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2   *Requirement of HE-PIXE at High Z Elements in Charnockite Matrix Composition*

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13   **Abstract;**

14   The maximum of Proton Induced X-ray Emission analytical technique on metamorphic
15   rocks in geology has used 3 MeV range proton beams for excitation of thick targets. Protons
16   of such energies do not accurately excite K-X –rays for high Z elements in matrix geological
17   compositions like charnockite. In this analysis, low-energy PIXE (LE-PIXE) uses K-X-rays
18   of Low Z elements and L-X-ray series for high Z elements. The resulting spectra between K-
19   X-rays of light elements and L-X-rays of heavy elements can require striping techniques to
20   resolve overlap difficulties in matrix composition. The results high Z elements in charnockite
21   are to be expected, as the cross section for K-shell ionization of high-Z elements have greater
22   values in the proton energy range of greater than 3 MeV in case of charnockite matrix
23   composition. It has been suggested that the overlap of these discrete, gamma-rays with the X-
24   ray spectrum may be serious problem in charnockite high energy PIXE (HE-PIXE) work,
25   sufficient to preclude its use as a viable analytical technique. The conclusion proves that for a
26   very complex matrix charnockite material of unknown chemistry, a HE-PIXE analytical
27   spectrum may contain various X-ray and gamma peaks, some of which may overlap, making
28   the analysis of line identities and the evaluation of X-ray counts intractable. It does not
29   however represent any intrinsic drawback in HE-PIXE, nor does it mean that HE-PIXE is any
30   more or less intractable than many other nuclear analytical techniques. Alternatively, the
31   same analytical tool use could be made of gamma-rays in HE-PIXE as in low energy
32   analytical tools like PIGE, NRA or INAA to obtain the results of charnockite at high Z
33   completely.

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35   Keywords; LE-PIXE, Charnockite matrix, Overlap problems, HE-PIXE, K-X-rays, Detection
36   probability,

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1. Introduction

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40   Almost all of inner-shell ionisation cross section data is obtained out of total X-ray
41 production cross sections, since X-ray detector systems are less complex. The X-ray spectrum
42 associated with atom-energetic ion bombardment can be detected and quantified
43 experimentally by means of general nuclear instruments. High resolution detection is often
44 required and usually lithium drifted Silicon Si (Li) for minor and trace elements and high
45 purity germanium (HPGe) detectors for detecting heavier atoms offer proper and resilient
46 detection possibility suitable for complex nature of X-ray spectra. Data is always received
47 and transferred from detection system to a computer using suitable network procedure in
48 order to work out the quantifying that involves the analytical interpretation of the X-ray
49 spectrum and peak area measurements.

50   Particle Induced X-ray Emission (PIXE) (Johansson and Campbell, 1988) is the
51 technique where X-rays are induced by the impact of energetic ions due to the coulomb
52 interaction between the incident ion and inner-shell bound electron, giving rise to vacancy in
53 the sample atom. This created vacancy is as a result filled by an outer shell electron, and the
54 atom subsequently de-excites by emitting a characteristic X-ray. In multi-elemental samples,
55 each element in the sample can be identified and quantified by referring to its characteristic
56 X-rays. The study of X-rays produced by light ions bombardments has received a great
57 impetus by the modifications of analytical techniques. Protons of energy 2-5 MeV are found
58 to be the most suitable ionising agents to use for the PIXE principle as one of the leading
59 multi-elemental analysis technique. PIXE has comparably large cross sections when
60 compared to the other excitation processes. As a result, the characteristic X-rays are produced
61 in concentration with relatively low background interference and only a low amount of
62 sample's composition is required for the analysis. If everything works well under valid
63 conditions, it is possible to detect 1-2 parts per million in quantities over a number of
64 elements.

