International Journal of Scientific Research in Physics and Applied Sciences **Research Paper**
Vol.8, Issue.3, pp.36-40, June (2020) **E-ISSN:** 2348-3423
DOI: https://doi.org/10.26438/ijsrpas/v8i3.3640

Need of Complementary Analytical Technique at PIXE-Complex Matrix Composition Analysis

A.V.S. Satyanarayana[1*], M. Jagannadha Rao[2], K. Sai Satya Mounika[3]

[1]Dept. of Engineering Physics, Andhra University, Visakhapatnam, AP, India
[2,3]Dept. of Geology, Andhra University, Visakhapatnam, AP, India

**Corresponding Author: savs.viit@gmail.com*

Available online at: www.isroset.org

Received: 27/May/2020, Accepted: 05/June/2020, Online: 30/June/2020

Abstract—PIXE is one of the nuclear techniques used to analyze the samples of geological materials routinely, but its validity in case of simple materials or non-matrix samples may give good results depending on elements present in composition. The applicability in case of complex matrix material rocks or minerals, the validity of results is not accurate if material contains a wide range of elements and results obtained by PIXE as single methodologies, should compare with other analytic nuclear technique. Simultaneously, to obtain a wide range of results of the complex geological material by using any nuclear technique, complimentary techniques should apply to the material analysis in case of complex geological materials.

Keywords—Geological materials, Non-matrix samples, Good results, Complex matrix material, Complementary Technique.

.

I. INTRODUCTION

The applicability of the PIXE technique, especially in geochemistry especially mineral and rocks [1] has been gaining importance in recent time and recent advances in PIXE) can successfully use in the elemental analysis of geological materials. When we observe the related scientific literature, a number of researchers from earth sciences have established its applicability in the analysis of materials from geological sciences; these include rocks, minerals, ores [2] petrology, crystallization process and fluid inclusions. Again, it contains an important of elemental analysis with accuracy, precision, resolution [3] and methodology applied to the geological samples. During the discussion of these results it is observed that though the PIXE is giving results of geological materials for their major, minor, trace and REE concentrations of complex matrix [4] are not with good precious and accurate. So PIXE technique and it's limiting in analyzing a given geological material particular very complex high grade [5] metamorphic rock which is contains wide range of elements.

II. OBJECTIVES OF THE STUDY

For this purpose investigation of belongs in to granulitic facis of Eastern Ghats has been chosen. This is a complex metamorphic igneous rock from the Eastern Ghats mobile belt. The rock selected for this study is from the study area Visakhapatnam of A.P state, India. Rock samples belonging to proto crust at which yields valuable information on the evaluation and geological history of the earth are rare when an opportunity to study a rock and present study was undertaken with the following specific objectives.

1) To study and record the recent advances in the methodology of PIXE in its application towards geochemical analysis of rocks or related materials complex and simple geo materials.
2) To understand such applications worldwide by conducting an extensive literature survey.
3) To evaluate the performance of PIXE in geochemical analysis of a rock formation by conducting a case study of samples from the Eastern Ghats terrain of Visakhapatnam.
4) To make an attempt to utilize the data generated to establish the genetic history or process of Charnockite from the study the application of PIXE and other complementary analysis techniques like AAS in the elemental analysis of geological materials particularly in case of rocks, petrological and mineralogical compositions, crystallization process and fluid inclusions.
5) It has been an argument that some of the elements present in complex matrix geological samples are completely determined or could not be determined at all by the PIXE. This may be due to various reasons including the complexity of matrix in geological materials like high grade metamorphic rock, etc. Due to this challenge it is felt that a systematic investigation needs to be designed and implemented to understand the performance of PIXE technique in case of matrix

materials in the determination of certain elements from major, minor, trace and REE concentrations.

A second attempt is made to analyze the same metamorphic rocks using complementary like Atomic Absorption photo spectrometer and the data generated by AAS method has been used to compare the PIXE results. This helped us to compare the data obtained by PIXE with that of published data to identify the elements which are completely determined or could not be determined at all. Another important factor for selecting this rock is based on the fact that the Charnockites of this area are well investigated and data are published in various scientific publications. The data generated the AAS method has been used to compare the PIXE results for its evaluation purpose. It is observed that the results obtained by AAS are more close to published data on Charnockites from various journals.

