ELEMENTAL ANALYSIS OF EAST INDIAN GEMSTONES BY EXTERNAL PIXE AND XRD TECHNIQUES - A CASE STUDY OF ISOMORPHOUS MOONSTONES FROM ANDHRA PRADESH

A.W. Iqbal

part time research scholor, Department of Engineering Physics,
College of Engineering, Andhra University, Visakhapatnam, A.P., India.

Y.RamaKrishna

Professor, Department of Engineering Physics, College of Engineering,
Andhra University, Visakhapatnam, A.P., India.

R.Venkateswara Rao

Senior Assistant Professor, Department of Physics,
Lendi Institute of Engineering & Technology, Jonnada, Vizianagaram, A.P, India

K.SrinivasaRao

Assistant Professor, Department of Physics,
College of Engineering, ANITS, Sangivalasa, Visakhapatnam, A.P., India.

C.Kasipathi

Professor, Department of Geology, Andhra University, Visakhapatnam, A.P, India.

T.R. Rautray

Professor, Biomaterials and Tissue Regeneration Laboratory,
CETMS, Siksha 'O' Anusandhan University, Khandagiri Square, Bhubaneswar, Odisha, India

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Abstract: Moonstone gemstones were collected from parts of Eastern Ghats geological formations of Andhra Pradesh, India and their gemological studies were carried out. Their study of chemistry is not possible as they represent mixtures of isomorphic nature, and none of the individual specimens indicate independent chemistry. Hence, non-destructive instrumental methodology of external PIXE technique was employed to understand their chemistry and identify the minerals. A 3 MeV proton beam was employed to excite the samples. In the present study, geochemical characteristics of moonstone gemstones were studied by external Proton Induced X-ray Emission (PIXE) technique. Furthermore, preliminary XRD studies of different moonstone patterns were performed. The crystal structure and the lattice parameters of the moonstones were estimated using X-Ray Diffraction studies, trace and minor elements were determined using the external PIXE technique, and major compositional elements were confirmed by XRD. In the present work, the usefulness and versatility of the external PIXE technique for research in geo-scientific methodology is established.

Keywords: XRD, External PIXE, Orthoclase feldspar, Semi-Precious gemstones, Moonstone, Adularia, Albite, Anorthite, Andhra Pradesh, India.

1. Introduction: The Mineral Exploration Division of the Department of Geology at Andhra University in India has been actively engaged in integrated geoscientific exploration, evaluation, grading, characterization, mining and beneficiation studies on the precious and semi-precious stone resources of the Eastern Ghats of Andhra Pradesh in India since 1990 and has identified important gem tracts in areas of the Khammam, East Godavari, Visakhapatnam, Vizianagaram and Srikakulam districts [1,2]. Moonstones have been characterized by their colors and microscopic characters and through destructive wet analyses and instrumental techniques. However, once these minerals are categorized as gemstones, they cannot be destructed for analysis due to their rarity and price. In these circumstances, a complete, non-destructive mode of analysis is necessary for the specification and characterization of these stones. The use of conventional tests, such as hardness, density, refractive index and physical observation, may not always be reliable. Therefore, the determination of the crystal structure and analysis of the trace element concentrations of these stones are helpful in distinguishing among the different types of gemstones and in finding their sources of origin. This idea forms the backdrop of this paper.

Kasipathi and his associates have reported many such valuable gemstones from this region, viz. Alexandrite, Chrysoberyl, Chrysoberyl Cat's Eye, Ruby, Corundum, Emerald, Moonstone, Garnet, Tourmaline, Sillimanite Cat's Eye, Zircon, Amethyst, Rose Quartz, Citrine and Rock crystal. The gem minerals are observed to be associated with pegmatite – basic / ultra basic rock types and hosted within the gneissose bands of quartzo-feldspathic granulites and its secondary colluviums bodies. Due to their important characters of chemical stability, compactness, hardness and durable nature of the gem minerals, there is no impact of their movement from their in-situ position to the farther distances as a process of geological weathering. Kasipathi and his group have carried out intensive geoscientific studies and evaluated many gemstone bodies, which helped in opening a number of mines in this region.

Moonstone deposits are generally found in areas such as Brazil, the European Alps, India, Korea, Madagascar, Mexico, Myanmar, Sri Lanka, Tanzania and the USA (e.g., in Pennsylvania and Virginia). Sri Lanka produces moonstones of the highest quality. Moonstones are available in a variety of colors that range from colorless to white, gray, brown, yellow, orange, green, or pink, and their clarity ranges from transparent to translucent. Color is one of the most important characteristics of the majority of minerals and gems, and because color is a result of trace element inclusions [3-4]. The causes of colors in the majority of minerals must be investigated using different high-precision techniques. Moonstone derives its name from its resemblance to the color of the moon, and this gem was very popular during the Roman period because people thought it was formed from moonlight. Moonstone has also been used in Roman jewelry since 100 A.D.