65   The PIXE analytic technique is a non-destructive, non-invasive, no sample surface
66 contamination and do not affect the analysis since PIXE is usually insensitive to elements
67 with Z < 13. We examine experimental factors in the latest successes of proton Microprobe
68 (PMP) experiments in the geological materials. The PIXE analysis can now be efficient to
69 scientists belongs to geology (Campbell and Willcam, 1995) as a useful, common and
70 measurement tool. With modifying suitability of proton microprobes and awareness among
71 geo scientists of the efficiencies of PIXE, matrix geo material applications (Ryan, 2004) are
72 likely to increase rapidly. Ore deposit mineralogy studies are performed to achieve a wide
73 range of objectives like parameters useful for mineral exploration is to a complete minerals
74 characterization (Graham, et. al., 2002) necessary to give guidance for mineral beneficiation
75 and extraction. Trace-element information, to calculate partition coefficients between co-
76 existing minerals, or on fluid inclusions, provides geothermometric data on ore deposits.

77   PIXE through high sensitivity and accuracy multi element measurement (Christopher,
78 et. al., 2016) with picometer spatial resolution offers up new capabilities in inter disciplinary
79 research work. Trace element data achieved using the proton microprobe provides new

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80 analytical tools in ore genesis studies, exploration for precious metals, as well in the
81 processing of metal bearing ores. Introduction of this new methodology to the complex
82 materials however is controlled by economic factors which must be taken into consideration.
83 Matrix geological material has gained new studies with the availability and application of
84 PIXE, XRF and EMPA and NAA (Malmqvist, et. al., 1987) complementary analytical
85 techniques (Satyanarayana, et. al., 2020).

86 A lot of PIXE work on geological materials has used 3MeV energy range proton beams
87 for thick samples and excitation. Proton beams of such energies do not suitably excite K-X-
88 rays for high Z elements present in charnockite complex composition, and low-energy PIXE
89 generally uses the L-X-rays for high Z elements. The final spectra of complex matrix can
90 require techniques of striping to resolve interfere problems between X-rays of low to high Z
91 elements in charnockite composition. Previously, it was thought that PIXE technique of
92 geological materials was restricted to excitation protons in the 3 MeV energy range. Because,
93 PIXE with 3MeV failed to detect (Javier, 1996) very low Z elements due to detector limits
94 and also at high Z elements and hence overlapping of these L-X-rays of high Z with K-X-
95 rays of low and middle Z elements, detection not is possible (Satyanarayana, et. al., 2020).
96 Simultaneously K-X-rays cross sections are heavy, so 3 MeV proton is not sufficient to excite
97 the elements at high Z elements. To analyse the charnockite composition completely
98 including high Z elements using PIXE, according to previous literature of charnockite and
99 geological research, most probably HE-PIXE may enable.

100 Since, PIXE is a highly sensitive, accurate and non-destructive analytical method for
101 different elements in variety geological materials down to the levels of a few ppm. The
102 samples chosen for analytical method are collected from the middle portion of a charnockite
103 hill, Visakhapatnam airport A.P, during a demolition operation for expansion of the airport. A
104 big lenticular mass compositionally different from the host charnockite rock was identified in
105 the middle part of the hill. This body is believed to be the early crustal layer (possibly proto
106 crust). Such samples are rare, PIXE technique is chosen for the trace elemental analysis of
107 these rare samples.

108 **2. Methodology**

109 The elemental quantification of charnockite matrix in each sample was concentrated
110 using the proton beam PIXE measurements. Each target's was bombarded with beam of 3
111 MeV protons in our PIXE set-up (Johansson and Johansson, 1976) X-ray spectra was
112 obtained and noted for all the measurements. While taking these experiments there was
113 constant keeping close tabs on the beam current, dead-time and beam aperture as all these
114 play an important role in the quality of the received spectrum. Beam is lead to the beam line
115 through the analysing magnets; afterwards they pass through the collimator to keep the beam
116 in focus as they approach the sample. To measure proton beam current, Beam Profile Monitor
117 (BPM) is used, and is placed in vacuum before the exit window where the proton beam enters
118 the atmosphere of laboratory.

119 Experiments were carried out at the scanning nuclear microprobe arranged on the 0
120 beam line of the 3MV pelletron accelerator at Institute of Physics, Bhubaneswar, India.

