



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

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11 **Abstract**

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

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

31 **Introduction**

32 It has already been shown that the mineralogy and petrography of the charnockite gneiss in the study area are
33 similar to that of metamorphosed igneous rocks with a basic affinity. Presence of characteristic minerals like
34 almandine garnet, pyroxenes indicates that the charnockite gneiss is a high grade metamorphic rock. In this section
35 it is proposed to study its major and trace element chemistry with an object of understanding more about its genesis.
36 Pyroxene granulites are reported in all Precambrian high grade terrains, but little is known about the chemical
37 characteristics of these rocks and their precursors. In the limited studies published on this problem both igneous and
38 sedimentary origins were reported from the Eastern Ghats granulites belt, India and have described the pyroxene
39 granulites from Visakhapatnam and also presented the minor, major and REE data in inferring the tectonic
40 environment and nature of magma. However, the present investigation supplements in establishing the origin of
41 pyroxene granulites based on minor, major and trace element geochemistry using discriminate functions.



42 Application of research tools such as X-ray diffraction, Electron Micro Probe Analysis, Scanning Electron
43 Microscopy, Particle Induced Gamma ray Emission, Neutron Activation Analysis, X-ray Fluorescence etc. on
44 routine basis are important supplements to present microscopic studies and analysis, although it should be stressed
45 that these traditional methods remain essential in any study. More recently other innovative beam technique PIXE
46 playing an important role in case of interesting geo chemical evaluation. Such technique permits detection limits of
47 trace elements in geological materials not believed possible some years ago, and with increasingly good resolution,
48 precision, accuracy and nondestructive. Very few researches were undertaken in geochemical analysis of geological
49 material by using PIXE analysis and a survey of previous literature shows that the PIXE technique has been used by
50 few several researchers for the multi elemental analysis of geological materials.

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

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

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

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



87 has its own ionisation physics but shares the fluorescence (or, equivalently, Auger) probabilities with the other
88 atomic excitation methods.

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

97 2. Experimental Details

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

107 With respect to the proton beam direction, the samples which are to be excited are positioned on the target
108 holder at an angle of 45⁰ in this scattering chamber. The target position with respect to the beam direction is adjusted
109 properly by viewing through a window beryllium of 0.1 mm thickness provided on the scattering chamber. The
110 direction is placed at an angle of 90⁰ with respect to the beam direction also placed in the chamber at an angle of
111 135⁰ with respect to the beam direction. The Si (Li) X-ray detection output is connected to system of data
112 acquisition which gathers the X-ray spectrum. The spectrum of each sample is noted for a sufficiently enough time
113 so as to achieve valuable statistics.

114 The Guelph PIXE (GUPIX) (Maxwell, et. al., 1995) software package is employed to analyze the spectrums
115 utilizing a standard Marquardt non-linear least square fitting procedure. This software package advantages is to
116 identify different elemental quantifications present in the target material and to calculate their relative intensities.
117 Using this GUPIX software package the X-ray intensities of different elements are changed into the respective
118 quantifications using a standardized technique involving fundamental parameters, pre-determined instrument
119 constants and input parameters such as solid angle, beam current etc. Comparing the quantification values of
120 Yttrium achieved in the present work with the known concentration of Yttrium added to the sample, the working
121 condition of a various experimental factors of input are verified (Satyanarayana, et. al., 2016).

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

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129 3. Related work

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

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

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

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154 It has been concluded that some of the elements present in charnockite samples by using PIXE analysis are
155 completely measured or could not be measured at all, due to various experimental factors including the matrix
156 composition [5]. It is felt that a proper study needs to be explaining the limitation of PIXE in certain low Z elements.
157 The high-grade metamorphic charnockite rocks selected are analyzed both by PIXE as well as complimentary
158 previous technique and the results are authenticated by using a USGS Basalt reference material and studies of
159 charnockite literature. It is believed that the accuracy of problematic low Z elements (Satyanarayana, et. al., 2019),
160 especially from high grade rock can be improved and the conditions of PIXE can be standardized for various
161 elements under different combinations. The reasons behind the working condition at low Z elements using Proton
162 Induced X-ray Emission have been established.

