



ELEMENTAL CHARACTERISATION OF GEOLOGICAL AND BIOLOGICAL SAMPLES USING PARTICLE INDUCED X-RAY EMISSION

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Abstract

The particle-induced X-ray emission (PIXE) method has been employed to tackle several analytical challenges with a MeV accelerator. Some preliminary experimental results are included in the study, along with several topics that might be further investigated. Proton-induced X-ray emission (PIXE) was applied to characterize the elemental composition of edible vegetable seeds and leafy-vegetable seeds samples collected from Vizianagaram district, Andhra Pradesh, India. Across the investigated samples, the manuscript reports 22 elements: Si, P, S, Cl, K, Ca, Ti, V, Mn, Fe, Co, Ni, Zn, Ce, Cu, As, Zr, Hg, Pb, Ga, Sr and Se. The data also indicate the presence of nutritionally relevant elements such as K, Ca, Fe, Zn, Mn, Cu and Se together with potentially toxic elements including As, Hg and Pb. These findings demonstrate the utility of PIXE for rapid multi-element screening of plant-derived foods and provide baseline information for environmental and food-quality monitoring in the study region. PIXE was employed to study the Rock and lead-zinc ore samples gathered from many mines in Zawar, Udaipur District, Rajasthan, India. Sixteen elements including Co, Ni, Cu, Zn, Ga, As, Fe, Mn and Pb were established in these ore and rocks, which may be useful to interpret the various geochemical conditions and the probable cause of their inceptions in rock matrix. It was found that Ti, Mn and Ni are present in substantial amount with respect to other trace elements. It is interesting to observe that the concentration of nickel indicates the origin of these Pb-Zn ore & rocks in Proterozoic period.

Keywords: Particle-Induced X-ray Emission (PIXE), Elemental Analysis, Multi-Elemental Characterization, Trace Elements, Edible Vegetable Seeds, Leafy-Vegetable Seeds, Lead-Zinc Ores, Geochemical Analysis, Heavy Metal Contamination, Nutritional Elements, Food Quality Monitoring, Zawar Mines, Andhra Pradesh, Rajasthan.

1. Introduction

Several analytical methods that are used to analyze different materials and determine the main, minor, and trace elemental concentrations are briefly described. From ordinary samples to sophisticated materials, a variety of analytical methods are available for material characterization and determination of elemental composition. XRF, EMPA, INAA, AAS, ICP-MS, and PIXE are popular techniques among them. The samples cannot be utilized for additional research because some of these techniques are destructive. Certain methods provide information on only one component or require sample preparation prior to analysis. PIXE, on the other hand, offers unique characteristics such as being fast and non-destructive, enabling multi-elemental determination, and requiring little to no sample preparation.

Using distinctive X-rays formed by a few-MeV proton beam aimed at the specimen's surface, PIXE is a novel technique for doing non-destructive examination. Various sectors, including biological, environmental, archeometrical, ecological, geological, nanotechnology, archeological, and biomedical, have effectively utilized this approach for analysis[1-19]. One of the most promising multi-elemental analytical techniques that has been developed recently is PIXE. There are several instances that demonstrate the PIXE method's suitability for geological applications [20].

Trace elements in a sample can be found and measured using PIXE, a comparatively straightforward yet effective analytical method. It is a nuclear analytical method with ppm sensitivity for quick measurement of various trace elements. It is used in geology and geophysics to study mineral trace elements in geological specimens due to its high sensitivity. Even when atomic numbers are smaller, utilizing protons offers great sensitivity since proton bremsstrahlung is less than electron excitation. Due to the growing demand for elemental analysis of extremely tiny sample quantities, such as in geological materials like gemstones and precious minerals, the PIXE approach has quickly acquired recognition as a useful analytical tool.

By detecting distinctive X-rays produced by a millimeter-thick proton beam (MeV energy scale) focused onto a specimen's surface, proton-induced X-ray emission (PIXE) is a novel method for doing non-destructive analysis [1]. For almost thirty years, this method has been effectively used to the analysis of a variety of materials, including environmental [2], biological [3], archaeological [4], and geological [5]. The well-known characteristics of the PIXE technique—such as its multi-elemental capabilities, low sample mass need, dynamic range, high sensitivity, and easy sample handling or almost no sample preparation—make it a preferred approach for sample analysis. The vacuum PIXE technique is destructive when working with certain archaeological (manuscripts, etc.) [22], geological (large rocks, etc.) [23], and biological (fish, teeth, etc. [24]) materials because it requires either a sub-sample or a part for compatibility, which destroys the original material at the stage of sample preparation. Environmental samples mostly contain micron- to submicron-sized percentages of anthropogenic elements such as sulphur, potassium, lead, and bromine. They frequently form a thin coating on larger natural particles, such as silicates, carbonates, and sea spray. In addition to making sample handling and placement in the air simple, this method offers a number of other benefits. Large items with intricate structures and shapes may be analyzed in-situ without the requirement for sample; this is especially useful for art pieces. Additionally, materials with volatile chemicals that would not normally tolerate a vacuum can be studied. Effective cooling from the air or helium flow significantly lowers the danger of heating-related damage. Nevertheless, there is no requirement for a thin conducting layer that is necessary while working under vacuum since charging of insulating materials is entirely prevented. In fact, potentials of many tens of keV can be produced via charging processes, which accelerates secondary electrons and expands the bremsstrahlung background to higher energies. The detection limit would therefore be significantly increased [6]. At the Institute of Physics (IOP), Bhubaneswar, the Ion Beam Laboratory was employed the PIXE method of ion beam analysis for the first time in 1992. Since then, IOP has conducted and occasionally reported PIXE analyzes of a variety of environmental, geological [7], and biological [8] materials, such as plant soil, iron pond ash, and water, fly ash, blood, hair, kidney stone, chromium ores, human and animal tissue, gallstone, etc. Samples are held in a vacuum and exposed to radiation using the PIXE process, which uses a 3 MV Tandem Pelletron accelerator. The

recent creation of the PIXE setup at the Institute of Physics and some preliminary experiments conducted are described in this paper.

2. Experimental facility

A graphite collimator was used to collimate the 3 MeV proton beam from the 3 MV tandem-type Pelletron accelerator into a beam with a diameter of 3 mm. At the chamber's exit, Kapton foil (8 microns thick) was used to remove the beam. KaptonTM foil is used as an exit window due to its unique properties, including radiation-damage resistance, little energy loss, and low beam-induced background emission. As seen in Fig. 1, a 2.4 MeV proton beam was utilized to irradiate the targets and the external PIXE setup while the beam was permitted to traverse roughly 3 cm in the air. The targets were maintained in the air at a 450-degree angle to beam direction over a sample stand (capacity: 5 kg). A maximum beam current of 20 nA was used to irradiate the samples, and it left via an 8 μ m thick KaptonTM window that was made to resist air pressure. A Si (Li) detector (active area 30 mm²) of CANBERRA with a full-width at half maximum (FWHM) of 165 eV at 5.9 keV was used to detect the targets' characteristic X-rays (active area 30 mm², beryllium window thickness 8 μ m, located at 900 with respect to the beam direction). A 25-meter-thick aluminized Mylar absorber with a 6% hole was placed in front of the detector to lower the bremsstrahlung background and the main low-energy X-ray peaks. A CANBERRA S-100 multichannel analyzer calibrated with a ²⁴¹Am X-ray source was used to record spectra.