121   Concerning the measurement conditions, a proton beam of 3 MeV energy focused down to
122   diameter 80mm ² with a 20 nA beam current used to bombard the targets. In order to avoid
123   the charging up of the samples, the proton beam current had to be kept under same. For the
124   low Z elements PIXE measurements, relative to the incident beam, X-ray detector placed at
125   135° geometry were used to detect the induced characteristic X-rays. A Gresham type Si(Li)
126   X-ray Be windowed detection with 80 mm2 active diameter setup was used to calculate the
127   medium and high energy characteristic X-rays (Atomic number > 19, energy 3–30 keV).
128   From the scattered protons, the detector protected by a permanent magnet and with a beam
129   chopper, the accumulated charge was monitored.

130   At an angle of 45° with direction to the proton beam, the charnockite targets which are
131   to be positioned on the target holder in this scattering chamber. The position of the target
132   relative to the beam direction is arranged suitably by observing through a window in the
133   scattering chamber. The detector is positioned at an angle of 90° with respect to the beam
134   direction. A Si (Li) with high detection (160 eV FWHM at 5.9 KeV) is used in the present
135   study to count the X-ray spectrum. Detailed explanation of the measurement setup can be
136   found and signal from all detection were collected by the data acquisition system. PIXE
137   spectra with better resolution and lower dead time were recorded.

138   The recorded PIXE spectra were evaluated with the GUPIX software (Maxwell, 1995)
139   to determine the multi elemental composition of the targets or samples. At first, the
140   composition of the matrix was calculated from the spectra of the Si (Li) detection, and then
141   the spectra of the Be windowed detector was analysed in element mode. On the spectra of
142   detection, the X-ray energy range of 2–8.5 keV is common, therefore characteristic X-rays
143   within this energy range was used to normalize the elemental quantifications. In the starting
144   and at the completion of the measurement experiments, analyses of standard reference
145   materials were carried out in order to verify the performance of the dose calculation and of
146   the precision, accuracy of the PIXE analysis setup. The standard USGS reference material
147   Basalt standards were used.

148   **3. Results**

149   The PIXE spectrum of the seven matrix charnockite samples collected from the interior
150   of the hill. The quantifications in ppm of these wide ranges of elements in each target were
151   calculated using the GUPIX software with Si (Li) detection (Satyanarayana, et. al., 2016).
152   These concentrations are tabulated with errors in table-1 by using the analysis of PIXE
153   spectrum. The missing elements in the PIXE spectrum of Charnockite samples with respect to
154   previous analytical techniques and hence the experimental factors behind the analysis of
155   charnockite matrix samples by PIXE at 3 MeV are discussed. With the comparison present
156   results table-1 and table-2 of previous studies (Rao, et. al., 1969, Rao and Babu, 1978,
157   Kamineni, et. al., 1982, Rao, et. al., 1993) the elements in charnockite composition is
158   discussed and suggestions for high Z elements detection in charnockite are made with
159   probable HE-PIXE.

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161   Table -1; Analytical results of all matrix charnockite 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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168   Table-2; Results of charnockites of same area of previous analyses and present PIXE

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_2O=1.591(Wt%)	-
Mg	12	ND	MgO=4.022(Wt%)	MgO=1.18(Wt%)
Al	13	ND	Al_2O_3=18.137(Wt%)	Al_2O_3==14.79(Wt%)
Si	14	ND	SiO_2=50.345(Wt%)	SiO_2=31.24(Wt%)
P	15	ND	P_2O_5=0.213(Wt%)	-
Cl	17	424.2±18.62ppm	0.130ppm	-
K	19	4887.28±29.91ppm	K_2O=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_2O_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_2O_3=1.123(Wt%) FeO =10.649(Wt%)	Fe_2O_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
G	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_2O_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_3O_8=0.01 (Wt%)
REE	57 to71	ND	-	*$(Ce,La,Nd)_2O_3$= 23.29(Wt%)

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4. Discussion

From the applications of LE-PIXE 3 MeV using Si (Li) detectors and above charnockite analysis (Satyanarayana and Ravi Kumar, 2017) suggested that it would be advantageous to keep excitation energies as low as possible to "reduce the number of different nuclear reactions" that might contribute low-energy gamma-ray peaks to the spectrum. The occurrence of various gamma-ray interferences is distinct from problems related to background (Murozono, et. al., 1999). The important sources for continuous background radiation in the low energy PIXE spectrum are atomic, secondary electron and quasi-free electron bremsstrahlung. These backgrounds mainly determine the limit of detection in PIXE spectrum by underlying the characteristic X-ray peaks in the case of elements with $Z < 35$. Other factors forming the background are nuclear bremsstrahlung (Ishii, et. al., 2005) the Compton tail of γ-rays, which is induced by the nuclear reactions.