The knowledge of major, minor and trace elements present in gemstones and their correlations in geological samples are very important because these factors provide a key to the history of minerals. In geological research, gemstone classification is performed by identifying the presence of major elements such as Na, Mg, Al, Si, P, K, Ca, Ti, Mn and Fe. Similar information on trace elements can be obtained using analytical techniques. Because of their low concentrations, it is difficult to obtain information on trace elements unless a suitable technique is adopted.

The various available analytical techniques that are adopted in georesearch for obtaining information about elemental concentrations (i.e., major, minor and trace) are : Instrumental Neutron Activation Analysis (INAA), X-ray Fluorescence (XRF), Inductively Coupled Plasma Mass Spectroscopy (ICP-MS), Electron Micro Probe Analysis (EMPA), Atomic Absorption Spectrometry (AAS) and Particle Induced X-ray Emission (PIXE) [5-10]. Some of these methods are destructive, which results in the inability to use the samples for further studies, and some of these techniques only provide information for one element or require sample preparation before the analysis. In comparison, PIXE with external proton beam is non-destructive, quick, allows for multi-elemental determination and requires no or little sample preparation [11-17].

The unique advantage of this technique lies in determining all the elements with greater accuracy in samples of different fields such as environmental science, biology, archeology, biomedicine, archeometry, geology and nanotechnology, among others [11-17, 18 -21]. PIXE technique seems to be favored for geological applications as it is one of the most promising methods of multi elemental analysis introduced in recent years [22-24]. The need of external PIXE basically arises from the want of geological and archeological materials as those are precious and difficult to be recovered, if damaged. This technique is a method of choice for analysis of samples with its well-known features like multi elemental capabilities, small sample mass, high sensitivity, dynamic range and sample or no sample preparation. It is a nuclear analytical technique, which is very much suitable for quantitative elemental characterization in a wide range of complex materials, especially in the range of the middle Z elements.

The PIXE technique has rapidly gained acceptance as a valuable analytical tool because of the ever-increasing need for the elemental analysis of very small amounts of sample, as in the case of geological materials such as gemstones [24]. PIXE with external beam is a relatively simple, yet powerful analytical technique that can be used to identify and quantify trace elements in a sample. PIXE is a nuclear analytical technique for rapid analysis of a wide range of trace elements with ppm sensitivity. Due to its high sensitivity, it is used in the field of geology for investigating trace elements in geological specimens [25-27]. The use of protons offers a good sensitivity, even at lower atomic numbers, because the bremsstrahlung, which is caused by protons, is low compared to the electron excitation. In the present work, we determined the concentrations of trace elements in the gem mineral moonstone with the external PIXE technique.

In the general case of geological material, a good amount of sampling is made and it would be very much useful for all laboratory investigations. But, in the case of gemstones, the sample size is very minute and collecting a sample of about a gram or so is very difficult from the field and at the same time, it would be difficult to destruct the sample for microscopic and analytical techniques. In most of the cases, characterization is enough to name the minerals. The External PIXE technique helps a lot in determining the chemistry of the gem minerals, as it is a non-destructive type of analyses and it aids in full characterization of the gem minerals.

2. Materials and Methods:

2.1 Study Area: The present study area Asakapalli (83°-84° N Lat.; 17°- 18° E Long.) is located in Visakhapatnam District, Andhra Pradesh on the southeastern seacoast of India (Fig.1 & Fig.2). It extends over a length of 5 km, trending NE-SW with an average width of more than 1.5 km. The Bay of Bengal in the southern side and Eastern Ghats Group of rocks in the northern and northwestern side bound this area.

2.2 Collection and processing of Samples: The samples of moonstone in the present work were collected from Asakapalli village, Sabbavaram Mandal, Visakhapatnam district, Andhra Pradesh, India; an important segment of Eastern Ghats (Fig.1 & Fig.2) which are recently known for the moonstone occurrences. Moonstones are found in association with chrysoberyl, chrysoberyl cat's eye, garnet, amethyst, rose quartz, apatite and citrine.

The moonstone samples were washed with tap water followed by distilled water and cleaned properly with acetone for the removal of contaminants on the surfaces of the specimens. Cleaned and processed moonstone samples were placed over the target ladder. The moonstone samples were then used as targets for the collimated beam, which was aimed on the samples, and the emitted characteristic X-rays were collected using a Si (Li) detector that was maintained at the temperature of liquid nitrogen.

