





41 The charnockite series is a group of igneous rocks French, et. al., (2008) variably  
42 metamorphosed. They are widely distributed and occupy an important place in the geology of  
43 India is the main sources for creation of continental crust. Calc-alkaline rocks typically are  
44 found above subduction zones, commonly in volcanic areas, and particularly on such area on  
45 continental crust. A widely accepted theory of the development of earth's crust states that the  
46 early earth would have had a proto crust formed from ultra mafic and felsic layers.

47  
48 The samples analysed using PIXE in the present study are collected in a very  
49 interesting context. Geologically the Visakhapatnam city is characterized by rocks termed as  
50 Eastern Ghats. The rocks are Precambrian age and comprise mainly Khondalites, Lepitynites,  
51 Poryxene Granulites and Charnockites and all of them have undergone metamorphosis.  
52 Among these, charnockites are termed as upper mantle basic igneous rocks and are emplaced  
53 into proto crustal rocks during Precambrian times. In this way the charnockites sometimes  
54 may contain the relict bodies of earlier crustal rocks (proto crust).The proto crust is derived  
55 from primitive oceans which are also called intra-cratonic sea water bodies.

56  
57 The samples chosen for analysis are collected from the central portion of a charnockite  
58 hill Rao, and Babu, (2008) near Visakhapatnam airport during a demolition operation for  
59 extension of the airport. A big lenticular mass of relict lithological body which is  
60 compositionally and physically different from the host charnockite was observed in this  
61 central portion of the hill. This body is believed to be the caught up body of the early crustal  
62 layer (possibly proto crust).Such samples are rare. PIXE technique is chosen for the trace  
63 elemental analysis Kullerud, and Steffen, (1979) of these rare samples as it is a highly  
64 sensitive and non destructive method for the simultaneous multi elemental analysis. Elements  
65 present in ppm levels can be detected efficiently with this technique.

66  
67 The experimental work was carried out using the 3Mev particle accelerator facility at  
68 the institute of physics, Bhubaneswar. The characteristic X-rays were detected with Si (Li)  
69 detector. The data analysis was carried out and concentrations of various elements detected  
70 were determined using GUPIX software and different elements were detected in varied  
71 concentrations. On the basis of the concentrations of these different trace elements obtained  
72 using PIXE Technique, a geochemical analysis of the rock samples was performed and  
73 interpreted for the genetic significance substantiating the information from previous  
74 literature.

## 75 76 **2. Experimental Details and Data Analysis.**

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78 Some of the trace elements are present in minute amounts in geological samples. Earlier  
79 it was very difficult to measure their precise concentrations because of non availability of  
80 sophisticated analytical methods. They were therefore described as occurring in traces, hence  
81 the term 'trace element'. With the invention of many modern analytical techniques Sie, et. al.,  
82 (1989) like Atomic Absorption Spectrometry (AAS) Instrumental Neutron Activation  
83 Analysis (INAA), Rutherford Back Scattering (RBS), X-Ray Fluorescence (XRF),Energy  
84 Dispersive X-Ray Fluorescence (EDXRF), Auger Electron Spectroscopy (AES), Particle  
85 Induced Gamma Ray Emission (PIGE),Particle Induced X-Ray Emission (PIXE),  
86 Wavelength Dispersive X-Ray Fluorescence (WDXRF) etc. It has become possible to  
87 estimate the concentrations of trace elements in ppm and ppb levels. These analytical  
88 techniques have the capability to measure all the trace elements present even in the smallest  
89 geological samples Malmqvist, (1987) with great precession and accuracy. The term trace is a



90 traditionally followed through it has become scientifically obsolete owing to the availability  
91 improved techniques. Among all the afore-mentioned techniques, PIXE Technique has its  
92 own advantages over the other techniques. From analytical point of view, techniques for the  
93 identification of trace elements and evaluation of their concentrations are categorized into  
94 destructive and non destructive techniques. Tangi, (1998) Chemical analysis and AAS are the  
95 two well known methods under the former category. Generally these methods require large  
96 amounts of sample and are tedious as they involve element-by-element analysis.

97  
98 PIXE and XRF are the both the methods based on x-ray emission are have several  
99 features in common. From sensitive point of view PIXE has certain superiority .Moreover the  
100 bremsstrahlung produced in PIXE is a secondary effect and hence is also the principle  
101 determinant of detection limits. The low bremsstrahlung in PIXE enables parts per million  
102 sensitivities, superior to its sister techniques. Due to high sensitivity and multi elemental  
103 analysis capability, PIXE has found applications in trace elemental analysis Luciana (1999)  
104 of samples from almost every conceivable field of scientific or technical interest. Some of  
105 these fields are Biomedicine, Environment, Archaeology, Material science, Forensic studies,  
106 Industrial applications and Geology.

107  
108 The present study is aimed at estimating the concentrations of different trace elements  
109 in geological samples of Precambrian charnockite hill near Visakhapatnam airport using  
110 particle induced X-ray emission (PIXE) technique. These experiments are carried out using  
111 3MV pelletron accelerator facility at the Institute of physics, Bhubaneswar. Protons with  
112 3Mev energy are used to excite the samples. The samples are mounted on an Aluminium  
113 target holder (a ladder arrangement).Then the target holder is inserted into the scattering  
114 chamber and the irradiation is carried out in vacuum conditions. A collimated proton beam of  
115 2 mm diameter is made to fall on to the sample. The beam current is kept at 20 nA. The  
116 samples on the target holder which are to be excited or positioned in this scattering chamber at  
117 an angle of  $45^{\circ}$  with respect to the direction of the proton beam. The position of the sample  
118 relative to the beam direction is adjusted properly by viewing through a window provided in  
119 the scattering chamber. A high resolution Si (Li) detector (160 eV FWHM at 5.9 KeV  
120 energy) is employed in the present experiments to record the X-ray spectrum. The detector is  
121 placed at an angle of  $90^{\circ}$  with respect to the beam direction. The output of the Si (Li) detector  
122 is coupled to data acquisition system, which records the X-ray spectrum. The spectrum of  
123 each sample is recorded for a sufficiently long time so as to ensure good statistics. During  
124 the irradiation of each sample the charge collected and the average beam current is noted.

125  
126 The Guelph PIXE (GUPIX) software package is used to analyse the spectra utilizing a  
127 standard Marquardt non-linear least square fitting procedure. This package is provision to  
128 identify different elements present in the sample and to estimate their relative intensities.  
129 Using this GUPIX software package the X-ray intensities of different elements are converted  
130 into the respective concentrations using a standardization technique involving fundamental  
131 parameters, pre determined instrument constants and input parameters such as solid angle,  
132 charge collected etc. Comparing the concentrations of Yttrium obtained in the present work  
133 with the known concentration of Yttrium added to the sample, the reliability of the input  
134 parameters is checked. To assure the reliability of experimental system and other parameters,  
135 in the same experimental conditions, the PIXE spectrum is recorded with NIST certified  
136 reference material and the relative concentrations of different elements are estimated using  
137 GUPIX software package. The relative concentrations of different elements thus obtained in  
138 the present experiment for the above standard samples are compared with the certified  
139 concentrations supplied by NIST. Good agreement Table-1 with in experimental uncertainties



140 is observed and this shows the reliability of the present experimental system and use of  
 141 GUPIX software package in the data analysis.

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143 Table-1. PIXE spectrum is recorded with NIST certified reference material-Apple Leaves-  
 144 1515.