By compare the results between PIXE and other techniques of Charnockites, there is a need to identification of complementary analytical technique to analyze the complex matrix composition at low performance of PIXE technique.

III. METHODOLOGY

The attraction of non-destructive, simultaneous multi elemental determinations has led to an extensive application of accurate, precise and sensitive atomic and nuclear analytical technique such as PIXE. These investigations are carried out using the pelletron accelerator facility at the Ion Beam Laboratory, IoP, Bhubaneswar. A collimated proton beam of 2 mm diameter is made to fall into the sample, and the beam current is kept at 20 nA. A high resolution Si (Li) detector (160 eV FWHM at 5.9 keV energy) for PIXE analysis at Bhubaneswar, energy proton created by using 3 MV pelletron accelerator facilities and 3 MeV X-ray proton beam is magnetically focused and beam current to as proton the line surface of the specimen. This spot, which may be treated under box magnification, is ultimately viewed optically with a 300 x microscope equipped with a change completed-device television camera. A large area 80 mm^2 X-ray detectors placed as close as possible to the specimen (25 mm). The specimen stage insulated to permit integration of the incident beam charge. The samples on the target holder which are to be excited (or) positioned in this scattering chamber at an angle of 45^0 with respect to the direction of the proton beam. The position of the sample relative to the beam direction is adjusted properly by viewing through a window beryllium of 0.1 mm thickness provided in the scattering chamber. The direction is adjusted 90^0 and also placed in the chamber at 135^0 with respect to the beam direction. The Si (Li) detector output is connected with data acquisition system which records the X-ray spectrum. The spectrum of each sample is recorded for a sufficiently long time, so as to obtain good values is employed in the present studies and the Guelph PIXE [6].

In AAS [7] hollow cathode lamp is most widely used as a light source should produce a narrow spectrum with little background noise, stable and have enough intensity. Inside the lamp, the cathode is coated with a metal of analyst to be analyzed. For instance, if magnesium is to be analyzed from the sample, a cathode coated with magnesium is used. Similarly, for all the other elements like Na, Ca, K, Zn, etc. analysis respective metal coated cathodes are used in the lamp. The lamp is filled with argon or neon gas which is ionized by an electric arc. The ions get attracted toward cathodes and strike it leading to excitation of metal ions. This leads to the emission of radiation with a characteristic wavelength of analyte metal.

IV. RESULTS AND DISCUSSION

An attempt is made to interpret the geochemical data of the Charnockite samples investigated. The reasons behind the poor performance of PIXE with respect to certain elements have been tried to explain. The possibility of increasing accuracy of PIXE in analyzing samples of complex matrix like Charnockite has been discussed and suggestions are made. The values of concentration of elements with precision are presented in table -1, 2. For this purpose one sample from each series is taken. Accuracy, precision and detection limits of measurements of trace elements of Basalt reference and Precambrian Charnockites by proton induced X-ray emission (PIXE) was studied.

To assure the reliability of experimental system and other parameters, in the same experimental conditions, the PIXE spectrum is recorded with NIST certified reference material and the relative concentrations of different elements are estimated using GUPIX software package. The relative concentrations of different elements, thus obtained in the present experiment for the above standard samples are compared with the certified concentrations supplied by NIST. Good agreement with experimental uncertainties is observed in case simple materials and this shows the reliability of the present experimental system and use of GUPIX software package in the data analysis.

Table-1; PIXE spectrum is recorded with NIST certified reference material [4]

Elements	***Concentration (ppm)***	
	Certified values	**Measured values**
K	1.48±0.05	1.60±0.02
Ca	1.615±0.26	1.53±0.02
Mn	48.5±2.4	54.0±3.0
Fe	88.1±4.5	83.0±5.0
Cu	5.3±0.4	5.60±0.24
Zn	12.9±0.7	12.5±0.03
Se	0.06±0.01	0.05±0.009
Rb	9.3±1.0	10.2±1.50
Pb	0.54±0.08	0.47±0.02

In the above table-1, the concentration of simple materials is in excellent agreement between certified values and measured values. This is because of the material contained very few series of elements from Cl to Pb. Therefore, if analyzing material is simple, PIXE analysis, gives better values of concentration values of the elements. The next step is the elemental analysis of complex matrix by using PIXE, and it should compare the results with other analytical technique such as AAS. Basing on that there is a choice to know the limitations of PIXE in case of complex materials and also what complementary technique is suitable which used to analyze the complex material completely. This helped us to compare the data obtained by PIXE with that of published data to identify the elements which are poorly determined or could not be determined at all. Another important factor for selecting this rock is based on the fact that the Charnockites of this area are well investigated and data are published in various scientific publications. The data generated the AAS method has been used to compare the PIXE results shown in table-3 for its evaluation purpose. It is observed that the results obtained by AAS are more close to published data on charnockites.