3. Applications and performance of the PIXE configuration:

Numerous disciplines, including geology, environmental science, biomedicine, biology, and nanotechnology [24], have effectively employed the PIXE approach for analysis. However, we only cover a few uses of this method in geology, biology, and environmental science [25, 26 & 27] in this study.

3.1 Environment

The PIXE method is being used in many laboratories nowadays for environmental research. This method was used at the laboratory of the IOP, Bhubaneswar, to characterize fly ash, an important environmental substance mainly because of its potential for usage by plants and animals. Along with significant concentrations of hazardous elements like Hg, Pb, V, As, Ni, Cr, and Ba, fly ash [26] is linked to a number of beneficial components, including Mg, Cu, Ba, S, Zn, Mn, Ca, Fe, and P. The parent coal's composition, the circumstances of combustion, and the effectiveness of emission control systems all affect the trace element content in ash, which varies greatly. A fly ash spectrum obtained using the external PIXE setup is shown in Figure 1. According to the study, fly ash may be successfully characterized using the PIXE approach with an external proton beam and a good sample turnover time. Another often researched environmental item that may be examined using the vacuum PIXE method is aerosols. However, this method results in the loss of volatile metals like mercury. The beam current used for aerosol samples in traditional PIXE is often lower, but it can be boosted by about 4 $\times$ in external PIXE, posing another practical challenge.

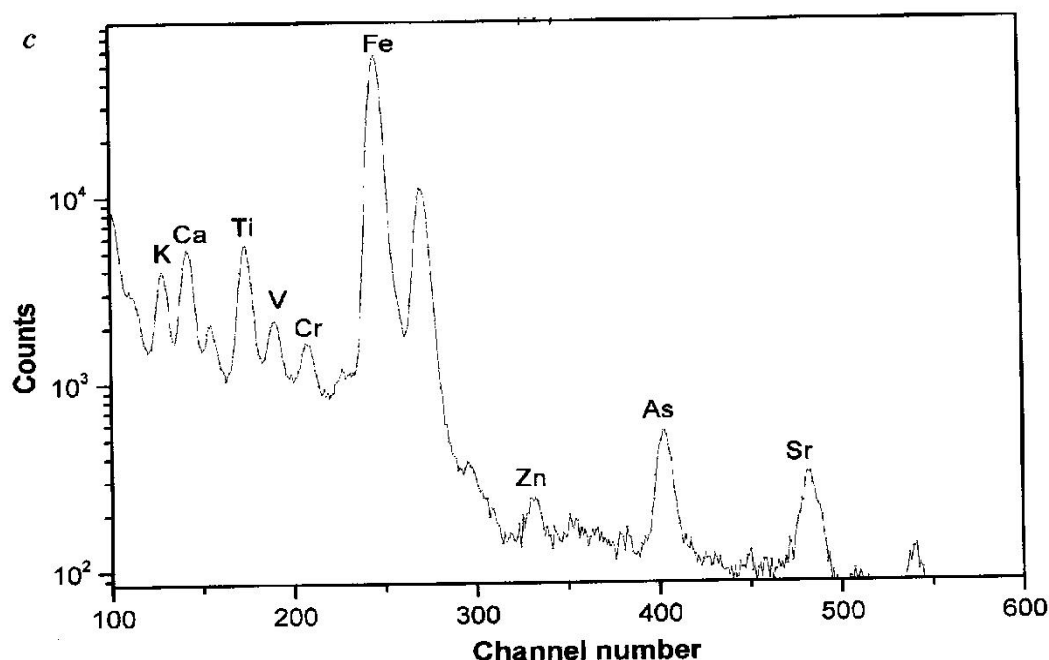


Figure 1. Fly ash as an environmental sample with an external PIXE spectrum.

3.2 Geology

Many researchers have employed PIXE extensively in geochemical exploration, including the groundbreaking work on a variety of minerals, including diamond, by the CSIRO (Australia) and Schonland research (South Africa) groups. However, the traditional PIXE method needs longer time for sample turnover since several samples must be irradiated in order to obtain better statistics. Characterizing particular areas in a geological material and then identifying them using ore microscopy is another important factor that should not be disregarded. In order to evaluate the depositional basin environment, Vijayan and his team have reported employing PIXE and other X-ray methods on geological rocks to estimate trace elements ratios [7, 11 and 27]. It is believed that the external PIXE approach might effectively solve the issue of analyzing big samples. An external PIXE spectrum of soapstone produced without sample pretreatment using the current setup at IOP, Bhubaneswar, is shown in Figure 2. Fe is found to be the most abundant element in this sample, among others. After analyzing various spots and inclusions found in geological materials using the external PIXE setup [10, 12], we want to apply cross-sectional cutting to look at the distribution of trace elements.

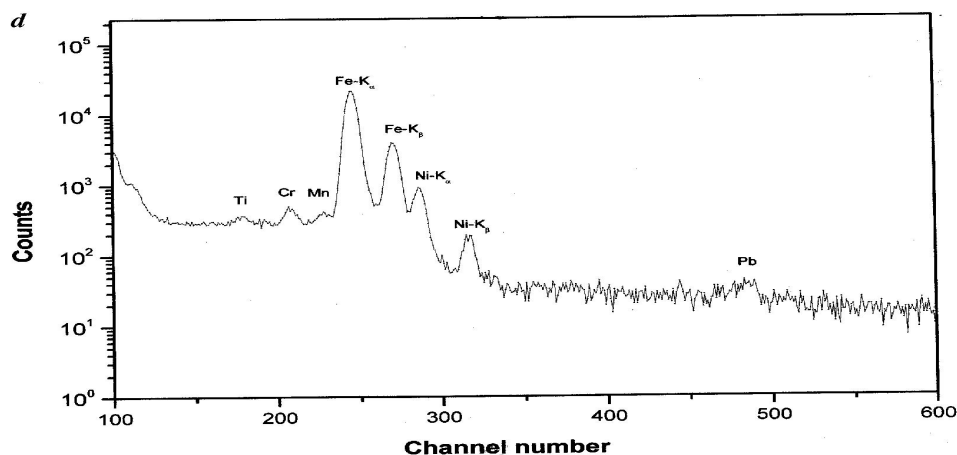


Figure 2. Soapstone's spectrum was examined with External PIXE.

Rock and lead-zinc ore samples have been gathered from many mines in Zawar, Udaipur District, Rajasthan, India. Zawar (24°21' N; 73°43' E) is situated around 38 kilometers south of Udaipur city in the Aravalli highlands of Rajasthan on the bank of the Tiri River. It is the only known historic zinc smelting site in India. Our team has used complementary and non-destructive PIXE (Proton-Induced X-ray Emission) methods to study these lead-zinc ores and rocks. The distinctive X-rays released were used to quantify the samples elemental concentrations. Tables 1 and 2 provide the estimated concentrations of minor, main, and trace elements in parts per million.

To determine the elemental contents, a total of seventeen samples twelve Pb-Zn ore samples and five rock samples were subjected to proton beam. These Pb-Zn ore and rock specimens included sixteen elements, which are listed in Tables 1 and 2 along with allowable errors. The LZR-5 rock sample has the highest concentrations of elements Ti, Cu, Pb, K, and Rb among all the samples that were collected, whereas the same rock sample also has the lowest amounts of Fe, Ge, As, Zn, Mn, and Sr. The tables below provide the experimental errors for each measured concentration along with the concentrations. The two primary sources of error in PIXE results are the number of counts and the least-squares fitting of the peak regions, which accounts for the background subtraction uncertainty. The results are consistent within permissible errors, as

Tables 1 and 2 demonstrate. TABLE-1.A: The element concentrations of Lead – Zinc ore samples by PIXE analysis.

