

## GEOCHEMISTRY AND MINERALOGY OF QUARRY DUSTS AT SOME SELECTED LOCATIONS OF SOUTHWESTERN NIGERIA

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**Abstract:** Toxic metals in quarry dusts have caused different health challenges to quarry workers and communities. Therefore, metal distribution and risk in humans linked to toxic-metal-contaminated quarry dusts have been examined from both inside and outside the twelve different quarries. Bauxitic portions ( $Al_2O_3$ -15.4) from dusts specify high clay percentage while the plot of  $SiO_2$ ,  $Al_2O_3$ + $TiO_2$  and  $Fe_2O_3$  signify highly and more clastic rock aggregates. High CaO in Sagamu signifies the presence of carbonate rocks but the plot of  $(SiO_2)$ - $(Al_2O_3+TiO_2)$ - $(Fe_2O_3)$  specifies silica rich rocks that is dominated by bauxitic clay when weathered. Zr-Cr-Ga plot revealed the dust origin and parental affinities as acidic rocks. Furthermore, ternary plot of Y-La-Ce revealed abundance of Ce signifying the presence of  $Ce > 7$  ppm in lepidolite, pollucite, and rhodizite within gneisses and pegmatitic rocks with values that range from 37.04 ppm - 656.8 ppm. Inputs of Pb-20.51ppm and As-14.50ppm at Kopek and Labstar quarries may signify anthropogenic sources while the presence of Cu, Pb, As, and Ni at Kunlun quarry might specify mineralization. The Value for Chemical Index of Alteration (CIA=60.1-72.8) and Chemical Index of Weathering (CIW=60.8-75.6) indicate high muscovite and feldspar content. The dusts generated from these quarries might have anthropogenic inputs of Cu, Pb, Zn, As and Cd in two to three folds above the baseline concentration levels.

Keywords: Quarry-dust, clastic, geogenic, anthropogenic, risks.

### Introduction

High demand and supply of rock aggregate materials for construction purposes can be linked to increase in urban growth, infrastructural development and response to population increase. This has caused increase in siting of quarries on different rock units. There are various works on the impact of atmospheric pollution on the environment which include dust, particulate matter and other noxious gases (Grantz *et al.*, 2003; Amos *et al.*, 2014). Then, this form of contamination is caused by industrial activities during mining production. The major impacts of quarrying on the environment are transmission of dusts and gases. These particles or dusts are very abundant and varied in size, shape, weight and colour. This multiplicity is assigned to different sources of broadcast and transmission. There are two types of particles/dust; they can be classified as: the primary particles that are found

directly in the atmosphere and the secondary particles that are formed in the atmosphere following chemical transformations. Dusts can be transferred into soil as dry, moist and damp deposits; that can undermine its physicochemical properties. Dust components are multifarious material and are controlled by size, shape, constituents, atmospheric stability, and roughness of the surfaces as well as the diameter of its particles. Enormous quantities of gravel, limestone and other materials for industrial and construction applications are produced in a quarry (Duan *et al.*, 2008). Quarrying activities have created a significant engagement for both youths and middle age class that can contribute and improve the wealth/economy through provision of raw materials to meet societal needs towards improving infrastructures with supply of materials. These materials are used in hard core and pave flooring, with granite, limestone,

marble, sandstone, slate and even clay to make ceramic tiles. Also, they can have environmental and health impacts like many other man-made activities or anthropogenic factors (Lameed & Ayodele, 2010). Some of the deleterious controls of quarrying operations include land deterioration, damage on water table, reduction of ground water quality, soil degradation, dust generation, and poisonous gases production. Suspended particulate matter is quite unresolved among all impurities springing from quarrying operations. Dusts or particulate matters from quarry sites are the main source of air pollution in and around such neighbourhood and the degree of noxious waste depends on climatic conditions of such area. Also, the concentration of dust particles in ambient air, as well as the size of dust particles and their composition vary based on climatic conditions (Bada *et al.*, 2013).

However, the industries unfortunately, discharge dusts that settle not only on land, plants and trees but also on surface waters for drinking and other domestic chores by the community (OSHA, 2006). Based on size of dust or particulate matter; some settled particles close to quarry sites are suspended in the air and some travel far away from the quarry sites before settling down. Finer dust particles can be inhaled, ingested and absorbed into the body through the skin and based on the composition of dust particles as well as the concentration of elements contained in the dust; humans are prone to health hazards (Bada *et al.*, 2013). Quarry workers are daily exposed to polluted air in which finer dust particles can be inhaled, breathed into the lungs, and cause harm, through pulmonary diseases (Sayara, 2016). Preliminary assessment study of the trace metals composition of dust from central part of Nigeria and their possible health implications indicate enrichment of metals in the environment, infestation of air, soil, both ground and surface water quality which may affect humans, animals and plants. Exposures through inhalation, ingestion and percutaneous absorption causing various health concerns in human have been observed (Binnur & Karakus, 2012). The harmful elements in the dust settled on soil and plants can bio-accumulate these

metals. Their effects on plant growth can also be transmitted through the plants and cause adverse medical conditions when consumed by humans (Laniyan & Adewumi, 2020). Dissolution of dust in water resources can change the quality of this water through settling of particulates dusts, and toxic wastes. Therefore, since existence of life can be linked to good portable water; quality of life for both humans and animals can be reduced near or along downstream from drained quarry sites.

Impacts of quarrying, ecological risks of heavy metal concentration in the environment and health effects of quarry operations which have made inhabitants health standard to be compromised, their abode endangered with their major source of living (farming) jeopardized around quarry sites have been reported (Abimbola *et al.*, 2007). Also, pulmonary function deterioration, because of exposure to dust containing high silica, suggests a need for protective measures of quarry workers (Oyinloye & Olofinyo, 2017). This dust affects the health of the people living very close to the site, thereby, making life difficult to the residents. Plants and vegetation around these local quarrying sites were covered; thereby, affect photosynthesis leading to low production and plant deaths. Different parts of the world have been experiencing the same challenges where quarry dusts have been linked with high prevalent rate of diseases (Sayara, 2016; Ojo *et al.*, 2018). High Hg, As, Cu, Zn, and Pb contents associated to quarry dust have been observed (Binnur & Karakus, 2012; Sayara, 2016; Ojo *et al.*, 2018).

The Rare Earth Elements (REE) are composed of Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu (Balaram, 2019). They are typically dispersed and not often found concentrated in the rare earth minerals due to their geochemical properties because of economically exploitable ore deposits which are less common (Haxel *et al.*, 2002). They have their source in mineral form and present as stable, in addition to radioactive isotopic forms. Human health can degenerate into inexplicable

state, if these metals are encountered and found their way into human systems (Balaram, 2019).

Different studies have shown that REE may accumulate in the soil surface due to their sorption onto soil colloids (Gonzalez, 2014), which consequently can lead to low bioavailability. This is directly controlled by various factors such as pH and presence of organic and inorganic substances. Under these circumstances, incidence of ingestion of REE-contaminated soil may not cause total content of the elements to represent the real risk (Gonzalez, 2014). The geochemistry of these elements focused on plant, animal and the environment. Studies involving effects of REE on bioavailability and accumulation of these elements in human system with long ingestion overtime in plants, bones, liver, and lungs of human and animal systems (USEPA, 2009; Rim, 2013). These could also cause some impairment in humans and animals.

Rare earth elements have been linked to some environmental hazards based on their presence in mine tailings, mine dumps, soil, water, industrial production, agriculture, fertilizers and diets to promote the growth of cultivated plants and livestock (Hu *et al.*, 2004; Migaszewski & Galuszka, 2015; Migaszewski *et al.*, 2016). All these and other human activities lead to the inflowing of REE to the environment causing different threats; with effects on biota and humans (USEPA, 2012).

Therefore, the focus of this study is to establish quarry industrial zones within the south-western Nigeria; to determine quarry dusts elemental composition at both inside (uncontaminated) and outside (contaminated) quarry operational areas. It is also to establish the release of anthropogenic metals that are harmful with the use of geochemical maps for spatial metal risk assessment.

This study lies within Oyo and Ogun provinces, South Western Nigeria; with latitudes 6° 19' - 9° 11' N and longitudes 2° 27' - 4° 33' E as coordinates. The quarry areas are characterized by savannah vegetation, rain forest belt and

mangrove swamp; covering the northern, central and the southern parts respectively. The northern part falls within the basement complex rocks while the southern part lies within transitional zone/sedimentary rocks.

### ***Geology of the Study area***

The area is dotted with various lithologies which comprise of wavering crystalline rock that makes up the basement complex with exception of Sagamu which lies in the sedimentary terrain of Nigeria. Some quarries were underlain with quartzites and silicified rocks while Onigambari and Imosan are composed of Meta-sediments. Ago-Iwoye, Isara, Kajola and Ajebo fall within the Migmatite-Gneiss Complex while Sagamu composed of carbonate rocks. The migmatite-gneiss-quartzite complex is the most widespread rock units in Nigerian basement (Dada, 2008) characterised with heterogeneous assemblage comprising of migmatites, orthogneisses, paragneisses and a series of basic and ultra basic metamorphosed rocks. Petrographic evidence indicates that deformational episode reworking led to recrystallization of many of the constituent minerals of Migmatite-Gneiss complex by partial melting with majority of the rock types displaying medium to upper amphibolite facies metamorphism. Records of major geological processes were observed on these rocks: the first is regarded as the banded grey gneiss of mantle origin, indicating crustal growth by sedimentation and the development of granite gneisses (Figures 1 and 2), with structural deformation of older rocks while age-reset had given rise to new form of granite gneisses, migmatites and other related rock units (Okonkwo & Ganev, 2012).

### ***Dust Sampling and Analytical Methods***

Twenty-four (24) dust samples were collected from 12 quarries from both inside and outside the quarry sites and covered Ogun and Oyo provinces (Figure 1). Samples were collected with the use of hand brush into a glass bottle and covered immediately to prevent further contamination. These were prepared and

analysed using multi-acid inductively coupled plasma-mass spectroscopy (ICP/ES-MS) with MA-250 analytical method having precision limit of 0.01 - 0.3 at Bureau Veritas Minerals (BVM) (Acme Laboratories), Vancouver, Canada. Two replicates analysis on dust pulp from Sixsix-Imosan (MS) quarry were also examined to test the precision and accuracy of the instrument.

Multi-acid digestion which uses a combination of acids such as: HCl (hydrochloric acid), HNO<sub>3</sub> (nitric acid) HClO<sub>4</sub> (perchloric acid) and HF (hydrofluoric acid) were employed.

This is known as an effective dissolution procedure because of its capability of dissolving most minerals. Prepared sample was digested to complete dryness with an acid solution of (2:2:1:1) H<sub>2</sub>O-HF-HClO<sub>4</sub>-HNO<sub>3</sub>, 50% HCl was added to the residue and heated using a mixing hot block. After cooling, the solutions were transferred to test-tubes and brought to volume using dilute HCl. Sample splits of 0.25g were analysed as replicates in order to examine the error(s); and determine the accuracy of analytical method. ICP/ES-MS analysis was used, since it gives near total values for most elements and it is a technique for multi-

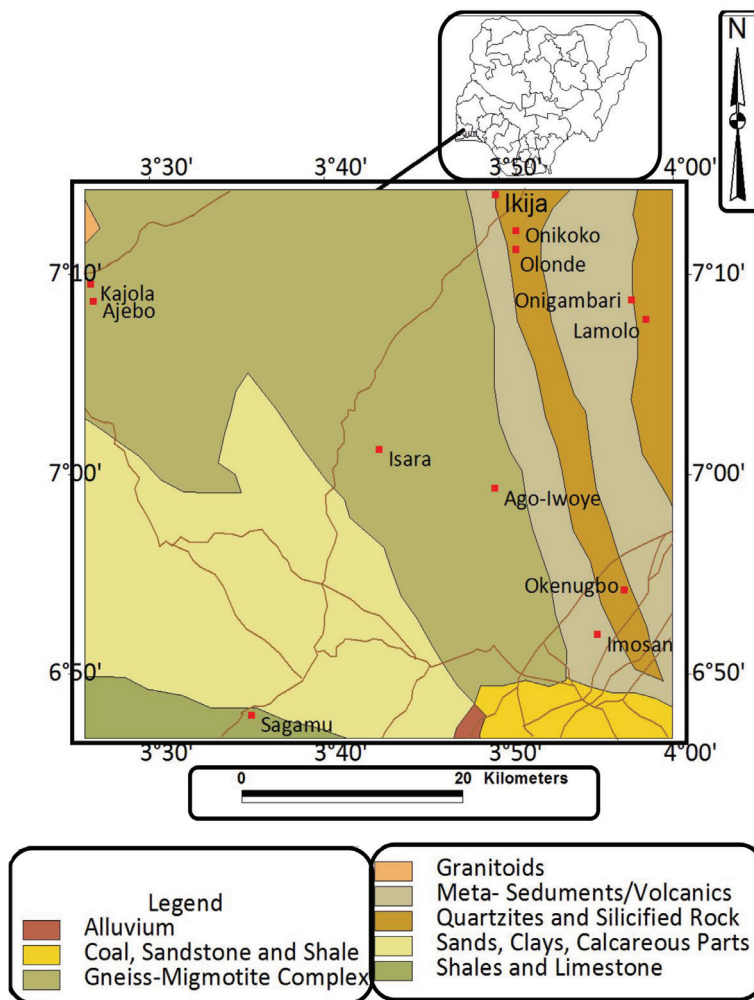
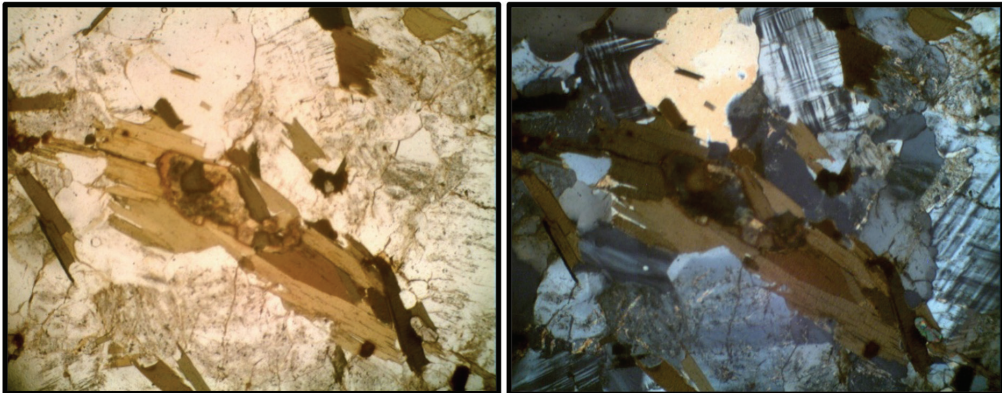