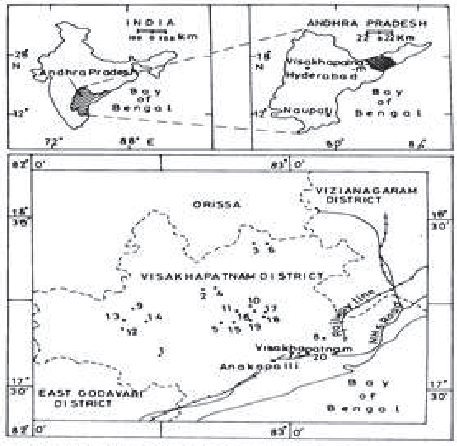

Fig. 1 LOCATION OF GEMSTONE OCCURRENCES IN PARTS OF VISAKHAPATNAM ANDHRA PRADESH, INDIA. (After Kasipathi et.al.1998)

1.Pappusettipalem, 2. Paderu, 3. Araku, 4. Turaiguda, 5. Pittagedda, 6. Matsyapuram 7. Venkataramana peta, 8. Asakapalli, 9. Lothugedda, 10. Goppulapalem 11. Khutikonda, 12. Pinapadu, 13. Geelugumetta , 14 Peddakonda ,15 Peddapitta gedda, 16 Ravipalem , 17. Korramamidipalem , 18. Goppuru , 19. Siripuram 20. Yeduvakala.

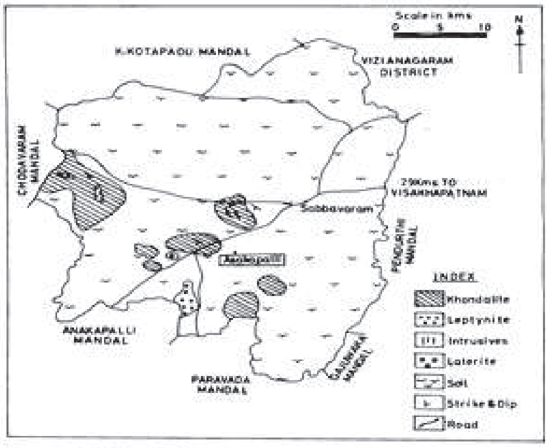

Fig.2. GEOLOGY OF SABBAVARAM MANDAL, VISAKHAPATNAM DISTRICT, ANDHRA PRADESH, INDIA.

2.3 Mineralogy and chemistry of Moonstone: The gem mineral of ‘Moonstone’ is a variety of complex perthite mixture of sodium and potassium feldspar minerals, comprising Na-K-Al silicates with dominating silica content of about 65%. The perthite forms of moonstone show various forms of string lets, strings, rods, beads, fractured beads, interlocking, interpenetration and replacements as their characteristics under the polarizing microscope. Moonstone [(K, Na) $AlSi_3O_8$] is a soft milky white stone, the most valuable variety of feldspar with a rainbow sheen. Moonstone shows a silvery or bluish iridescence that is caused by the intergrowth of two different types of feldspar with different refractive indices. The term moonstone also has been applied to the plagioclase feldspars peristerite and labradorite, which also exhibit iridescence. The moonstone is mostly white, grey, yellow, orange, pink and colorless and represents pearly and schillery appearance. Their density is variable between 2.55 to 2.62 and the hardness varies from 6.0 to 6.5. The sheen reflections of this stone are also referred to adularia and this character is known as adularescence. The characterizations between these two types of moonstones are presented in Table.1. The crystal forms of both orthoclase and albite moonstone are different.

Table 1: Mineralogy of the Two Different Moonstones

S.No	Character	Orthoclase Moonstone	Albite Moonstone
1.	Crystal System	Monoclinic	Triclinic
2.	Twins	1) Carlsbad (irregular penetration) or contact type 2) Baveno Twins (nearly square Prisms) 3) Manebach (Contact twin)	Triclinic – In addition show albite law (contact twins and polysynthetic twins result striations on ‘C’ axis) and pericline law (Contrast twins along rhombic section, polysynthetic represents striation of ‘B’ axis
3.	Crystal form	Fine crystals of larger size form sometimes complex twin crystals occur, Prismatic, orthorhombic, thick tabular, massive and granular	Tabular, lamellar, massive, granular and often curved
4.	Cleavage	(001) perfect, (110) imperfect	(001) perfect, (110) imperfect
5.	Parting	Distinct along (100)	Distinct along (010)
6.	Fracture	Conchoidal to uneven, brittle	Uneven to Conchoidal
7.	Hardness	6.0	6.0-6.5
8.	Specific gravity	2.56	2.60-2.62
9.	Luster	Vitrioius and pearly, sometimes satin or Schiller like	Viereous and pearly
10.	Colour	Colourless, White, pale brown, milky sheen exhibits at the truncations of the prism as per its position	White, Grey, Bluish, Opalscence or play of colours
11.	Streak	Colourless	Colourless
12.	Transparency	Transparent to translucent	Transparent to subtranslucent