S.No	Sample	K	Ti	Mn	Fe	Zn	Ga	Ge	As
1	LZO-1	345.9 ± 1.72	74 ± 0.59	1068.9 ± 6.94	1745 ± 8.72	38957 ± 155.82	287.4 ± 2.29	247.1 ± 1.97	218 ± 1.63
2	LZO-2	1581.6 ± 7.90	288 ± 2.30	115 ± 0.74	2767.9 ± 13.83	2792.2 ± 11.16	---	4149.9 ± 33.19	65.3 ± 0.48
3	LZO-3	1783 ± 8.91	108.9 ± 0.87	2045.9 ± 13.29	12695.5 ± 63.47	73122.3 ± 292.48	297.1 ± 2.37	112.3 ± 0.89	73 ± 0.54
4	LZO-4	894.9 ± 4.47	92.5 ± 0.74	2420.8 ± 15.73	26745 ± 133.72	15908.4 ± 63.63	1171 ± 9.36	364 ± 2.91	177 ± 1.32
5	LZO-5	1071 ± 5.35	168.9 ± 1.35	137.7 ± 0.89	11091.9 ± 55.45	437014.8 ± 1748.05	1783 ± 14.26	1018 ± 8.14	761 ± 5.70
6	LZO-6	1356.4 ± 6.78	56.1 ± 0.44	225.5 ± 1.46	21718.6 ± 108.59	370959.4 ± 1483.83	1592 ± 12.73	618.5 ± 4.94	863.1 ± 6.47
7	LZO-7	1055 ± 5.27	74.1 ± 0.59	1924 ± 12.50	47830 ± 239.15	534670.4 ± 2138.68	1942 ± 15.53	718 ± 5.74	776 ± 5.82
8	LZO-8	1167.3 ± 5.83	12.4 ± 0.09	550.1 ± 3.57	29508.7 ± 147.54	20184.9 ± 80.73	155.5 ± 1.24	516 ± 4.12	493.5 ± 3.70
9	LZO-9	1713 ± 8.56	274.4 ± 2.19	796.5 ± 5.17	15346.2 ± 76.73	175079.8 ± 700.31	1068.9 ± 8.55	531.6 ± 4.25	2383.3 ± 17.87
10	LZO-10	3883.2 ± 19.41	---	3040 ± 19.76	19862.6 ± 99.31	310.4 ± 1.24	18 ± 0.14	6.5 ± 0.05	39 ± 0.29
11	LZO-11	1068.9 ± 5.34	129.4 ± 1.03	46.7 ± 0.30	8640 ± 43.2	199765.6 ± 799.06	1448.1 ± 11.58	893.2 ± 7.14	3218.1 ± 24.13
12	LZO-12	870.8 ± 4.35	271.7 ± 2.17	800.9 ± 5.20	22857 ± 114.28	284146.9 ± 1136.58	837.1 ± 6.69	509 ± 4.07	817 ± 6.12

TABLE-1.B: The element concentrations of Lead – Zinc ore samples by PIXE analysis.

S.No	Sample	Pb	Ba	Co	Ni	Cu	Sr	Rb	Zr
1	LZO-1	30872.8 ± 185.23	199.1 ± 0.79	28 ± 0.14	893.2 ± 2.67	209.9 ± 0.41	72 ± 0.53	115 ± 1	38.2 ± 0.18
2	LZO-2	3697.2 ± 22.18	42.6 ± 0.17	38.9 ± 0.19	14.4 ± 0.04	101.6 ± 0.20	27 ± 0.19	172 ± 1.49	42.1 ± 0.20
3	LZO-3	1372.5 ± 8.23	619.9 ± 2.47	25.5 ± 0.12	20.1 ± 0.06	125.3 ± 0.25	65 ± 0.48	24.5 ± 0.21	21.1 ± 0.10
4	LZO-4	634.1 ± 3.80	18.8 ± 0.07	120.2 ± 0.60	203.2 ± 0.60	154.2 ± 0.30	172 ± 1.27	102 ± 0.88	98.3 ± 0.47
5	LZO-5	31403 ± 188.41	209.7 ± 0.83	65.6 ± 0.32	58.9 ± 0.17	75.4 ± 0.15	9.2 ± 0.06	115 ± 1	128.4 ± 0.61
6	LZO-6	2199 ± 13.19	630 ± 2.52	75.9 ± 0.37	131.3 ± 0.39	15.5 ± 0.03	78.6 ± 0.58	55.8 ± 0.48	632.7 ± 3.03
7	LZO-7	4317 ± 25.90	78.9 ± 0.31	192.7 ± 0.96	204.9 ± 0.61	893.2 ± 1.78	217 ± 1.60	19.5 ± 0.16	347 ± 1.66
8	LZO-8	23933.6 ± 143.60	14.4 ± 0.05	65.3 ± 0.32	133.7 ± 0.40	115.6 ± 0.23	15.7 ± 0.11	23 ± 0.20	160.9 ± 0.77
9	LZO-9	47579.7 ± 285.47	239.4 ± 0.95	28.1 ± 0.14	445.1 ± 1.33	---	378.9 ± 2.80	63.4 ± 0.55	138.9 ± 0.66
10	LZO-10	21068.9 ± 126.41	96 ± 0.38	63.8 ± 0.31	59.5 ± 0.17	41.8 ± 0.08	28.1 ± 0.20	38.3 ± 0.33	186.6 ± 0.89
11	LZO-11	113660.9 ± 681.96	511 ± 2.04	149.7 ± 0.74	60 ± 0.18	322735.6 ± 645.47	559 ± 4.13	115 ± 1	65.5 ± 0.31
12	LZO-12	1910.6 ± 11.46	91.4 ± 0.36	23.7 ± 0.11	15.9 ± 0.04	62.2 ± 0.12	49.3 ± 0.36	118 ± 1.02	74.4 ± 0.35

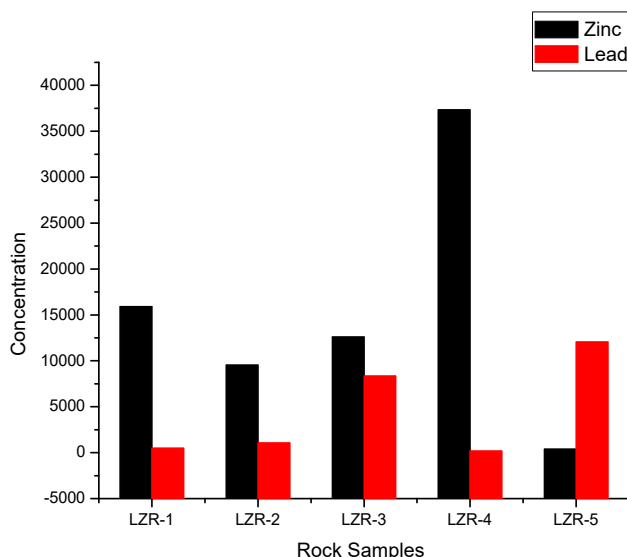
TABLE-2.A: PIXE study of the elemental concentrations in lead-zinc rock samples.

