Low Z Elements of High Grade Metamorphic Rocks by PIXE Analysis - A Comprehensive Review

Avupati Venkata Surya Satyanarayana¹, Mokka. Jagannadha Rao², Byreddy Seetharami Reddy³,

1 Department of Engineering Physics, Andhra University, Visakhapatnam, AP, India.
2 Department of Geology, Andhra University, Visakhapatnam, AP, India.
3 Department of Nuclear Physics, Andhra University, Visakhapatnam, AP, India.

Correspondence; Avupati. V. S. Satyanarayana, E-mail; savs.viit@gmail.com

Abstract

The majority of PIXE analytical study on geosciences has used 3 MeV proton beams for excitation and these studies generally uses the K-X-rays for low Z elements and L-X-rays for high Z elements. The present study of resulting spectra of metamorphic high grade rocks like charnockite can require striping techniques to resolve interference problems between low and high Z elements on the applications of light energy-PIXE using Si (Li) detector. In all forms of X-ray analysis, including thick-target light energy-PIXE, the X-ray signal is a dependent of the ionization cross section and for low-energy protons, the cross section is high for the K shells of light elements and the L shells of heavy elements in charnockite rock providing sufficient fluorescent yield for analytical purposes. For Z > 55, 3 MeV protons cannot ionize K-shell electrons and analysis depends on the use of L-X-ray lines in charnockite rock. Such L-X-ray spectra are complicated and can be affected by interferences K-X-rays from low Z elements. The low Z elements present in the charnockite were identified by previous complementary analytical techniques, but not identified in this study due to the above PIXE experiment limitations, and also particularly due to the dimensions of Si (Li) detector because of low energy K-X-rays of the elements absorbed by the detector window. Both interferences complexity and detector efficiency can lead to difficulties and ambiguity in the interpretation of spectra of low Z charnockite composition, a problem that is exacerbated by uncertainty in relative K-X-ray line intensities of low Z elements. From this investigation, the light energy-PIXE is ideal for the analysis of low Z<55 elements except lower K-X-rays of Z<17 elements using K-X-ray lines without high Z elements present in charnockite samples.

Keywords:- Metamorphic high grade rock, Thick-target LE-PIXE, Low Z elements, Complexity, Spectral overlap, Detector efficiency, Review.

Introduction

It has already been shown that the mineralogy and petrography of the charnockite gneiss in the study area are similar to that of metamorphosed igneous rocks with a basic affinity. Presence of characteristic minerals like almandine garnet, pyroxenes indicates that the charnockite gneiss is a high grade metamorphic rock. In this section it is proposed to study its major and trace element chemistry with an object of understanding more about its genesis. Pyroxene granulites are reported in all Precambrian high grade terrains, but little is known about the chemical characteristics of these rocks and their precursors. In the limited studies published on this problem both igneous and sedimentary origins were reported from the Eastern Ghats granulites belt, India and have described the pyroxene granulites from Visakhapatnam and also presented the minor, major and REE data in inferring the tectonic environment and nature of magma. However, the present investigation supplements in establishing the origin of pyroxene granulites based on minor, major and trace element geochemistry using discriminate functions.
Application of research tools such as X-ray diffraction, Electron Micro Probe Analysis, Scanning Electron Microscopy, Particle Induced Gamma ray Emission, Neutron Activation Analysis, X-ray Fluorescence etc. on routine basis are important supplements to present microscopic studies and analysis, although it should be stressed that these traditional methods remain essential in any study. More recently other innovative beam technique PIXE playing an important role in case of interesting geo chemical evaluation. Such technique permits detection limits of trace elements in geological materials not believed possible some years ago, and with increasingly good resolution, precision, accuracy and nondestructive. Very few researches were undertaken in geochemical analysis of geological material by using PIXE analysis and a survey of previous literature shows that the PIXE technique has been used by few several researchers for the multi elemental analysis of geological materials.

Some of geological materials are generally complex forms with mineral grains and inclusions. Geo-chemical nature of the different regions has been significant for explaining the fundamental process of formation. The characterization of mineral composition in terms of their texture chemical nature, morphology, and other physical attributes is playing an important role in studies of mineral deposits of all types. The growing need for complete idea about the mineralogical composition of a deposit determines that mineral characterization studies from an integral and often critical part of investigations of deposits. In many instances these are very important advantages in trace elements, minor and major elements while contracting models of the genesis of geological system, non destructive techniques include atomic and nuclear processes.

H. Moseley experimented out the characteristic X-rays induced when materials were bombarded with cathode rays. Since electrons are particles too, this is the first report of Particle Induced X-ray Emission. In the first described the spectrometer and pointed out that his elemental samples were contaminated with impurities saying presciently. The prevalence of X-ray lines due to impurities suggests that this may prove a powerful chemical analysis. In his second, he systematically measured K and L line wavelengths or energies. But Charles Barkla is responsible for the first recognition of characteristic X-ray lines of elements, it was in his paper that he first named X-ray "fluorescence", and introduced the "K" and "L" notation: mid alphabet letters being used since both longer and shorter wave-lengths were expected. The first report of modern PIXE using Si (Li) detectors was by Johansson and others who suggested that trace-element detection limits could be as low as ng/g, and analysed geological materials.