Figure 1: The location and geology of quarry sites



\*plane polars\*\*crossed polars

Figure 2: Granite gneiss features under plane polars and crossed polars

elemental and isotopic concentrations in liquid and solids. The quarry sites include: CCECC-Ago-Iwoye(Gw); Zhong Tai-Okenugbo(Kn); Sixsix-Imosan(Ms); CCECC-Isara(Sr); Lafarge-Sagamu(Sgm); Labstar-Ajebo(Jb); Multiverse-Kajola(KI); Prestige-Lamolo(Lm); Kunlun-Onigambari(Gr); Ratcon-Ikija(Kj); Kopek-Olonde(Ld) and Platinum-Onikoko(Nk).

## Results and Discussions

Varying concentrations of major oxides values examined in different quarry dusts showed high  $\text{SiO}_2$  contents in all locations except Lafarge-Sagamu, specifying that the rocks were crystalline and granitic. Also, high CaO in Lafarge (SG) signifies the presence of carbonate rocks than siliceous rocks at the quarry site (Figure 3). Some of the major oxides concentrations from both inside and outside quarry dusts were in close range with average crustal abundance (ACA) values except for the carbonate rocks in Lafarge (SG) which is a reflection of the rock type that was being quarried (Table 1, Figure 3). The ternary plot of  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{+TiO}_2\text{-Fe}_2\text{O}_3$  was used to know the amount of bauxite in the dust's samples (Putzolu *et al.*, 2018). This plot specifies that the rocks being quarried at these quarry sites were silica-rich-rocks that are dominated by bauxitic clay when weathered (Figure 4). Zr-

Cr-Ga Ternary plot (Ozlu, 1983; Gamaletsos, 2019) revealed the origin and parental affinities of the rocks that generated these dusts. These can be used as determination of precursor material for samples with Zr associated with the acidic, Cr-intermediate and Ga with basic rock types. The quarried rock materials ranged and plotted around the intermediate, magmatic, basic to ultra-basic rocks with most of the rock aggregates plotting around the acidic rock types (Figure 4); signifying that acidic rocks were the most common rocks that dominated the quarry area. It also signified their field relationship, spatial distribution and mode of formation.

## Heavy Metals

The graphical representation of the heavy metals concentrations for both outside and inside quarry dust with their respective ACA values signifying disparity between these values (Figure 5). Copper is elevated above the ACA values inside some quarry sites except in Lafarge-Sagamu, CCECC-Isara, Kunlun-Onigambari and Platinum-Onikoko specifying the presence of Cu minerals-CuFeS<sub>2</sub> but contamination did not occur at both inside and outside Lafarge and Platinum quarry dusts. Also, Pb and Zn were above their respective ACA values in most quarry sites; especially in Kunlun and Multiverse quarry dusts respectively; this indicates the presence of Pb-Zn ores in the rocks

Table 1: Concentration of the major oxides analyzed in the quarry dusts

Loc/(%)	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O
GW-1a	64.25	8.05	5.27	3.08	0.92	14.26	3.81	0.35
GW-1b	69.38	6.44	3.5	1.91	0.78	13.75	3.87	0.37
KN-2a	70.49	5.15	3.75	1.86	0.71	13.7	3.96	0.4
KN-2b	73.78	4.66	3.16	1.29	0.66	12.49	3.69	0.26
MS-3a	66.4	5.93	5.74	3.86	0.75	13.77	3.15	0.38
MS-3b	61.8	7.78	6.39	3.86	1.29	15.4	3.19	0.28
SR-4a	74.97	4.12	2.73	0.85	0.48	12.77	3.79	0.3
SR-4b	77.26	3.25	2.87	0.48	0.42	11.98	3.45	0.3
SG-5a	34.06	3.3	55.96	1.74	0.27	4.61	0.03	0.02
SG-5b	52.99	2.4	39.66	1.13	0.25	3.44	0.09	0.04
JB-6a	73.79	4.1	2.69	0.98	0.56	14.07	3.14	0.67
JB-6b	72.48	4.95	1.87	1.08	0.71	15.13	3.0	0.79
KL-7a	74.14	4.25	2.52	0.86	0.71	13.68	3.0	0.85
KL-7b	69.74	6.89	2.11	1.64	0.92	14.96	2.76	0.98
LM-8a	75.51	1.13	1.75	0.38	0.27	15.17	4.92	0.87
LM-8b	74.09	2.04	1.85	0.78	0.42	15.13	4.85	0.84
GR-9a	74.59	2.46	2.08	0.93	0.58	14.04	4.36	0.96
GR-9b	75.97	2.46	1.29	0.8	0.46	14.36	3.85	0.82
KJ-10a	74.08	3.4	2.41	1.74	0.58	13.68	3.33	0.78
KJ-10b	80.88	1.73	1.71	0.51	0.28	11.05	3.2	0.64
LD-11a	69.17	6.18	4.28	2.25	0.8	13.45	3.6	0.27
LD-11b	70.65	5.21	4.77	1.89	0.66	12.98	3.5	0.35
NK-12a	77.06	2.53	1.5	0.56	0.27	13.62	3.47	0.99
NK-12b	76.24	3.89	2.62	1.16	0.49	11.94	3.15	0.52
ACA	61.50	6.28	5.50	3.70	0.68	15.10	3.20	2.40

\*a = Inside\*\*b = Outside\*\*\*ACA=Average Crustal Abundance

CCECC-Ago-Iwoye(Gw); Zhong Tai-Okenugbo(Kn); Sixsix-Imosan(Ms); CCECC-Isara(Sr); Lafarge-Sagamu(Sgm); Labstar-Ajebo(Jb); Multiverse-Kajola(Kl); Prestige-Lamololo(Lm); Kunlun-Onigambari(Gr); Ratcon-Ikija(Kj); Kopek-Olonde(Ld) and Platinum-Onikoko(Nk).

(Table 2, Figure 5). It also signifies substantial contamination of Pb at Lafarge-Sagamu and Kunlun-Onigambari quarries than others. Meanwhile, arsenic is a little above the ACA in all quarries but Lafarge and Labstar were extremely enriched and concentrated above the ACA. Cadmium was extremely high in the limestone dust from Lafarge than that of other

rock aggregate samples from various quarry sites. However, nickel (Ni) concentration in Average Crustal Abundance was far above the recorded values in the dusts from all the quarries at both inside and outside phases but exception was observed from inside dust at CCECC-(Ago-Iwoye) and Labstar, specifying enrichment of this metal at background levels. This may also

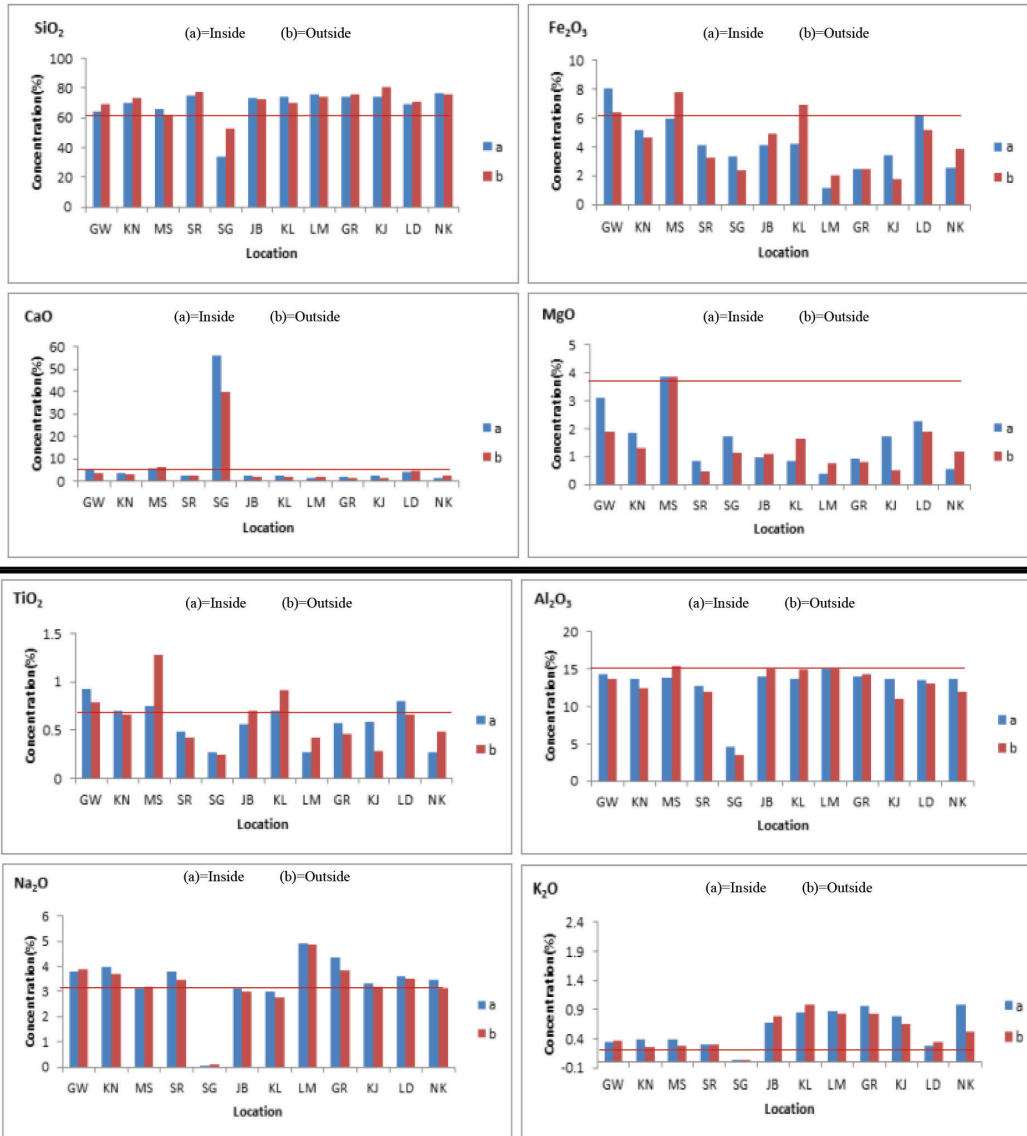


Figure 3: Comparison of major oxides in quarry dust with ACA

indicate the presence of ore containing nickel in the rock aggregates. Slight contamination of nickel was observed at Labstar, Multiverse, Kopek and Platinum quarry sites (Table 2, Figure 5). Also, cobalt (Co) concentration in average crustal abundance was far-off above the verified values in the dusts from all the quarries examined at both inside and outside the quarry operational areas except samples from inside CCECC(Ago-iwoye) and both outside and

inside of Sixsix-Imosan stipulating enrichment and depletion from the two quarry sites. Cobalt contamination occurred at Labstar, Multiverse, Prestige and Platinum quarries. Cr content from all the dust samples were below the ACA values indicating depletion of these metals. It also specifies contamination of the metal at Labstar, Multiverse, Prestige, Kopek and Platinum quarries (Table 2, Figure 5).