S.No	Sample	K	Ti	Mn	Fe	Zn	Ga	Ge	As
1	LZR-1	684 ± 4.02	146 ± 0.85	1397.1 ± 8.38	13767.1 ± 110.13	15934.5 ± 79.67	73.6 ± 0.29	120.3 ± 0.9	86.6 ± 0.64
2	LZR-2	758 ± 4.46	108.9 ± 1.8	1985 ± 11.91	17581 ± 140.64	9548 ± 47.74	59.1 ± 0.23	45.5 ± 0.34	178.9 ± 1.34
3	LZR-3	1303 ± 7.67	35.1 ± 0.20	516 ± 3.096	48515.9 ± 388.12	12613.6 ± 63.06	121.8 ± 0.48	112.5 ± 0.84	402.5 ± 3.01
4	LZR-4	549.8 ± 3.23	6.1 ± 0.03	420.5 ± 2.52	31859.6 ± 254.87	373369 ± 1866.84	1284 ± 5.13	593 ± 4.4	310 ± 2.32
5	LZR-5	1448.1 ± 8.52	1559.8 ± 9.18	196.4 ± 1.17	7361.9 ± 58.89	392 ± 1.96	23.8 ± 0.09	14.4 ± 0.10	34.1 ± 0.25

TABLE-2.B: PIXE study of the elemental concentrations in lead-zinc rock samples.

S.No	Sample	Pb	Ba	Co	Ni	Cu	Sr	Rb	Zr
1	LZR-1	491.4 ± 2.5	23.7 ± 0.15	15.9 ± 0.12	62.2 ± 0.43	49.3 ± 0.32	115 ± .97	74.4 ± .68	22.5 ± 0.18
2	LZR-2	1068.9 ± 1.1	28.1 ± 0.14	222.2 ± 1.65	483.3 ± 3.85	133.9 ± 1.29	146 ± 1.23	172 ± 1.35	253.7 ± 2.11
3	LZR-3	8356.5 ± 74.45	432.7 ± 2.35	140 ± 1.28	403 ± 3.89	93 ± .67	88.8 ± .65	37.5 ± 0.19	475.6 ± 4.3
4	LZR-4	1738 ± 1.32	893.2 ± 7.65	141.9 ± 1.34	65.9 ± .46	14.4 ± 0.11	161 ± 1.31	58 ± 0.37	210.4 ± 1.97
5	LZR-5	12068.9 ± 112.52	75.9 ± .68	131.31 ± 1.12	15.5 ± .12	654.2 ± 5.69	55.8 ± .48	172 ± 1.57	148.4 ± 1.23

In the literature, it is reported that the average values of nickel (Ni) in igneous rocks of the Proterozoic period are above 200 ppm [29-30]. It is found that the concentration of nickel (Ni) in our six Pb-Zn ore and rock samples shows the higher values than the previous researcher literature values for the rocks of igneous origin. It indicates that our samples are of igneous origin belonging to the Proterozoic period. We would further like to bring the attention of the readers towards the fact that a significant number of geologists consider that Pb-Zn ore deposits as the product of magmatic differentiation of basalt melts [29] which are segregated at the beginning of the process, due to fractional crystallization of dry magmas or at the end of the process segregated from residual melt enriched with volatiles that reduces the crystallization temperature of Pb-Zn ore deposits. Hence, in order to understand the probability of this differentiation process that may lead to association of various trace metals with major elements, a series of elemental correlation has been attempted from the results of the concentrations of various elements and only the outstanding and the extra ordinary correlations have been plotted and considered for further understanding and discussion.

**Fig.3. The concentrations of Pb & Zn elements in rock samples**

The comparison of concentrations of lead and zinc elements in rock samples is as shown in figure 3. From the figure it is clear that the element zinc has more concentration in all rock samples except LZR-5. The variation of element Zn is very large and random. In comparison with Zn, Lead has small variations in concentrations. The maximum concentration of lead is occurred in LZR-5 and second higher concentration is observed in LZR-3. In remaining samples, in which lead occurs, it ranges from 491.4 ppm to 12068.9 ppm.

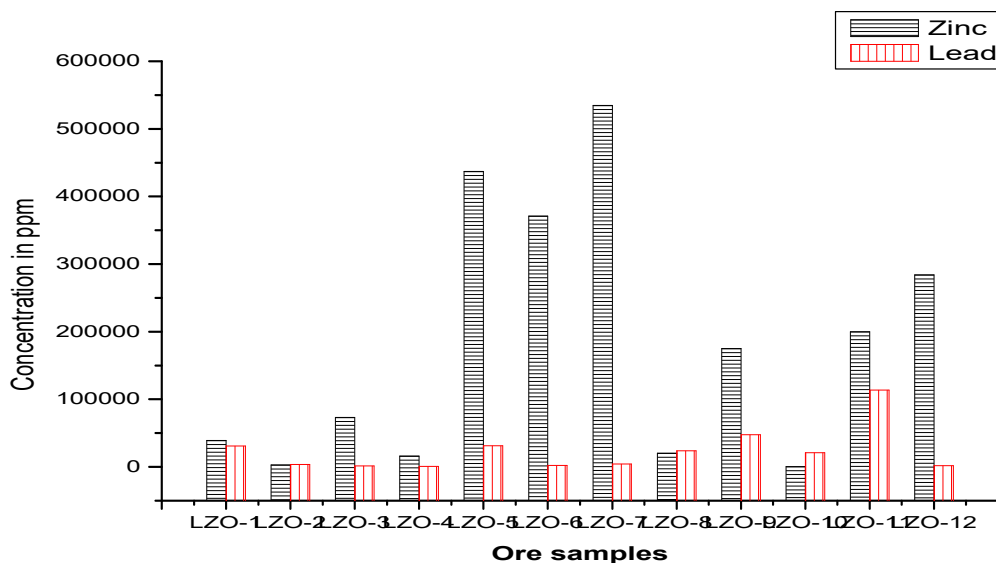


Fig.4: The mean concentration of the elements lead & zinc in all Pb-Zn ore samples.

The concentrations of the elements lead & zinc in all the ore samples are plotted and their variation from sample to sample is clearly visible in figure 4. The concentration of the element zinc is more when compared to lead in all ore samples. Furthermore, the concentration of zinc is very high in the sample LZO-7 and is low in the sample LZO-10. The element zinc varies from 310.4 ppm to 534670.4 ppm in all the remaining ore samples. Comparatively the concentration of element lead is low in all the ore samples; its concentration is maximum in the sample LZO-11 and is minimum in the sample LZO-4.

3.3 Biology.

The PIXE technique is employed to determine a total of 22 elements in this study, including major elements Si, Ca, S, Cl, Ti, Fe, V, Co, Ni, Mn, P, K, Zn & Ce a total of 14, minor elements Cu, As, Zr, Hg and Pb a total of 5 and finally trace elements Ga, Sr and Se a total of 3 in various vegetable seeds and leafy-vegetable seed samples. The vegetable seed and leafy vegetable seed samples were collected from Vizianagaram district, Andhra Pradesh, India. Mainly considered vegetable seeds, namely Mullangi, Makkajonna single cross, double cross, Beans, cluster beans (Goruchikkudu), Carrot, Tella vanga, bendakaya & bheerakaya, and also leafy-vegetable seeds of Bacchali, Pudeena, Karivepaku, Munagaku. Palakura, Tella gongura, thotakura, menthikura and chukkakura. The elements concentrations of the different vegetable seeds and leaf-vegetable seed samples were measured and are displayed in Tables 3 and 4, respectively, to compare their elemental distribution.

Table 3.A: Elements concentrations present in the samples in PPM of vegetable seeds.