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

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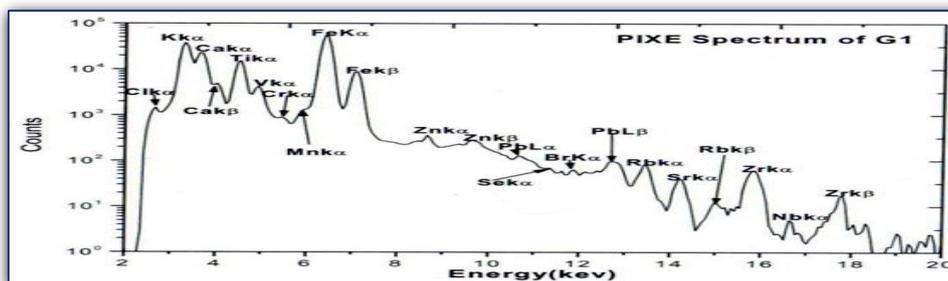
148 This deals with the detailed explanation of the advantages of PIXE over other analytical  
 149 techniques, principle and technical minutiae of the PIXE technique, experimental setup,  
 150 sample preparation and data analysis.

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### 152 3. Results and discussions

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154 The PIXE spectrum fig; 1-7 of the geological samples G1 to G7 collected from the  
 155 interior of the charnockite rock recorded by Si (Li) detector. The concentrations in ppm of  
 156 these various elements in each sample were determined using the GUPIX software .These  
 157 concentrations are presented with errors in tables 2-13.



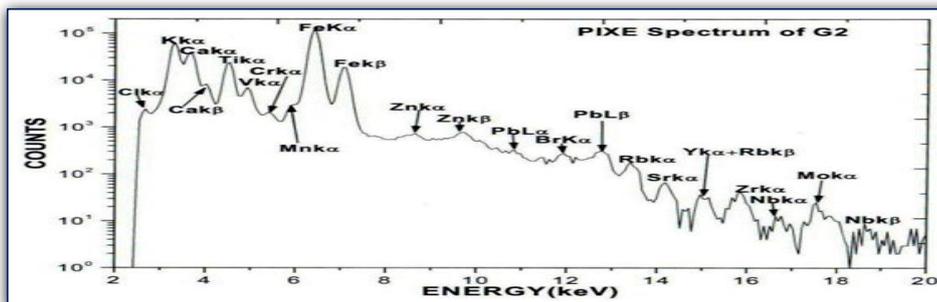
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Figure-1; PIXE Spectrum of sample G1

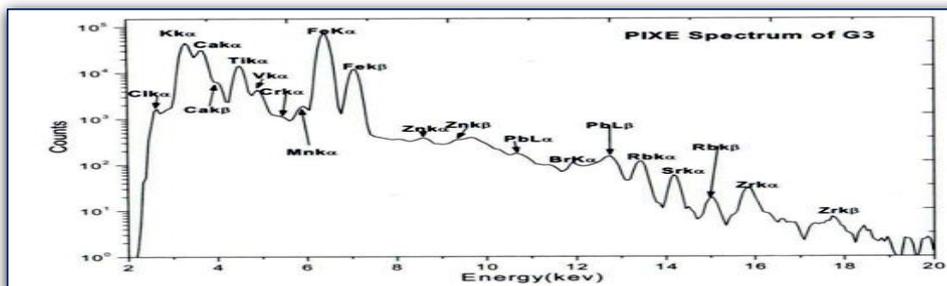


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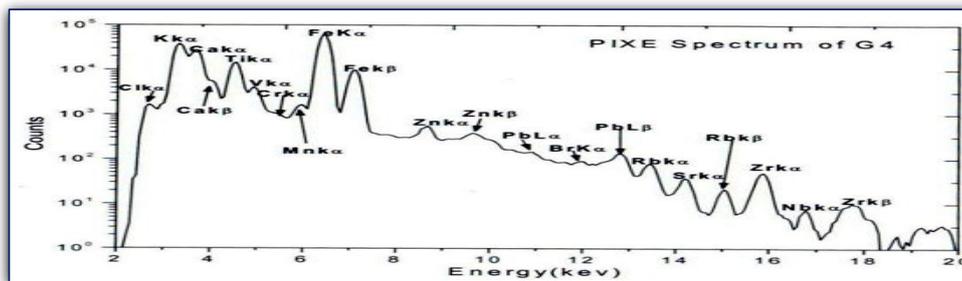
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Figure-2; PIXE Spectrum of sample G2



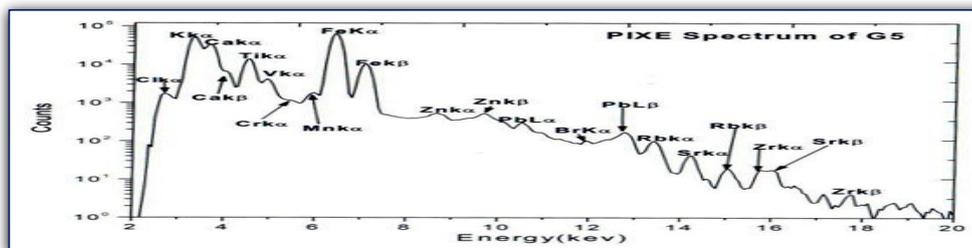
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Figure-3; PIXE Spectrum of sample G3



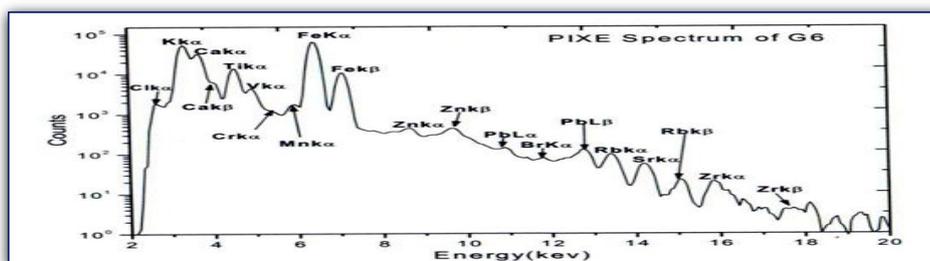
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Figure-4; PIXE Spectrum of sample G4



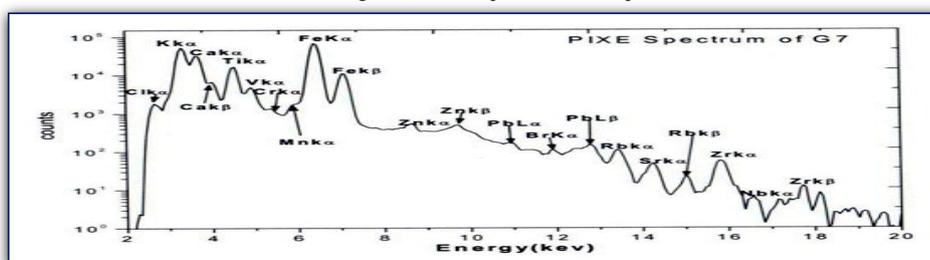
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Figure-5; PIXE Spectrum of sample G5



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Figure-6; PIXE Spectrum of sample G6



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Figure-7; PIXE Spectrum of sample G7

174 The PIXE spectrum of the geological samples G1 to G7 collected from the interior of  
175 the Charnockite rock recorded by Si (Li) detector. These concentrations are presented with  
176 errors in Table-9. Another attempt is made to analyze the samples using an atomic absorption  
177 photo spectrometer and same elements are reported using the method of AAS and the same  
178 standard also employed for a method of AAS also. The data generated the AAS method has  
179 been used to compare the PIXE results for its evaluation purpose. In this paragraph, each  
180 element is considered in evaluating PIXE as per that element is concentrated. It is observed  
181 that the results obtained by AAS are close which already published data on Charnockites in  
182 various journals.