Among various elemental analytic tools (Olabanji, et. al., 1996, Felix, et. al., 2017) PIXE is the most significant which are based on the use of the material to be quantified as a target for a beam of accelerated particles. The determination of the characteristic energy emitted by the incident beam is then used to identify and quantify the presence of the various elements in the material. In PIXE (Christopher, et. al., 2016) what are exploited are, in particular, the X-rays emitted from the target material, whose energies are characteristic of the emitting atomic species. A technical description then follows of how proper beams for PIXE are produced and of the experimental setups commonly used. The X-ray detector characteristics, the electronics for constructing the energy spectra, and the software processes for their deconvolution, leading to the extraction of quantitative data, are then briefly described in case of analysis of low Z elements of Charnockite composition.

Moseley employed good resolution technique, wavelength dispersive spectroscopy which is a quite suitable of detection differences in the atomic electron structure due to different bonding states. This valence information is routinely used in the electron spectroscopy and absorption spectroscopy. It can also be used in PIXE, if a high resolution detector is used which could be WDX or one of high resolution calorimetric EDS detectors. Of course high resolution also allows disentangling of overlapping peaks which often accuse, especially for the L lines and is one main reason of the degradation of sensitivity. Three physical effects have to be quantified to use PIXE for analysis, 1) Ionisation cross-section 2) Fluorescence probability and 3) Mass absorption; these are all quite complex and need describing separately. To this needs to be added the energy loss of the incident particles in the sample, which is of course exactly the same as for the particle reaction technique. We should note here that PIXE
has its own ionisation physics but shares the fluorescence (or, equivalently, Auger) probabilities with the other atomic excitation methods.

Among all the previous analytical methods, PIXE technique has its own merits and demerits (Javier, 2016) over the other techniques. Using the analysis of the present study, it could be concluded the level of working of PIXE (Satyanarayana, et. al., 2019) at low Z elements with respect to previous analytical tools of same location of the charnockite samples by comparisons. An attempt also made to present the genetic aspect of the charnockites studied by obtaining geo chemical data through review of the PIXE spectrum compare with previous analytical methods. The aim of the present investigation is calculating the quantification values of all elements and also review in matrix Precambrian samples of low Z elements in charnockite samples of hill near Visakhapatnam airport using particle induced X-ray emission technique with 3 MeV.

2. Experimental Details

For PIXE analysis is at ion beam laboratory energy proton created by using 3 MV pelletron accelerator facilities at institute of physics, Bhubaneswar, India. A 3 MeV, X-ray proton beam is magnetically focused proton beam of 2 mm diameters beam current to as proton the line surface of the target. The samples are mounted on an aluminum target holder with a ladder arrangement. Then the target holder is inserted into the scattering chamber and the irradiation is carried out in vacuum conditions. The beam current is kept at 20 nA and this spot which may be treated under box magnification is ultimately viewed optically by a 300 x microscope equipped with a change completed device television camera. A large area 80 mm² X-ray detecting nominal resolution 160 eV at 5.9 keV is placed as close as possible to the specimen (25 mm). The specimen stage insulated to permit integration of the incident beam charge.

With respect to the proton beam direction, the samples which are to be excited are positioned on the target holder at an angle of 45° in this scattering chamber. The target position with respect to the beam direction is adjusted properly by viewing through a window beryllium of 0.1 mm thickness provided on the scattering chamber. The direction is placed at an angle of 90° with respect to the beam direction also placed in the chamber at an angle of 135° with respect to the beam direction. The Si (Li) X-ray detection output is connected to system of data acquisition which gathers the X-ray spectrum. The spectrum of each sample is noted for a sufficiently enough time so as to achieve valuable statistics.

The Guelph PIXE (GUPIX) (Maxwell, et. al., 1995) software package is employed to analyze the spectrums utilizing a standard Marquardt non-linear least square fitting procedure. This software package advantages is to identify different elemental quantifications present in the target material and to calculate their relative intensities.

Using this GUPIX software package the X-ray intensities of different elements are changed into the respective quantifications using a standardized technique involving fundamental parameters, pre-determined instrument constants and input parameters such as solid angle, beam current etc. Comparing the quantification values of Yttrium achieved in the present work with the known concentration of Yttrium added to the sample, the working condition of a various experimental factors of input are verified (Satyanarayana, et. al., 2016).

To know the performance of experimental system and other parameters, in the similar experimental conditions, the PIXE spectrum is recorded with USGS standard certified reference material and the relative quantifications of multi-elements are quantified using Guelph PIXE software package. The relative quantifications of different elements in the present experiments are determined. The above standard samples are compared with the certified quantifications supplied by USGS. Good agreement at the performance of present experimental system and use GUPIX software package in the data analysis. (Kabir, 2007).
3. Related work

The first known occurrence of allanite from charnockite hill, Eastern Ghats, Visakhapatnam, India is reported. X-ray powder data, chemical and spectrographic analysis (Rao and Babu, 1978) are presented. The allanite belongs to a late paragenetic sequence in the coarse paligenetic charnockites and charnockite pegmatites which are derived during granulite-grade metamorphism from the structurally emplaced igneous charnockites. Porphyritic basic charnockite has been observed within the ‘charnockite region’ of the Eastern Ghats of the Precambrian formations of India. From the X-ray and chemical data (Rao., et. al., 1969) the phenocrysts are considered, based on petrographic and chemical evidence it is inferred that the basic charnockites of Chipurupalli area in Visakhapatnam district are formed from tholeiitic magma as a gabbroic mass under deep seated plutonic conditions.

High energy proton induced X-ray emission (HE-PIXE) for samples in which high Z elements, all K X-ray lines are well-resolved in the energy range of 60-80 keV and is not suitable for low Z elements due to the cross section problems of light elements. When more heavy elements are present in the composition, K-lines of light elements overlap with L-X-rays of high Z elements occurs, but the resolution of all K-line components for each element should allow quantitative relative intensities to be derived. Additional complications also can arise from nuclear reactions within a sample. Previous evaluations have overestimated the problems associated with X-ray generation in high-energy particle bombardment of geological materials. A brief comparison of low energy PIXE, high-energy PIXE (Norman, et. al., 1995) indicates that high-energy PIXE (HE-PIXE) should be a useful to the methods of high Z-element in geological material analysis only.