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

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4. Results and Discussions

Table-1; USGS Standard reference material (verified by PIXE)

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



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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	2229±25.9	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	9.118±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	8.717±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±65±2.5	BDL	BDL	0.9499±1.7	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	9.08±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	33.91±4.9	35.53±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	77.82±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

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181 Table-3; Analytical results of charnockites of same area of previous techniques and present PIXE

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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	Na ₂ O=1.591(Wt%)	-
Mg	12	ND	MgO=4.022(Wt%)	MgO=1.18(Wt%)
Al	13	ND	Al ₂ O ₃ =18.137(Wt%)	Al ₂ O ₃ =14.79(Wt%)
Si	14	ND	SiO ₂ =50.345(Wt%)	SiO ₂ =31.24(Wt%)
P	15	ND	P ₂ O ₅ =0.213(Wt%)	-
Cl	17	424.2±18.62ppm	0.130ppm	-
K	19	4887.28±29.91ppm	K ₂ O=0.428(Wt%)	-
Ca	20	2808±26.31ppm	CaO=11.376(Wt%)	CaO=11.01(Wt%)
Sc	21	ND	23ppm	150ppm
Ti	22	1133.09±10.97ppm	TiO ₂ =1.314(Wt%)	TiO ₂ =1.62(Wt%)
V	23	18.26±5.88ppm	240ppm	V ₂ O ₃ =0.09(Wt%)
Cr	24	18.31±2.4ppm	180ppm	70ppm
Mn	25	31.934±4.1ppm	MnO=0.089(Wt%)	MnO=0.28(Wt%)
Fe	26	5961.42±21.5ppm	Fe ₂ O ₃ =1.123(Wt%) FeO =10.649(Wt%)	Fe ₂ O ₃ =5.10(Wt%) FeO=8.49 (Wt %)
Co	27	ND	74ppm	150ppm
Ni	28	13.755±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
Se	34	3.65±2.1ppm	-	-
Br	35	9.92±3.45ppm	-	-
Rb	37	47.36±6.37ppm	66.52ppm	-
Sr	38	35.26±5.37ppm	325ppm	480ppm
Y	39	15.385±4.75ppm	-	*Y ₂ O ₃ = 0.15 (Wt%)
Zr	40	43.64±7.41ppm	78ppm	*ZrO ₂ =0.15(Wt%)
Nb	41	7.6±3.43ppm	-	900ppm
Mo	42	17.59±5.17ppm	-	60ppm
Ru	44	9.97±3.59ppm	-	-
Ag	47	12.36±9.0ppm	-	-
Sn	50	ND	-	*SnO ₂ =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	*ThO ₂ = 0.50(Wt%)
U	92	ND	2.83ppm	*U ₃ O ₈ =0.01 (Wt%)
REE	57 to71	ND	-	*(Ce,La,Nd) ₂ O ₃ = 23.29(Wt%)



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184 The PIXE analysis of the charnockite samples G1 to G7 collected from the interior of the Charnockite hill are
185 obtained by Si (Li) detector. These quantification values are presented with errors in table-2 assuming standard
186 deviation values ($n = 7$ and BDL (Below Detection Limit). The results obtained from PIXE analysis-charnockite
187 composition compared with the previously experimented analytical tools (Rao, et. al., 1969, Rao, et. al., 1978,
188 Kamineni, et. al., 1982, Rao, et.al., 1993) shown in table-3 for review (Mac Arthur and Xin-Pei, 1991) of low Z
189 elements present in the complex matrix charnockite composition.

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

196 In the previous analytical results, the low Z elements in charnockite composition are started from analysis Li
197 and Be, but these are not detected in this present PIXE at 3MeV spectrum because of low energy K X-rays induced
198 from low Z elements in charnockite, and these are absorbed by detector window of the Si (Li) detection and in
199 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-
200 rays, $Z=72$ to 83.
201

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

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

222 Therefore, PIXE unable to detect the low Z elements present like, Li, B, F, Na, Mg, Al, Si and minor P in
223 charnockite composition due to detector limits. X-rays below or near the chlorine are not identified because they are
224 absorbed in either the detector window atmosphere or though any filter used. A possible limitation to running in this
225 configuration is that low energy X-rays from low Z elements attenuated in air. The spectrum in above started from
226 peak of Cl because $K\alpha = 2.622$ keV, because detector configured limits starts from Cl element. From the element Cl