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184 The possibility of increasing accuracy of PIXE in analysing samples of complex  
185 matrix like Charnockite has been discussed and suggestions are made. So, the following  
186 tables presents the elements which are close to elements having moderate errors and elements  
187 which are highly erroneous not detected. Using this data, the Charnockite hill from where the  
188 samples are collected has been attempted. to understand the chemical nature followed by  
189 genetic implications. The reasons behind the poor performance of PIXE with respect to  
190 certain elements have been tried to explain.

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202 Table-2; G1 sample elements and  
203 concentrations  
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<i>S.NO</i>	<i>Element</i>	<i>G1</i>
<i>1</i>	Cl	394.1±16.5
<i>2</i>	K	4080±28.2
<i>3</i>	Ca	2229±25.9
<i>4</i>	Ti	1394±11.6
<i>5</i>	V	17.92±4.8
<i>6</i>	Cr	16.63±2.3
<i>7</i>	Mn	18.623.9±
<i>8</i>	Fe	5200±20.3
<i>9</i>	Ni	10.96±3.7
<i>10</i>	Cu	BDL
<i>11</i>	Zn	9.147±3.3
<i>12</i>	Se	6.3±65±2.5
<i>13</i>	Br	4±2.2
<i>14</i>	Rb	48.87±6.0
<i>15</i>	Sr	38.5±5.4
<i>16</i>	Y	BDL
<i>17</i>	Zr	95.91±9.8
<i>18</i>	Nb	7.035±3.1
<i>19</i>	Mo	BDL
<i>20</i>	Ru	BDL
<i>21</i>	Ag	BDL
<i>22</i>	Pb	32.93±15.6

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207 Table-3; G2 sample elements and  
208 concentrations  
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<i>S.No</i>	<i>Element</i>	<i>G2</i>
<i>1</i>	Cl	399.6±17.1
<i>2</i>	K	4187±25.1
<i>3</i>	Ca	2281±22.8
<i>4</i>	Ti	1271±9.3
<i>5</i>	V	23.69±4.1
<i>6</i>	Cr	38.53±2.1
<i>7</i>	Mn	34.71±3.7
<i>8</i>	Fe	6575±21.0
<i>9</i>	Ni	11.43±3.7
<i>10</i>	Cu	BDL
<i>11</i>	Zn	18.21±3.5
<i>12</i>	Se	BDL
<i>13</i>	Br	12.17±2.93
<i>14</i>	Rb	42.08±6.1
<i>15</i>	Sr	28.6±4.6
<i>16</i>	Y	12.64±4.5
<i>17</i>	Zr	20.86±6.0
<i>18</i>	Nb	9.812±3.9
<i>19</i>	Mo	24.34±6.3
<i>20</i>	Ru	BDL
<i>21</i>	Ag	12.36±9.0
<i>22</i>	Pb	38.35±17.3

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213 Table-4; G3 sample elements and  
214 concentrations  
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<i>S.NO</i>	<i>Element</i>	<i>G3</i>
<i>1</i>	Cl	379±16.5
<i>2</i>	K	4148±26.1
<i>3</i>	Ca	2637±25.6
<i>4</i>	Ti	1109±9.3
<i>5</i>	V	7.85±4.0
<i>6</i>	Cr	15.16±2.1
<i>7</i>	Mn	34.31±3.7
<i>8</i>	Fe	5649±19.8
<i>9</i>	Ni	10.06±3.39
<i>10</i>	Cu	6.1±2.7
<i>11</i>	Zn	14.23±3.0
<i>12</i>	Se	BDL
<i>13</i>	Br	11.82±2.85
<i>14</i>	Rb	62.73±6.0
<i>15</i>	Sr	44.61±4.9
<i>16</i>	Y	BDL
<i>17</i>	Zr	23.6±6.1
<i>18</i>	Nb	BDL
<i>19</i>	Mo	BDL
<i>20</i>	Ru	BDL
<i>21</i>	Ag	BDL
<i>22</i>	Pb	17.68±7.7

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218 Table-5; G4 sample elements and  
219 concentrations  
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<i>S.NO</i>	<i>Element</i>	<i>G4</i>
<i>1</i>	Cl	403.5±19.5
<i>2</i>	K	4246±29.3
<i>3</i>	Ca	2754±28.1
<i>4</i>	Ti	13.67±11.3
<i>5</i>	V	BDL
<i>6</i>	Cr	16.93±2.5
<i>7</i>	Mn	33.68±4.1
<i>8</i>	Fe	5838±22.2
<i>9</i>	Ni	8.94±3.92
<i>10</i>	Cu	BDL
<i>11</i>	Zn	14.41±3.5
<i>12</i>	Se	0.9499±1.7
<i>13</i>	Br	13.47±6.2
<i>14</i>	Rb	34.71±6.2
<i>15</i>	Sr	27.65±5.2
<i>16</i>	Y	18.13±5.0
<i>17</i>	Zr	63.7±8.7
<i>18</i>	Nb	6.09±3.29
<i>19</i>	Mo	10.84±4.04
<i>20</i>	Ru	BDL
<i>21</i>	Ag	BDL
<i>22</i>	Pb	28.82±11.2

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224 Table-6; G5 sample elements and  
 225 concentrations  
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<i>S.NO</i>	<i>Element</i>	<i>G5</i>
<i>1</i>	Cl	546.9±23.5
<i>2</i>	K	6699±40.2
<i>3</i>	Ca	4120±23.5
<i>4</i>	Ti	1590±13.8
<i>5</i>	V	37.78±6.0
<i>6</i>	Cr	17.71±3.1
<i>7</i>	Mn	47.43±5.3
<i>8</i>	Fe	7325±26.4
<i>9</i>	Ni	28.29±5.02
<i>10</i>	Cu	BDL
<i>11</i>	Zn	11.96. ±4.6
<i>12</i>	Se	BDL
<i>13</i>	Br	10.32. ±4.031
<i>14</i>	Rb	56.14 ±7.9
<i>15</i>	Sr	38.02±6.5
<i>16</i>	Y	BDL
<i>17</i>	Zr	11.44±7.0
<i>18</i>	Nb	BDL
<i>19</i>	Mo	BDL
<i>20</i>	Ru	BDL
<i>21</i>	Ag	BDL
<i>22</i>	Pb	41.58±14.48

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229 Table-7; G6 sample elements and  
 230 concentrations  
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<i>S.NO</i>	<i>Element</i>	<i>G6</i>
<i>1</i>	Cl	383.7±16.7
<i>2</i>	K	5458±27.1
<i>3</i>	Ca	2544±26.2
<i>4</i>	Ti	1044±9.1
<i>5</i>	V	10.79±4.0
<i>6</i>	Cr	9.118±2.1
<i>7</i>	Mn	27.36±3.5
<i>8</i>	Fe	4905±17.7
<i>9</i>	Ni	10.11±3.1644
<i>10</i>	Cu	BDL
<i>11</i>	Zn	24.73±2.9
<i>12</i>	Se	BDL
<i>13</i>	Br	8.61±2.455
<i>14</i>	Rb	34.58±5.3
<i>15</i>	Sr	33.91±4.9
<i>16</i>	Y	BDL
<i>17</i>	Zr	12.16±5.0
<i>18</i>	Nb	BDL
<i>19</i>	Mo	BDL
<i>20</i>	Ru	9.977±3.59
<i>21</i>	Ag	BDL
<i>22</i>	Pb	BDL