Table-2; USGS standard reference material verified by PIXE and AAS [5]

Element	*Certified Values* ppm	±	*Measured value* ppm (PIXE)	±	*Measured value* ppm (AAS)	±
Al	71600	800	-		70208	787
Ca	81700	1200	7834.26	93	80232	1172
Fe	86300	400	7982	74	86907	1421
K	64300	100	9830	80	65103	96
Mg	43600	700	-	-	43864	711
Na	16400	600	-	-	16104	589
P	61200	100	-	-	60352	91
Si	233000	3000	-	-	230724	2936
Ti	16300	2000	3286	64	15173	1890
Ba	130	13	-	-	126	12
Ce	38	2	-	--	-	-
La	15	1	-	-	-	-
Co	45	3	10.5	1	44	3
Cr	280	19	295.2	25	290.08	21
Cu	127	7	133.23	10.14	135.63	8
Ga	21.7	0.9	22.52	2.6	22.52	2.6
Hf	4.1	0.3	-	-	-	-
Mn	1290	40	42	1.8	1.8	37
Nd	25	1.8	-	-	-	-
NI	119	1.8	41.2	2	118	2
Rb	9.8	1.0	8.62	1.2	10	1
Sc	3.2	1	3.11	1	3	1
Sr	389	23	97.8	17	392	23
V	317	11	26.4	1.8	307	12
Y	26	2	8.27	2.1	25	3
Zn	103	6	119.48	8.1	107	7
Zr	172	11	67.48	3.9	168	10
Nb	18	2	13.46	3.1	19	2

Table-3; Analytical results of all complex geological samples (PIXE and AAS) [5]

S.No	Element	PIXE(Average values of seven samples, ppm)	AAS (Average values of seven samples, ppm)
1	Na	-	23221.70
2	Mg	-	19911.42
3	Al	-	90242.71
4	Si	-	265686.71
5	P	-	1293
6	Cl	424.2±18.62	-
7	K	4887.28±29.91	20231.42
8	Ca	2808±26.31	32563
9	Ti	1133.09±10.97	7292.57
10	V	18.26±5.88	131.85
11	Cr	18.31±2.4	36
12	Mn	31.934±4.1	2161.28
13	Fe	5961.42±21.5	83156.71
14	Co	-	8.42
15	Ni	13.755±3.89	39.5
16	Cu	7.40±3.08	9.85
17	Zn	13.85±3.25	11.3
18	Se	3.65±2.1	5.65
19	Br	9.92±3.45	-
20	Rb	47.36±6.37	75.12
21	Sr	35.26±5.37	134.28
22	Y	15.385±4.75	49.585
23	Zr	43.64±7.41	140.9
24	Nb	7.6±3.43	13.14
25	Mo	17.59±5.17	6.442
26	Ru	9.97±3.59	4.20
27	Ag	12.36±9.0	5.5
28	Pb	30.64±13.13	29.97
29	Ba	-	841.57

Using the data obtained from the present investigation, it could be established the performance of PIXE with respect to different elements of the Charnockite samples. Another attempt is made to analyze the same samples using AAS. The data generated the AAS method has been used to compare the PIXE results for its evaluation purpose. It is observed that the results obtained by AAS are more close to published data on Charnockites from various journals [8] [9]. The results are authenticated by the published data on Charnockite of the study area as well as Charnockite from sample areas based on the comparison of the finalized data on the Charnockite samples presented. An attempt also made to present the genetic aspect of the Charnockites studied by obtaining Geo chemical data. Using this data the Charnockite hill from where the samples are collected have been attempted to understand the chemical nature followed by its genetic implications.