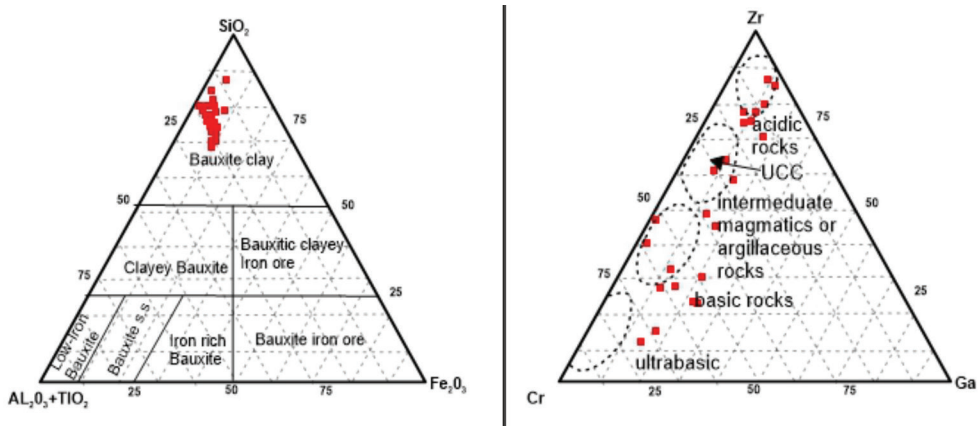


Figure 4: Ternary plots of (A)  $\text{SiO}_2\text{-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{+TiO}_2$  (B) Zr-Cr-Ga

### Rare Earth Elements

The charts employed to represent the REEs for both the (outside) contaminated and (inside) uncontaminated dusts with their ACA values revealed REEs in Lafarge limestone dust below the ACA value but were higher in other rock aggregates (Tables 3 and 4). This conformed to previous work, specifying that REE contents naturally found in soils basically depend on the parent material; with decreasing contents from granite-basalt-sandstone (Buessler *et al.*, 2011). The REEs were mostly above the average crustal abundance in Sixsix, Labstar, Multiverse, Ratcon and Kopek quarries (Tables 3 and 4). This revealed higher concentrations of LREE than MREE and HREEs. It also exposed the low REE contents in Sagamu-limestone dust when compared to other rock aggregate dust. Furthermore, the ternary plot of Y-La-Ce indicated the abundance of Ce in all the rock aggregate dust. Ce occurred in small quantities (7 ppm) in lepidolite, pollucite, and rhodizite that were present within granite gneiss and pegmatitic rocks (Buessler *et al.*, 2011) but the values range from 37.04ppm - 656.8ppm these quarries signifying rock aggregates derived similar lithology while very high content of lepidolite, pollucite, and rhodizite. Depletion and enrichments of Ce occurred in all the quarries indicating two different sources likely to be geogenic and anthropogenic types. Ce

could also be found together with Rb in the environment, and it may be mixed with other alkali metals (Buessler *et al.*, 2011).

The plots of LREE-MREE-HREE disclosed the distribution of REE in the rock dusts, with the abundance of LREE in all quarry sites. Further plot of LREE-MREE-HREE+Y also showed distribution of REE which fell on the LREE field and tending towards the HREE+Y side of the triangle (Figure 6).

### Chondrite-Normalized Plots

The REE chondrite-normalized plot presented in agreement to Oddo-Harkins rule, that elements with an even atomic number have higher abundance than elements with an odd atomic number (Oddo, 1914). Therefore, REEs in rocks were normalized with their abundance in the chondritic meteorites for elimination of Oddo-Harkins effect (Nakamura, 1974). This Normalization was achieved through the ratio of REE and chondrite concentration values. Consequently, chondrite values/standard for REE, trace metals and major oxides normalization (McDonough & Sun, 1995) were employed. The chondrite-normalized REE pattern indicated Light REE (LREE) enrichment, Heavy REE (HREE) depletion and Eu-negative anomaly indicated modified rocks. The various patterns of chondrite normalized REEs showed the origin and in-situ processes



Table 2: Concentration of the heavy metals analysed in the quarry dusts

Loc/ (ppm)	Cu	Pb	Zn	Cd	Mn	As	Ni	Co	Cr
GW-1a	94.0	7.98	113.6	0.09	870	1.9	61.1	25.8	110
GW-1b	65.0	11.69	118.8	0.07	715	3.6	33.5	19	97
KN-2a	36.7	9.68	90.2	0.02	540	1.4	30.6	15.2	49
KN-2b	31.6	10.54	75.6	0.07	458	1.8	19.6	11.7	45
MS-3a	81.9	18.42	99.9	0.06	795	1.7	69.1	28.3	94
MS-3b	65.3	13.25	104.4	0.05	1147	2.0	45.2	26.6	75
SR-4a	22.4	10.69	88.4	0.08	443	2.4	7.6	9.3	87
SR-4b	24.0	21.18	56.2	0.07	411	2.7	5.5	7.0	58
Sg-5a	5.1	1.54	65.5	0.02	350	18.2	18.4	6.5	123
Sg-5b	14.4	20.43	96.2	0.69	282	15.1	13	4.7	89
JB-6a	64.7	42.88	87.4	0.02	419	7.8	19.3	12	34
JB-6b	63.8	49.51	107.3	0.02	504	22.3	21.7	13.7	41
KL-7a	71.0	44.08	110	0.04	503	2.8	11.7	10	19
KL-7b	57.6	37.92	152.4	0.09	674	2.2	24.2	18	49
LM-8a	42.6	62.86	42.3	0.02	198	2.8	4.2	2.8	6
LM-8b	45.2	58.13	74.4	0.02	334	2.2	11.9	5.6	15
GR-9a	15.9	88.83	69.4	0.12	441	3.6	16.7	6.2	29
GR-9b	14.7	107.3	69.6	0.02	373	3.4	16.5	5.6	27
KJ-10a	32.1	38.83	78.1	0.02	601	1.2	42.4	10.5	55
KJ-10b	16.7	37.85	37.6	0.03	266	2.9	11.2	3.9	16
LD-11a	66.8	7.76	100.8	0.14	733	2.2	33.3	21	42
LD-11b	43.7	28.27	94.8	0.14	622	3.3	36.4	17.2	52
NK-12a	15.2	37.46	116.2	0.05	568	1.2	7.3	4.1	10
NK-12b	22.8	20.75	78.7	0.02	474	2.6	21.5	12.8	37
ACA	25	14.8	65	0.1	716	1.7	56	24	126

\*a = Inside \*\*b = Outside \*\*\*ACA=Average Crustal Abundance

CCECC-Ago-Iwoye(GW); Zhong Tai-Okenugbo(KN); Sixsix-Imosan(MS); CCECC-Isara(SR); Lafarge-Sagamu(SG); Labstar-Ajebo(JB); Multiverse-Kajola(KL); Prestige-Lamolo(LM); Kunlun-Onigambari(GR); Ratcon-Ikija(KJ); Kopek-Olonde(LD) and Platinum-Onikoko(NK).

of enrichment or depletion. The REE pattern also revealed the level of magma fractionation. Plagioclase fractionation normally controls the anomalous nature of Eu, specifying significant and probable fractionation of plagioclase out of magmatic melt (Figure 7).

The chondrite-normalized values for major elements concentrations showed significant

variations among the rock aggregate and limestone dusts. The CaO content is enriched while the Na<sub>2</sub>O and K<sub>2</sub>O contents are depleted in the Sagamu-limestone dusts; compared to concentration of these oxides in the rock aggregate dusts. The chondrite-normalized for heavy metal contents signify that: Pb and Arsenic were moderately enriched in the dusts from the entire locations suggesting their anthropogenic

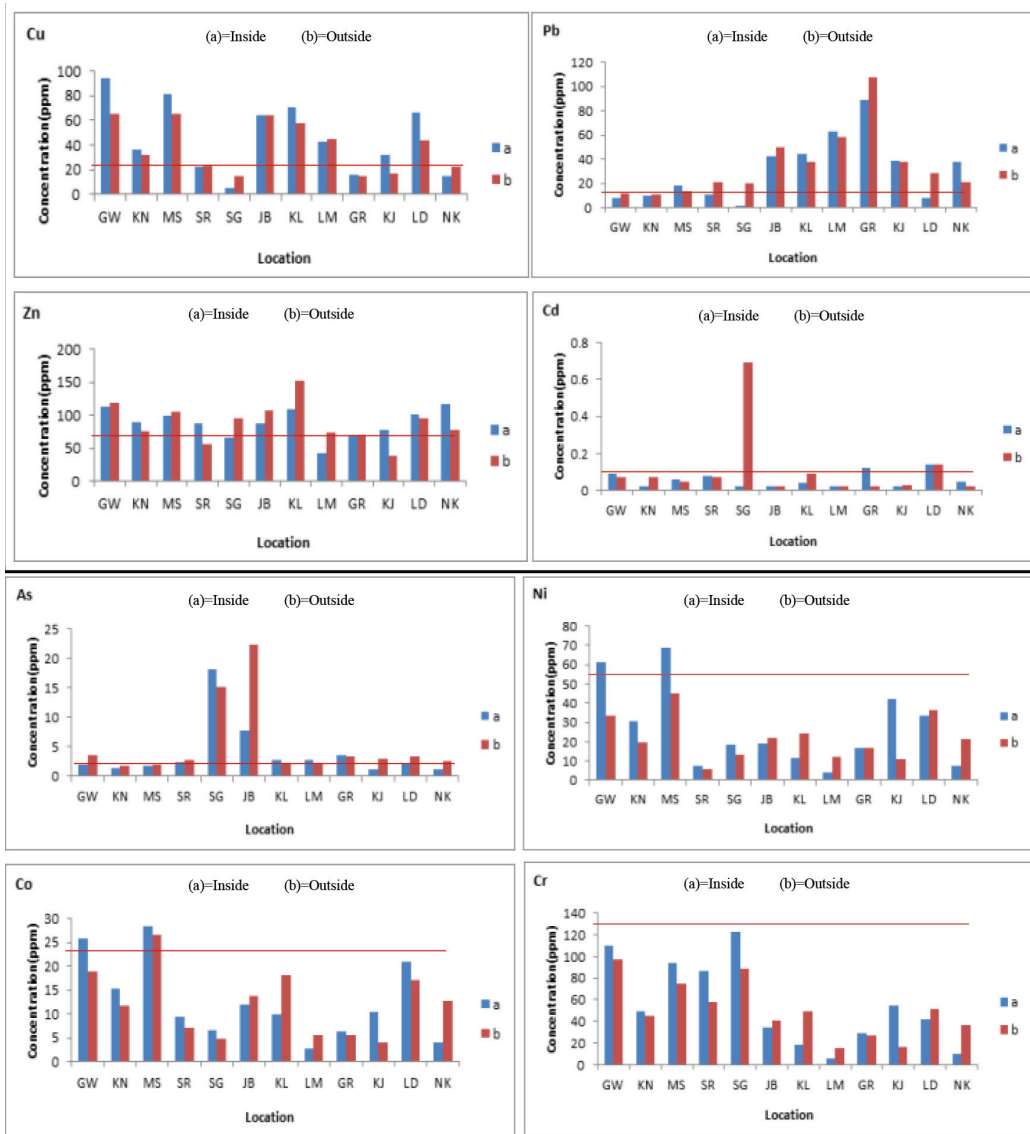


Figure 5: Comparison of metal concentration in quarry dusts with ACA

source while on the other hand, Ni is depleted from the quarry dusts.

**Chemical Alterations in Quarry Dust**

**Chemical Index of Alteration (CIA):** The Chemical Index of Alteration (CIA) proposed by Nesbitt & Young, (1982) as a measure of role played by chemical weathering in the

production of soils and clastic sediments; is the most acceptable weathering indices. This illustrates  $Al_2O_3$  ratio, mostly immobile during weathering to the mobile  $Na^+$ ,  $K^+$  and  $Ca^{2+}$  cations (Nadłonek & Bojakowska, 2018). However, high CIA values indicate leaching of mobile  $Ca^{2+}$ ,  $Na^+$  and  $K^+$  cations during weathering in relation to immobile components ( $Al^{3+}$ ,  $Ti^{4+}$ ). The low values suggest lack of