232



233 Table-8; G7 sample elements and  
 234 concentrations

<i>S.NO</i>	<i>Element</i>	<i>G7</i>
<i>1</i>	Cl	462.6±20.6
<i>2</i>	K	5393±33.4
<i>3</i>	Ca	3091±32.1
<i>4</i>	Ti	1510±12.4
<i>5</i>	V	11.55±12.4
<i>6</i>	Cr	14.13±2.6
<i>7</i>	Mn	27.03±4.5
<i>8</i>	Fe	6238±23.1
<i>9</i>	Ni	16.5±4.3692
<i>10</i>	Cu	8.717±3.47
<i>11</i>	Zn	4.29±2.0
<i>12</i>	Se	BDL
<i>13</i>	Br	9.08±3.503
<i>14</i>	Rb	52.46±7.1
<i>15</i>	Sr	35.53±6.1
<i>16</i>	Y	BDL
<i>17</i>	Zr	77.82±9.3
<i>18</i>	Nb	BDL±6. ±6.
<i>19</i>	Mo	BDL
<i>20</i>	Ru	BDL
<i>21</i>	Ag	BDL
<i>22</i>	Pb	24.49±12.5

235 The PIXE spectrum of the geological  
 236 samples G1 to G7 collected from the  
 237 interior of the Charnockite rock recorded  
 238 by Si (Li) detector. These concentrations  
 239 are presented with errors in Table-9  
 240 assuming Standard Deviation values (n) =  
 241 7 and BDL (Below Detection Limit).

242 Another attempt is made to analyze  
 243 the samples using an atomic absorption  
 244 photo spectrometer and same elements are  
 245 reported using the method of AAS and the  
 246 same standard also employed for a method  
 247 of AAS also. The data generated the AAS  
 248 method has been used to compare the  
 249 PIXE results for its evaluation purpose. In  
 250 this paragraph, each element is considered  
 251 in evaluating PIXE as per that element is  
 252 concentrated.

253 It is observed that the results  
 254 obtained by AAS are close which already  
 255 published data on Charnockites in various  
 256 journals. The possibility of increasing  
 257 accuracy of PIXE in analyzing samples of  
 258 complex matrix like Charnockite has been  
 259 discussed and suggestions are made.

260 So, the following tables presents the  
 261 elements which are close to elements  
 262 having moderate errors and elements  
 263 which are highly erroneous not detected.  
 264 Using this data, the Charnockite hill from  
 265 where the samples are collected have been  
 266 attempted to understand the chemical  
 267 nature followed by genetic implications.  
 268 The reasons behind the poor performance  
 269 of PIXE with respect to certain elements  
 270 have been tried to explain.

271 The following tables give overall  
 272 analysis of Charnockite samples by using  
 273 PIXE analysis and also AAS analysis.  
 274 Later the validity of AAS analysis verified  
 275 through wt% in the major elemental  
 276 components in the form of oxides in below  
 277 tables. Finally reviewed the Charnockite  
 278 composition, by using PIXE with  
 279 comparing results with AAS (tables 9-13).



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Table- 9; Analytical results of all geological samples (PIXE)

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.
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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Table-10; Analytical results of all geological samples (AAS).

Element	G11	G21	G31	G41	G51	G61	G71
Na	23483	15561	22300	23718	26679	25505	25306
Mg	20568	16467	20026	20209	20501	24063	17546
Al	89081	90776	87760	96543	88132	89302	90105
Si	260631	274683	265398	269366	265905	262318	261506
P	1367	1402	916	1103	1231	1450	1582
Cl	-	-	-	-	-	-	-
K	24813	29466	27052	25739	9268	11374	13908
Ca	33709	28918	30776	29412	29418	36403	39305
Ti	7001	7403	7606	7842	6582	7409	7205
V	127	125	136	129	143	137	126
Cr	38	34	39	33	38	31	39
Mn	2023	2706	1855	1784	1548	2202	3011
Fe	87176	69983	88511	71342	90979	86904	87202
Co	8	10	7	9	7	11	7
Ni	38	34	42	45	39	37	42
Cu	8.8	12.8	11.9	9.2	6.6	8.6	11.1
Zn	11.3	12.3	9.3	15.4	10.6	10.9	9.3
Se	6.3	7	4	6	7.4	3.9	5
Br	-	-	-	-	-	-	-
Rb	60.8	70.1	74.6	89	82.9	77.5	71
Sr	144	132	143	126	119	128	148
Y	56	39.5	47.3	49.1	45.8	63.2	46.2
Zr	194.1	189.6	198.9	190.6	189	12.1	12
Nb	15.9	14.5	13.1	12.1	10.9	12.9	12.6
Mo	5.8	6	6	5.3	8	8	6
Ru	4.9	5.9	4.3	4.2	4	6	4.4
Ag	10	4.2	4.1	4.2	7	5	4
Pb	29.3	27.9	31.3	32.4	28	28	32.9
Ba	852	843	839	858	823	857	819

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Table-11; Total Analytical results of all samples (AAS).

Element (Wt.%)	G11	G21	G31	G41	G51	G61	G71
Si	26.063	27.68	26.539	26.936	26.590	26.23	26.15
Al	8.908	9.077	8.776	9.654	8.813	8.93	9.01
Ti	0.7	0.940	0.760	0.784	0.658	0.74	0.72
Fe (total)	8.717	6.99	8.851	7.134	9.097	7.88	8.72
Mg	2.056	1.646	2.002	2.020	2.050	2.406	1.754
Mn	0.202	0.270	0.185	0.178	0.154	0.22	0.301
K	2.481	2.946	2.7058	2.573	0.9268	1.137	1.39
Ca	3.37	2.891	3.027	2.941	2.949	3.648	3.93
Na	2.346	1.556	2.230	2.371	2.667	2.55	2.53
P	0.136	0.140	0.092	0.110	0.123	0.145	0.158

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Table-12; Major Elements of all samples (AAS) Wt%.

Element (wt.%)	G11	G21	G31	G41	G51	G61	G71
SiO <sub>2</sub>	55.81	58.82	56.83	57.68	56.94	56.17	56.01
Al <sub>2</sub> O <sub>3</sub>	16.84	17.16	16.59	18.25	16.66	16.89	17.05
TiO <sub>2</sub>	1.17	1.57	1.27	1.31	1.10	1.24	1.21
Fe <sub>2</sub> O <sub>3</sub>	1.65	1.39	1.72	1.094	1.289	0.81	0.82
Feo	9.74	7.77	9.85	7.78	10.05	10.15	10.18
Mgo	3.41	2.73	3.321	3.35	3.42	3.51	2.91
Mno	0.262	0.35	0.241	0.23	0.20	0.29	0.39
K <sub>2</sub> O	2.99	3.55	3.26	3.10	1.16	1.37	1.67
CaO	4.72	4.05	4.31	4.12	5.42	5.11	5.31
Na <sub>2</sub> O	3.17	2.10	3.01	3.20	3.60	3.45	3.42
P <sub>2</sub> O <sub>5</sub>	0.31	0.32	0.21	0.25	0.28	0.33	0.36
Total	100.078	99.81	100.423	100.84	100.58	100.57	100.27

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Table-13; Analytical results of all geological samples (PIXE and AAS).

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

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299 Another attempt is made to analyze the samples using Atomic Absorption photo  
 300 spectrometer for PIXE fig; 1-7 evaluation or standardization Christopher et. al., (2016) in  
 301 high grade matrix composition and the same elements are reported and same standard also  
 302 employed for a method of AAS. The data generated the AAS method table-10 to 13 has been  
 303 used to compare the PIXE results Oti Wilberforce JO (2016) for its standardization purpose.  
 304 In this paragraph each element is considered in evaluating PIXE as per that element is  
 305 concentrated. It is observed that the results obtained by AAS are close which already  
 306 published data Rao and Babu (1978) Sriramadas and Rao (1979) Charnockites in various  
 307 journals Saradhi (2000) Rajib Kar (2001) With respect to certain elements, the reasons behind  
 308 the improper performance of PIXE in case of matrix composition of geological materials  
 309 have been tried to explain Gerlad , et. al., (1993).