4.1 Elemental Discussion

The PIXE Method generally offers maximum sensitivity when an atomic number of Z of a detected element roughly is in the range 20 to 40, but in this investigation of Charnockites the elements identified from 17 (Cl) to 82 (Pb). The disadvantage of the once again investigated in the evaluation of PIXE method of complex matrix material is that the low Z elements like Na, Al, Mg, Si and P with 3 MeV. Particle-Induced X-ray Emission (PIXE) failed in the situation where the species of interest has a low atomic number because the low K X-ray fluorescence yields are strongly attenuated by the absorption edge of higher atomic number elements present in the complex matrix sample. Similarly, in case of concentration of K, Ca, Ti, Fe and others represented in the above. In the case of the complex matrix composition analysis of the elements with $Z \leq 32$ an interference is frequently encountered between the Kα (Z+1) X-ray and the Kβ (Z) X-ray, which have virtually the same energy or between the X-ray K lines of media elements and X-ray L lines of heavy elements. Therefore the concentrations obtained by PIXE are not equal to the concentrations obtained by AAS at K, Ca, Ti, Fe major concentration elements middle Z elements and PIXE not given proper concentration values of complex matrix composition shown in table-2.3.

The possible advantages it presents, such as less background radiation, good sensitivity for media elements, and lower secondary excitation in thick targets, are explained and also in matrix composition REE cannot be detected in important Basalt reference and Charnockites rock research. The generation of X-ray by 3 MeV and previous keV energy electrons are quantitatively similar. However, the bremsstrahlung back ground, which is the primary determinant of detection limits of the abundances of many elements from Cl to Pb down to parts per million. The detection limit of Se is 0.9 ppm, which represents very good sensitivity of the system. Trace element less than 0.0001% wt analysis is possible in case of Charnockites. PIXE is not the technique of choice for the REE present in Charnockite of Eastern Ghats whose levels of uninterested are after at the ppm level or below. PIXE with Si (Li) detector not suitable to detect REE: Determination of REE in geological samples is a very significant subject but hard to detect. By PIXE, the L X-rays energies of REE elements from 4-9 keV not resolved with K X-rays energies of low Z elements from 17 to 32 Z, because the energies ranges are equal and the determination of concentration of REE by PIXE becomes not easy and in accurate as a results of the needed complex spectrum deconvolution.

The results are authenticated by the published data on Charnockite of the study area as well as Charnockite from sample areas based on the comparison of the finalized data on the Charnockite samples presented in the lesson. From the results between PIXE and other analytical results, we conclude that, in addition to the PIXE, there is a need to identify other complementary technique to analyze the complex matrix geo materials.

4.2. Experimental Discussion

The results are authenticated by the published data on Charnockite of the study area as well as Charnockite from sample areas based on the comparison of the finalized data on the Charnockite samples presented in the lesson. The main reasons from experimental facts in the analysis of complex matrix materials are the following. The first group contains the uncertainties in the stopping power, the X-ray attenuation coefficient, the production cross section, the energy of incident proton, the angles, the solid angle, and the detector efficiency. lt also contains the systematic parts of the uncertainties in the number of bombarding particles, and in the X-ray yield. The second group contains the matrix composition (only for thick targets) and the statistical parts of the uncertainties in the number of bombarding particles and the X-ray yield.

V. CONCLUSIONS

From the above analysis, PIXE analysis is very much suitable at simple material which contain not nearby or element by the elements. Because in this case elements are clearly resolved and elements are clearly traceable and not overlapped in the spectrum. So good results are achieved in case of simple geo materials. In the second case of complex matrix composition like Charnockite composition, which contains continuous series of elements from low Z to high Z, elements are not resolved properly due same characteristic energies between different series. In this case, PIXE is limited and unable to detect low Z elements and erroneous at middle Z elements due to overlapped and same energy X-rays and failed to detect REE elements which are very important in Charnockite composition. Simultaneously, there is a need to apply complimentary analytical techniques like PIGE, or EPMA at low Z elements and NAA at middle Z and REE where the PIXE shows low performance and failed to give the complete analysis of complex geological materials.

ACKNOWLEDGMENT

I deem it a privilege to express my deep sense of gratitude and heartiest thanks to my research director. I am thankful to Prof A.Durga Prasad Rao, Head of the Department, Department of Nuclear Physics, Andhra University, Visakhapatnam and teaching staff. The deep sense of gratitude and heartiest thanks to my Head of the department, Engineering Physics, Andhra University, Visakhapatnam. I thank Dr. D.P.Mahapatro, Director, Institute of Physics, and Bhubaneswar, providing accelerator facility to carry out the research work and for all amenities provided during our stay at the institute of physics.