The drawback of PIXE at 3 MeV to studying in this configuration is that below or near the chlorine (Satyanarayana, et. al., 2020) from spectrums of PIXE are not detected in this work due to low energy X-rays, because they are absorbed in either the detector window atmosphere or through any filter used. In case of PIXE analysis of the elements present in charnockite with $Z\leq31$ an interference is encountered between the Kα next element X-ray and the Kβ previous element X-ray, which have virtually the same energy and also between the X-ray K lines of media elements and X-ray L lines of heavy elements. Due to this the concentration values of Ca, K, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ru, Ag, Pb are not exactly equal to the concentrations when compare to the another analytical techniques. Few elements like Li, Be, F, Co, Ga, Ge, Ce, Sn, Ba, Au, Th, U and REE are not detected due to the same reason.

Particle Induced X-ray Emission (PIXE) has been used to an analytical tool for long range of major, minor, trace and REE elemental analysis in Precambrian charnockites. PIXE is sensitive, accurate and non-destructive method for some elemental analysis in a variety of metamorphic charnockite rocks down to levels of a few ppm and it is not valid for all remaining elements in the composition. The elements in the Precambrian charnokite rock Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ru, Ag, Pb are identified without exact values by PIXE but the minor and major elements Li. Be, F, Na, Mg, Al, Si, P, Ba and traces of Sc, Ce, Co, Sn, W, Ge, Ga, Au, Th, U and REE are not at all detected due to the various factors even though there present in the charnockite composition, because of PIXE which is operated at 3MeV proton energy and characterization of charnockite compositional investigated. In elemental characterization of charnockite rocks, elemental errors in concentration explained by comparing nuclear technique studies.

The element tin 3.444, 3.663 keV (L-X-rays) are similar to the potassium K-X-rays. Therefore tin is not detected in charnockite composition by PIXE analysis. The element barium 4.466, 4.828 22 keV (L-X-rays) since K-X-rays limited in case of PIXE and for L-X-rays, similar to titanium 4.512, 4.933 keV (K-X-rays). Therefore barium is present in the charnockite composition, but not detected in PIXE analysis due to the above reason. The

211 element cerium have 4.839, 5.262 keV (L-X–rays), these L-X-ray energies are same as
212 titanium 4.933 keV (K-X-rays), Vanadium 4.953 5.428 keV (L-X -rays). Therefore cerium is
213 not identified in PIXE spectrum and overlapped with either titanium or vanadium.

214   The rare earth elements are also very important but not detected by using PIXE with 3
215 MeV analyses. The M-X-rays of rare earth elements and Hf, Ta, and W have less energy
216 characteristic X-rays and absorbed by the detector window. The element Hf have L-X-ray
217 energies 7.899, 9.023 (keV) and M-X-ray energies 1.646, 1.700 (keV), Ta have L-X-ray
218 energies 8.146, 9.343 (keV) and M-X-ray energies 1.712, 1.770 (keV), W have L-X-ray
219 energies 8.398, 9.672 (keV) and M-X-ray energies 1.775, 1.838 (keV). Similarly Co have K-
220 X-ray energy 7.649 (keV), Ni have K-X-ray energy 8.267 (keV), Cu have K-X-ray energy
221 8.046, 8.904 (keV), Zn have K-X-ray energy 9.570 (keV) and Ga have K-X-ray energy 9.251
222 (keV). From the above discussion, M-X-ray energies of the elements Hf, Ta, W have less
223 characteristic energies are detected by PIXE and L-X-ray energies are nearly equal to K-X-
224 ray energies of Co, Ni, Cu, Zn, Ga and Ge. Since Ga have 9.251, 10.267 (K-X-rays) and
225 1.098, 1.125 (L-X-rays), Ge have 9.886, 10.982 (K-X-rays) and 1.188, 1.218 (L-X-rays).
226 Therefore Hf, Ta, W and rare earth element are not identified in the PIXE spectrum of
227 charnockite composition in this PIXE at 3MeV methodology. Similarly Au have L-X-rays
228 9.713, 11.443 keV, Ge have 9.886, 10.982 keV L-X-rays, Ga have 9.251, 10.267 keV L-X-
229 rays at similar characteristic X-ray energies. Therefore the elements Au, Ge and Ga are not
230 detected in PIXE experiments but these are already presented in the charnockite composition
231 in the form of traces by other previous techniques.