A high resolution Si (Li) detector (160eV FWHM at 5.9 keV energy) is employed in the experimental work and to analyse the spectra, the Guelph PIXE (GUPIX) software package is used. The elemental quantification identified in this Precambrian charnockite rock are Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ru, Ag, Pb. From this observation (Satyanarayana., et. al., 2016) these minerals are proto crustal rocks. These samples are to belong to a very important geological phase and further work at problematic elements like low Z elements in geology of the metamorphic rock is indeed to firmly establish its exact ppm range.

It has been concluded that some of the elements present in charnockite samples by using PIXE analysis are completely measured or could not be measured at all, due to various experimental factors including the matrix composition [5]. It is felt that a proper study needs to be explaining the limitation of PIXE in certain low Z elements.

The high-grade metamorphic charnockite rocks selected are analyzed both by PIXE as well as complimentary previous technique and the results are authenticated by using a USGS Basalt reference material and studies of charnockite literature. It is believed that the accuracy of problematic low Z elements (Satyanarayana, et. al., 2019), especially from high grade rock can be improved and the conditions of PIXE can be standardized for various elements under different combinations. The reasons behind the working condition at low Z elements using Proton Induced X-ray Emission have been established.

PIXE is one of the nuclear analytic tools employed to analyze the samples of geological materials routinely, but its validity in case of simple non-matrix materials may given good results depending on elements present in composition. The applicability in case of complex matrix material rocks, the validity of results is not accurate if target contains a wide range of elements and results obtained by PIXE as single methodologies, should compare with other analytic nuclear technique (Satyanarayana, et. al., 2020). Simultaneously, to obtain a wide range of results of the complex geological material by using any nuclear technique like PIXE, complimentary techniques should apply to the analysis in case of complex geological materials.
### 4. Results and Discussions

Table 1: USGS Standard reference material (verified by PIXE)

| Element | Certified Values ppm | ± | Measured value ppm | ± |
|---------|----------------------|---|---------------------|---|
| Al      | 71600                | 800 |                      |   |
| Ca      | 81700                | 1200 | 7834.26             | 93 |
| Fe      | 86300                | 400 | 7982                | 74 |
| K       | 64300                | 100 | 9830                | 80 |
| Mg      | 43600                | 700 |                      |   |
| Na      | 16400                | 600 | -                   |   |
| P       | 61200                | 100 | -                   |   |
| Si      | 233000               | 3000 | -                   |   |
| Ti      | 16300                | 2000 | 3286               | 64 |
| Ba      | 130                  | 13  | -                   |   |
| Ce      | 38                   | 2   | -                   |   |
| La      | 15                   | 1   | -                   |   |
| Co      | 45                   | 3   | 10.5                | 1  |
| Cr      | 280                  | 19  | 295.2               | 25 |
| Cu      | 127                  | 7   | 133.23              | 10.14 |
| Ga      | 21.7                 | 0.9 | 22.52               | 2.6 |
| Hf      | 4.1                  | 0.3 | -                   |   |
| Mn      | 1290                 | 40  | 42                  | 1.8 |
| Nd      | 25                   | 1.8 | -                   |   |
| Ni      | 119                  | 1.8 | 41.2                | 2  |
| Rb      | 9.8                  | 1.0 | 8.62                | 1.2 |
| Sc      | 3.2                  | 1   | 3.11                | 1  |
| Sr      | 389                  | 23  | 97.8                | 17 |
| V       | 317                  | 11  | 26.4                | 1.8 |
| Y       | 26                   | 2   | 8.27                | 2.1 |
| Zn      | 103                  | 6   | 119.48              | 8.1 |
| Zr      | 172                  | 11  | 67.48               | 3.9 |
| Nb      | 18                   | 2   | 13.46               | 3.1 |
Table-2; Analytical results of charnockites of present PIXE techniques