REFERENCES

[1] Christopher. M. Heirwesh, John. L. Campbell, Gerald. K. Czamanske, Refinement of major, minor element PIXE analysis of rocks and mineral. Nuclear Instruments and Methods in

Physics Research Section B: Beam Interactions with Materials and Atoms. 366, pp. 40-50, 2016.
[2] C. W. Graham, C. R. John, L. C. John, N. Zdenek, & J. T. William, Application of PIXE to mineral characterization. Nuclear instruments and methods in physics research B; Beam Interactions with Materials and Atoms. 189, pp. 387-393, 2002.
[3] D. D. Cohen, R. Siegele, I, Orlic, Ed. Stelcer, Long term accuracy and precision of PIXE and PIGE measurements for thin and thick sample analyses. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms. 189, pp. 81, 2002.
[4] A.V.S. Satyanarayana, S. Ravi Kumar, & S.V.R.A.N. Sharma, An application of PIXE technique to Proto Crustal Rocks: Geo chemical Evaluation of Granulitic Charnockites of Eastern Ghats, Andhra Pradesh, India. *Journal of Nuclear Physics, Material Sciences, Radiation and Applications*, *3*(2), 147-155, 2016.
[5] A. V. S. Satyanarayana, M. Jagannadharao, K. Chandra Mouli and B. Seetarami Reddy, Performance of PIXE Technique through a Geochemical Analysis of High Grade Rocks J. Nucl. Phys. Mat. Sci. Rad. A. Vol. 7, No. 1, pp.11–27, 2019.
[6] M. H. Kabir, Particle Induced X-ray Emission (PIXE) Setup and Quantitative Elemental Analysis (Ph.D. Dissertation) Kochi University of Technology Japan, 2007.
[7] W. B. Barnett, A Calibration Algorithm for Atomic Absorption. Spectrochimica Acta. Part B, Atomic Spectroscopy. 39, Issue-6, pp. 829-836, 1984.
[8] A. Sriramadas and A.T. Rao, Charnockites of Visakhapatnam, Andhra Pradesh. Journal of Geological Society of India. 20, pp. 512-517, 1979.
[9] A. T. Rao and V. R. R. M. Babu, Allanite in Charnockites rock airport hill near Visakhapatnam, Andhra Pradesh. American Mineralogist. 63, pp. 330-331, 1978.

AUTHORS PROFILE

Dr. A. V. S. Satyanarayana, has been qualified with higher degrees M.Sc., M.Phil, and Ph.D. Physical Science from Andhra University. He has significant teaching and research contributions in different areas of Physical Sciences, Atomic and Nuclear Physics, Advances of Nuclear Techniques in Elemental Analysis, Material Science, Geo-Chemistry and Geo-Physics. He has 20 years of teaching experience and 15 years of research experience. He has published research papers in reputed national and international journals.

Prof. Mokka Jagannadha Rao has been qualified with higher degrees from India and abroad, working on various aspects of Geological research and having more than three decades of experience. He has significant teaching and research contributions in different earth science specializations including, Mineral Resources, Coastal Geology, Environmental Geology, Remote Sensing, Computer Applications, Geo-Chemistry, Regional Geology and related fields. He has published more than 150 research articles in various national and international journals. He has undertaken 10 funded projects and 2 consultancy projects funded by various funding agencies and industry. He filed a patent entitled “Innovative Model that explains the genesis of Bay of Bengal”. Thirty students got their Ph.Ds’ under his guidance including students from other disciplines like computer sciences, Geo-Physics, Geo-Engineering and Nuclear Physics. He has been a member of various professional bodies and recipient of many awards and recognitions.

Ms. K.S.S.Mounika has been working for her Ph.D under the guidance of Professor M.Jagannadha Rao. She is presently finalizing her thesis and her thesis topic is related to Coastal processes, Geomorphology and Coastal Erosion along Visakhapatnam-Bheemunipatnam coast. She did her Masters in Geology from Andhra University and has been active in her research career. Her research interests include Geomorphology, Coastal processes, Coastal erosion, Environmental Geology and Applications of Remote sensing.