310 It is established that the recent advances in PIXE can successfully used in analyzing  
311 samples with high accuracy, precision, low detection limits and high resolution from different  
312 fields like geology of high grade metamorphic rocks. Low energy PIXE, high energy PIXE,  
313 micro PIXE and external beam PIXE are recent developments which are used to determine  
314 the various elements present in samples in the form of major, minor and trace amounts from  
315 low to high atomic ( $Z$ ) elements. During recent advances in PIXE, it is indicated that the  
316 spatial resolution of peaks of various elements in samples of materials can be obtained in the  
317 order of micro meter by developed micro PIXE and hence elimination of overlapping of  
318 peaks in matrix effects are possible.

319 The detailed study table-1-13 of Charnockite samples from Visakhapatnam have been  
320 established that there is certain accuracies pertaining to the concentration of certain elements.  
321 Potassium is a major element in the Charnockite composition. The concentration of K in the  
322 Charnockite composition by PIXE ranges from 4000 to 6000 ppm range in various locations.  
323 But actually according to contents of Charnockite composition its value should be 20,000  
324 ppm range. This is due to overlapped peaks of Ca K X-ray with K K X-ray in spectrum  
325 obtained in this investigation. From this analysis PIXE is unable to detect major elements in  
326 Charnockites of Visakhapatnam due to detector limits. Calcium is also a major composition  
327 of Charnockite composition like potassium and in the analysis of Charnockites by using  
328 PIXE, its value is 2500-3000 ppm range in all G1 series to G7 series samples. But in the  
329 analysis of AAS its value is 30,000 ppm range. Therefore, PIXE once again fails to detect  
330 exact value of ppm of major elements like K and Ca in Charnockite composition. The K and  
331 Ca escape peaks in Si (Li) detector interfere with X-ray lines of Al, Pand S; K and Ca  
332 summing peaks could interfere with X-ray lines of Fe, Ni and Cu. So in case of Charnockites  
333 also high K and Ca contents, could be automatically resolved by GUPIX. The K and Ca  
334 escape peaks in Si (Li) detector interfere with X-ray lines of Al, Si, P, Na and Mg; K and Ca  
335 summing peaks could interfere with X-ray lines of Ti, V, Fe, Ni and Cu in Charnockite  
336 composition.

337 The concentration of Ti in Charnockite by using PIXE method nearly 1200 -1400 ppm in  
338 all types of samples. The error percentage of Ti is 3.6% only by standard reference. But  
339 according to previous literature weight ratio in Charnockites it should be 7000 ppm and also  
340 by present AAS analysis. From this PIXE analysis the error due to Ti- $K\alpha$  and Fe- $K\alpha$  have  
341 closely 4.5 keV energy X-rays (4.509 and 4.647 keV) and also Ti-Ba have same X-ray  
342 energies (4.469 and 4.509 keV). So PIXE not given proper value in case of major elements  
343 like Ti due to above overlapping peaks. The value of Fe detection in Charnockite samples by  
344 PIXE is around 6550 ppm but by the investigation through AAS its value is 86,000 ppm,  
345 which is equal to wt% of Charnockite composition study. PIXE could not perform well in the  
346 determination of Fe. Because the overlapped of Co- $K\alpha$  and Fe-  $K\beta$  causes the inability of proper  
347 detection and in addition to that Ti- $K\alpha$  and Fe- $K\alpha$  are same energy or nearly K X-ray energies,  
348 (4.509 keV and 4.647 keV.) Some times it is difficult to resolve two peaks from neighboring  
349 elements. Some corrections are needed to calculate the exact concentration value of Fe in  
350 Charnockites by PIXE.



351 PIXE unable to detect the low  $Z$  elements present like Li, Be, F, Na, Mg Al, Si and P in  
352 Charnockites due to detector limits. X-rays below or near the sodium cannot be seen because  
353 they are absorbed in either the detector window atmosphere or through any filter used. A  
354 possible disadvantage to running in this configuration is that low energy X-rays from lighter  
355 elements attenuated in air. By increasing efficiency of detector or placing more suitable  
356 detectors or by changing the incident proton beam energy or other technique like AAS used  
357 in this investigation, these low atomic number ( $Z$ ) elements are determined. Another reason  
358 also is K and Ca escape peaks of in this investigation in Si (Li) detector interfere with X-ray  
359 lines of Be, F, Na, Mg, Al, Si, and P Ana, et. al., (2011). The concentration of element V in  
360 this PIXE analysis, 28-30 ppm and by AAS the value is 125ppm. From the above values  
361 PIXE nearly gives results in case of minor elements and middle  $Z$  elements due to non-  
362 overlapping of peaks and spectrum obtained by PIXE. The remaining 100 ppm due to Ti  
363 overlapped peaks in the spectrums of Charnockite samples. So PIXE is more suitable in the  
364 analysis of minor elements, middle atomic number ( $Z$ ) elements. The error percentage of V is  
365 around 15% through standard reference material.

366 PIXE results showed very good approximation in case of minor element. In case of Co  
367 elemental analysis of Charnockite rocks by present PIXE investigation; the ppm value is not  
368 detected. But Co trace presented in Charnockites according to previous literature and  
369 composition of Charnockite by AAS. Non determination by PIXE of Co in Charnockites is  
370 due to mainly two reasons; 1) Co-  $K\alpha$  and Fe-  $K\beta$  2) Ni  $K\alpha$  and Co  $K\beta$  from the interferences  
371 of above two peaks trace of cobalt not detected, but in case of AAS analysis Co also  
372 presented in Charnockites and its value only is 8 to 10 ppm. In this case also Fe is the major  
373 component so that the X-ray emitted from this element will dominate the energy spectrum, In  
374 the PIXE analysis of Charnockites, the elemental concentration of Cu is very low and only  
375 traces of one or two samples are obtained. But by using AAS analysis traces of Cu up to 12  
376 ppm are present. The above reason is due to the interference of Cu peak with Zn peak in case  
377 of Charnockites samples from Figure 3.1 to 3.7. It is Cu  $K\alpha$  and Zn  $K\beta$  interference matrix, i.  
378 e,  $K\alpha$  ( $Z+1$ ) X-ray and the  $K\beta$  ( $Z$ ) X-ray and by correction small interference value, PIXE  
379 once again proved in the detection case of trace elemental analysis.

380 By present PIXE analysis, the concentration value of Cr in Charnockite samples is 10-20  
381 ppm and by AAS analysis, the value is also the same 40 ppm. Like V, in this case also  
382 obtained the same result by PIXE analysis. Here no overlapping of peaks with V element in  
383 the spectrums as shown in Figure 1 to 7. PIXE again given nearly good results in case of  
384 minor elements as stated above in case minor elements, middle  $Z$  elements with small matrix  
385 corrections. The concentration value of Mn obtained by PIXE analysis investigation is 20- 40  
386 ppm and AAS analysis its value is 2000 ppm. In this case variation is due to the matrix of  
387 non-resolution of peaks between Mn  $K\beta$  and Fe  $K\alpha$  overlapped. The error in this by using  
388 standard reference material is 1%. So correction is required in case of Mn concentration  
389 which is determined by PIXE analysis and also suitable to measure the concentration of Mn  
390 major element with correction of matrix effects. Because in Charnockites Fe is the major  
391 component. So the X-ray emitted from this element will dominate the energy spectrum as can  
392 be seen from Figure; 1 to.7 and influence the Mn peak and concentration.