| S.NO | Element | G1     | G2     | G3     | G4     | G5     | G6     | G7     |
|------|---------|--------|--------|--------|--------|--------|--------|--------|
| 1    | Cl      | 394.1±16.5 | 399.6±17.1 | 379±16.5 | 403.5±19.5 | 546.9±23.5 | 383.7±16.7 | 462.6±20.6 |
| 2    | K       | 4080±28.2  | 4187±25.1  | 4148±26.1 | 4246±29.3 | 6699±40.2  | 5458±27.1  | 5393±33.4  |
| 3    | Ca      | 223925.9   | 2281±22.8  | 2637±25.6 | 2754±28.1 | 4120±23.5  | 2544±26.2  | 3091±32.1  |
| 4    | Ti      | 1394±11.6  | 1271±9.3   | 1109±9.3  | 13.67±11.3 | 1590±13.8  | 1044±9.1   | 1510±12.4  |
| 5    | V       | 17.92±4.8  | 23.69±4.1  | 7.85±4.0  | BDL     | 37.78±6.0  | 10.79±4.0  | 11.55±12.4 |
| 6    | Cr      | 16.63±2.3  | 38.53±2.1  | 15.16±2.1 | 16.93±2.5 | 17.71±3.1  | 9.11±2.1   | 14.13±2.6  |
| 7    | Mn      | 18.62±3.9  | 34.71±3.7  | 34.31±3.7 | 33.68±4.1 | 47.43±5.3  | 27.36±3.5  | 27.03±4.5  |
| 8    | Fe      | 5200±20.3  | 6575±21.0  | 5649±19.8 | 5838±22.2 | 7325±26.4  | 4905±17.7  | 6238±23.1  |
| 9    | Ni      | 10.96±3.7  | 11.43±3.7  | 10.06±3.39 | 8.94±3.92 | 28.29±5.02 | 10.11±3.1644 | 16.5±4.3692 |
| 10   | Cu      | BDL       | BDL       | 6.1±2.7  | BDL     | BDL     | BDL     | 8.71±3.47  |
| 11   | Zn      | 9.147±3.3  | 18.21±3.5  | 14.23±3.0  | 14.41±3.5 | 11.96±4.6  | 24.73±2.9  | 4.29±2.0   |
| 12   | Se      | 6.3±6.5±2.5 | BDL     | BDL     | 0.94±9.1 | BDL     | BDL     | BDL     |
| 13   | Br      | 4±2.2     | 12.17±2.93 | 11.82±2.85 | 13.47±6.2 | 10.32±4.031 | 8.61±2.455 | 9.0±8±3.503 |
| 14   | Rb      | 48.87±6.0  | 42.08±6.1  | 62.73±6.0  | 34.71±6.2 | 56.14±7.9  | 34.58±5.3  | 52.46±7.1  |
| 15   | Sr      | 38.5±5.4  | 28.6±4.6  | 44.61±4.9  | 27.65±5.2 | 38.02±6.5  | 33.9±4.9  | 35.5±6.1   |
| 16   | Y       | BDL       | 12.64±4.5  | BDL     | 18.13±5.0 | BDL     | BDL     | BDL     |
| 17   | Zr      | 95.91±9.8  | 20.86±6.0  | 23.6±6.1  | 63.7±8.7  | 11.44±7.0  | 12.16±5.0  | 77.8±9.3   |
| 18   | Nb      | 7.035±3.1  | 9.812±3.9  | BDL     | 6.09±3.29 | BDL     | BDL     | BDL±6. ±6. |
| 19   | Mo      | BDL       | 24.34±6.3  | BDL     | 10.84±4.04 | BDL     | BDL     | BDL     |
| 20   | Ru      | BDL       | BDL       | BDL     | BDL     | BDL     | 9.977±3.59 | BDL     |
| 21   | Ag      | BDL       | 12.36±9.0  | BDL     | BDL     | BDL     | BDL     | BDL     |
| 22   | Pb      | 32.93±15.6 | 38.35±17.3 | 17.68±7.7 | 28.82±11.2 | 41.58±14.48 | BDL     | 24.49±12.5 |
| Element | Atomic Number | Present PIXE Analysis, average of 7 samples | Previous Chemical analysis of pyroxene granulites from charnockitic rocks, Visakhapatnam (Rao, et. al., 1993) | Previous, Chemical analysis of allanite from Air Port Hill charnockite, Visakhapatnam (Rao and Babu, 1978) |
|---------|---------------|---------------------------------------------|-----------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------|
| Li      | 3             | ND                                         | 18.08ppm                                                                                     | -                                                                                                  |
| Be      | 4             | ND                                         | -                                                                                             | <4                                                                                                |
| F       | 9             | ND                                         | 0.400ppm                                                                                     | -                                                                                                  |
| Na      | 11            | ND                                         | Na2O=1.591(Wt%)                                                                              | -                                                                                                  |
| Mg      | 12            | ND                                         | MgO=4.022(Wt%)                                                                               | MgO=1.18(Wt%)                                                                                     |
| Al      | 13            | ND                                         | Al2O3=18.137(Wt%)                                                                            | Al2O3=14.79(Wt%)                                                                                 |
| Si      | 14            | ND                                         | SiO2=50.345(Wt%)                                                                             | SiO2=31.24(Wt%)                                                                                  |
| P       | 15            | ND                                         | P2O5=0.213(Wt%)                                                                              | -                                                                                                  |
| Cl      | 17            | 424±18.62ppm                               | 0.130ppm                                                                                     | -                                                                                                  |
| K       | 19            | 4887±29.91ppm                              | K2O=0.428(Wt%)                                                                               | -                                                                                                  |
| Ca      | 20            | 2808±26.31ppm                              | CaO=11.376(Wt%)                                                                              | CaO=11.01(Wt%)                                                                                   |
| Sc      | 21            | ND                                         | 23ppm                                                                                         | 150ppm                                                                                            |
| Ti      | 22            | 1133±10.97ppm                              | TiO2=1.314(Wt%)                                                                              | TiO2=1.62(Wt%)                                                                                   |
| V       | 23            | 18.26±5.88ppm                              | 240ppm                                                                                       | V2O5=0.09(Wt%)                                                                                    |
| Cr      | 24            | 18.31±2.4ppm                               | 180ppm                                                                                       | 70ppm                                                                                             |
| Mn      | 25            | 31.93±4.1ppm                               | MnO=0.089(Wt%)                                                                               | MnO=0.28(Wt%)                                                                                    |
| Fe      | 26            | 5961±15.5ppm                               | Fe2O3=1.123(Wt%)                                                                             | Fe2O3=5.10(Wt%)                                                                                  |
| Co      | 27            | ND                                         | 74ppm                                                                                         | 150ppm                                                                                            |
| Ni      | 28            | 13.75±3.89ppm                              | 170ppm                                                                                       | 66ppm                                                                                             |
| Cu      | 29            | 7.40±3.08ppm                               | 262ppm                                                                                       | 150ppm                                                                                            |
| Zn      | 30            | 13.85±3.25ppm                              | 80ppm                                                                                         | 140ppm                                                                                            |
| Ga      | 31            | ND                                         | 36ppm                                                                                         | 30ppm                                                                                             |
| Ge      | 32            | ND                                         | -                                                                                             | 80ppm                                                                                             |
| Sc      | 34            | 3.65±2.1ppm                                | -                                                                                             | -                                                                                                  |
| Br      | 35            | 9.92±4.55ppm                               | -                                                                                             | -                                                                                                  |
| Rb      | 37            | 47.36±6.37ppm                              | 66.52ppm                                                                                     | -                                                                                                  |
| Sr      | 38            | 35.26±5.37ppm                              | 325ppm                                                                                       | 480ppm                                                                                            |
| Y       | 39            | 15.38±4.75ppm                              | -                                                                                             | *Y2O3= 0.15 (Wt%)                                                                                |
| Zr      | 40            | 43.64±7.41ppm                              | 78ppm                                                                                         | *ZrO2=0.15 (Wt%)                                                                                 |
| Nb      | 41            | 7.6±3.43ppm                                | -                                                                                             | 900ppm                                                                                            |
| Mo      | 42            | 17.59±5.17ppm                              | -                                                                                             | 600ppm                                                                                            |
| Ru      | 44            | 9.97±3.59ppm                               | -                                                                                             | -                                                                                                  |
| Ag      | 47            | 12.36±9.0ppm                               | -                                                                                             | -                                                                                                  |
| Sn      | 50            | ND                                         | *SnO2=0.03(Wt%)                                                                               | -                                                                                                  |
| Ba      | 56            | ND                                         | 338.40ppm                                                                                     | -                                                                                                  |
| Hf      | 72            | ND                                         | 3.23ppm                                                                                       | -                                                                                                  |
| Ta      | 73            | ND                                         | 0.69ppm                                                                                       | -                                                                                                  |
| W       | 74            | ND                                         | -                                                                                             | <40ppm                                                                                            |
| Au      | 79            | ND                                         | -                                                                                             | 10ppm                                                                                             |
| Pb      | 82            | 30.64±13.13ppm                             | -                                                                                             | *PbO=0.04(Wt%)                                                                                   |
| Th      | 90            | ND                                         | 7.07ppm                                                                                       | *ThO2= 0.50(Wt%)                                                                                  |
| U       | 92            | ND                                         | 2.83ppm                                                                                       | *U3O8=0.01 (Wt%)                                                                                 |
|REE      | 57 to 71      | ND                                         | -                                                                                             | *(Ce,La,Nd)2O3= 23.29(Wt%)                                                                        |
The PIXE analysis of the charnockite samples G1 to G7 collected from the interior of the Charnockite hill are obtained by Si (Li) detector. These quantification values are presented with errors in table-2 assuming standard deviation values \((n) = 7\) and BDL (Below Detection Limit). The results obtained from PIXE analysis-charnockite composition compared with the previously experimented analytical tools (Rao, et. al., 1969, Rao, et. al., 1978, Kamineni, et. al., 1982, Rao, et.al., 1993) shown in table-3 for review (Mac Arthur and Xin-Pei, 1991) of low Z elements present in the complex matrix charnockite composition.