2.4 Experimental Set Up: In the present work, the experiment was carried out at the Institute of Physics (IOP), Bhubaneswar, India. A proton beam of energy 3MeV is obtained from 3MV tandem type pelletron accelerator. This accelerator has been routinely used for carrying out material analysis using PIXE and external beam PIXE techniques. This beam was collimated by a graphite collimator to a beam size of 3mm diameter. Using a Kapton foil, the beam was extracted at the exit point of the chamber (8μm diameter). The scattering chamber has an inner diameter of 80cm and was designed to cater the requirements of the external beam. The beam is first focused and centered at the target location inside the scattering chamber and then let through the thin Kapton foil placed at the exit port. The chamber is pumped by a high throughput diffstack pump to maintain a vacuum in the range of 10^{-7} m bar in the chamber and the beam line. The Kapton foil is used as exit window due to its several special characteristics like low beam induced background emission, minimal energy loss and radiation damage resistance. The beams from exit point of chamber were allowed to travel about 3cm in air and about 3MeV proton beam were used to irradiate the targets. Beam charge measurement was carried out using a rotating chopper as described by Mando, 1994 and Chiari et al, 2002 [25, 30]. The chopper disc of diameter 15cm is placed between the exit window and the sample at a distance of 3mm from the exit window. The chopper vane is fully isolated from the electrical motor as well the beam line using insulation and is connected to the current integrator for recording the charge. The charge measurement of the chopper is calibrated using the pure copper foil.

The samples were irradiated with maximum beam current of 15nA passing through the 8μm thick Kapton window, at an angle of 45° to the beam direction in the air. A Si (Li) detector of Canberra with FWHM of 170eV at 5.9KeV placed at 90° with respect to the beam direction was used to detect characterized x-rays emitted from the sample. The detector has an active area of 30 mm^2 and an entrance beryllium window of 8μm thickness. A 50μm thick aluminized Mylar absorber (with 6% hole) was kept in front of the detector to attenuate the bremsstrahlung background and dominant low energy x-ray peaks. Spectra were recorded by using a Canberra S-100 MCA (a multi channel analyzer), which was calibrated with ^{241}Am X-ray source. The processed moonstone samples were placed over the target ladder. Now the collimated beam was made to fall on the samples and emitted respective x-rays are collected using Si (Li) detector. The data were analyzed with the GUPIX software program [31].

2.5 Analysis of Data: External PIXE spectral analysis was carried out using GUPIX software [32-33] that provides non linear least square fitting of the spectrum. GUPIX utilizes the fundamental parameter method (FPM) for quantitative analysis that requires parameters of experimental geometry and detector (H parameter), chamber window thickness, target major matrix, the energy of the incident particle, and the net charge collected. To check the adopted analysis procedure and input parameters external standard method was adopted using macrometer standard and other certified reference materials, and accordingly H values were normalized. The further details about the analysis procedure can be obtained from above mentioned references [32-33]. Using this software package, different elements present in each of the moonstone gem were identified and their concentrations were determined. To ensure the reliability of this method in reproducing concentrations of elements, we have checked the accuracy of this technique by analyzing NIST standard Coal fly ash [1633b]. This shows the reliability of the concentration values obtained in the present work.

2.6 X-ray Diffraction: The moonstone samples were ground to a fine powder using a pestle and agate mortar for recording the XRD spectra. The X-ray diffraction (XRD) experiment was performed at Andhra University in Visakhapatnam, India. The powdered XRD patterns of the moonstones were determined using a miniflux X-ray diffractometer (Rigaku America's corporation, USA) with rotating copper target of voltage 40 KV and current 100 mA. X-rays of wavelengths $\lambda_{k\alpha 1}$ = 1.5406 A^o, $\lambda_{k\alpha 2}$ = 1.5443A^o were selected using (002) graphite crystal scattering at goniometer receiving slit. The divergence slit angle, scattering slit angle and receiving slit width were selected as 0.5^o, 0.5^o and 0.15mm respectively. The XRD instrument consisted of an X-ray generator, goniometer, gas proportional detector and a counting system.

3. Results and Discussion: The gems (Moonstones) collected from different parts in and around the Asakapalli Village of Sabbavaram Mandal in Visakhapatnam District of Andhra Pradesh; Eastern Ghats of India are analyzed with external beam PIXE and XRD techniques. The minor and trace elements present in the samples are detected with external proton beam obtained from tandem type pelletron accelerator at Institute of Physics (IOP), Bhubaneswar, India. Along with the lattice parameters and the crystal structure of the moonstone gems the major compositional elements are also confirmed by X-ray diffraction (XRD) technique.

External PIXE is used to determine the constituents' viz. K, Ca, Ti, V, Cr, Mn, Fe, Zn, Ba and Pb which are within the general range of their chemical composition. The instrument determines the chemistry of any specific point of the mineral and variations can be summarized by the color and nature of the mineral group.