393 The concentration value of Ni by PIXE analysis is 10-20 ppm and AAS analysis is 40  
394 ppm. In this element PIXE analysis given excellent result when compared with AAS and  
395 remaining 20 ppm is due to the interference and non-resolution of peaks obtained by PIXE  
396 with cobalt traces due to Ni  $K\alpha$  with Co  $K\beta$ . The error percentage in this case is 2% and  
397 except 20 ppm correction compared to AAS and previous literature, PIXE given excellent  
398 result in nickel minor elemental concentration of Charnockites, The concentration of Zn  
399 element in samples of Charnockites by PIXE analysis, value is 10- 20 ppm range but the  
400 results obtained by AAS its value is 10-15 in eastern ghats, Charnockites, Visakhapatnam.  
401 The variation between the above two analysis, the error percentage of Zn though standard  
402 reference is 16% and 5-10 ppm the variation between the above two analyses, which is very  
403 low and good results obtained by PIXE analysis. So the variation of above value with AAS is  
404 due the above Cu and Zn peaks overlapped in spectrums of Charnockites obtained by PIXE  
405 analysis. In this case of Sr, the PIXE analysis 30-40 ppm range and AAS analysis 140 ppm  
406 and difference 80 ppm, Sr  $K\alpha$  and Rb  $K\beta$  and also with Y  $K\alpha$  X-rays overlapped corrections  
407 due to error value 3.5%. The PIXE had given the same results like above minor elements.  
408 The concentration values of Rb obtained by PIXE and AAS are 40-50 ppm and 60 ppm. The  
409 difference is nearly 20 ppm range and this is due to the overlapped peaks of Y  $K\alpha$  and Rb  $K\beta$ ,  
410 Sr  $K\alpha$  and R  $K\beta$  in the analysis of spectrum of the peaks of Charnockites. So by correct the  
411 matrix 20-30 ppm value of Rb and compared to AAS, PIXE has given good results in case of  
412 Rb.

413 Using PIXE analysis, the concentration value of Y is 10-15 ppm which is low. From  
414 Charnockite composition and present AAS analysis, its value is 60 ppm range and the  
415 difference arises due to Y  $K\alpha$  and Rb  $K\beta$  overlapped of peaks and matrix effects. From the  
416 above two elements if the concentration value increases, PIXE performance value decreases.  
417 By PIXE analysis the concentration value is 90 ppm and by AAS analysis its value is 190  
418 ppm. From these analyses PIXE analysis is very poor in the detection of Zr and resolution of  
419 peaks with Nb. The poor results obtained in PIXE analysis of element Zr in the Charnockites  
420 as concentration value of element in Charnockite composition increases, poor results also  
421 increase in PIXE analysis. It is same as above two cases. The error value increases with as  
422 concentration value increases.

423 The concentration value of Nb in Charnockites is 5-11 ppm in PIXE and in case of AAS  
424 its value is 15 ppm range, the concentration variation is only 10 ppm and it is due to small  
425 matrix effect of Zr and Mo. Of course, PIXE analysis is good in case of trace elements like  
426 Nb except small corrections due to resolutions of peaks and matrix effects. The element Pb is  
427 an important element in rock formation, which is determined by PIXE and its value 20-30  
428 ppm range and in the investigation of Pb, PIXE given good results. It gives valuable  
429 information in rock crystallization process. In PIXE analysis, the concentration value  
430 identified is only 1-2 series samples of Charnockites. So in PIXE analysis traces of Mo not  
431 exactly found due to corrections of interferences with Nb but its value by AAS is also given  
432 very low traces due to matrix effect of Nb.



433 The traces of Ru found by using PIXE like Ag in Charnockites. AAS analysis is also given  
434 only traces of Ru in one or two sample series of Charnockites. It is a precious metal  
435 previously not detected in Charnockite, in this PIXE also not trace out exactly because in ppb  
436 levels and most of above series samples are at BDL. So PIXE is suitable to measure the  
437 concentration of precious metal like Ag. The traces of Ag investigated also in the AAS  
438 analysis. It is an important element in Charnockites in Visakhapatnam and these are halogen  
439 rich minerals. PIXE is a very suitable technique in the determination of gaseous phase  
440 elements like Cl. Its value is 400 ppm which is the similar result obtained by previous  
441 analysis. But AAS is not able to detect the Cl element directly. Br is also a trace element in  
442 halogen rich minerals of Charnockites. PIXE is very suitable in the detection of Br and Cl but  
443 not F present in the composition due X- ray energy limitation. The gaseous elements give  
444 information about rock formation. The traces of Br identified by the PIXE are in the range 5-  
445 13 ppm and Br is not detected by AAS. PIXE is very much suitable technique in case of  
446 middle Z elements like Zn, Rb, Cr, gaseous elements Cl and Br, in the detection of precious  
447 metals Nb, Mo and Ru and other elements with corrections.

448 The presented PIXE technique is known for its sensitivity, accuracy, precision simplicity  
449 and fast of thick target preparation and to perform multi elemental analysis of a large number  
450 of complex geological materials like Precambrian, proto crustal rocks compared with the  
451 previous study EPMA. By the identification of elements from upper mantle, crust and the  
452 trace elemental data show that rock samples analyzed have a composition different from that  
453 of the host Charnockite. These include the large ion lithophile elements (Rb, Sr) high field  
454 strength elements (Ti, Zr, Nb) precious elements Ag, Cu and various elements of importance  
455 in geo thermo barometry. However for REE elements, the LOD are markedly poorer. This is  
456 particularly the case for the REE s Hajivaliei, et. al., (2000):

457 The elements K, Ca, Rb and Sr present in high concentration, low value of Ni in the  
458 samples supports calcium alkaline phase. The element Fe has the highest concentration, Cr,  
459 Zn and Zr are detected in the samples strongly indicates the ultramafic percentage from upper  
460 mantle. In this aspect these rocks are entirely different from the host Charnockite and these  
461 were evolved from upper mantle to crust during Precambrian period. The light and medium  
462 heavy elements therefore determined by their K X-ray as the heavy ones by L X-rays which  
463 are shown in figures. PIXE has certain drawbacks in detection of light elements Be, F, Na,  
464 Mg, Al, Si, and P and the REE. For light elements, the problem is mainly due to absorption of  
465 the low energy X-ray Durocher, et. al., (1988) by detector Si (Li) windows and the tails of the  
466 heavier major elements peaks.

467 PIXE, especially with micro beam, has proven to be a versatile and powerful analytical  
468 tool in many areas of geology. PIXE within a short span of time has demonstrated its  
469 versatility and usefulness by the diversity of applications to which it has been applied. The  
470 detection limits of the PIXE measurements were calculated assuming that the minimum  
471 detectable peak is three times the square root of the background at FWHM. The detection  
472 limits in the PIXE measurements 0–1ppm by weight with the exception (from all the tables  
473 and values presented). We are aware of no attempts having been made to apply PIXE analysis



474 to the petrogenesis of intermediate to silicic igneous rocks. Our results show that such studies  
475 are feasible.

476 The ability to analyze diverse phases using a single standard and uniform operating  
477 conditions largely obviates the need to perform laborious mineral separations, formerly  
478 necessary for studies of the trace-element inventory of such rocks. Among the most exciting  
479 potential applications of PIXE analysis to silicate minerals and element-partitioning  
480 measurements relevant to mineral melt, mineral-mineral, or melt-melt systems useful in  
481 understanding melting and crystallization processes, trace element zoning studies in igneous  
482 or metamorphic volcanic minerals to assess the crystallization behavior of magmas or to  
483 assess tectonic and metamorphic histories and diffusion-profile measurements in minerals,  
484 melts.