In this, an attempt is made to evaluate the working condition of PIXE at light atomic number elements with respect to the geochemistry of previously analyses charnockite samples. The results of charnockite obtained by PIXE analytical method for the elements testing have been authenticated by comparing these values with that of USGS standard material Basalt. The analysis of USGS standard, each element has been compared with USGS particularly low Z elements. So, the following table-1 presents the elements which are near to USGS standard elements having moderate error values and elements which are highly erroneous values not detected.

In the previous analytical results, the low Z elements in charnockite composition are started from analysis Li and Be, but these are not detected in this present PIXE at 3MeV spectrum because of low energy K X-rays induced from low Z elements in charnockite, and these are absorbed by detector window of the Si (Li) detection and in general PIXE experiments fit the elements for K X-rays, \(Z = 6\) to \(Z = 60\) nearly, for L-X-rays, \(Z = 22\) to 92, for M-X-rays, \(Z = 72\) to 83.

The smooth Si (Li) detection volume ranges from order of 10 mm diameter, and order of 5 inch thickness depend on the achieved application. The smaller diameter detectors given good energy resolution of elements at low characteristic X-ray energies, and the thicker detectors have higher detection efficiency at energies above 20 keV of the characteristic X-rays. The X-ray enters the cryostat through a thin Be window to reach the detector. The beryllium windows of detection are typically range of 8-25.4 pm thick. The thickness of the window sets the lower energy limit for photons that can be detection by the detector. The induced X-rays of the order of 2 keV energies of low Z elements can be determined using this Si (Li) detector with the window thickness. Recently instead of beryllium foils, very thin films of the order of 0.5 p of polycarbonate have been used which can withstand greater pressure, and is resistant to environmental degradation. With these windows low Z elements like carbon (0.282 keV K X-rays) has been measured (Szegedi, et. al., 1996).