The gemstone 'Moonstone' contains K, Ca, Ti, V, Cr, Mn, Fe, Ni, Zn, Ba and Pb. Because of the limitation of the Si (Li) detector the elements Si and Al were unestimated by external PIXE method. The concentrations (in ppm by weight) and the experimental errors of these elements in the 'Moonstone' gem as obtained by external PIXE are given in Table.2. Errors in external PIXE results are based on number of counts and on the least-square fitting of the peak areas, which include the uncertainties in the background subscription. It can be seen from Table.2 that the results are consistent within the permissible range of errors.

The range of concentration of Ti was found in these samples between 0.019% and 0.089%, where as the elements V, Cr, Mn and Fe are in the ranges from 0.0097% -0.052%, 0.061% - 0.18%, 0.11% - 0.19% and 0.20% - 0.33% respectively (Table. 2). On the other hand the range of variation in the concentration for the elements K and Ca are quite large, which varies from 3.904% to 7.873% and 0.769% to 1.983% respectively. Furthermore, the concentrations of trace elements (Table. 2) show interesting behavior with large variation except for the elements gallium and lead, which are present in some 10's of ppm to 100's of ppm (range:29-356 ppm and 108-169 ppm respectively) in these samples.

Table 2: Concentration of elements in moonstone samples (values are in ppm).

	K	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Ga	Ba	Pb	Zn
GMS-1	5795± 409.0	1699± 66.26	899± 44.05	113± 6.10	1029± 44.24	1423± 45.53	3317± 129.36	924± 29.56	828± 26.49	72± 4.53	801± 31.23	136± 8.97	413± 28.49
GMS-2	4019± 364.60	1812± 57.98	494± 26.67	413± 20.23	1593± 68.49	1842± 71.83	2813± 109.7	453± 14.49	719± 23.00	197± 12.41	589± 22.97	108± 7.12	308± 21.25
GMS-3	3904± 265.56	1382± 3.89	512± 27.76	312± 15.28	1460± 62.78	1796± 70.04	2960± 94.72	702± 22.46	512± 16.38	356± 22.42	1130± 44.07	--	78± 5.38
GMS-4	4483± 357.83	1158± 45.16	631± 34.07	249± 12.20	914± 39.30	1397± 44.70	2974± 95.16	689± 22.09	329± 10.52	243± 15.30	612± 23.86	169± 1.11	101± 6.96
GMS-5	5435± 452.92	1047± 40.83	435± 21.31	230± 12.24	709± 30.14	1329± 42.52	2481± 79.39	735± 22.52	641± 24.99	114± 7.18	1035± 40.36	--	31± 2.13
GMS-6	7873± 473.04	1328± 51.79	143± 7.00	329± 17.75	807± 34.70	1523± 48.73	2009± 78.35	819± 26.20	929± 36.23	86± 5.41	721± 28.11	119± 7.85	--
GMS-7	6114± 367.64	1239± 48.12	536± 26.26	427± 23.05	1421± 61.10	1283± 41.05	3120± 121.68	569± 18.20	607± 23.67	29± 1.82	940± 36.66	--	59± 4.07
GMS-8	3992± 265.98	769± 29.99	198± 6.33	97± 5.23	1239± 53.27	1181± 37.79	2042± 79.91	512± 16.38	923± 29.53	261± 16.44	1281± 50.27	108± 7.12	89± 6.14
GMS-9	4618± 283.77	1279± 49.88	204± 6.52	468± 25.27	1193± 51.29	1568± 61.15	3124± 99.96	269± 8.60	734± 23.48	134± 8.44	830± 32.37	--	221± 15.24
GMS-10	4789± 365.87	1038± 40.48	469± 15.00	309± 16.68	809± 34.78	1521± 51.87	2643± 90.97	921± 29.47	491± 15.90	129± 8.12	652± 25.42	123± 8.11	185± 12.76
GMS-11	5745± 368.04	1343± 52.30	524± 16.76	104± 5.16	618± 26.57	1959± 76.40	2492±79.74	453± 14.49	512± 16.38	108± 6.80	496± 31.24	146± 9.63	--
GMS-12	5149± 292.10	1983± 63.45	896± 28.67	529± 28.56	1873± 59.93	1947± 62.30	2438± 78.01	896± 28.67	634± 20.28	94± 5.92	953± 60.03	110± 7.26	301± 20.76

The proportion of end-member molecules of analyzed moonstones inferred from the physical properties lie within the range of accuracy to those calculated from chemical determinations. The moonstones from pyroxene granulites have been analyzed Table 3. he numbers of ions on the basis of 6(O) are calculated from the chemical analyses and data are furnished in table 3.