232   PIXE with 3 MeV energy protons is not the technique of choice for the REE in
233 complex matrix charnockite shown in table-1 whose levels of uninterested are after at the
234 ppm level or below. Because the REE elements present in matrix charnockite composition,
235 But charnockite have characteristic X-rays Lanthanum Kα 33.442 keV and Lα 4.64 keV,
236 Cerium Lα 4.839 keV and Mα 0.884 keV, Praseodymium Lα 5.035 keV and Mα 0.927 keV,
237 Neodymium Lα 5.228 keV and Mα 0.979 keV, Promethium Lα 5.432 keV and Mα 1.023
238 keV, Samarium Lα 5.633 keV and Mα 1.078 keV, Europium Lα 5.849 keV and Mα 1.131
239 keV, Gadolinium Lα 6.053 keV and Mα 1.181 keV, Terbium Lα 6.273 keV and Mα 1.240
240 keV, Dysprosium Lα 6.498 keV and Mα 1.293 keV, Holmium Lα 6.720 keV and Mα 1.348
241 keV, Erbium Lα 6.949 keV and Mα 1.404 keV, Thulium Lα 7.180 keV and Mα 1.462 keV,
242 Ytterbium Lα 7.416 keV and Mα 1.526 keV, Lutetium Lα 7.655 keV and Mα 1.580 keV.

243   In the above REE elements, K-X ray energies are very high and due to the cross
244 sections these are not detected by PIXE with 3 MeV. The M-X rays of REE are very low,
245 absorbed by the Si (Li) detector. Finally L-X-ray energies are in the range of PIXE
246 experiment at 3MeV, but these LX-ray energies of REE 4.6-7.6 KeV are overlapped with the
247 following K-X-ray media Z elements like Titanium Kα 4.512 keV and Lα 0.452 keV,
248 Vanadium Kα 4.953 keV and Lα 0.510 keV, Chromium Kα 5.415 keV and Lα 0.572 keV,
249 Manganese Kα 5.900 keV and Lα 0.637 keV, Iron Kα 6.405 keV and Lα 0.705 keV, Cobalt
250 Kα 6.931 keV and Lα 0.775 keV, Nickel Kα 7.480 keV and Lα 0.849 keV, Copper Kα 8.046
251 keV and Lα 0.928 keV.

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252   Thorium and Uranium traces are not detected by using present analysis. Because of
253   uranium, contain 98.440 keV, 111.303 keV (K-X-rays), 13.614 keV 17.220 keV (L-X-rays)
254   and 3.171 keV 3.336 keV (M-X-rays), similarly thorium contain 93.351 keV 105.605 keV
255   (K-X-rays), 12.968 keV 16.202 keV (L-X-rays) and 2.996 keV 3.149 keV (M-X-rays). The
256   X- ray energy detection from PIXE with Si (Li) detector experiment should only lay 1-20
257   keV. The energy of K-X-ray energies of high Z elements in charnockite composition are
258   more, therefore detection is not possible through K-X rays due to the Si (Li) detector
259   limitation. But the atomic number of Th and U > 83, according to PIXE theory, M-X-rays are
260   limited to PIXE technique because for M-X-rays, validity is 72<Z<83. Finally L X-rays
261   energies of Th and U are similar to K X-rays energies of Br 13.292 keV, Rb 13.396 keV, Sr
262   15.835 keV, and Mo 17.480 keV, which are present in the composition shown in table-1.
263   Therefore, due to above reason or overlapping U and Th are not detected in charnockite
264   composition by PIXE with 3 MeV spectrum analyses.