Elem.	Si	P	S	Cl	K	Ca	Ti	V	Mn	Fe	Co
BV1	21.21 ± 0.10	9571 ±57.42	840.81 ± 4.20	12675 ± 76.05	787.86 ± 3.93	2309.12 ± 11.54	1.33 ± 0.002	0.01 ± 0.00	19.87 ± 0.07	37.31 ± 0.18	0.10 ±0.001
BV3	347.84 ± 1.73	4771.9 ±28.63	896.75 ± 4.48	23672 ±142.03	1532.76 ± 7.66	120.98 ± 0.60	1.2 ± 0.002	0.07 ±0.001	8.89 ± 0.03	31.00 ± 0.14	0.10 ± 0.000
BV4	397.12 ± 1.98	2279.1 ±13.67	788.57 ± 3.94	1818.26 ± 10.90	2697.96 ± 13.48	102.56 ± 0.51	0.98 ± 0.001	0.04 ± 0.001	4.08 ± 0.02	47.15 ± 0.21	0.94 ± 0.001
BV5	53.26 ± 0.26	1931.9 ±11.59	1677.7 ± 8.38	577.53 ± 3.46	4954.84 ± 24.77	220.57 ± 1.10	0.97 ± 0.001	0.04 ± 0.001	23.48 ± 0.11	39.73 ± 0.23	0.97 ± 0.001
BV6	187.13 ± 0.93	940.39 ± 5.64	1687 ± 8.43	422.94 ± 2.53	11936.38 ± 59.68	3723.99 ± 18.61	1.63 ± 0.003	0.06 ± 0.001	18.29 ± 0.08	38.31 ± .22	0.49 ± 0.001
BV7	55.61 ± 0.27	45.218 ± 0.27	435.2 ± 2.17	1345.72 ± 8.07	142.16 ± 0.71	120.98 ± 0.60	1.36 ± 0.002	0.03 ± 0.001	34.122 ± 0.15	15.11 ± 0.09	1.97 ± 0.003
BV10	88.11 ± 0.44	117.1 ± 0.70	3985 ±19.92	21456 ±128.73	151.44 ± 0.75	84.72 ± 0.42	0.50 ± 0.001	0.02 ± 0.001	2.99 ± 0.01	39.78 ± 0.27	0.01 ± 0.00
BV14	79.65 ± 0.39	345.62 ± 2.07	295 ± 1.47	14567 ± 87.40	21358.27 ± 106.79	797.09 ± 3.98	1.06 ± 0.002	0.02 ± 0.001	109.87 ± 0.78	397.31 ± 1.54	0.47 ± 0.00
BV17	271.14 ± 1.35	118.11 ± 0.70	120 ± 0.6	15327 ± 91.96	284.19 ± 1.42	18.07 ± 0.09	0.2 ± 0.003	0.042 ±0.001	26.54 ± 0.12	38.73 ± 0.12	0.39 ± 0.001

Table 3.B: Elements concentrations present in the samples in PPM of vegetable seeds.

Elem.	Ni	Cu	Zn	Ga	As	Se	Sr	Zr	Ce	Hg	Pb
BV1	5.67 ± 0.01	1.63 ± 0.007	16.54 ± 0.01	2.59 ± 0.01	1.83 ± 0.01	1.83 ± 0.01	2.88 ± 0.01	1.92 ± 0.01	1.102 ± 0.006	0.01 ± 0.0002	0.1 ± 0.001
BV3	0.34 ± 0.0008	20.9 ± 0.14	16.86 ± 0.01	0.01 ± 0.001	1.08 ± 0.01	1.08 ± 0.01	0.65 ± 0.003	1.34 ± 0.01	1.72 ± 0.009	0.01 ± 0.0002	0.23 ± 0.002
BV4	4.86 ± 0.012	7.34 ± 0.03	11.09 ±0.007	0.05 ± 0.001	2.18 ± 0.018	2.18 ± 0.011	1.47 ± 0.008	1.67 ± 0.008	0.31 ± 0.002	0.01 ± 0.0001	0.25 ± 0.003
BV5	6.533 ± 0.01	2.83 ± 0.018	16.58 ±0.012	0.06 ± 0.001	0.09 ± 0.01	0.09 ± 0.005	2.41 ± 0.01	1.54 ± 0.007	0.72 ± 0.004	0.01 ± 0.0001	0.14 ± 0.001
BV6	2.56 ± 0.006	5.31 ± 0.03	10.12 ±0.006	0.19 ± 0.001	0.73 ± 0.06	0.73 ± 0.004	1.82 ± 0.001	1.72 ± 0.008	0.82 ± 0.004	0.015 ± 0.0002	0.15 ± 0.001
BV7	4.25 ± 0.010	20.7 ± 0.15	13.14 ± 0.06	0.06 ± 0.001	0.18 ± 0.001	0.18 ± 0.001	2.37 ± 0.012	1.07 ± 0.006	0.89 ± 0.004	0.041 ± 0.0004	0.11 ± 0.001
BV10	2.37 ± 0.005	0.30 ± 0.001	9.3 ± 0.04	0.05 ± 0.001	0.17 ± 0.001	0.17 ± 0.001	0.61 ± 0.003	1.8 ± 0.01	0.20 ± 0.001	0.016 ± 0.0002	0.11 ± 0.001
BV14	2.29 ± 0.005	10.8 ± 0.007	12.65 ± 0.07	0.02 ± 0.001	0.21 ± 0.01	0.21 ± 0.001	0.93 ± 0.005	0.93 ± 0.005	0.56 ± 0.003	0.010 ± 0.0001	0.26 ± 0.002
BV17	5.79 ± 0.014	35.68 ± 0.23	13.10 ± 0.08	0.03 ± 0.001	0.64 ± 0.01	0.64 ± 0.003	0.89 ± 0.004	0.59 ± 0.003	0.56 ± 0.003	0.019 ± 0.0002	0.243 ± 0.001

Table 4.A: Element concentrations present in the samples in PPM of leafy-vegetable seeds

Elem.	Si	P	S	Cl	K	Ca	Ti	V	Mn	Fe	Co
BVL1	21.21 ± 0.10	9571 ± 71.78	840.81 ± 5.46	12675 ± 63.37	787.86 ± 3.54	2309.12 ± 10.39	1.33 ± 0.007	0.01 ± 0.0002	19.87 ± 0.07	37.315 ± 0.11	0.1065 ±0.001
BVL2	564.32 ± 2.82	2321.9 ± 17.41	3997 ± 25.98	6532.36 ± 32.66	18730.4 ± 84.28	2448.14 ± 11.01	0.9 ± 0.005	0.01 ± 0.0002	60.44 ± 0.24	86.08 ± 0.25	0.05 ± 0.001
BVL3	784.1 ± 3.92	18678 ±140.05	2317 ± 15.06	200.26 ± 1.01	834.26 ± 3.75	10123.4 ± 45.55	0.51 ±0.003	0.043 ±0.009	18.7055 ± 0.07	46.653 ± 0.13	0.133 ±0.001
BVL4	93.713 ± 0.46	15890 ±119.17	1078.34 ± 7.00	42.167 ± 0.21	784 ± 3.52	630 ± 2.83	1.04 ± 0.005	0.037 ±0.008	14.567 ± 0.05	140.53 ± 0.42	0.064 ±0.001
BVL5	168.14 ± 0.84	4071 ± 30.53	1586.43 ± 10.31	209.84 ± 1.04	24947.79 ± 112.26	17197.99 ± 77.39	1.654 ±0.008	0.042 ±0.001	47.613 ± 0.19	49.873 ± 0.14	0.129 ±0.001
BVL6	113.14 ± 0.56	18610 ±139.57	3456 ± 22.46	1467.24 ± 7.33	25728.44 ± 115.77	24918 ± 112.13	1.786 ±0.008	0.054 ±0.001	20.345 ± 0.08	94.534 ± 0.28	0.145 ±0.001
BVL8	123.11 ± 0.61	5200.45 ± 39.00	3747 ± 24.35	140.31 ± 0.70	3338.51 ± 15.02	1203.45 ± 5.41	1.056 ±0.005	0.09 ± 0.002	47.89 ± 0.19	113.65 ± 0.34	0.433 ±0.004
BVL9	101.14 ± 0.50	5154.12 ± 38.65	4147 ± 26.95	2056.67 ± 10.28	12211.08 ± 54.94	1685.82 ± 7.58	1.345 ±0.006	0.055 ±0.001	18.76 ± 0.07	87.89 ± 0.26	3.478 ±0.034
BVL10	173.14 ± 0.86	3191 ± 23.93	1546.23 ± 10.05	2178 ± 10.89	24147.4 ± 108.66	2333.22 ± 10.49	1.252 ±0.006	0.0455 ±0.001	18.88 ± 0.07	78.747 ± 0.23	0.087 ±0.001