Table 3: Chemical Analysis of Moonstones from Asakapalli area, India

Element	1	2	3	4	5
SiO_2	66.20	66.24	66.28	66.34	67.41
Al_2O_3	18.16	18.86	19.17	19.36	20.32
FeO	0.02	0.05	0.09	0.96	0.08
CaO	0.04	0.17	0.14	0.02	0.05
Na_2O	7.98	5.34	6.07	8.34	6.92
K_2O	7.84	9.48	8.09	5.78	4.54
Total	100.24	100.14	99.84	100.8	99.32
	NUMBER OF IONS ON THE BASIS OF 6 (O)				
Si	3.952	3.869	3.794	3.934	3.813
Al	0.891	0.824	0.916	0.727	0.812
Fe	0.007	0.008	0.004	0.006	0.005
Ca	0.005	0.006	0.010	0.044	0.007
Na	0.351	0.348	0.352	0.347	0.943
K	0.766	0.837	0.918	0.894	0.296
Total	5.972	5.892	5.994	5.952	5.876
	TERNARY FELDSPAR COMPOSITIONS (MOL %)				
Anorthite	4.28	3.22	2.97	3.73	2.96
Albite	29.89	27.82	30.14	34.82	29.98
Orthoclase	65.42	68.94	66.99	61.46	66.54

To compare the elemental concentration profile among the various moonstone samples, the ranges and the mean elemental concentrations have been determined from each of these samples. The mean concentration profiles for the elements Ca, Cr, Mn and Fe are shown in Fig.3 and the average of the concentration profiles for minor and trace elements is as shown in Fig.4. The minor elemental concentrations were found to be very similar among all the moonstone samples.

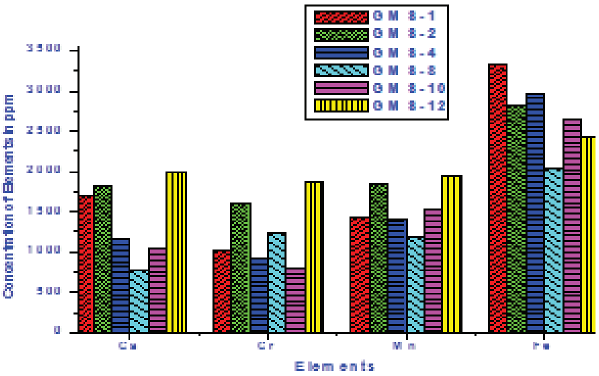

Fig. 3: The Bar Diagram For The Elemental Profile In Moonstones.

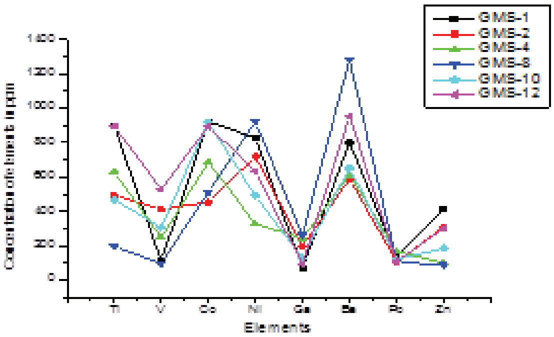

Fig. 4: Minor And Trace Elemental Concentration Profile In Moonstones.

It can be noticed from the Fig.5 that the mean concentrations of Ca is almost similar for the pair of samples GMS1, GMS2 and for GMS4, GMS10, the concentration values are high and low respectively for these pairs of moonstone samples. And there is a noticeable variation in the concentration of Ca among the moonstones and the value is least for the samples GMS8 as well as highest for GMS12. The concentrations of Cr in all moonstones are found to be almost same except for GMS2, GMS8 and GMS12. It is also observed from Fig.3 that, the distribution of Mn is not uniform for all samples and there is a considerable increment in GMS12 and decrement for GMS8. Similarly, the observation on Fe concentration from Fig.3 reveals that its value is more in all moonstones and is little bit high for GMS1 and GMS4. And from the Fig.3 it is clear that the average concentration of Cr and the Fe is low and high in all moonstones respectively, whereas the average concentrations of Ca and Mn are medium for all gems.

It can be observed from Fig.4 among the identified trace elements, the mean concentration of Ba in almost all the moonstones are high where as the concentrations of Ga and Pb are low in all the gemstone samples. And the concentration of remaining elements such as V, Ti, Co, Ni and Zn are lies in between them.

The pie diagram of the element potassium is as given in Fig.5. From the Fig.5 it is clear that the concentration of the element potassium is maximum for the moonstone sample labeled GMS-1 and minimum for the moonstone samples labeled GMS-2 and GMS-8. It can also be noticed from table 2, the average concentrations of K is maximum for all moonstone specimens indicating that may be these moonstones belonging to Adularia category.