265   In case of PIXE spectrum analysis of the elements present in charnockite, the elements
266   Z≤31 an overlap is occurred between the Kα immediate element X-ray and the Kβ previous
267   element X-ray, which have virtually the same characteristic energy or between the X-ray K
268   lines of media elements and X-ray L lines of heavy elements. Determination of rare earth
269   elements in charnockite samples is a very important, but is not easy to tackle in this
270   investigation. By PIXE at 3 MeV, the L X-rays energies of low Z elements from 4-9 keV
271   range of REE in charnockite strongly interfere with K X-rays energies of low Z elements (20
272   to 31 Z) and the quantification of REE by PIXE with 3 MeV becomes very difficult detect in
273   this study.

274   Interferences of various peaks of low Z to high Z elements present in charnockite
275   caused by overlap of L-X-ray line and X-ray lines are not easily resolved, mainly when one is
276   important in analysis of the rare earth elements. As the REEs are of very important to the
277   geologists and there is not yet an interesting technique for their analysis, it is important that
278   the full potential of be realized for this group. The full complexity of the difficulties is
279   revealed by the interpreted spectrum of charnockite, a rare earth containing charnockite
280   composition, presented in this study. That this complex spectrum could be interpreted with
281   such precision was a major toured force but not the type of experiment that would be
282   appropriate for routine analysis. To eliminate these interfere separation of REE from the
283   matrix or by analysing the K-X-rays instead of the L-X-rays for the rare earth elements in a
284   charnockite sample approach should be modified at the proton energies.

285   From the above study held that the maximum energy for PIXE analysis laid 3MeV
286   range. Above 3MeV range increasing backgrounds arising due to compound nuclear reaction
287   gamma rays offset the advantage of higher X-ray production cross sections. In general above
288   proton energies 20 MeV, various particle processes overcomes and different gamma–rays are
289   lost in background spectra. In the range above proton energy 60 MeV for elements at high Z,
290   the maximum in cross sections for K-X-ray production is reached (Norman, et. al., 1995).
291   The mixing of higher production cross section and continuum gamma ray background results

292 compared to lower energy PIXE, in geological materials in orders of magnitude development
293 in limits of detection E=40 MeV (Durocher, et. al., 1998) for high Z elements.

294   The interpretation of K-X-ray peaks in the spectrum for rare earth elements detected
295 using an intrinsic Ge detector (Chaves, et. al., 2014) considerably easy in comparison to
296 fitting of L-X-rays below 10 keV. The systematically calculated the X-ray production cross
297 sections of the REE from 40-70 MeV and will use the results to geo materials like
298 charnockite. The possibility of using off–line counting of delayed rays, following activation
299 of the sample by the high energy protons provides further analytical possibilities. While the
300 use of high energy proton PIXE may dominates the experimental uncertainties of multi-
301 element interferences, the expense and limited access to high energy experiments will prevent
302 this becoming wider spread analytical techniques.

303   So, it might be expected that PIXE with high-energy proton bombardment of
304 charnockite complex geological materials may cause a number of nuclear reactions, with the
305 result that low-energy gamma-rays from those reactions could interfere with the X-ray
306 spectra of the elements of interest. This is to some extent borne out by the experiment who
307 observed peaks in their spectra that they interpreted to be "of nuclear origin." In this case, the
308 projectiles used were protons, and the peaks of nuclear origin were produced when the energy
309 of the protons was raised. However, reported well-resolved K line spectra for the rare-earth
310 elements (REEs) in several geological materials, showing that interference due to low-energy
311 gamma-rays and from nuclear reactions is not a necessary result of using high-energy protons
312 for excitation.