Table 3: Concentration of the rare earth elements analysed in the quarry dust

Loc/ (ppm)	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
GW-1a	12.6	14.4	45.2	86.53	9.4	35.8	6	1.3	4.6	0.5	3.5	0.6	1.7	0.2	1.4	0.2
GW-1b	9.4	14.3	47.8	97.09	10.3	37.5	7	1.1	5.4	0.6	3.3	0.6	1.4	0.2	1.1	0.2
KN-2a	7.8	10.7	48.4	99.73	10.2	37.9	6.7	1.4	4.6	0.5	2.5	0.5	1.2	0.1	0.9	0.1
KN-2b	6.2	11	48.3	93.53	9.4	35.1	6.6	1.3	4.5	0.4	2.6	0.3	1.1	0.1	0.9	0.1
MS-3a	16.1	18.2	30.7	62.05	7.3	29.8	5.5	1.1	4.5	0.6	3.7	0.8	1.9	0.3	2	0.3
MS-3b	22.1	26.7	41.9	88.94	9.7	39.2	8.7	1.9	7.9	0.9	5.3	0.9	2.8	0.5	2.8	0.4
SR-4a	5	12.3	52	95.99	10	33	5.6	0.8	4.4	0.5	2.8	0.5	1.2	0.2	0.9	0.1
SR-4b	5.7	16.8	49.8	103.7	9.8	36.1	5.5	0.9	5.2	0.7	4	0.6	1.6	0.3	1.8	0.2
SG-5a	4.7	20.2	26.5	50.02	6.2	24.3	4.6	1	3.8	0.5	3.3	0.6	1.7	0.3	1.6	0.2
SG-5b	3.1	13.4	19.5	37.04	4.4	17.9	3.5	0.7	3.4	0.3	2.4	0.4	1.2	0.2	1	0.2
JB-6a	7.3	20.9	196.8	390.3	45	147	24.5	1.5	13.3	1.6	6.3	0.7	2	0.2	1.4	0.1
JB-6b	8.9	23.9	238.5	487.6	56.4	185	31.1	1.6	16.6	1.7	7.5	0.7	2.1	0.3	1.3	0.2
KL-7a	5.6	29.9	324.8	656.8	73.6	250	34.2	1.3	16.2	1.8	7.9	1	2.5	0.3	2.4	0.3
KL-7b	11.1	27	231	477.9	53.5	180	26.1	1.4	12.9	1.6	7.3	0.9	2.7	0.3	2	0.3
LM-8a	2.3	9.8	63.1	121.1	14.6	50.8	8.5	0.9	5.1	0.4	2.2	0.3	1.1	0.1	1	0.1
LM-8b	4.1	8.5	45.6	91.81	9.7	37	5.9	0.9	3.5	0.3	2.2	0.3	0.8	0.1	0.9	0.1
GR-9a	5.9	16.8	46	89.96	11.3	40.1	7.1	1.6	5.5	0.6	3.5	0.6	1.8	0.3	1.8	0.3
GR-9b	5.5	14.5	45.7	83.03	10	33.4	6.3	1.2	4.2	0.4	2.6	0.5	1.5	0.2	1.5	0.2
KJ-10a	7.6	21.8	69.7	140.5	16	59.3	10.7	1.6	7.3	0.8	5.2	0.8	2.3	0.3	1.9	0.3
KJ-10b	3.9	13.2	29.8	63.06	7.5	26.1	5.1	1	4.6	0.4	2.8	0.5	1.4	0.2	1.3	0.1
LD-11a	13.4	12	26.8	51.14	5.6	20.7	3.8	1.2	3.6	0.3	2.1	0.5	1.4	0.2	1	0.1
LD-11b	10.9	13.2	31.3	65.99	7.2	24.8	5.1	1.3	4.2	0.4	3.3	0.4	1.7	0.2	1.2	0.2
NK-12a	6.1	24.6	89.6	180.8	19.9	70.7	13.4	0.8	9.9	1.2	6	0.9	2.6	0.3	2.2	0.4
NK-12b	6.9	9.6	23.1	52.12	5.5	18.8	2.9	0.6	2.6	0.3	2.4	0.4	1	0.2	1.1	0.1
ACA	16	24	30	60	6.7	27	5.3	1.3	4	0.7	3.8	0.8	2.1	0.3	2	0.4

\*a = Inside\*\*b = Outside \*\*\*ACA=Average Crustal Abundance

chemical alterations at cool and/or arid climate conditions (Fedó *et al*, 1996). The greatest value CIA=100 is typical of kaolinite weathering. Therefore, these calculated CIA values indicated low kaolinite weathering: for illite, CIA=75-90; muscovite CIA=75, feldspars-50; while fresh basalts showed CIA values in the range of 30-45; and fresh granites and granodiorites varied from 45-50 (Fedó *et al*, 1996).

$$CIA = \{Al_2O_3 / (Al_2O_3 + CaO + Na_2O + K_2O)\} \times 100$$

#### **Chemical Index of Weathering (CIW):**

Harnois's Chemical Index of Weathering (CIW) is calculated similarly to the CIA, eliminating only K<sub>2</sub>O contributions. In this arrangement, Al<sup>3+</sup>, which is associated with K<sup>+</sup> feldspars, is not separated; thus, the CIW can reach very high values in the case of rocks that are rich in these minerals, no matter whether the rocks are chemically weathered or not (Fedó *et al*, 1996).

$$CIW = \{Al_2O_3 / (Al_2O_3 + CaO + Na_2O)\} \times 100$$

(Harnois, 1988)

Table 4: Average Crustal Abundance (A.C.A) for the major oxides and heavy metals

Chondrite values by Lodders and Fegley, 1998			Average Crustal Abundance (A.C.A) for the major oxides and heavy metals by Wedepohl, 1995				Chondrite REE values by (a) Sun & McDonough (1995), ** (b) Wakita, Rey and Shmitt (1971) and Abundance of Elements in the Earth's crust by (c)Wedepohl (1995)			
Major Oxide	Chondrite abundance (%)	A.C.A (%)	Heavy Metal	Chondrite abundance (ppm)	A.C.A (ppm)	REE	(a) Chondrite abundance (ppm)	(b) Chondrite abundance (ppm)	(c)Crustal abundance (ppm)	
SiO <sub>2</sub>	Si	10.64	Zn	315	65	La	0.237	0.34	30	
TiO <sub>2</sub>	Ti	0.044	Ni	11,000	56	Ce	0.613	0.91	60	
Al <sub>2</sub> O <sub>3</sub>	Al	0.865	Cu	125	25	Pr	0.0928	0.121	6.7	
Fe <sub>2</sub> O <sub>3</sub>	Fe	18.2	Co	505	24	Nd	0.457	0.64	27	
MgO	Mg	9.7	Cr	2650	126	Pm	na	na	Na	
CaO	Ca	0.926	Pb	2.53	14.8	Sm	0.148	0.195	5.3	
Na <sub>2</sub> O	Na	0.5	Cd	0.69	0.1	Eu	0.0563	0.073	1.3	
K <sub>2</sub> O	K	0.055	As	1.85	1.7	Gd	0.199	0.26	4	
			Mn	1940	716	Tb	0.0361	0.047	0.7	
						Dy	0.246	0.3	3.8	
						Ho	0.0546	0.078	0.8	
						Er	0.16	0.2	2.1	
						Tm	0.0247	0.032	0.3	
						Yb	0.161	0.22	2	
						Lu	0.0246	0.034	0.4	
						Sc	na	na	16	
						Y	na	na	24	

\*Average Crustal Abundance (A.C.A) for the major oxides and heavy metals (Wedepohl, 1995 and Chondrite values by Lodders and Fegley, 1998).

\*\*Chondrite REE values by Sun & McDonough (1995), \*\*Wakita, Rey and Shmitt (1971) and Abundance of Elements in the Earth's crust by Wedepohl (1995), Na=not available.

Hence, for outside quarry dust, the CIA and CIW values ranged from 7.95-72.77 and 7.96-75.63% respectively (Table 5). These values signify dusts derived from highly weathered rocks and the values showed indication of the presence of high muscovite and feldspar content. However, for inside quarry dust, the CIA and CIW values ranged from 7.60-68.39% and 7.61-69.47% correspondingly (Table 5); signifying dusts from highly weathered rocks and further indication revealed the presence of high feldspar content. The outside and inside dusts assessment

using the CIA and CIW values for Lafarge quarry dusts revealed very low CIA and CIW values which indicated the material contents of the dust. It also showed that limestone quarry dusts are chemical but not clastic like the rock aggregate quarry dusts.

#### ***Geochemical Maps and Anthropogenic Assessment of Quarry Dusts***

Heavy metal dissemination in rock aggregates at the quarry sites was exposed with the help of geochemical maps. This displayed the natural

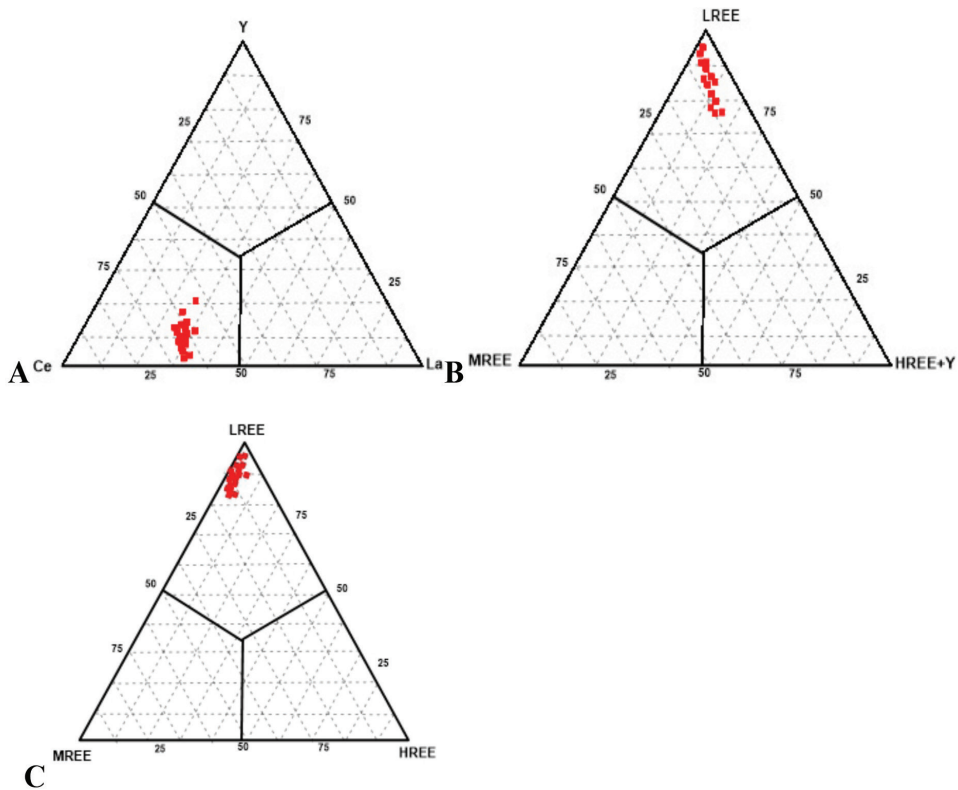


Figure 6: Ternary plots of (A) Y-La-Ce (B) LREE- HREE+Y-MREE (C) LREE-HREE-MREE (LREE= $\sum$ La-Pm MREE= $\sum$ Sm-Dy HREE= $\sum$ Ho-Lu)

level of metals in the form of enrichment and depletion of elements in the quarry dusts. The concentrations in ppm of heavy metals were further explicitly revealed on geochemical maps with colour range to identify varying concentrations of elements at the various quarry sites which gave a clearer view and pictorial representation of areas with the high and low metal contents.

CCECC-Ago-Iwoye (Cu-94.0) and Sixsix-Imosan (Cu-81.90) quarry recorded very high Cu content in the rock dust derived from inside-quarry dust indicating the presence of Cu-sulphide mineral in the gneiss and the pegmatitic rock of the area while Sixsix-Imosan (Cu-63.50) and Labstar recorded elevated Cu concentrations (Cu-65.0) from outside-quarry dust (Table 2; Figure 8). This specified depletion

of sulphides by the environmental bacterial (Gerardi and Zimmerman 2005; Wu et al. 2012). Highest concentration of Pb (Pb-88.83 ppm and Pb-107.30 ppm) observed inside and outside-Kunlun quarry dusts respectively. The presence of high Pb inside this quarry dusts might be indicative of Pb-minerals in the migmatite gneiss and biotite gneiss lithology that served as source rock for the aggregates while Pb-107.30 from outside-quarry dusts signified additional input of this metal from anthropogenic sources specifying contamination of the dust (Table 2; Figure 8). Zinc with 116.2 ppm showed the highest concentrations from inside Platinum quarry dusts, indicating Zn-minerals in the rock dusts of the area: whereas Prestige-quarry revealed the highest Zn-152.48ppm content from outside-quarry dusts signifying additional anthropogenic Zn-input that might have been

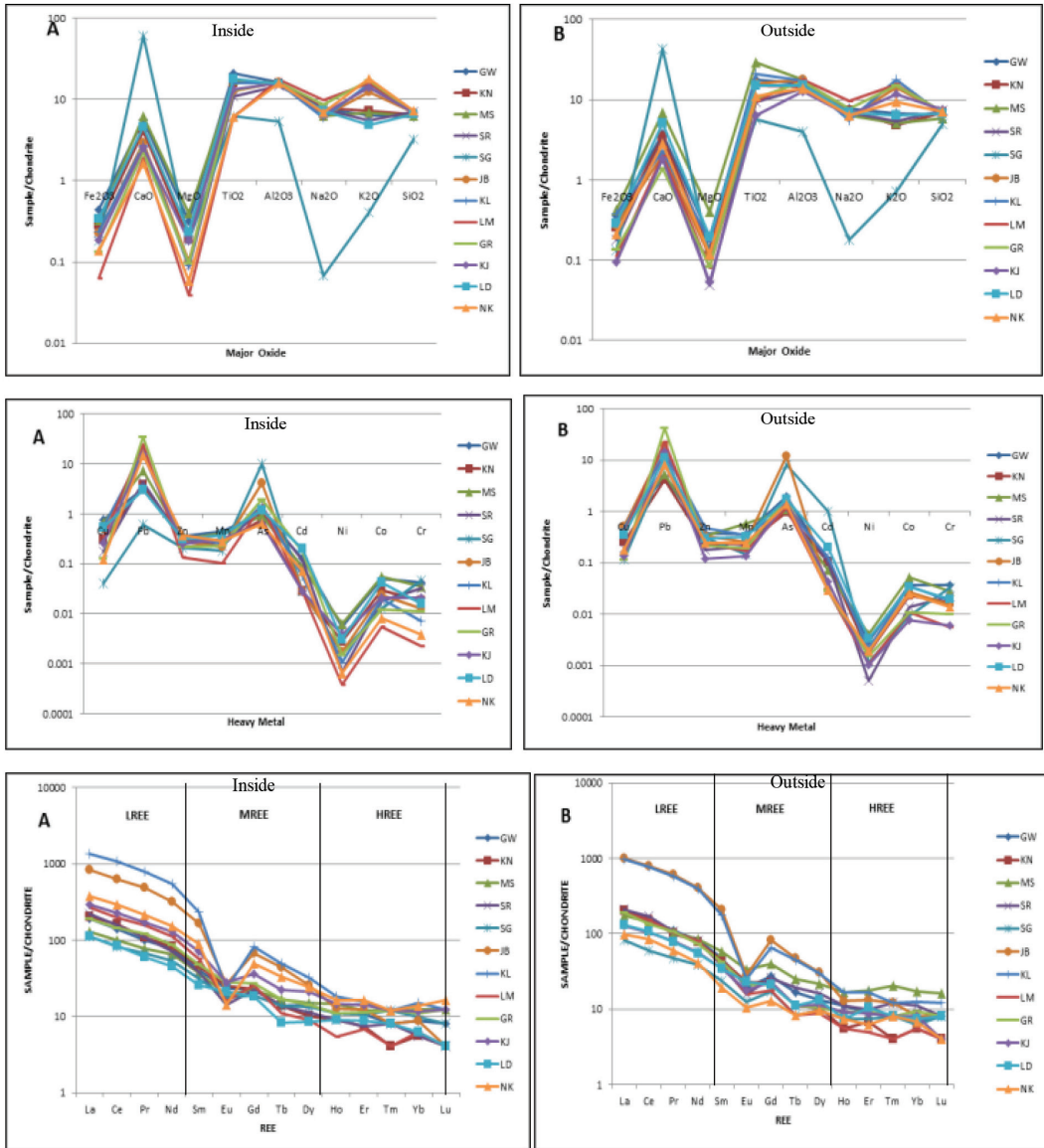


Figure 7: Normalized plots for oxides, trace metals and REE (A) inside (B) outside