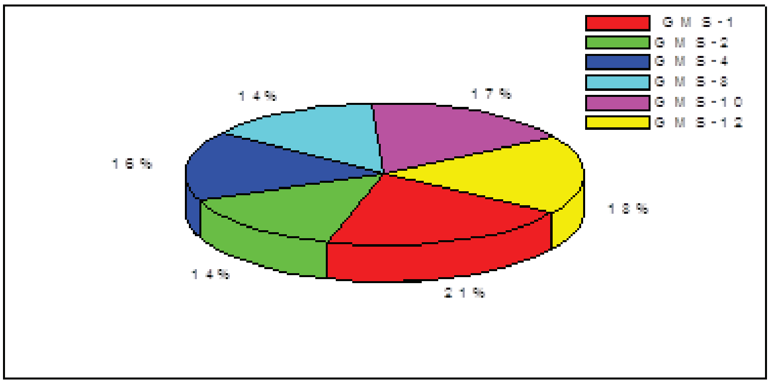

Fig. 5: The Pie Diagram of the Element Potassium in Moonstones

In order to understand the significant role of elements in the gem moonstone, a series of inter-elemental correlation (various plots of minor verses trace elements) has been attempted from the results of the concentrations of various elements and only the excellent correlations have been plotted (Fig.6) and considered for further understanding and discussions. From the Fig.8 it is clear that the concentration of iron shows sympathetic relation with lead, and nickel also exhibits the same sympathetic trend with zinc, whereas the elements iron and cobalt follow antipathetic relation with the elements nickel and lead respectively.