Table 4.B: Element concentrations present in the samples in PPM of leafy-vegetable seeds.

Elem.	Ni	Cu	Zn	Ga	As	Se	Sr	Zr	Ce	Hg	Pb
BVL1	5.67 ± 0.04	1.6347 ± 0.008	16.54 ± 0.13	2.59 ± 0.018	1.8372 ± 0.015	0.01219 ± 0.001	2.88 ± 0.01	1.92 ± 0.012	1.102 ± 0.007	0.0133 ± 0.001	0.16 ± 0.002
BVL2	0.34 ± 0.002	33.21 ± 0.166	17.31 ± 0.13	0.05 ± 0.001	0.39 ± 0.001	0.1 ± 0.001	0.41 ± 0.002	0.56 ± 0.003	0.7 ± 0.003	0.09 ± 0.001	0.16 ± 0.002
BVL3	4.86 ± 0.03	7.57 ± 0.037	34.132 ± 0.27	0.032 ± 0.0002	0.466 ± 0.002	0.0801 ± 0.001	0.527 ± 0.002	1.34 ± 0.008	0.12 ± 0.001	0.0271 ± 0.001	0.3 ± 0.001
BVL4	6.533 ± 0.05	9.71 ± 0.048	71.2 ± 0.56	0.042 ± 0.0003	0.135 ± 0.001	0.019 ± 0.001	0.656 ± 0.003	0.368 ± 0.001	0.8 ± 0.004	0.048 ± 0.005	0.187 ± 0.002
BVL5	2.56 ± 0.02	6.07 ± 0.030	6.436 ± 0.05	0.054 ± 0.0002	0.0873 ± 0.001	0.25 ± 0.001	1.55 ± 0.008	0.452 ± 0.002	0.39 ± 0.001	0.085 ± 0.001	0.246 ± 0.001
BVL6	4.25 ± 0.03	7.98 ± 0.039	53.11 ± 0.42	0.0543 ± 0.001	0.0436 ± 0.001	0.073 ± 0.001	1.567 ± 0.009	0.635 ± 0.004	0.376 ± 0.001	0.074 ± 0.001	0.386 ± 0.001
BVL8	2.37 ± 0.01	4.356 ± 0.021	30.7 ± 0.24	0.0152 ± 0.001	0.222 ± 0.001	0.091 ± 0.001	1.235 ± 0.007	0.748 ± 0.003	0.88 ± 0.004	0.0092 ± 0.001	0.68 ± 0.003
BVL9	2.29 ± 0.01	8.97 ± 0.044	76.9 ± 0.61	0.0143 ± 0.0012	0.397 ± 0.001	0.05 ± 0.001	0.4123 ± 0.002	0.813 ± 0.004	0.4 ± 0.002	0.009 ± 0.001	0.17 ± 0.001
BVL10	5.79 ± 0.04	13.498 ± 0.067	82.31 ± 0.65	0.0723 ± 0.001	0.486 ± 0.002	0.0213 ± 0.001	0.5 ± 0.002	0.934 ± 0.005	0.492 ± 0.003	0.0134 ± 0.001	0.197 ± 0.001

In the above tables 3 & 4, the major element highest composition is K and it ranges in vegetable seeds samples as 142.16 ppm in BV7 (Carrot) and 21358.27 ppm in BV14 (Lady's finger), similarly in leafy-vegetable samples the element K ranges from 784 ppm in BVL4 (Drumstick tree leaves) to 25728.44ppm in BVL6 (Sorrel-leaf type). Next to potassium, higher concentration is associated with the element, phosphorous in vegetable seeds samples as 45.218 ppm in BV7 (Carrot) to 9571 ppm in BV1 (Radish) and similarly in leafy-vegetable seeds samples, it ranges from 2321 ppm in BVL2 (Mint) to 18678 ppm in BVL3 (Curry leaves). Next to Phosphorous, the element Calcium (Ca) in vegetable seeds is ranging from 18.07 ppm in BV17 (Ridge gourd) to 3723.99 ppm in BV6 (Cluster beans) and in leafy-vegetable seeds samples, it ranges from 630 ppm in BVL4 (Drumstick tree leaves) to 24918 ppm in BVL6 (Sorrel-leaf type). The next element after Calcium is Sulphur, which is ranging in vegetable seeds sample as 120 ppm in BV17 (Ridge gourd) to 3985 ppm in BV10 (White eggplant) and similarly in leafy-vegetable samples, it is ranging from 840.81 ppm in BVL1 (Malabar spinach) to 4147 ppm in BVL9 (Fenugreek greens).

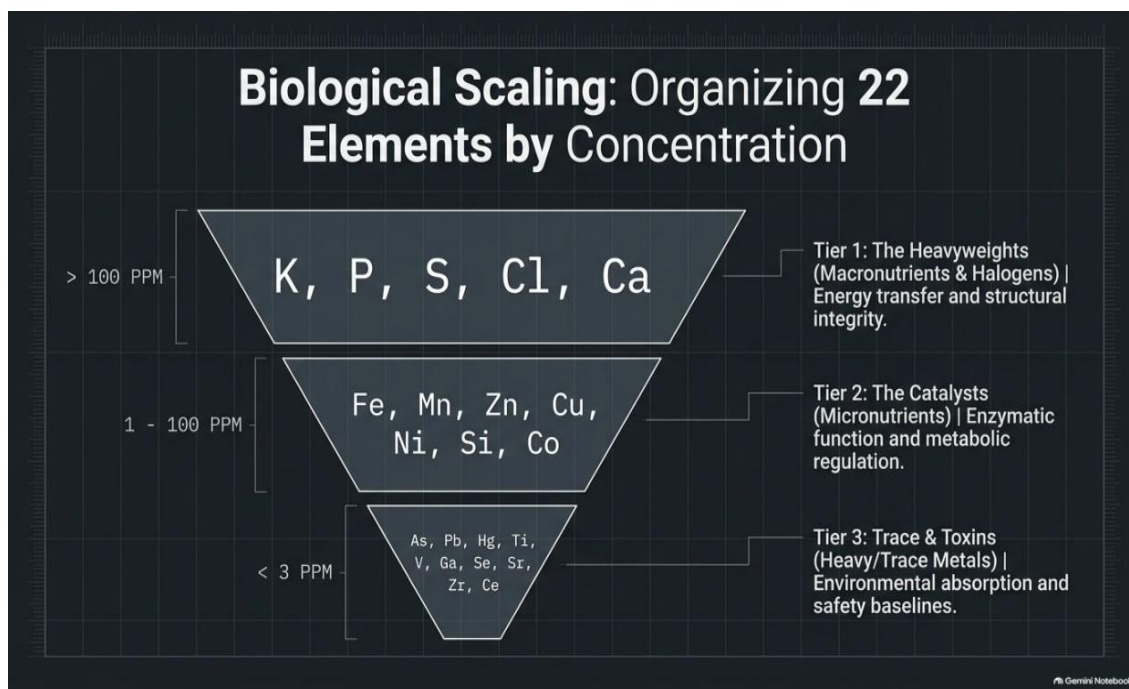


Fig-5: Classification of major, micro, trace & ultra-trace nutrient elements in all the seeds.