485 In the coming years PIXE should find itself being applied more and more to a variety of  
486 samples, when a rapid non-destructive and multi-elemental method is looked for and it should  
487 take its rightful place as an equal or better technique among the numerous other standard  
488 analytical techniques available. We also demonstrated that nuclear microscopy, due to its  
489 high spatial resolution and the low detection limits proved to be a powerful tool for the  
490 characterization of minerals with complex chemistry and it serves as an ideal complementary  
491 technique of optical mineralogy, SEM and EPMA. During to its longer probe depth (ten of  
492 micro meter) the PIXE can be performed for a large range of elements ( $K < Z < Pb$ ) in the  
493 periodic table. So PIXE useful fast, precise, accurate and sensitive (limit in ppm). Both  
494 matrix and trace elements PIXE gives higher signal to background ratio as compared to  
495 EPMA and spectrum 100 times better sensitive and has higher resolution like previously  
496 stated.

497 Compared to electron based X-ray analytical techniques such as energy dispersive  
498 spectroscopy(EDS) and EPMA, PIXE offers better peak to noise ratios and consequently  
499 much higher trace element sensitivities as seen in spectrum Figure 1 to 7. PIXE is capable of  
500 multi-elemental analysis and a large number of elements (Twenty two) may be seen  
501 simultaneously. PIXE, being a non-destructive technique and because the original shape and  
502 size of the sample is not destroyed, makes it a unique facility for a number of applications.  
503 PIXE and XRF are both methods based on X-ray emission and have several features in  
504 common. From sensitivity point of view, PIXE has certain superiority, moreover the  
505 bremsstrahlung produced in PIXE is a secondary effect where as in case of Electron  
506 Microprobes and XRF it is primary contributor and the principal source of proton back  
507 ground against which the character X-rays of elemental constituents must be distinguished  
508 and hence is also the principal determinant of detection limits. The low bremsstrahlung in  
509 PIXE enables parts per million sensitivities, superior to its sister techniques in geological  
510 materials are obtained (From previous literature and previous EPMA and XRF).

511 The results obtained indicate that it is competitive with other more classical analytical  
512 methods, and that it may be, in addition, a very useful complementary technique when  
513 combined with other ion beam methods like PIGE, EPMA, XRF and NAA is, in general, a



514 very sensitive method but has limited use for light elements. Also, Particle-Induced X-ray  
515 Emission (PIXE) fails in the situation where the species of interest has a low atomic number  
516 because the low K X-ray fluorescence yields are strongly attenuated by the absorption edge  
517 of higher atomic number elements present in the sample. Prompt  $\gamma$ -ray analysis (PIGE) offers  
518 an alternative in measuring light elements which are not detected by PIXE and has the  
519 advantage that  $\gamma$ -rays from the different light elements can be easily distinguished by their  
520 energies. The sensitivity of PIGE analysis can be improved by coincidences measurements.

521 From this it results that by coupling PIGE, PIXE and NAA methods, a very good overall  
522 picture of the elemental composition of a complex target such as steel may be obtained. PIXE  
523 and NAA are complements of PIGE when the determination of medium and heavy elements  
524 with high sensitivity is necessary in geological materials. Neutron activation is a very  
525 efficient tool of high sensitivity, but it is expensive and seldom used; also this technique is  
526 not convenient for detection of some elements of great interest in geochemistry such as Al, Si  
527 or Pb. But detection of Pb possible in this PIXE, off course light elements like Al, Si not  
528 detected but light elements are possible by using PIGE.

529 The method is a very sensitive one having a minimum detectable concentration of about  
530 0.1–1 ppm under optimum conditions. In the coming years PIXE should find itself being  
531 applied more and more to a variety of samples, when a rapid non-destructive and multi-  
532 elemental method is looked for and it should take its rightful place as an equal or better  
533 technique among the numerous other standard analytical techniques available. PIXE analyses  
534 of silicate samples are of excellent quality for a broad range of elements at abundance levels  
535 of one to hundreds of parts per million, depending on counting times. PIXE with Si (Li)  
536 detector not suitable to detect REE because in the determination of REE in geological  
537 samples is a very important subject but hard to tackle. By PIXE the L X-rays energies from 4-  
538 9 keV strongly overlap with K X-rays energies of light elements (20 to 30 Z).

539 The quantification of REE by PIXE becomes very difficult and inaccurate as results of the  
540 needed complex spectrum deconvolution. In fact in the context of REE L X-ray using  
541 standard PIXE set by compared results obtained with PIXE, XRF and NAA for geological  
542 samples and concluded that with the PIXE technique the limits are 30 ppm for REE, higher  
543 than with other techniques as NAA. The use K X-ray of REE elements could be a solution  
544 but at that energies Si (Li) detection can no longer is used. To overcome this problem the use  
545 of large Ge detection to detect the L X-ray of REE was attempted but due to large  
546 dimensions, a large Compton back ground is present which degrades the detection limits in  
547 the high X-ray energy region. Small Ge detection represent in improvement relative to this  
548 problem. But their overall size is still significant to this problem. But their overall crystals  
549 reduced solid angle Cd Te detects have average atomic numbers of 50 allow the construction  
550 of small detection.

551 PIXE roughly analyses the element whose atomic numbers, the light and medium-heavy  
552 identified by their K X-ray and the heavy elements by L X-ray due to the effective detection  
553 of the K X-ray which can be obtained in the range  $20 < Z < 50$ , L X-ray for  $Z > 50$  and  $20 < Z < 50$



554 for M X-ray. So due to above reason Na, Al, Si, and Mg not detected due to low Z elements  
555 ( $Z < 17$ ) in this investigation.

556 PIXE fails in the situation where the species of interest has a low atomic number because  
557 the low K X-ray fluorescence yields are strongly attenuated by the absorption edge of higher  
558 atomic number elements in the present investigation. From the above results, PIXE at IOP,  
559 Bhubaneswar, India, Charnockites elemental analysis lower atomic number ( $Z$ ) in all  
560 spectrums is Cl ( $Z=17$ ) and higher atomic number ( $Z$ ) in all spectrums is Ag ( $Z=47$ ) for K X-  
561 ray. For L X-rays only Pb is present in charnockites ( $Z$  greater than 50). The comparison with  
562 roughly PIXE ( $20 < Z < 50$  for K X-ray and  $Z > 50$  for L X-ray), good results obtained by PIXE  
563 in the elemental analysis of Charnockites of airport hill Visakhapatnam.

564 The element Sc is a trace which is detected previously by nuclear techniques other than  
565 PIXE. But in this investigation above element is not detected due to the X-ray  $K\alpha=4.093$  keV  
566 is equal to the  $K\beta=4.013$  keV of Ca and hence resolution of Si (Li) detector at 160eV at  
567 5.9keV. Similarly  $K\beta=4.464$  keV of Sc is equal to  $K\alpha=4.512$  keV of Ti. The element Y is  
568 also trace is not detected properly by present PIXE because Y  $K\alpha=14.958$  is equal to Rb  
569  $K\beta=14.961$  keV and Y  $K\beta=16.739$  keV is equal to Nb  $K\alpha=16.615$  keV.