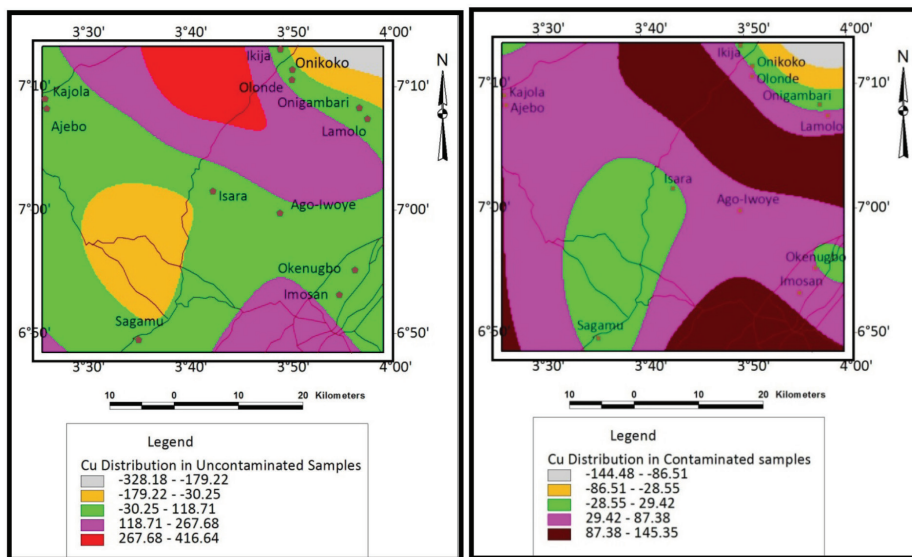
sourced from domestic activities by quarry support workers outside the quarry operational enclave (Table 2; Figure 9).

Cadmium-0.14ppm was observed as highest concentration at Kopek quarry from both inside and outside quarry-dusts whereas, the least was recorded at KN, SG, JB, LM, GR, KJ and NK quarries at both inside and outside

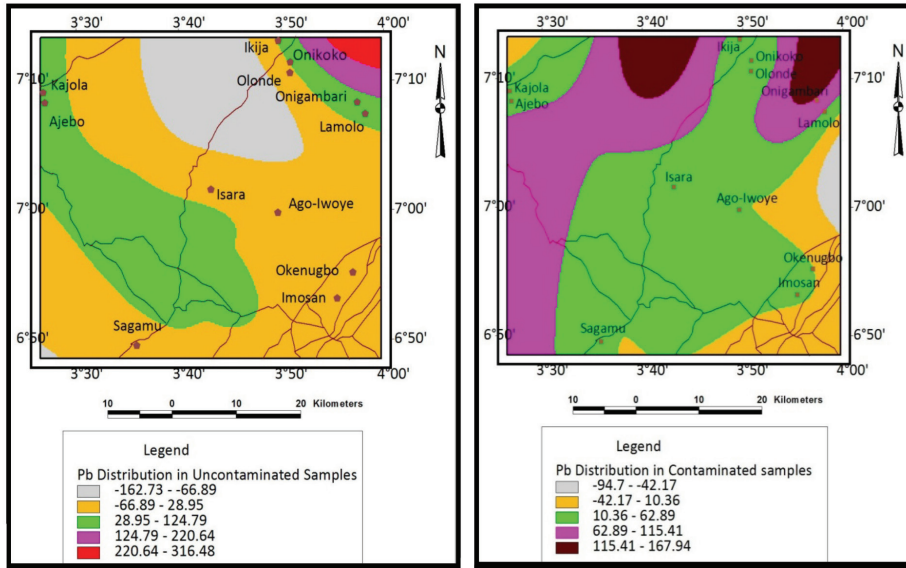
dusts. These may represent both geogenic and anthropogenic inputs in both quarry dusts respectively (Table 2; Figure 9). Lafarge quarry that specifically quarries limestone for cement production recorded the highest Arsenic-18.20ppm derived from inside quarry-dust that was generated during operation; this indicated arsenic background levels at the quarry site.

Table 5: Chemical weathering indices for each quarry

Location	CIA	CIW	CIA	CIW
	a=inside		b=outside	
%				
GW	60.19	61.10	63.99	65.11
KN	62.83	63.99	63.70	64.57
MS	59.76	60.77	60.94	61.63
SR	65.19	66.21	64.41	65.46
SG	7.60	7.61	7.95	7.96
JB	68.39	70.70	72.77	75.63
KL	68.22	71.24	71.90	75.44
LM	66.80	69.47	66.76	69.32
GR	65.47	68.52	70.67	73.66
KJ	67.73	70.45	66.57	69.25
LD	62.27	63.05	60.10	61.08
NK	69.55	73.26	65.51	67.43

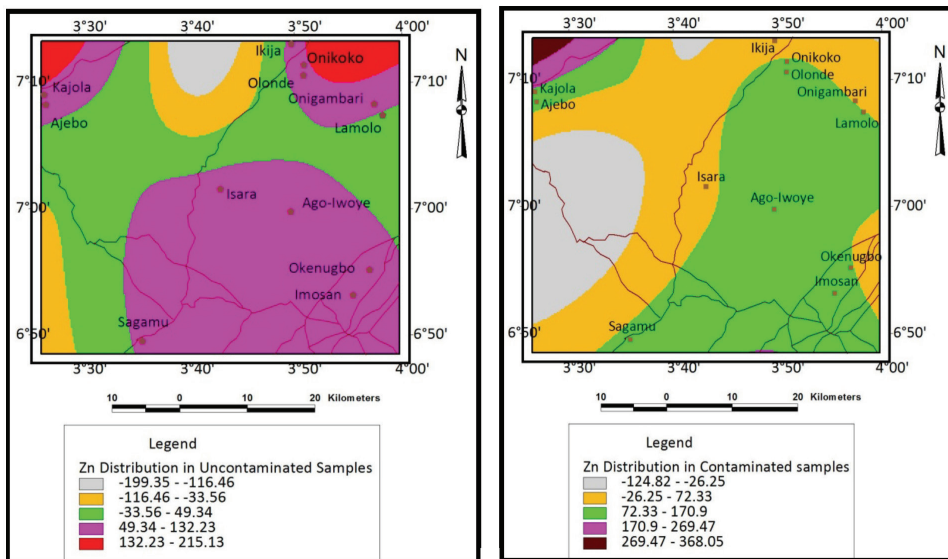


(a): Distribution of Cu in the quarry



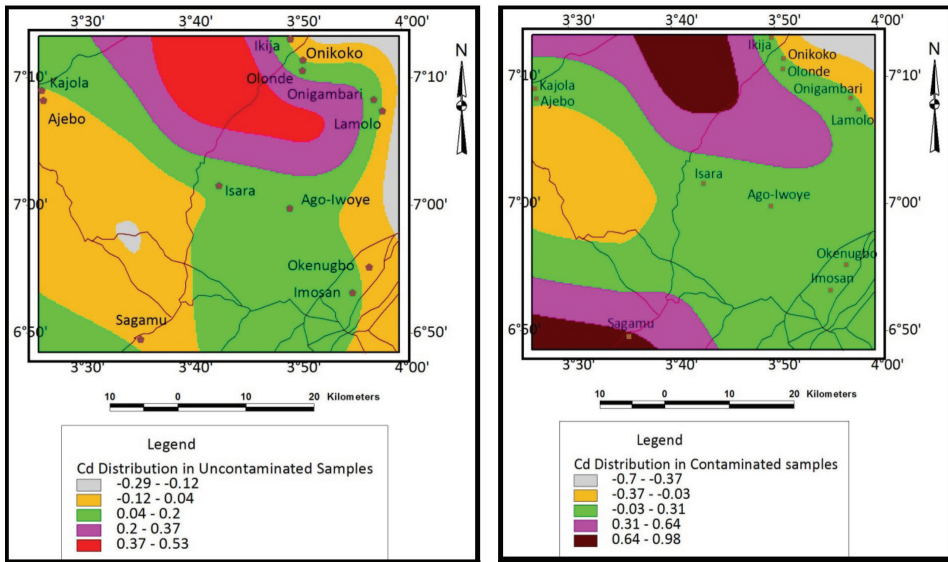
(b): Distribution of Pb in the quarry

Figure 8: Spatial distribution of Cu and Pb in the quarry operational areas



(a): Distribution of Zn in the quarry





(b): Distribution of Cd in the quarry

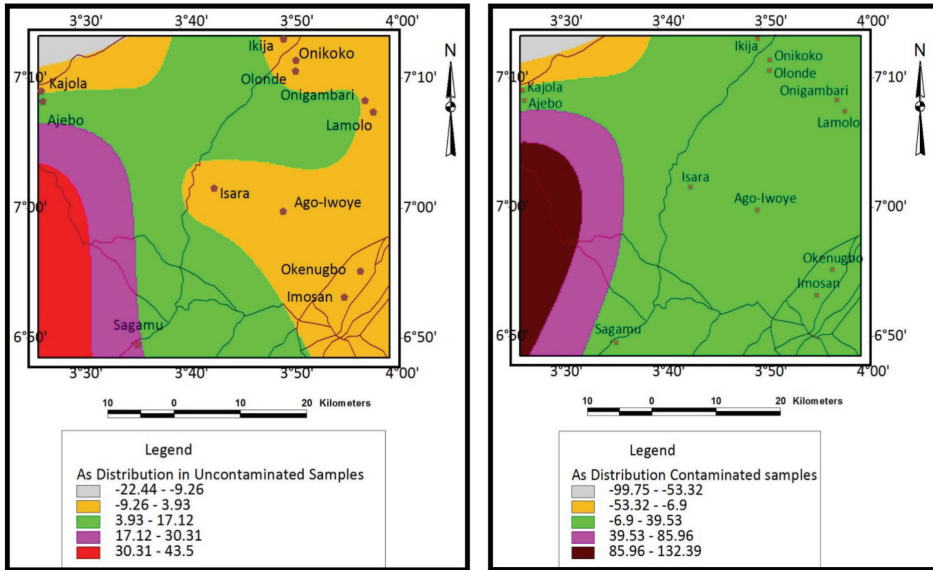
Figure 9: Spatial distribution of Zn and Cd in the quarry operational areas

This metal might have been sourced geogenically; therefore, making Lafarge-quarry dust to be toxic (Table 2, Figure 10). Also, very high Arsenic content observed at Labstar-22.30ppm and Larfarge-18.20ppm at both inside and outside, showing presence of As-minerals in the Labstar rock aggregate. Precisely, these arsenic minerals are likely found in the gneissic rocks that are being quarried at Labstar quarry as rock aggregates. Therefore, this metal might have been sourced geogenically from the limestone based on its proximity (Table 2, Figure 10). Also, there are significant disparities between arsenic values from both inside and outside quarry dusts.