The figure-5 represents about biological scaling which has been done with respect to the ppm levels. The Macronutrients and Halogens (K, P, S, Cl, Ca) are present in the tier 1, whose ppm range is greater than 100. These are very useful in human system for energy transfer and structural integrity reactions. The Micronutrients (Fe, Mn, Zn, Cu, Ni, Si, Co) are present in the tier 2, whose ppm range is from 1 – 100. These are also useful in enzymatic function and metabolic regulations. The trace and toxins (As, Pb, Hg, Ti, V, Ga, Se, Sr, Zr, Ce) which are also known as heavy/trace metals present in tier 3, whose ppm range is less than 3. AS, Pb, Hg, Sr are the toxic elements which are harmful to the mankind at higher ranges.

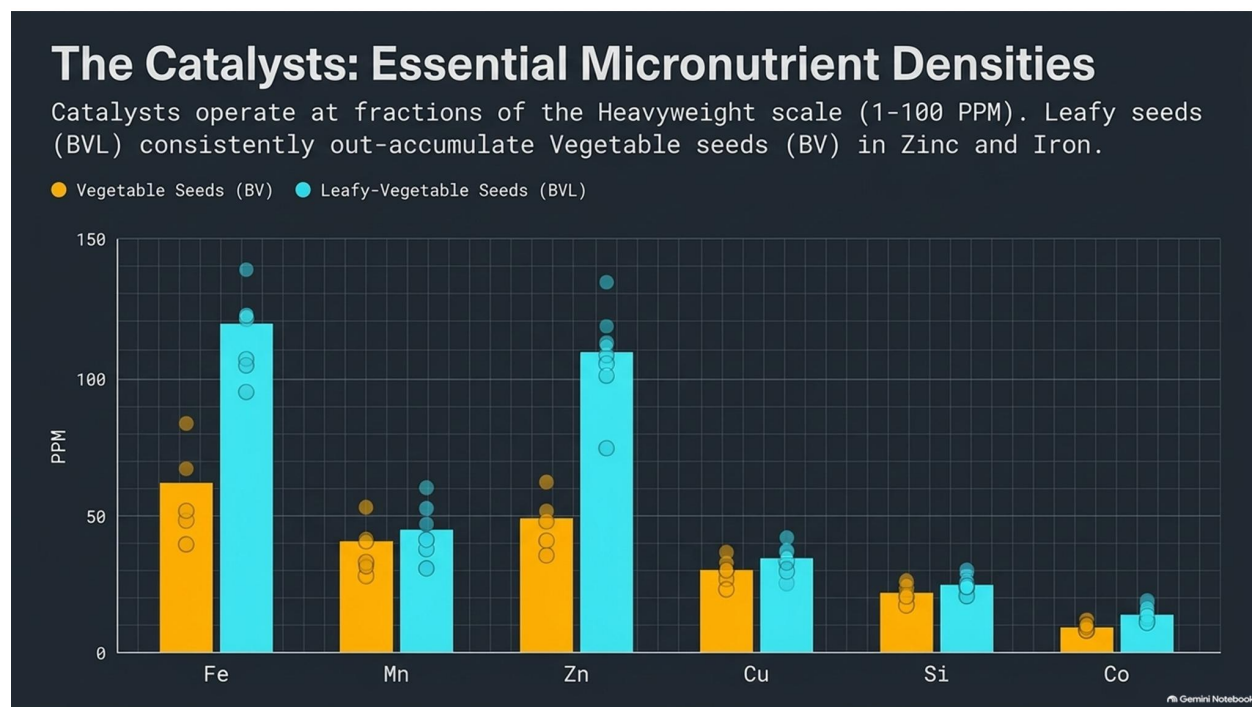


Fig-6: Bar diagram of micro nutrient elements in all the seeds.

A bar diagram has been drawn for minor nutrient elements which are present in vegetable seeds and as well as leafy-vegetable seeds and is given in figure-6. The element Iron (Fe) is more in leafy-vegetable seeds than the vegetable seeds samples. Next element Zn is high in leafy-vegetable samples and vegetable seeds samples. It is also found that the Fe, Mn, Zn, Cu, Si, Co elements are high in leafy-vegetable samples than the vegetable seeds samples. Many of the nutrienists suggests intake of leafy vegetables is good for health; our findings (figure-6) also supported it.

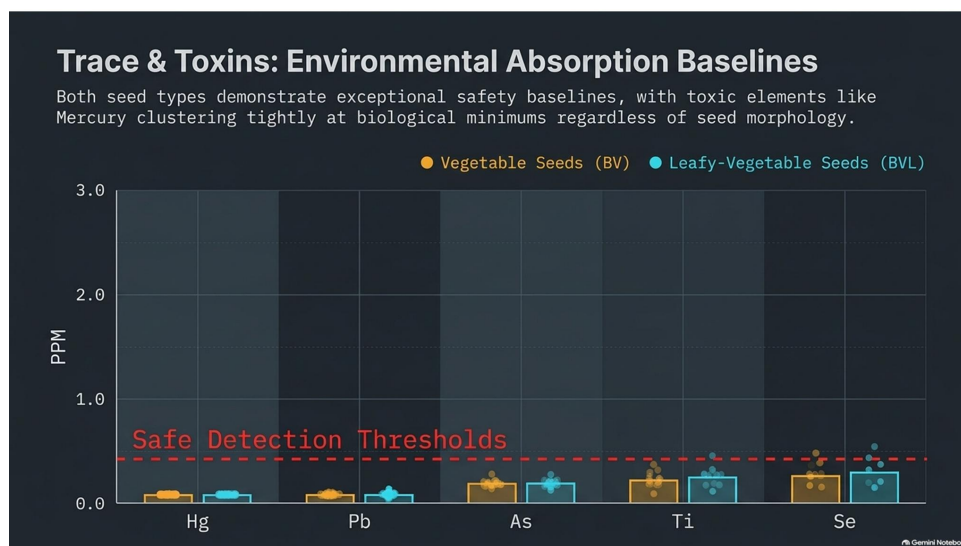


Fig-7: Bar diagram of toxic elements in all the vegetable & leaf vegetable seeds with indication of safe thresholds.

A bar diagram has been drawn for trace and toxic elements present in all the vegetable and leafy vegetable samples as shown in figure-7. It has been found that all the trace and toxic elemental concentrations are nearly same in vegetable seeds and leafy-vegetable seeds samples and which are within the safe ranges.