313   It has been concluded also that the "gamma-rays Compton scattering within the Ge
314 detection might importantly increase the background for studies run at high energies proton
315 30 MeV (Ishii, 1995), to the extent that this component of the background might effectively
316 obscure K X-ray peaks. We have shown that this is not the case. From the previous
317 experiments in case of geological materials, we see that the K-X-rays from various elements
318 are clearly resolved with high peak-to-background ratios, and that high levels of
319 bremsstrahlung are not an important problem. These experiments are to be expected, as the
320 ionization cross section for K-shell of REE and high-Z elements reaches a maximum in the
321 proton energy range 30-60 MeV (Hajivaliei, et. al., 2000). Because of the present study in the
322 determination of high Z elements in charnockite composition, it seemed worthwhile to focus
323 the analytical potential in this area of HE-PIXE.

324   Therefore, the matrix chanockite analysis by using PIXE with 3 MeV proved good
325 results (Macarthur and Ma, 1991) at media Z elements. Of course interferences are takes
326 place due to matrix charnockite contained wide range of elements. PIXE with 3MeV failed to
327 detect very low Z elements due to detector limits and also at high Z elements due to
328 overlapping of these L-X-rays of high Z with K-X- rays of low and middle Z elements,
329 detection not is possible. Simultaneously K-X-rays cross sections are heavy at low energy
330 protons, so 3MeV proton is not sufficient to excite the elements at high Z elements. HE-PIXE
331 is required for the analysis of high Z elements present in the charnockite composition with
332 alternation for gamma rays in addition to the high energy K-X-ray detection.

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333   **5. Conclusions**

334   The elements in the Precambrian charnokite complex composition Cl, K, Ca, Ti, V, Cr,
335   Mn, Fe, Ni, Cu, Zn, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ru, Ag, Pb are measured with errors due
336   to interferences by PIXE spectrum. The elements minor and major elements Li. B, F, Na, Mg,
337   Al, Si, P, Ba and traces of Sc, Ce, Co, Sn, W, Ge, Ga, Au, Th, U and REE are not detected
338   due to the experimental factors even though there present in the charnockite composition
339   from previous analytical techniques. Because of characterization of Charnockite mineral the
340   investigation at PIXE which is operation at 3MeV energy.

341   From the above discussion, the results of high Z elements are to be expected, as the
342   cross section for K-shell ionization of medium to high-Z elements reaches a maximum in the
343   proton energy range of 30-50 MeV in case charnockite matrix composition. It has been
344   suggested that the interference of these discrete, gamma-rays with the X-ray spectrum is a
345   serious problem in HE-PIXE work, sufficient to preclude its use as a viable analytical
346   technique.

347   The systematically measured the X-ray production cross sections of the high Z and REE
348   from 40-70 MeV and will apply the results to geological samples. The approach is possible to
349   avoid these interferences separation of REE from the matrix or by analysing the K-X-rays
350   instead of the L-X-rays for the REE in a bulk sample. The interpretation of K-X-ray peaks for
351   the REE detection using an intrinsic Ge detector is valuably simple in comparison to Si (Li)
352   interpretation of L-X-rays below 10 keV.

353   PIXE with 3MeV failed to detect very low Z elements due to detector limits and also at
354   high Z elements and hence overlapping of these L-X-rays of high Z with K-X- rays of low
355   and middle Z elements, detection not is possible. Simultaneously K-X-rays cross sections are
356   heavy, so 3 MeV proton is not sufficient to excite the elements at high Z elements. To
357   analyse the charnockite composition completely using PIXE, by using previous literature of
358   charnockite and geological research, most probably HE-PIXE may enable.

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453 **Conflict of Interest; Authors have no conflict of interest**

454 **Code and Data Availability;**

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463 **Competing interests;-**

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

470 **Authors have no conflict of interest**

471 **Funding;-**

473 **Authors' contributions;-**

474 The first author Dr. A.V.S. Satyanarayana, being a Nuclear Physics graduate he is
475 instrumental in the design of the experiment, sample preparation, selection of appropriate

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476   standards for the PIXE analysis, having discussions with the scientists of PIXE facility to
477   come up with standard analytical conditions for the rock with complex matrix to be analyzed
478   that is charnockite and compared with complementary present AAS & previous others. He
479   contributed all the technical aspects of PIXE analytical work, including physically working
480   with experts at PIXE facility.

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

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

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