227 onwards, all the elements within the detector limits of X-rays, and all are detected in above spectrum of chanoackite
228 sample by using PIXE.
229

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

239 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
240 ionization cross section for the K, L, and, M electron shells. Numerical values of cross-sections for ionization
241 measured data of protons are available in the literature. The cross-section values coming from ECPSSR theory for
242 K-shell ionization are generally used in PIXE. The L-shell case is relatively more problematic than the K-shell case.
243 It is required to convert calculating X-ray production cross-section to ionization cross-sections using L-sub shell
244 fluorescence and Coster-Kronig yield.

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

258 The K lines are used for elements $17 < Z < 55$ in the above chanoackite, and L X-ray lines are used for $Z > 55$.
259 Below Fe, the minimum detection level increases due to the increasing attenuation of the X-rays with low energy
260 3MeV protons. At the beginning of $Z > 55$, the minimum detection level increases due to decreasing efficiency of
261 detection with increasing X-ray energy, compounded by decreasing X-ray yield with increasing Z. Normally PIXE
262 is experimented out with energy dispersive spectrometers since micro beams of protons are not intense enough to
263 exploit wave length dispersive spectrometers effectively. In order to protect the energy dispersive spectroscopy
264 detector from radiation damage by the scattered proton beam, an absorber has been placed in front of the detector,
265 which limits the detectable element to $Z > 11$ from previous literature. The greater penetration depth > 20 microns of
266 3 MeV energy protons typically used for PIXE also simplifies the X-ray yield measurements and self-absorption
267 corrections. The 20 nA beam currents of proton required for analysis do not usually cause important damage to the
268 specimens. Hence PIXE analytical method is a capable tool in its readily quantified, non-destructive, in situ multi-
269 element analytical ability, with ppm sensitivity. PIXE commonly is in the 1 ppm range from the table-2 results and
270 less spatial resolution for various elements in matrix composition when compared to other techniques.



271 In general, for low Z elements, the PIXE experiments-geological materials, two X-ray detectors placed at 135°
272 geometry relative to the incident proton beam were used to detect the characteristic X-rays. Si (Li) detection with
273 AP.3 ultra-thin polymer window (SGX Sensortech) with active surface area 30 mm² was employed to detect low
274 and medium Z elements energy X-rays (0.2–12 keV, Z > 5). A detector is protected by permanent magnet from the
275 scattered protons. Si (Li) with Gresham type Be windowed X-ray detection with an active surface area 30 mm²
276 equipped, adding kapton filter of thickness 125 μm was employed to measure the medium and high Z energy X-rays
277 (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
278 elements, the limit of detection varied from 10 to 50 ppm, which is typical for this arrangement.

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

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

291 5. Conclusions

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

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

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

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



313 mm² active surface area equipped adding kapton filter of thickness 125 μm was employed to detect the medium and
314 high Z energy X-rays (3–30 keV, Z < 19).

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

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385 **Code and Data Availability;**

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393 **Competing interests:-**

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

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402 **Authors' contributions:-**

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

409 The second author Prof. M. Jagannadha Rao is a Geologist having vast knowledge of Eastern Ghats from which
410 the analyzed Rock samples of charnockites are collected. His contribution is selection of standard samples from
411 field keeping in mind the sample location which is very important in understanding its genesis, based on the
412 geochemical data obtained from PIXE. He also suggested suitable international standards which are close to the
413 charnockite. Both the authors together finalized the data, including error calculation, interpretation and formatting
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415 The third author Prof. B. Seetharami Reddy is a Physicist having vast knowledge of Nuclear Techniques especially
416 in PIXE from which the analyzed Rock samples of charnockites are collected. His contribution is selection of
417 standard samples and analysis from field keeping in mind the sample location which is very important in
418 understanding its genesis, based on the geochemical data obtained from PIXE spectrum and experimental factors.
419 He also suggested suitable international standards which are close to the charnockite.

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