The element Li have no X-ray and Be with X-ray energy \(K_a = 0.108\) keV are not detected even though these elements are previously detected in chemical analysis of charnockites. The next element F is a trace or minor element in composition, the elements F emit the X-ray energy \(K_a = 0.677\) keV (Satynarayana, et. al., 2020) but not trace out in this PIXE analysis due to the low characteristic X-ray energy less than 2 keV and Na (\(K_a = 1.040\) keV) to P (\(K_a = 2.010\) keV) are also not detected in the present study due to above detection limits, but these elements are detected by previous analytical methods. Actually, the analysis is started in the PIXE spectrum from element S (\(K_a = 2.309\)) with the present detector, but S is not present in charnockite composition. Similarly the major elements Na, Mg, Al, Si, and minor or trace P are present in the composition of charnockite by previous analytical techniques, but not detected in this investigation due to PIXE experiment limitations and hence low characteristic energy K-X rays of the elements absorbed by the detection window.

Therefore, PIXE unable to detect the low Z elements present like, Li, B, F, Na, Mg, Al, Si and minor P in charnockite composition due to detector limits. X-rays below or near the chlorine are not identified because they are absorbed in either the detector window atmosphere or though any filter used. A possible limitation to running in this configuration is that low energy X-rays from low Z elements attenuated in air. The spectrum in above started from peak of Cl because \(K_a = 2.622\) keV, because detector configurated limits starts from Cl element. From the element Cl
onwards, all the elements within the detector limits of X-rays, and all are detected in above spectrum of chanockite sample by using PIXE.

From this investigation of chanockite matrix composition, the idea of production cross sections of X-ray for low Z elements is required for quantitative analysis by PIXE method. This is a simplest and basic widely accepted universal expression of ionization cross-section for proton induced X-ray emission. The cross-sections of K and L shell ionization basing of incident proton energy and target atoms. In this, the K-shell X-ray production cross section should take an account for low-Z elements in the composition, are comparable when bombarded by incident slow protons with energies. All these results have significant for fundamental physics considerations as well as for low-energy PIXE (probably 1MeV-3MeV) and in general, for application in which thick targets need to be used. The applicability of these energies has certain advantages, especially when analyzing light elements because the bremsstrahlung background in the spectra is much lower and better within this proton energy region.

In thick-target LE-PIXE (E: 2-5 MeV), and all forms of X-ray analysis, the X-ray induced is a function of the ionization cross section for the K, L, and M electron shells. Numerical values of cross-sections for ionization measured data of protons are available in the literature. The cross-section values coming from ECPSSR theory for K-shell ionization are generally used in PIXE. The L-shell case is relatively more problematic than the K-shell case. It is required to convert calculating X-ray production cross-section to ionization cross-sections using L-sub shell fluorescence and Coster-Kronig yield.

For protons with low energy, the cross section is high for the K shells of low Z elements and the L shells of high Z elements, providing sufficient fluorescent yield for analytical purposes. For heavy elements (Z > 55), protons with low energy cannot ionize K-shell electrons (Hajivaliei, et. al., 1993) and analysis depends on the use of L X-ray lines from the above results. Such L X-ray spectra (Z > 55) are complicated and can be affected by interferences K X-rays from lighter elements greater than Z=20 in the above results of chanockite samples. Both spectral interferences (Pantelica, et. al., 2011) and complexity can lead to problematic and ambiguity in the interpretation of K-line spectra of low Z>20 elements, a problem that is exacerbated in relative L X-ray line intensities of higher Z elements. Also in thick-target light energy-PIXE, the proton beam is stopped by the sample, producing an important background radiation from proton scattering and matrix effects; this can obscure X-ray signals from elements present in low concentrations. Light energy-PIXE probes can provide in situ analysis with less spatial resolution, and lower limits of detection than that obtained by previous chanockite electron probe microanalysis. From the above results discussion of chanockite samples, light energy-PIXE is ideal for the analysis of trace elements (Z < 55) except above Z<17 using K X-ray lines of elements present in the above chanockite samples.

The K lines are used for elements 17 < Z < 55 in the above chanockite, and L X-ray lines are used for Z > 55. Below Fe, the minimum detection level increases due to the increasing attenuation of the X-rays with low energy 3MeV protons. At the beginning of Z>55, the minimum detection level increases due to decreasing efficiency of detection with increasing X-ray energy, compounded by decreasing X-ray yield with increasing Z. Normally PIXE is experimented out with energy dispersive spectrometers since micro beams of protons are not intense enough to exploit wave length dispersive spectrometers effectively. In order to protect the energy dispersive spectroscopy detector from radiation damage by the scattered proton beam, an absorber has been placed in front of the detector, which limits the detectable element to Z > 11 from previous literature. The greater penetration depth > 20 microns of 3 MeV energy protons typically used for PIXE also simplifies the X-ray yield measurements and self-absorption corrections. The 20 nA beam currents of proton required for analysis do not usually cause important damage to the specimens. Hence PIXE analytical method is a capable tool in its readily quantified, non-destructive, in situ multi-element analytical ability, with ppm sensitivity. PIXE commonly is in the 1 ppm range from the table-2 results and less spatial resolution for various elements in matrix composition when compared to other techniques.
In general, for low Z elements, the PIXE experiments-geological materials, two X-ray detectors placed at 135° geometry relative to the incident proton beam were used to detect the characteristic X-rays. Si (Li) detection with AP.3 ultra-thin polymer window (SGX Sensortech) with active surface area 30 mm2 was employed to detect low and medium Z elements energy X-rays (0.2–12 keV, Z > 5). A detector is protected by a permanent magnet from the scattered protons. Si (Li) with Gresham type Be windowed X-ray detection with an active surface area 30 mm2 equipped, adding kapton filter of thickness 125 μm was employed to measure the medium and high Z energy X-rays (3–30 keV, Z < 19). The detection limit values decreased from 300 to 30 ppm in the Na to Ca range and for the trace elements, the limit of detection varied from 10 to 50 ppm, which is typical for this arrangement.