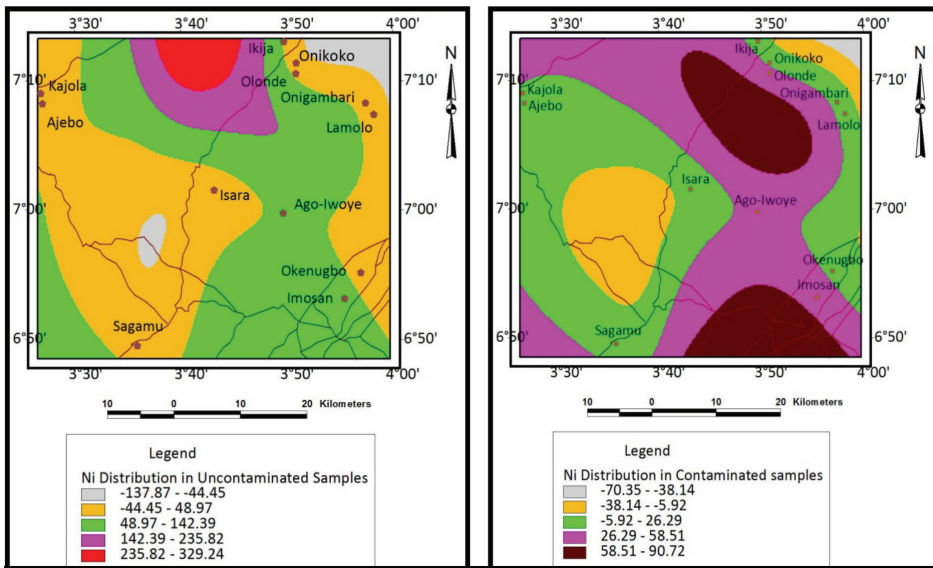
CCECC-Ago-Iwoye and Sixsix-Imosan quarries recorded very high concentration of Ni-61.1ppm and Ni-69.1ppm correspondingly within inside quarry dust which laid down the presence of Ni-rich mineral in the rock dusts with reference to ACA Ni-values; whereas Kopek and Sixsix nickel contents obtained from outside-quarry dusts were found to be 36.4ppm and 45.2ppm which specified depletion of nickel

in the rock dusts (Table 2, Figure 10). Sixsix and CCECC-Ago-Iwoye quarry presented moderately high concentrations of cobalt (Co-28.3ppm and 25.8ppm) from inside-quarry rock dust (Table 2; Fig 11). This is indicative of the presence of Co-mineral in the banded gneiss and other gneissic rock of the area while Co-26.6ppm and Co-19.0ppm were observed as the highest concentrations from outside-quarry-rock dust, derived from both quarry sites; signifying depletion of Co in the contaminated environment (Table 2, Figure 11).

Lafarge (Cr-1123.0ppm) and CCECC (Cr-110.0ppm) quarry displayed high contents of chromium from inside-quarry-dusts but lower than the ACA value. These values must have been sourced from chromite minerals present within the gneissic rocks that produced the rock aggregates at the quarry sites especially CCECC quarry dust. These Cr values were below the ACA at all the quarry operational areas in both inside and outside-quarry-dusts (Table 2; Figure 11).



(a): Distribution of As in the quarry

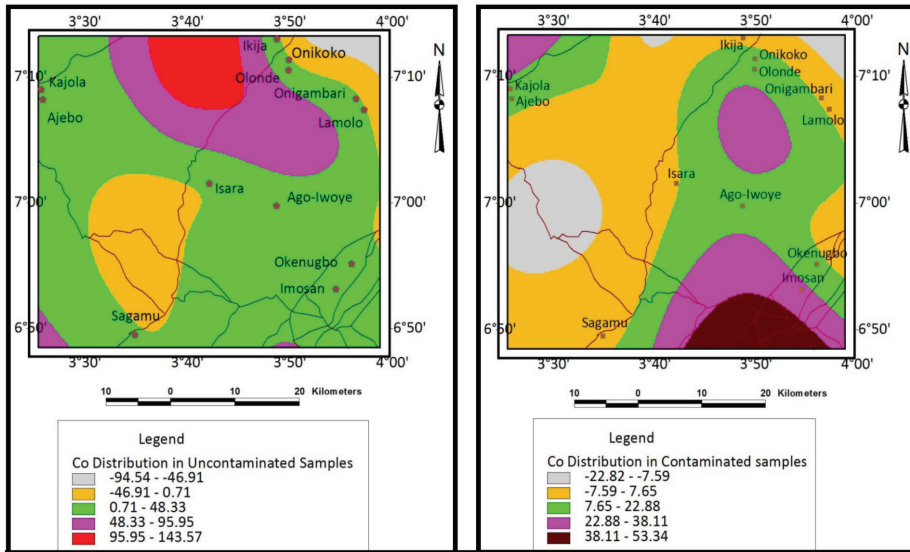


(b): Distribution of Ni in the quarry

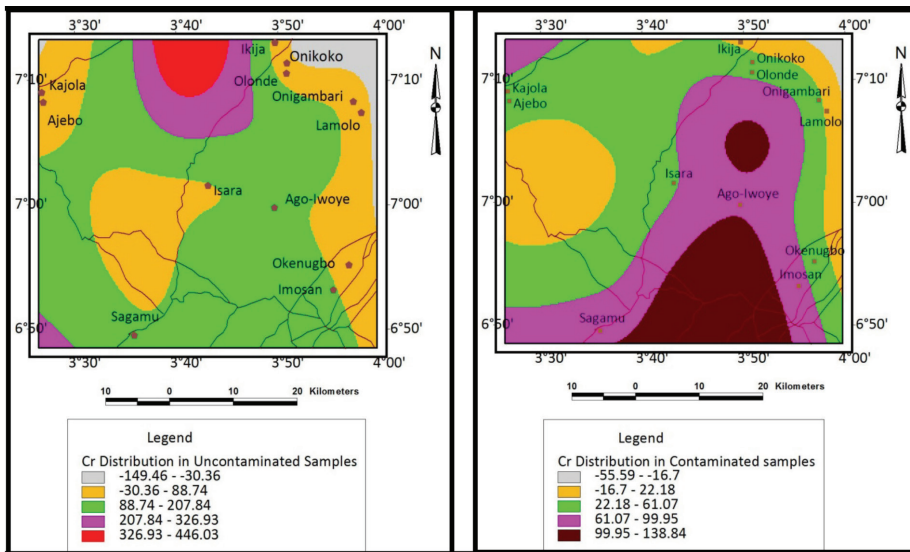
Figure 10: Spatial distribution of As and Ni in the quarry operational areas

Kopek and Sixsix-quarry sites revealed elevated concentration of Mn which consist of 733.0ppm and 870.0ppm derived from dusts from inside the quarry respectively; signifying enrichment when compared with ACA Mn-value; whereas 1147.0ppm Mn from CCECC

obtained from the outside-quarry dusts indicate anthropogenic input of this metal. The amount of manganese depleted must have been used up by different plants in the farmland around the quarry vicinity (Table 2; Figure 12).



(a): Distribution of Co in the quarry



(b): Spatial distribution of Cr in the quarry

Figure 11: Spatial distribution of Co and Cr in the quarry operational areas

**Mean Enrichment of metal and Contamination of Samples**

The difference in concentration of the outside quarry dust and the inside quarry dust (b-a) with negative signs showed enrichment in the concentration of the element or metal (Table 6). It was expected that the outside quarry dust

be greater in concentration than the inside but when the reverse occurs, it indicates that these elements are added by anthropogenic activities but may get weathered or leached out from the environment. The values of the difference in concentration of the outside quarry dust and the inside quarry dust (b-a) that were positive

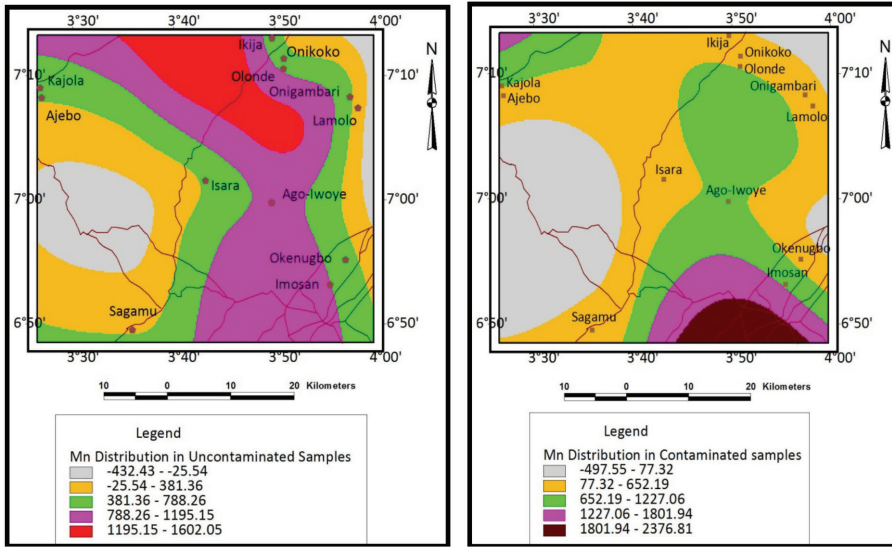


Figure 12: Spatial distribution of Mn in the quarry operational areas

(Table 6); revealed contamination of the element or metal and this showed that the increase was caused by anthropogenic activities around quarry operational sites.

From the above data,  $Al_2O_3$ ,  $CaO$ ,  $MgO$ ,  $K_2O$  and  $Na_2O$  were enriched in the inside than the outside quarry dusts; whereas,  $Fe_2O_3$ ,  $TiO_2$  and  $SiO_2$  were depleted. However, as regards the heavy metals, it was observed that  $Cu$ ,  $Mn$ ,  $Ni$ ,  $Co$  and  $Cr$  were enriched in the inside quarry dust and  $Pb$ ,  $Zn$ ,  $As$  and  $Cd$  revealed contamination. These metals are noteworthy because they are potentially harmful elements which have health implications when taken into the body system. For the REE, all except  $Sc$  were enriched in the inside quarry dust. This implies that REEs were rarely added by anthropogenic activities (Table 7).

**Enrichment of Metal and Contamination of Samples per Site**

$Cu$  enrichment varied between 1.6 - 9.3 ppm and occurred at four quarry sites specifying about 33.3% of all the quarry sites. The enrichment is high at Lafarge-SG indicating the presence of  $Cu$ -minerals in the limestone in the quarry (Table 8; Figure 13).  $Pb$  and  $Zn$  showed as the

most significant elements, because most of their values were generally greater than the ACA of 14.8 and 65.0 ppm values respectively. The enrichments varied from 3.71- 18.89 and 0.2 - 42.4ppm respectively taking place at seven quarries suggesting 58.3% of the enrichment and specified enrichment of geogenic origin while 41.7% of the quarry sites were contaminated (Table 8; Figure 13). The enrichment is high at CCECC-Isara, Lafarge, Kunlun and Kopek quarries specifying the presence of  $Pb$  and  $Zn$ -minerals in the limestone, gneiss and pegmatitic rocks. (Table 8). Contamination changes from 0.98 - 16.71ppm and 6 - 40.5ppm for  $Pb$  and  $Zn$  correspondingly (Table 8; Figure 13). Cadmium and Arsenic are among the potentially harmful elements that affects the environment negatively.

Cadmium and Arsenic are among the potentially harmful elements that affects the environment negatively. The contrast between  $Cd$  enrichments ranged from 0.0 - 0.7 ppm and occurred at four quarry sites signifying 33.3% of all the quarry sites.

The enrichment is high at Lafarge-SG indicating the presence of  $Cd$ -minerals in the limestone in the quarry (Table 8; Figure 13) while the contaminated quarry sites with

Table 6: Mean Anthropogenic inputs assessment in the quarry dust

Major Oxides	Outside Dust (b)	Inside Dust (a)	Difference (b-a)
Al <sub>2</sub> O <sub>3</sub>	12.72	13.07	-0.35
CaO	5.98	7.56	-1.57
MgO	1.38	1.59	-0.21
K <sub>2</sub> O	0.52	0.57	-0.05
Fe <sub>2</sub> O <sub>3</sub>	4.31	4.22	<b>0.09</b>
Na <sub>2</sub> O	3.22	3.38	-0.16
TiO <sub>2</sub>	0.61	0.57	<b>0.04</b>
SiO <sub>2</sub>	71.27	69.04	<b>2.23</b>
Heavy Metals	Outside Dust (b)	Inside Dust (a)	Difference (b-a)
Cu	38.73	45.70	-6.97
Pb	34.74	30.92	<b>3.82</b>
Zn	88.83	88.48	<b>0.35</b>
Mn	521.67	538.42	-16.75
As	5.34	3.93	<b>1.41</b>
Cd	0.11	0.06	<b>0.05</b>
Ni	21.68	26.81	-5.13
Co	12.15	12.64	-0.49
Cr	50.08	54.83	-4.75

Table 7: Anthropogenic inputs Assessment of REE in the quarry dust

REE	Outside Dust (b)	Inside Dust (a)	Difference (b-a)
Sc	8.15	7.87	<b>0.28</b>
Y	16.01	17.63	-1.63
La	71.03	84.97	-13.94
Ce	145.15	168.74	-23.59
Pr	16.12	19.09	-2.98
Nd	55.93	66.57	-10.63
Sm	9.48	10.88	-1.40
Eu	1.16	1.21	-0.05
Gd	6.25	6.90	-0.65
Tb	0.67	0.78	-0.11
Dy	3.81	4.08	-0.28
Ho	0.54	0.65	-0.11
Er	1.61	1.78	-0.18
Tm	0.23	0.23	0.00
Yb	1.41	1.54	-0.13
Lu	0.19	0.21	-0.02

Table 8: Enrichment of metal and contamination of samples per site

Site/(ppm)	Cu	Pb	Zn	Cd	Mn	As	Ni	Co	Cr
GW	29	-3.71	-5.2	0.02	155	-1.7	27.6	6.8	13
KN	5.1	-0.86	14.6	-0.1	82	-0.4	11	3.5	4
MS	16.6	5.17	-4.5	0.01	-352	-0.3	23.9	1.7	19
SR	-1.6	-10.49	32.2	0.01	32	-0.3	2.1	2.3	29
Sg	-9.3	-18.89	-30.7	-0.7	68	3.1	5.4	1.8	34
JB	0.9	-6.63	-19.9	0	-85	-15	-2.4	-2	-7
KL	13.4	6.16	-42.4	-0.1	-171	0.6	-13	-8	-30
LM	-2.6	4.73	-32.1	0	-136	0.6	-7.7	-3	-9
GR	1.2	-18.47	-0.2	0.1	68	0.2	0.2	0.6	2
KJ	15.4	0.98	40.5	-0	335	-1.7	31.2	6.6	39
LD	23.1	-20.51	6	0	111	-1.1	-3.1	3.8	-10
NK	-7.6	16.71	37.5	0.03	94	-1.4	-14	-9	-27

CCECC-Ago-Iwoye(Gw); Zhong Tai-Okenugbo(Kn); Sixsix-Imosan(Ms); CCECC-Isara(Sr); Lafarge-Sagamu(Sgm); Labstar-Ajebo(Jb); Multiverse-Kajola(Kl); Prestige-Lamolo(Lm); Kunlun-Onigambari(Gr); Ratcon-Ikija(Kj); Kopek-Olonde(Ld) and Platinum-Onikoko(Nk).