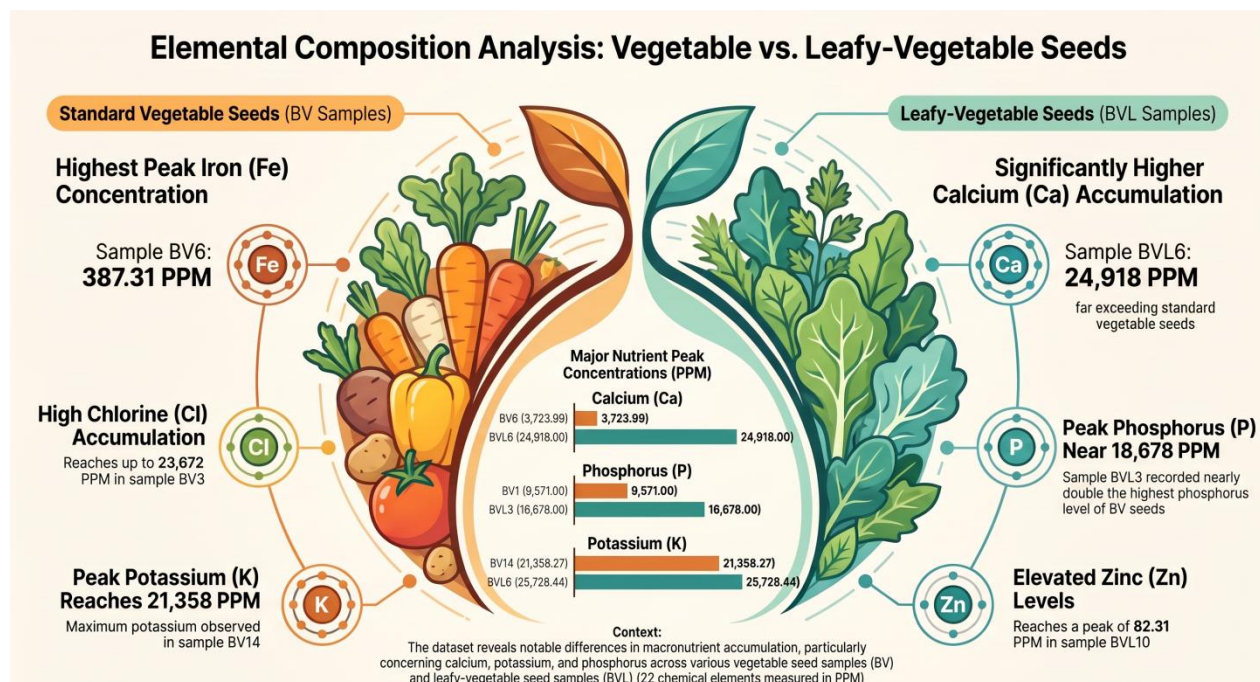


Fig-8: Elemental composition analysis in all the vegetable & leaf vegetable seeds.

The overall comparison of the major nutrient peak concentrations of Calcium, Phosphorous and Potassium in vegetable seeds and leafy-vegetable seeds samples were represented in figure-8. Among all the vegetable seeds and leafy-vegetable seeds, the iron concentration is maximum in BV6 (Cluster beans) with 387.31 ppm, similarly the chlorine is high in BV3 (Single-cross hybrid maize) with 23,672 ppm and the Potassium is high in BV14 (Lady's finger) with 21, 358 ppm. The calcium highest is in BVL6 (Sorrel- leaf type) with 24,918 ppm and the phosphorous high value in BVL3 (Curry leaf), with 18,678 ppm. The zinc is high in BVL10 (Indian Sorrel) with 82.31ppm. Hence it is advisable to consume more vegetables and leafy vegetables for those who are having iron deficiency such as pregnant ladies, anemia patients, etc.

Many major, Minor and trace elements required for the growth and development of human metabolism in the human body. Results also show that some of the vegetables and vegetable leaves contain toxic elements like Arsenic, Cesium, Mercury and lead but they are below the accepted toxic levels [31].

Conclusion:

The many analytical methods used in geo-research and the mining business to gather data on elemental concentrations (minor, major, and trace) are briefly described. Instrumental X-ray Fluorescence (XRF), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Neutron Activation Analysis (INAA), Atomic Absorption Spectrometry (AAS), Electron Microprobe Analysis (EMPA), and Particle-Induced X-ray Emission (PIXE) are all commonly used techniques. The samples cannot be utilized for additional research because some of these techniques are destructive. Certain methods only offer information on one component or need sample preparation prior to analysis. PIXE, on the other hand, offers unique characteristics such as being fast and non-destructive, enabling multi-elemental determination, and requiring small to no sample preparation. Trace elements in a sample can be found and measured using PIXE, a comparatively straightforward yet effective analytical method. It is a nuclear analytical method with ppm sensitivity for quick measurement of different trace elements. Its high sensitivity makes it useful in geology and geophysics for examining trace elements in minerals in geological specimens. Because proton bremsstrahlung is less than electron excitation, using protons offers high sensitivity even at lower atomic numbers. Due to the growing demand for elemental analysis of enormously tiny sample quantities, such as in geological materials like gemstones and precious minerals, the PIXE approach

has quickly acquired recognition as a useful analytical tool. The different mineral deposits and geological and biological uses of the PIXE technology in and around Andhra Pradesh, India, were examined in this article. To quantify trace elements in high-grade ores regions, the research suggests using PIXE. The importance of trace elements throughout the Proterozoic may be better understood with more thorough research, though, as the current work is still preliminary.

The accelerator-based nuclear method of PIXE was used to describe certain natural Pb-Zn ores and rocks. These minerals are mostly used in research and technology. The quantities of a number of main, minor, and trace elements were found in these samples. The elemental contents of the Pb-Zn ores and rocks are used to identify them. Because the PIXE approach is a non-destructive analytical technique that helps complete characterization, it helps identify the chemistry and mineralogy of Pb-Zn ores and rocks. Therefore, the current work promotes the use of the PIXE approach for characterizing geological materials, particularly where several components are of particular relevance. Thus, the current work demonstrates the use and adaptability of the PIXE technology for geoscientific methodological research, especially in ore matrices and rock mechanics.

Proton-induced X-ray emission (PIXE) was also applied to characterize the elemental composition of edible vegetable seeds and leafy-vegetable seed samples collected from Vizianagaram district, Andhra Pradesh, India. At the Institute of Physics in Bhubaneswar, India, the materials were oven-dried, homogenized, combined with graphite, pelletized, and exposed to a 3 MeV proton beam produced by a 3 MV tandem Pelletron accelerator. A Si (Li) detector was used to identify characteristic X-rays, and GUPIX was used to analyze the spectra. The analytical procedure was checked using NIST Apple Leaf certified reference material, for which the original study reports agreement between measured and certified concentrations. Across the investigated samples, 22 elements were identified: P, S, K, Mn, Fe, Ca, Si, Cl, Ni, Zn, Ti, V, Co, Ce, Cu, As, Zr, Hg, Pb, Ga, Sr, and Se. Potassium was reported in every sample, whereas several other elements showed sample-dependent occurrence. The data also indicate the presence of nutritionally relevant elements such as K, Ca, Cu, Fe, Se, Mn, and Zn, together with potentially toxic elements including As, Hg, and Pb. These findings demonstrate the utility of PIXE for rapid multi-element screening of plant-derived foods and provide baseline information for environmental and food-quality monitoring in the study region. However, quantitative dietary-risk interpretation requires confirmation of concentration units, complete sample identification, replicate measurements, analytical uncertainties, and comparison with element-specific regulatory limits on an equivalent mass basis. The current study therefore demonstrates the value and adaptability of the PIXE approach for geoscientific methods and biological research.

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