0.15	1.15
Hg	BDL	BDL	BDL	0.04
K	295.1	BDL	BDL	0.10*
La	9.4	2.76	10.22	4.17
Lu	BDL	0.06	0.005	0.03
Mg	20.1	1.5*	BDL	0.248
Mn	35.9	0.01*	BDL	0.017*
Na	30.5	0.01*	0.019*	0.148
Rb	BDL	BDL	BDL	4.84
Sb	BDL	BDL	3.12	0.18
Sc	BDL	0.41	2.63	3.13
Sm	BDL	1.09	2.88	1.19
Sn	BDL	328	BDL	15.38
Sr	BDL	BDL	90	105
Ta	BDL	BDL	BDL	0.50
Tb	BDL	BDL	0.27	0.32
Th	BDL	0.18	0.95	0.46
Ti	BDL	BDL	BDL	6095
V	0.7	0.47	BDL	65.66
Yb	BDL	0.85	0.28	0.38
Zn	BDL	23.5	18.88	19.85

BDL = Below detection Limit * Conc in %

Table 7b: Global comparison of average composition of building stones obtained in current study (concentrations in µg/g unless otherwise specified).

Elements	Limestone [25]	Sandstone [26]	Stones (Ave. Present Study)
Al*	BDL	BDL	0.95
As	BDL	BDL	13.66
Br	BDL	BDL	6.03
Ce	3.38	3.38	14.14
Co	12	12	6.98
Cr	94	94	33.91
Eu	0.04	0.04	0.32
Fe*	4.8	4.8	1.70
Hf	2.07	2.07	0.76
Hg	BDL	BDL	BDL
K	BDL	800	909.05
La	1.5	1.5	8.80
Lu	0.13	0.13	0.05
Mg*	BDL	BDL	1.70*
Mn*	0.8	BDL	0.15
Na*	3.4	3.4	0.22
Rb	BDL	BDL	26.32
Sb	BDL	BDL	13.36
Sc	0.73	0.73	2.19
Sm	0.26	0.26	1.35
Sn	0.18	BDL	2.52
Sr	BDL	BDL	BDL
Ta	BDL	0.18	BDL
Tb	BDL	BDL	BDL
Th	9.6	0.89	1.70
Ti	BDL	BDL	BDL
V	BDL	BDL	27.66
Yb	0.4	0.40	BDL
Zn	89	BDL	26.92

BDL = Below detection Limit * Conc. in %

Table 7c: Global comparison of average composition of pottery samples obtained in current study (concentrations in µg/g unless otherwise specified).

Elements	Clay [27]	Bricks [28]	Tiles [28]	Pottery (Average Present Study)
Al*	BDL	6.47	7.39	6.6
As	219	3.6	0.5	21.92
Br	BDL	BDL	BDL	BDL
Ce	18.4	73.8	91.3	100
Co	3.3	5.2	7.9	20.0
Cr	274	79.8	65.4	93.84
Eu	16.5	1.10	1.52	1.38
Fe*	0.84	3.92	1.99	4.6
Hf	9.8	12.55	15.60	4.47
Hg	BDL	BDL	BDL	BDL
K*	6.9	1.36	1.59	3.5
La	183	37.8	45.4	47.90
Lu	77.4	0.509	0.661	0.80
Mg*	5.3	BDL	BDL	0.55
Mn*	29	BDL	BDL	0.08
Na*	26	0.18	0.32	1.10
Rb	5.9	94	99	169.74
Sb	BDL	0.62	1.62	2.26
Sc	842	11.8	12.3	16.89
Sm	106	6.1	7.7	7.78
Sn	15.11	BDL	BDL	4.49
Sr	BDL	BDL	BDL	BDL
Ta	7.0	1.47	1.64	BDL
Tb	BDL	0.87	1.46	BDL
Th	12.6	12.4	11.1	19.17
Ti*	3.71	0.70	0.88	BDL
V	BDL	115.0	89.9	160.78
Yb	31.3	3.5	4.7	BDL
Zn	0.1	50	80	233.79

BDL = Below Detection Limit

4. Conclusions

In this work the highest concentration of elements was found in pottery samples followed by stone and then marble samples which have comparatively lower concentrations of elements. Up to 24 elements are determined in pottery samples. Principal component analysis has shown that all marble samples are similar. Moreover, stone samples also share the same chemical characteristics and pottery samples resemble each other. It was also inferred that a large dataset which contains elemental data for building materials upon application of PCA can separate different types of samples; i.e., marbles, stones and ceramics. The number of samples analyzed in this work is limited. Therefore, further work may be undertaken to analyze a greater number of samples. It is recommended to apply other complementary techniques like atomic absorption spectroscopy (AAS) and inductively coupled plasma spectroscopy (ICP) to quantify those elements which INAA cannot determine such as Cd, Si, S, Pb, etc., and also to complement the INAA results. Si is a major component of soil so this additional information may prove useful. Further work is required to determine the radionuclide content of these building materials as they are commonly used and this data will provide information regarding the indoor dose being experienced within buildings constructed from such materials.

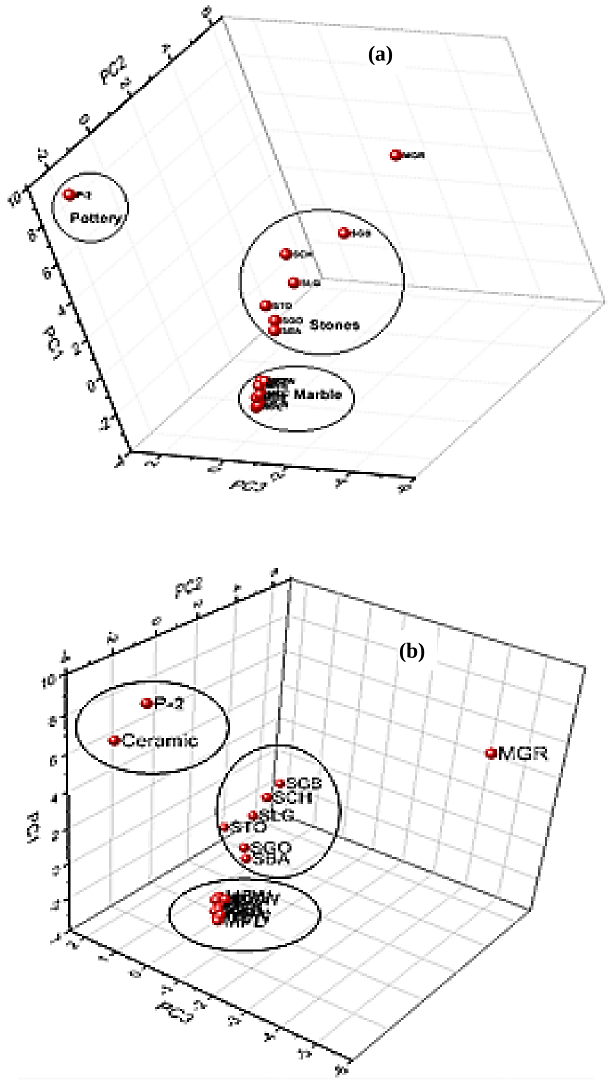

Fig. 2: (a) Three principal component plot of building materials and (b) building materials with a Chinese ceramic reference material.

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