Cd cover about 66.7%; making significant operations to be Cd prone and signify additions of anthropogenic Cd contributions. Also, Arsenic enrichments vary from 0.3 - 1.7ppm suggesting 66.7% of all the sites; these imply the presence of Cd in the rock formation. The remaining 33.3% of the quarry sites specify contamination with anthropogenic arsenic inputs (Table 8; Figure 13). The enrichment is high at Lafarge and Labstar quarries for Cd and As respectively which stipulate occurrence of Cd-minerals in the limestone, gneiss and pegmatitic rocks (Table 8).

Ni and Co are also enriched, and their enrichment covers 41.66% and 33.3% of all the quarry sites for Ni and Co in that order. Ni ranges from 2.4 - 14.0ppm while Co varies from 2-9ppm respectively (Table 8; Figure 13). The most enriched sites for Ni and Co are Platinum and Multiverse quarries respectively. Contamination of Ni and Co revealed 58.34% and 66.7% in that order; signifying moderately contaminated sites for Ni and Co. Contaminated sites Ni and Co include Ratcon and CCECC-Ago-iwoye respectively (Table 8).

Cr is toxic and harmful leaving negative effects on the environment. Cr enrichment varies from 4.4 - 14ppm covering about 41.67% of the quarry sites (Table 8; Figure 13). The most Cr enhanced quarry sites include Platinum (9ppm) and Multiverse (8ppm) which signify chromite enriched gneiss and migmatitic rocks respectively. Cr contaminated quarry sites covered about 58.33% indicating moderate level of chromium contamination from different human activities outside the quarry and other input from industrial materials. The amount of Mn in rock and soils vary greatly based on its complexes and toxicity which is common in soils/environment. The enrichment levels of Mn vary between 85-382ppm. Manganese is significantly enriched within the banded gneiss and other gneissic rocks at Sixsix (382ppm) and Multiverse (171ppm) quarries (Table 8; Figure 13). Mn enrichment covers 33.3% of all the quarry sites while 66.7% revealed manganese contaminated sites. The most Mn contaminated site is Ratcon (335ppm) specifying high input of anthropogenic Mn (Table 8).

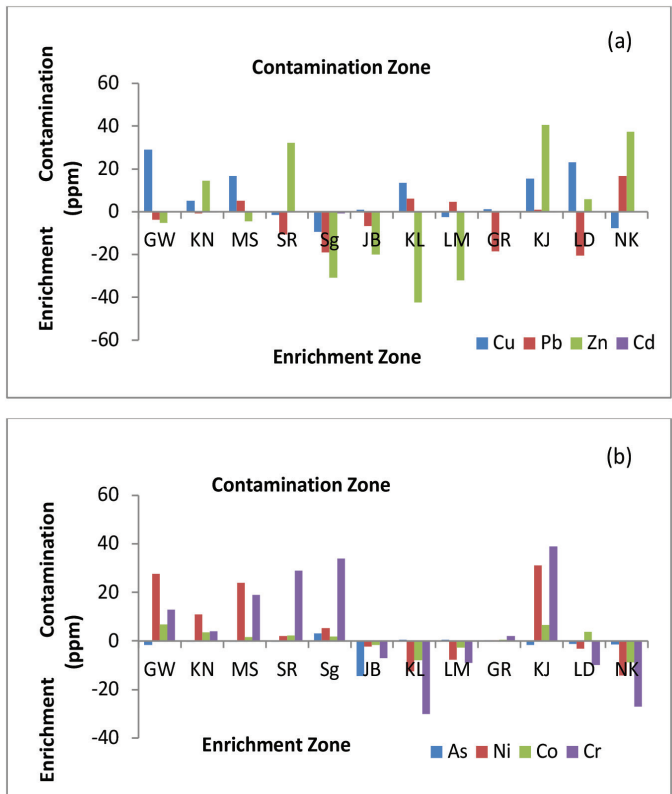


Figure 13: Metal enrichment and contamination levels of samples per site

**Medical Geology**

Generally, particulate dusts exist in different fractions and can be found on pervious and impervious urban surfaces which have become the most significant concern in environmental studies especially at urban centres. Dusts generated from the cities and urban centres have increased contents of PHEs-potentially harmful elements (Al-Khashman2004, 2007; Langer *et al*, 2010). This has instituted and concealed heavily; the precarious capabilities of metals which serve as a threat to human’s health and also endanger the environment (Li *et al*, 2001; Charlesworth *et al*, 2003; Duong & Lee, 2011). These PHEs (Pb, Zn, Cd, As, Se, Th, U) have been exposed to produce an outlook as paradigm that influence human health status negatively (Figure 14). Each of this metal can be linked to different health challenges and great hazards in the environment.

Since the uninterrupted deposition of heavy metals also known as potentially harmful elements generated from both limestone and rock aggregates; quarry may be regarded as another input or secondary source of contamination. All groups of people are susceptible to dangers posed by dust inhalation. Some people exposed to these dusts apart from the quarry workers include people living in proximity to the quarry site; hawkers; drivers and others who are consumers of water, food and farm products derived from quarry environments.

Hence, the aged and the toddlers adduced to be the most susceptible group who are constantly affected by these particulate dusts (Han *et al*, 2017). However, in respect to this work, the most exposed group is the people of the active age; especially, the quarry workers who solely depend on this for livelihood. They are willingly exposed on daily basis to earn a living.

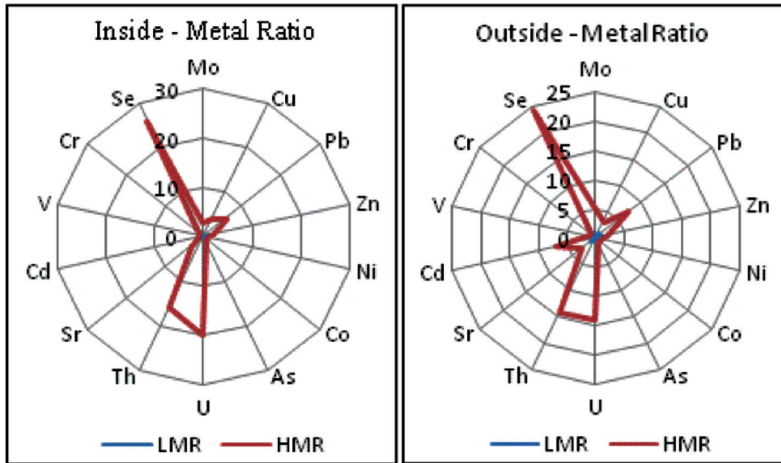


Figure 14: Exposition of PHEs with Low (LMR) and High (HMR) Metal Ratio

Indirect or direct ingestion of dusts always occurred among this group, and they are highly vulnerable to different group health challenges that may arise from this exposure (Sajid *et al*, 2012). Therefore, high concentration of heavy metals inhaled or ingested can accumulate in human body and cause serious health complications.

Hazards caused on human health by rare earth elements depend on the amount and duration of exposure; from the above findings, exposure to a large concentration of REE over a long period of time can be dangerous and harmful to human health. Furthermore, the finer the dust, the farther the ability to move far away and settle on plants, water, bodies, agricultural soil and even breathed inhalation and dermal absorption by humans and animals (Hu *et al*, 2006). Lack of certain standards makes it difficult to detect and evaluate the health risks developed from REEs. Thus, it is necessary to introduce guideline values of REEs in food, water, soil, air and all other environmental components. Apart from the regular health issues like sneezing, catarrh and cough that workers and residents around the quarry sites can have; there are other serious health issues which may show up years later through inhalation and accumulation of REE laden dusts in their body system.

Several studies on effects of REE in human and animal health, specifying accumulation of these elements with time have revealed bones, liver, and lungs as the main spots for build-up (Hirano & Suzuki, 1996; Li *et al*, 2013; Rim, 2013). Despite this, safe levels of REE exposure in humans cannot be determined with the little facts that have been gathered with values found being described as temporary (USEPA, 2012).

Comparisons of  $\sum$ REEs with estimate daily intake (EDI) divulge that: the concentrations already exceeded the estimate daily intake of REEs which was found to be damaging to human health as  $100\text{-}110\mu\text{gkg}^{-1}\text{d}^{-1}$  (Zang *et al*, 2000; Li *et al*, 2010; Li *et al*, 2013).

From these analytical results, the  $\sum$ REE values ranged from 108.64-1408.5ppm. These values were greater than the EDI= 0.1-0.11ppm/d. Therefore, if the dust containing REE is inhaled, ingested or contacted with the skin; it could have adverse effect on the health of man either through immediate or long-time exposure. Ingestion of these dusts into the system is even more dangerous because it goes directly into the body system.

Among the REEs, La, Gd, Ce and Eu are generally considered but the origin of anthropogenic REE consist of different technologies, medicine and fertilisers (Gwenzi



Table 9: Concentration of the Rare Earth Elements (REE) in the quarry dusts

Loc/ (ppm)	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	ΣLREE	ΣHREE	ΣREE
GW-1a	12.6	14.4	45.2	86.53	9.4	35.8	6	1.3	4.6	0.5	3.5	0.6	1.7	0.2	1.4	0.2	196.83	27.1	223.98
GW-1b	9.4	14.3	47.8	97.09	10.3	37.5	7	1.1	5.4	0.6	3.3	0.6	1.4	0.2	1.1	0.2	210.19	27.1	237.29
KN-2a	7.8	10.7	48.4	99.73	10.2	37.9	6.7	1.4	4.6	0.5	2.5	0.5	1.2	0.1	0.9	0.1	212.13	21.7	233.23
KN-2b	6.2	11	48.3	93.53	9.4	35.1	6.6	1.3	4.5	0.4	2.6	0.3	1.1	0.1	0.9	0.1	200.43	21	221.43
MS-3a	16.1	18.2	30.7	62.05	7.3	29.8	5.5	1.1	4.5	0.6	3.7	0.8	1.9	0.3	2	0.3	152.55	32.3	184.85
MS-3b	22.1	26.7	41.9	88.94	9.7	39.2	8.7	1.9	7.9	0.9	5.3	0.9	2.8	0.5	2.8	0.4	212.44	48.2	260.64
SR-4a	5	12.3	52	95.99	10	33	5.6	0.8	4.4	0.5	2.8	0.5	1.2	0.2	0.9	0.1	202.39	22.9	225.29
SR-4b	5.7	16.8	49.8	103.7	9.8	36.1	5.5	0.9	5.2	0.7	4	0.6	1.6	0.3	1.8	0.2	211.49	31.2	242.69
SG-5a	4.7	20.2	26.5	50.02	6.2	24.3	4.6	1	3.8	0.5	3.3	0.6	1.7	0.3	1.6	0.2	117.32	32.2	149.52
SG-5b	3.1	13.4	19.5	37.04	4.4	17.9	3.5	0.7	3.4	0.3	2.4	0.4	1.2	0.2	1	0.2	86.14	22.5	108.64
JB-6a	7.3	20.9	196.8	390.3	45	147	24.5	1.5	13.3	1.6	6.3	0.7	2	0.2	1.4	0.1	811.9	46.5	858.4
JB-6b	8.9	23.9	238.5	487.6	56.4	185	31.1	1.6	16.6	1.7	7.5	0.7	2.1	0.3	1.3	0.2	1008.99	54.3	1063.29
KL-7a	5.6	29.9	324.8	656.8	73.6	250	34.2	1.3	16.2	1.8	7.9	1	2.5	0.3	2.4	0.3	1346.2	62.3	1408.5
KL-7b	11.1	27	231	477.9	53.5	180	26.1	1.4	12.9	1.6	7.3	0.9	2.7	0.3	2	0.3	981.36	55	1036.36
LM-8a	2.3	9.8	63.1	121.1	14.6	50.8	8.5	0.9	5.1	0.4	2.2	0.3	1.1	0.1	1	0.1	261.34	20.1	281.44
LM-8b	4.1	8.5	45.6	91.81	9.7	37	5.9	0.9	3.5	0.3	2.2	0.3	0.8	0.1	0.9	0.1	195.01	16.7	211.71
GR-9a	5.9	16.8	46	89.96	11.3	40.1	7.1	1.6	5.5	0.6	3.5	0.6	1.8	0.3	1.8	0.3	201.96	31.2	233.16
GR-9b	5.5	14.5	45.7	83.03	10	33.4	6.3	1.2	4.2	0.4	2.6	0.5	1.5	0.2	1.5	0.2	185.13	25.6	210.73
KJ-10a	7.6	21.8	69.7	140.5	16	59.3	10.7	1.6	7.3	0.8	5.2	0.8	2.3	0.3	1.9	0.3	305.35	40.7	346.05
KJ-10b	3.9	13.2	29.8	63.06	7.5	26.1	5.1	1	4.6	0.4	2.8	0.5	1.4	0.2	1.3	0.1	136.46	24.5	160.96
LD-11a	13.4	12	26.8	51.14	5.6	20.7	3.8	1.2	3.6	0.3	2.1	0.5	1.4	0.2	1	0.1	122.64	21.2	143.84
LD-11b	10.9	13.2	31.3	65.99	7.2	24.8	5.1	1.3	4.2	0.4	3.3	0.4	1.7	0.2	1.2	0.2	146.59	24.8	171.39
NK-12a	6.1	24.6	89.6	180.8	19.9	70.7	13.4	0.8	9.9	1.2	6	0.9	2.6	0.3	2.2	0.4	381.26	48.1	429.36
NK-12b	6.9	9.6	23.1	52.12	5.5	18.8	2.9	0.6	2.6	0.3	2.4	0.4	1	0.2	1.1	0.1	109.92	17.7	127.62

*et al.*, 2018). REEs are moved when mobilised in the environment through water and air. REEs is contacted through food, water, medicine and gasp from the air. REEs can cause fibrosis, and severe damage and dysfunctional neurological disorder in humans (Gwenzi *et al.*, 2018).