570 Again from this analysis, PIXE once again proved with good accuracy with  $\pm 11\%$  in the  
571 detection of elements present in samples, better resolution in case of all elemental peaks with  
572 detection limits  $< 1$  ppm with precious trace elemental detection through sensitivity. Non  
573 detection of Th and U by PIXE in this investigation depend detector window. It can be  
574 performed for a large range of elements ( $K < Z < Pb$ ). The lower limit started from  $Z=17$ (Cl) is  
575 due to experimental detector limits because PIXE analysed the elements present in samples  
576 from  $Z=17$ (Cl) to  $Z=Pb$  (82) (from previous literature and present investigation also). So  
577 eventhough some elements are present in eastern ghat Charnockite from previous analysis  
578 like XRF and EPMA, here not detected because of detector efficiency. Ba was detected  
579 previously in the major element category of Charnockites like XRF analysis but it is not  
580 possible due to following explanation. In case of PIXE, the light and medium-heavy elements  
581 are identified by their K X-rays and the heavy elements by L X-rays. Due to the effective  
582 detection of the K X-ray which can be obtained in the range  $20 < Z < 50$  and of the L X-ray for  
583  $Z > 50$ . Since the value of atomic number ( $Z$ ) of Ba is 56, this element is not suitable to detect  
584 by PIXE. Similarly, the middle Z elements Sc, Ce, Sn, W, Ge, Ga and also Au not detected  
585 due to overlapped.

### 586 3.1. Rare Earth Elements Interpretation

587 Non detection of REE elements is due non suitability of Si (Li) detector to the REE  
588 elements in PIXE. These samples belong to a very important geological phase and further  
589 work on petrography and REE of the rock is indeed to firmly establish its exact parentage.  
590 PIXE has weaknesses in detection of media Z elements (Ti, V, Mn, Cr, Fe, Ni, Co) and the  
591 REE. For light elements, the problem is mainly due to absorption of the low energy X-ray by  
592 detector Si (Li) windows and the tails of the heavier major elements peaks. One approach,



593 such as that will be tried to use ultra thin window for X-ray detectors. This enables to extend  
594 the lower limit of detectable atomic number but measures must be taken to protect the  
595 detector from scattered proton beams, for example by using magnetic beam deflector.

596 Poor REE detection is due to the fact that the L-X-ray are either absorbed heavily or  
597 interfered with by the  $K\alpha$  line of Fe which is present in most geological rock samples with  
598 low energy proton. The K and L X-ray production cross section and intensity ratios of rare-  
599 earth elements for proton impact in the energy range 20–25 MeV are useful for detection of  
600 trace elements in rare earth region due to their high K X-ray ionization cross-section  
601 Hajivaliei, et. al., (2000). The use of their K X-ray is not practical because of the low yield  
602 and the low efficiency of the Si (Li) detector for X-ray >30 keV. Improvements in the future  
603 would address these problems and include the use of Ge detector or WDS detector in  
604 principle. PIXE, being a non-destructive technique and because the original shape and size of  
605 the sample is not destroyed, makes it a unique facility for a number of applications for the  
606 determination of REE of samples needed.

### 607 3.2. Other Traces Elemental Interpretation

608 The trace of element bromine is not all detected previously in Charnockite hill of  
609 Visakhapatnam by previous methods like EPMA and XRF. This investigation by PIXE  
610 clearly proved that this technique could detect not only regular elemental phase Cl in halogen  
611 rich minerals of Charnockites, and also the trace of Br. This aspect is highly interesting and  
612 potential geological applicability in similar investigations. From these fluids containing rich  
613 in Cl, F and also trace of Br are recognized to have contributed significantly to the evolution  
614 of proto crust. In this PIXE technique element, F is not detected due to PIXE has weaknesses  
615 in detection of light elements (F, Na, Mg, Al, Si, and P).

616 Here the silver identified in some few samples, it is an interesting investigation. Previous  
617 methods not identified this type of precious metal in analysis and no method from  
618 Charnockite analysis identified the precious metal Ag. So PIXE is wonderful technique used  
619 to identify the traces of Ag in Eastern Ghat Charnockites particularly in high metamorphic  
620 rocks. PIXE is a sensitive technique in the analysis elements even though if they are present 1  
621 micro gram/gram through scan the sample even small quantities are present in few samples.  
622 Nb is also present in few samples in the order of below 10 ppm. From this analysis PIXE has  
623 higher sensitivity with accuracy without destroy the sample and is very important in case of  
624 precious metals like Nb. Previous analytical techniques like XRF and EPMA except PXE,  
625 trace of Cu not detected in Charnockites of Visakhapatnam. The PIXE once again proved in  
626 case of traces present even though if they are present in one or two samples in ppm levels.

627 The importance of PIXE technique is used to find out the new trace elements if they are  
628 present even in small quantities at any corner of sample even in micro gram. Previously in  
629 Eastern Ghats analysis in any method Se and Mo not identified but in this investigation they  
630 are in clearly appreciable quantities in few samples. This kind of experimental research work  
631 may be compared with the previous work published in elsewhere, accuracy evaluation



632 absolute calibration in thick target PIXE. Data have been compared with the standard used  
633 mainly USGS. Similarly data are compared with elemental concentration obtained for the  
634 samples studied using another standard technique AAS. In the above paragraphs the PIXE  
635 has been evaluated based on the data pertaining to various elements determined. The  
636 evaluation has been made and comparing the accuracies of elemental concentration with  
637 respect to Charnockite sample. The traces of Th, U also present in charnockite composition,  
638 in the PIXE analysis not detected due to X-ray energy limits. Because of wide range of  
639 elements from low atomic number Z to high atomic number present in matrix composition of  
640 geological materials and characteristic X-rays of any series of elements present are at similar  
641 to characteristic X-rays of thorium and uranium in composition.

#### 642 **4. Conclusions**

643 In support of our observation also the theoretical back ground behind on performance of  
644 PIXE against induced elements has been discussed in detail. An analysis is made to  
645 understand the results behind the poor performance of PIXE with respect to certain elements.  
646 The possible reasons behind this have been brought out.

647 The general observation of PIXE methodology indicate that PIXE has been operated at  
648 one 3MeV proton energy with such condition the determination of different elements from  
649 low Z to high Z is not possible and perhaps this is the most important reasons behind the poor  
650 performance of PIXE with respect to the certain elements. It is suggested that with an  
651 investigation of PIXE by analysing pure samples of problematic elements. It means them  
652 100% pure elemental powders needed to be analysed with different concentrations at  
653 different levels using a non interfering matrix so that the optimum conditions for that element  
654 can be obtained. Further work is needed to understand the problems pertaining to  
655 combinations of elements. Such experiment is needed to design to determine different  
656 elements in a sample in combination to an optimum condition of analysis. In this way the  
657 conditions of PIXE can be standardized for low Z to high Z elements under different  
658 combinations. This kind of experimental research is highly necessary to fine tune the  
659 performance of PIXE especially when dealing with materials of complexity like high grade  
660 metamorphic such as Charnockite.

661 The present study could establish this aspect for the first time which will help in future  
662 for effective analysis of complex samples using PIXE. This experiment should contribute the  
663 conditions of PIXE operation for materials of different complexity and matrix.

664 The presented PIXE technique is known for its sensitivity, accuracy, precision simplicity  
665 of thick target preparation and to perform multi elemental analysis of a large number of  
666 complex geological materials, like Precambrian, proto crustal rocks. This investigation  
667 clearly proved that this technique could detect not only these elemental phases but also the  
668 concentrations of gaseous elements like Br, Cl. And K, Ca, Rb, Sr present in high  
669 concentration in the samples supports calcium alkaline phase and also Fe has the highest  
670 concentration, Cr, Zn, Zr are detected in the samples strongly indicates the ultramafic



671 percentage from upper mantle. This aspect is highly interesting and has partial geological  
672 applicability in similar investigations

673

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