At first, the composition of the matrix was calculated from the spectrum of the Si (Li) detector using the iterative matrix solution method, and then the spectrum of the Be windowed detector was analysed in trace element mode, using the previously obtained matrix and the measured irradiation dose. The X-ray energy range of 3.0–8.5 keV is common for the two PIXE detectors, therefore intensive X-ray lines within this range (e.g. Cl – below Ba) were used to normalize the elemental concentrations. Analyses of reference materials were carried out in the beginning and at the end of the measurement work in order to check the accuracy of the dose calculation and of the precision and accuracy of the PIXE system.

In the mineral prospecting-geochemistry, using PIXE and complementary techniques, PIXE showed better results at middle Z elements except interferences, along with other complementary analytical tools (Satyanarayana, et al., 2020). PIXE is very well suitable for the analysis of geo samples except few situations for low Z element analysis and high Z elements due to cross sections, the substituted analytic technique of particle-induced γ-radiation (PIGE) or NRA used at the low Z elements (Ene, et al., 2005).

5. Conclusions

From the investigation of PIXE, low Z elements detection is possible through K-X-rays. But these K-X-rays at low Z elements have less energetic which are lies in between 0 to 2 keV and detection is not possible in the above study though the Si (Li) detectors. Si (Li) detector with low diameter detection provide better energy resolution of elements at low characteristic X-ray energies, and the thicker detectors have better detection efficiency at energies of the X-rays above about 20 keV. The X-ray enters the cryostat through a thin beryllium window to reach the detector. The Be windows of detectors are typically 8–25.4 μm thick. The thickness of the window sets the lower energy limit for photons that can be detected by the detector.

The limitation of PIXE at 3 MeV is that below or near the Cl from spectrums of PIXE are not detected at all in this work due to low energy X-rays from low Z elements, because they are absorbed in either the detector window, atmosphere or through any filter used. Therefore the elements Li, Be, F, Na, Mg, Al, Si and P present in Charnockites are not detected due to the above explanation.

In case of PIXE analysis, maximum number of the elements present in charnockites, interference is encountered between the Kα of next element X-ray and the Kβ of previous element X-ray, which have virtually the near or same energy and also between the X-ray K lines of media elements and X-ray L lines of heavy elements. PIXE experimental work on minerals has used 3 MeV proton beams for excitation and low-energy normally uses the K-X-ray for low Z and L X-rays for high Z analysis. The present resulting spectra of charnockite rock can require stripping techniques to resolve overlap problems between light and heavy elements on the applications of light energy-PIXE using Si (Li) detector.

Si (Li) detection with AP.3 ultra-thin polymer window (SGX Sensortech) with active surface area 30 mm2 was employed to detect low and medium Z elements energy X-rays (0.2–12 keV, Z > 5). A detector is protected by permanent magnet from the scattered protons. Si (Li) with Gresham type Be windowed X-ray detection with 30
mm² active surface area equipped adding kapton filter of thickness 125 μm was employed to detect the medium and high Z energy X-rays (3–30 keV, Z < 19).

Both complexity due to the interferences and detector efficiency can lead to problematic and ambiguity in the conclusion of spectra, a problem that is exacerbated by uncertainty in relative K X-ray line intensities of low Z elements. From this experimental investigation, the LE-PIXE is suitable for the analysis of low Z < 55 elements except very low Z elements (Z<17) only using K X-ray lines without high Z elements present in geological samples. PIXE is very well suited for the analysis of geological samples except few conditions like above and for low Z element analysis, hence the complementary technique of particle-induced γ-ray emission or NRA is required at complex matrix composition-low Z elements.

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 thank to my Prof. Y. Rama Krishna, Head of the Department, Engineering Physics, Andhra University, Visakhapatnam and Prof. K. Chandra Mouli, Senior Professor, Engineering Physics Department. 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., (2016) 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.

[2] Ene. A., Popescu, I. V., Badica, T., Besliu, C., (2005) Comparative study of PIGE, PIXE and NAA analytical techniques for the determination of minor elements in steels. Romanian Reports in Physics. 51(5-6), pp. 595.

[3] Felix, S Olise., Oyediran, K Owoade., Solomon, A Adekola., Hezekiah, B Olaniyi., Christopher, B Mtshali., Wojciech, J Przybylowicz., Carlos, A P Vargas., Malik, Maaza, (2017) A combination of μ-PIXE, XRF, SEM-EDS and XRD Techniques in the Analyses of Sn-Mine Tailings. Journal of Radiation and Nuclear Applications. 2, No. 3, pp. 95-102.

[4] Hajivaliei, M., Adam, J., Green, T H., and Sie, S H., (1993) Proton microscope determined partitioning of Rb, Sr, Ba, Y, Zr, Nb and Ta between experimentally produced amphiboles and silicates melts with variable F content. Chem. Geol. 109, 29-49.

[5] Javier, M., (1996) Low energy PIXE: advantages, drawbacks, and applications. Nuclear Instruments and Methods in Physics Research B: Beam Interactions with Materials and Atoms. 118, pp. 346-351.

[6] Kamineni, D.C., Bandari, M., Rao, A.T. (1982) Halogen-bearing minerals from Airport Hill, Visakhapatnam, India. American Mineralogist. 67, pp. 1001-1004.

[7] Kabir, M.H., (2007) Particle Induced X-ray Emission (PIXE) Setup and Quantitative Elemental Analysis (Ph.D. Dissertation) Kochi University of Technology Japan.