Comparison of rare earth elements in dusts from other countries with the values of REEs in dust collected from outside the quarries in parts of southwestern Nigeria. This revealed that there are significant differences in them, with the values of the dust derived from outside the quarry sites being slightly higher than

others (Table 9 and 10). This is an implication of the effects these dusts can have on the soils where they are used for agricultural purposes. However, REE concentrations in plants vary according to the contents of these elements in the environment and among different plant species (Guo, 2007; Ramos *et al.*, 2016). Due to their higher mobility in soils, LREE are more easily absorbed by plants; thus, occurring at greater contents than HREE in plant tissues while some plants have been being described as REE bio-accumulators, accumulating especially, the LREE (Turra *et al.*, 2013). Arsenic and Lead have high concentration that humans can be

exposed to by inhalation of the contaminated dust and ingestion through water and plants. Contamination can still occur through dermal contact with the contaminated dust which can also be a threat to human health. Breathing high levels of arsenic can give sore throat or irritated

lungs. Ingesting and exposure of very high and low levels of arsenic may result to death. Exposure to lower levels can cause nausea and vomiting; decreased production of red and white blood cells (Agency for Toxic Substances and Disease Registry-ATSDR, 2007).

Table 10: Comparison of REE concentration in dusts of some countries (adapted from Salminen *et al.*, 2005)

Country	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb
Croatia	27-52(43)	55-128(91)	6.5-12(10)	24-45(39)	5.0-8.9(7.6)	1.01.8(1.5)	4.8-8.5(7.2)	0.7-1.3(1.1)
Denmark	2.6-12 (6.6)	5-23(13)	0.5-2.7(1.5)	2.0-10(5.5)	0.4-8.1(1.0)	0.1-0.4(0.2)	0.5-1.9(1.1)	0.1-0.3(0.2)
Spain	5.3-128(33)	11-246(63)	1.3-32(7.7)	4.6-132(28)	0.9-23(5.9)	0.2-7.0(1.1)	0.9-24(5.4)	0.1-3.7(0.8)
Estonia	5.5-3.7(26)	9.6-71(50)	1.2-9.7(6.1)	3.5-3.8(23)	0.9-8.4(4.5)	0.2-1.6(0.9)	0.7-9.3(4.6)	0.1-1.3(0.6)
Finland	4.8-45 (15)	8.5-90(28)	1.0-10(3.3)	3.4-41(13)	0.6-6.8(2.3)	0.3-1.3(0.6)	0.6-6.4(2.3)	0.07-0.9(0.3)
France	2.6-66 (31)	5.5-159(63)	4.4(7.3)	2.1-54(27)	0.4-11(5.1)	0.1-2.2(1.0)	0.4-11(5.0)	0.05-1.5(0.7)
Greece	13-64 (29)	23-102(57)	2.9-14(6.8)	11-53(26)	2.1-10(5.1)	0.5-2.4(1.1)	2.2-11(5.2)	0.4-1.6(0.7)
Netherlands	5.6-22(13)	12-43(27)	1.3-5.1(3.1)	4.7-19(12)	0.8-3.7(2.2)	0.2-0.8(0.5)	0.9-3.8(2.3)	0.1-0.5(0.3)
Hungary	7.5-4.2 (27)	15-87(55)	1.7-10(6.4)	6.4-37(24)	1.2-7.5(4.6)	0.3-1.4(0.9)	1.2-7.2(4.8)	0.2-1.1(0.7)
Ireland	12-36 (20)	23-78(39)	2.5-9.1(4.6)	9.0-35(17)	1.4-6.6(3.3)	0.2-1.3(0.7)	1.4-6.4(3.2)	0.23-1.0(0.5)
Italy	6.9-143(40)	14-267(78)	1.3-29(8.8)	5.4-94(32)	1.0-16(5.9)	0.2-3.2(1.2)	0.9-13(5.6)	0.2-1.7(0.8)
Latvia	11-31(21)	21-67(44)	2.3-8.1(4.9)	5.5-28(18)	1.2-5.5(3.3)	0.3-1.1(0.6)	1.8-5.4(3.2)	0.2-0.9(0.4)
Norway	2.9-101(21)	5.7-253(48)	0.7-23(5.2)	2.8-80(20)	0.5-13(3.7)	0.1-4.3(0.9)	0.6-11(3.7)	0.1-1.7(0.5)
Portugal	19-74(38)	38-151(77)	4.7-18(9.0)	16-63(32)	2.9-10(5.8)	0.4-2.0(0.9)	2.8-9.3(5.2)	0.4-1.4(0.7)
UK	1.1-103(23)	2.5-206(48)	0.3-30(5.6)	1.1-112(21)	0.2-30(4.0)	1.7(0.8)	0.2-36(4.1)	0.03-7.0(0.6)
Switzerland	1.7-8.5(27)	3.2-117(50)	0.4-16(6.0)	1.5-65(23)	0.3-13(4.4)	0.1-2.9(0.9)	0.2-15(4.5)	0.04-2.1(0.6)
Nigeria	19.324.8(77.9)	657(156.9)	73.6(17.6)	250(61.3)	34.2(10.2)	1.9(1.18)	16.6(6.58)	0.3-1.8(0.72)
		<b>Dy</b>	<b>Ho</b>	<b>Er</b>	<b>Tm</b>	<b>Yb</b>	<b>Lu</b>	<b>Sc</b>
Croatia		3.8-7.0 (6.0)	0.8-1.4 (1.2)	2.3-4.2 (3.6)	0.3-0.6 (0.5)	2.1-4.0 (3.5)	0.3-0.6 (0.5)	7.7-1.6 (13)
Denmark		0.5-2.2 (1.1)	0.1-0.4 (0.2)	0.3-1.3 (0.7)	0.05-0.2 (0.1)	0.4-1.5 (0.9)	0.05-0.2 (0.1)	0.9-3.9 (2.2)
Spain			0.1-4.8 (0.9)		0.04-2.1 (0.3)		0.03-2.0 (0.3)	
Estonia		0.7-7.2 (4.0)	0.2-1.3 (0.8)	0.5-3.8 (2.2)	0.07-0.5 (0.3)	0.6-3.2 (2.1)	0.1-0.5 (0.3)	1.3-10 (64)
Finland		0.5-4.8 (2.0)	0.1-1.1 (0.4)	0.3-3.2 (1.2)	0.05-0.5 (0.1)	0.4-3.4 (1.2)	0.04-0.5 (0.1)	2.0-21 (8.1)

	0.3-8.6 (4.2)	0.04-1.8 (0.8)		0.02-0.71 (0.3)	0.2-4.5 (2.3)	0.01-0.7 (0.3)	
France			0.2-5.0 (2.4)				0.3-29 (9.3)
	2.1-9.2 (4.5)	0.4-1.9 (0.9)		0.2-0.7 (0.3)	0.8-5.0 (2.4)	0.1-0.7 (0.3)	
Greece			1.2-5.3 (2.5)				4.4-23 (14)
	0.6-3.0 (1.9)	0.1-0.6 (0.4)		0.09-0.3 (0.2)	0.3-1.9 (1.1)	0.08-0.3 (0.1)	
Netherlands			0.4-1.8 (1.1)				0.9-9.5 (4.3)
	1.1-5.8 (3.9)	0.2-1.2 (0.8)		0.1-0.5 (0.3)	0.8-3.4 (2.3)	0.1-0.5 (0.3)	
Hungary			0.8-3.7 (2.4)				2.9-17 (9.0)
	1.3-5.8 (3.1)	0.3-1.2 (0.6)		0.1-0.5 (0.2)	0.9-3.0 (1.7)	0.2-0.4 (0.3)	
Ireland			0.8-3.1 (1.8)				3.2-12 (6.5)
	0.9-8.9 (4.5)	0.2-1.7 (0.9)		0.1-0.7 (0.3)	0.7-4.1 (2.3)	0.1_0.6 (0.3)	
Italy			0.6-4.9 (2.5)				5.5-21 (11)
	1.4-5.1 (2.9)	0.3-1.0 (0.6)		0.1-0.4 (0.3)	0.9-2.9 (1.8)	0.2-0.4 (0.3)	
Latvia			0.9-2.7 (1.6)				1.8-11 (5.8)
	1.1-4.6 (2.6)	0.2-0.8 (0.5)		0.1-0.4 (0.2)	0.8-2.6 (1.6)	0.1-0.3 (0.2)	
Lithuania			0.8-2.2 (1.5)				1.8-7.6 (4.3)
	0.8-9.0 (3.4)	0.9-1.8 (0.7)		0.09-0.8 (0.3)	0.6-5.8 (2.2)	0.1-0.8 (0.3)	
Norway			0.6-5.0 (2.1)				2.5-33 (11)
	1.8-7.1 (3.7)	0.3-1.3 (0.7)		0.1-6.0 (0.3)	0.7-3.5 (1.9)	0.1-0.5 (0.2)	
Portugal			0.9-3.6 (2.0)				1.9-20 (8.7)
	0.2-4.5 (3.8)	0.03-9.2 (0.8)		0.01-4.0 (0.3)	0.09-2.5 (2.3)	0.02-3.2 (0.3)	
UK			0.1-2.6 (2.3)				0.7-23 (9.4)
	0.2-1.3 (3.8)	0.1-2.7 (0.8)		0.02-1.1 (0.3)	0.1-7.1 (2.0)	0.02-1.0 (0.3)	
Switzerland			0.1-7.9 (2.2)				0.7-15 (8.8)
	2.10- 7.9(3.95)	0.3- 1.0(0.59)	0.8- 2.80(1.69)	0.1- 0.5(0.23)	0.9- 2.8(1.48)	0.10- 0.40(0.2)	8.5- 29.9(16.8)

Exposure to even low levels of lead could cause damage over time, especially in children. The greatest risk is in brain development, where irreversible damage occurs. Higher levels can damage the kidney and nervous system in both children and adults. Very high lead levels may cause seizures, unconsciousness and death. Inhalation and ingestion from contaminated dust, water and food can be linked to the above health challenges in the brain, liver, kidney and bones. It is also stored in the teeth and bones, where it accumulates over time. Lead is highly toxic to humans and their environments. It is hazardous to humans, especially young children and pregnant women because there is no safe limit for this metal. Once ingested into the body system, this metal can cause permanent damage to the neurological and cardiovascular systems because the main exposure and absorption route are inhalation, ingestion and

dermal contact (ATSDR, 2007). Uptake of Pb by plants occurs through soil fixation and in water bodies. Toxicity of Pb disturbs various plants physiological process; while unlike other metals, which possess no biological functions (Sharma & Dubey, 2005).

### Conclusion

Lead (Pb) and arsenic (As) concentration increase in the outside quarry dusts indicate anthropogenic input and contamination of these metals. The introduction of these Potentially Harmful Elements (PHEs) might contain little to high toxic effect at Sixsix-Imosan, Labstar-Ajebo and Multiverse-Kajola which may arise from human activities outside the quarry. In general, these potentially harmful elements (Pb and As) have been observed to be above the average crustal abundance (ACA) baseline

concentration values. The dust generated from these quarries have anthropogenic inputs of Cu, Pb, Zn, As and Cd in two to three folds. Based on the toxicity of these elements adequate care should be employed during quarrying operations since these metals are potentially harmful and can be hazardous to humans and animals that are exposed to them. Therefore, quarry workers good health should be guided and different toxins generated in and around the quarry must be kept in abeyance with use of various personal protective equipment. The Chemical Weathering Indices (CIA and CIW) revealed that the rock aggregate in quarry dusts were of greater feldspar and muscovite contents than the limestone quarry dusts.

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