[8] Mac Arthur, J. D., and Xin-Pei, Ma., (1991) A review of Particle Induced X-ray Emission in geology. International PIXE. 1, pp. 311-338.
[9] Maxwell, J. A., Teesdale, W., Campbell, J.L., (1995) The Guelph PIXE software package II. Nuclear Instruments and Methods in Physics Research B: Beam Interactions with Materials and Atoms. 95, pp. 407-421.

[10] Norman, M. Halden., John, L. Campbell., William, J. Teesdale (1995) PIXE analysis in mineralogy and geochemistry, The Canadian Mineralogist. 33, pp. 293-302.

[11] Olabanji, S.O., Haque, A. M. I., Zandolin, S., Ajay, T., Buoso, M. C., Ceccato, D., Cherubini, R., Zafiropoulos, D., Moschini, G., (1996) Applications of PIXE, PIGE, SEM and EDAX techniques to the study of geological samples. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms. 109-110, pp. 262-265.

[12] Pantelica, Ana., Ene, Antoaneta., Gugiu, M., Ciortea, C., Constantinescu, O., (2011) PIXE Analysis of some vegetable species. Romanian Reports in Physics. 63, No. 4, pp. 997–1008.

[13] Rao, A.T., and Babu., V.R.R.M., (1978) Allanite in Charnockites rock airport hill near Visakhapatnam, Andhra Pradesh. American Mineralogist. 63, pp. 330-331.

[14] Rao, K. S. R., Rao, A.T., and Sriramada., A., (1969) Porphyritic plagioclase-hornblende-pyroxene granulite from charnockitic rocks of Chipurupalli, Visakhapatnam district, Andhra Pradesh, South India, Mineral Geological Magazine.. 37, No. 288.

[15] Rao, A. T., Rao, J. U., Yoshida, Masaru., (1993) Geochemistry and Tectonic Evolution of the Pyroxene Granulites from Visakhapatnam Area in the Eastern Ghats Granulite Belt, India Journal of Geosciences, Osaka City University. 36(7), p. 135-150.

[16] Satyanarayana, A. V. S., Ravi Kumar, S., Sharma, S. V. R. A. N., (2016) 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.

[17] Satyanarayana, A. V. S., Jagannadhara, M., Chandra Mouli, K., Seetarami Reddy, B., (2019) The Performance of PIXE Technique through a Geochemical Analysis of High Grade Rocks. Journal of Nuclear Physics, Material Sciences, Radiation and Applications. 7(1), 13-28.

[18] Satyanarayana, A. V. S., Jagannadhara Rao, M., Chandra Mouli, K..., Sai Satya Mounika, K., (2020) Performance of PIXE Technique at Elemental Analysis of Halogens in Charnockite Matrix, International Journal of Scientific Research in Physics and Applied Sciences. 8(4), pp.1-6.

[19] Satyanarayana, A. V. S., Jagannadhara Rao, M., Sai Satya Mounika, K., (2020) Need of Complementary Analytical Technique at PIXE-Complex Matrix Composition Analysis, International Journal of Scientific Research in Physics and Applied Sciences. 8(3), pp.36-40.

[20] Szegedi, S., Ibrahim, S. M., (1996) J. Radioanal. Nucl. Chem., Possible use of low voltage accelerators in PIXE analysis. pp. 201-210.

Conflict of Interest; Authors have no conflict of interest

Code and Data Availability;

Satyanarayana, A V S., Jagannadharao, M., Chandra Mouli, K., Seetarami Reddy, B. (2020). The Performance of PIXE Technique through a Geochemical Analysis of High Grade Rocks. Journal of Nuclear Physics, Material Sciences, Radiation and Applications. 7(1), 13-28. https://doi.org/10.15415/jnp.2019.71002
Satyanarayana, A V S. Ravi Kumar, S and Sharma, S.V.R.A.N. (2016) 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. https://doi.org/10.15415/jnp.2016.32016

Competing interests:-
Sir, this is a part of research work at Andhra University, Visakhapatnam, and Andhra Pradesh, India. The topic related to material analysis by using PIXE technique and also the limitations of technique. The limitation arises due to selecting material which is very complex matrix material. Also it gives the idea where the PIXE fails to determine the elements, simultaneously gives the idea of another complementary technique which is used to give the complete analysis of the complex materials.

Authors have no conflict of interest

Funding:-
No funding, it is my own research work under the guidance of Prof. M. Jagannadha Rao

Authors’ contributions:-
The first author Dr. A.V.S. Satyanarayana, being a Nuclear Physics graduate he is instrumental in the design of the experiment, sample preparation, selection of appropriate standards for the PIXE analysis, having discussions with the scientists of PIXE facility to come up with standard analytical conditions for the rock with complex matrix to be analyzed that is charnockite and compared with complementary present AAS & previous others. He contributed all the technical aspects of PIXE analytical work, including physically working with experts at PIXE facility.

The second author Prof. M. Jagannadha Rao is a Geologist having vast knowledge of Eastern Ghats from which the analyzed Rock samples of charnockites are collected. His contribution is selection of standard samples from field keeping in mind the sample location which is very important in understanding its genesis, based on the geochemical data obtained from PIXE. He also suggested suitable international standards which are close to the charnockite. Both the authors together finalized the data, including error calculation, interpretation and formatting the paper.

The third author Prof. B. Seetharami Reddy is a Physicist having vast knowledge of Nuclear Techniques especially in PIXE from which the analyzed Rock samples of charnockites are collected. His contribution is selection of standard samples and analysis from field keeping in mind the sample location which is very important in understanding its genesis, based on the geochemical data obtained from PIXE spectrum and experimental factors. He also suggested suitable international standards which are close to the charnockite.