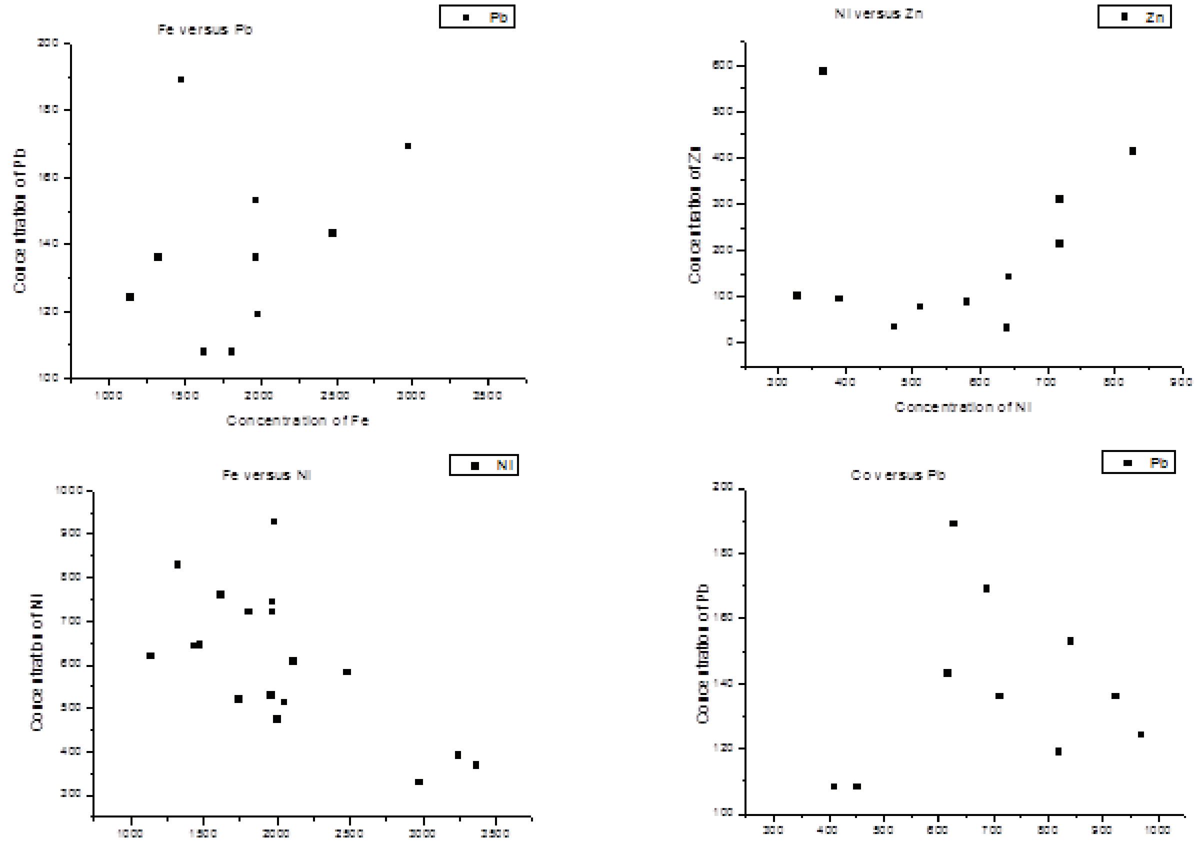

Fig. 6: Sympathetic and Antipathetic Nature of Elements in Moonstone Gems

From the plots, it is found that the concentration of K shows sympathetic nature with the elements Fe, Ni, Ga, Ba and Zn as well as antipathetic nature with Co and Pb. And the concentration of Mn follows antipathetic relation with Co, Ni, Ba and Pb and sympathetic relation with the elements Fe, Ga and Zn. There is a similar positive trend i.e., sympathetic nature of calcium with vanadium, titanium, chromium, manganese and iron and the antipathetic relation with cobalt, nickel, gallium, barium, zinc and lead were also found. It is also noticed from the plots Fe shows sympathetic trend with Ga, Ba and Pb and antipathetic nature with Co, Ni and Zn. And the element Co exhibits similar sympathetic relation with Ni, and Ba and antipathetic nature with Ga, Pb and Zn. And chromium exhibits the antipathetic relation with manganese, iron, gallium, barium and zinc and the sympathetic relation with cobalt and lead. It may be possible that there is a simultaneous precipitation in case of sympathetic nature of elements and simultaneous differentiation in the antipathetic nature of elements with that of the source solution.

A moonstone is made up of crystallites of three different feldspars. They are present in different moonstones to different extents. Generally the most dominant component is the monoclinic potash feldspar (orthoclase). The next important component is the triclinic soda feldspar (albite). Incidentally these two feldspars are similar in chemical composition though they have different crystal structures. The third component that exists in very small amounts is the triclinic lime feldspar (anorthite). It may be mentioned here that this feldspar is an isomorph of soda feldspar. In a moonstone these three feldspar crystallites are interwoven inside the medium and these are given in Figure-7.The minerallographic observations of orthoclase moonstone (adularia moonstone) show a microperthitic association of orthoclase and albite, where orthoclase is dominant. This microperthitic association resulted slight turbid transparency. In the present area of study, adularia moonstone is found to be dominant in occurrence than that of albite moonstone. In albite moonstone also microperthitic association between orthoclase and albite is observed but albite predominates in its content. Physically all these types can be distinguished by their density, hardness and color [Figure-7].

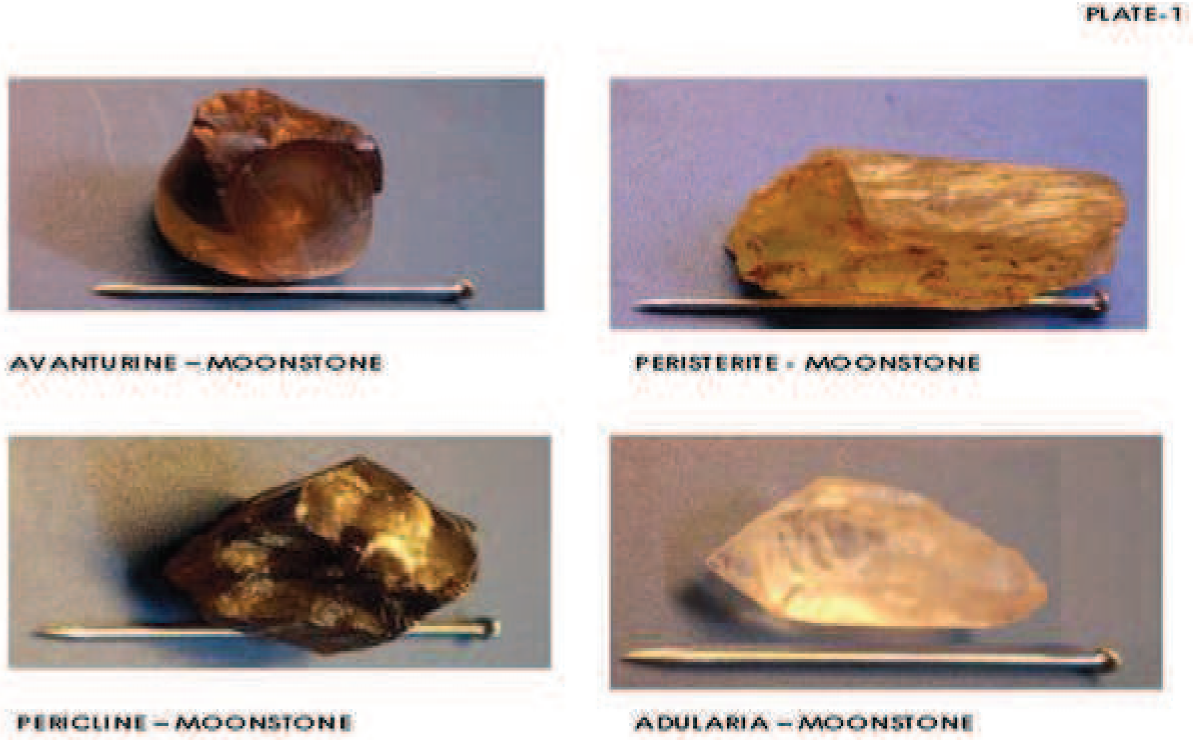

Fig. 7: Photograph of Natural Moonstone Collected from Present Study Area

For the laboratory investigation, sampled geological material will be much useful. In most of the cases, characterization is enough to name the minerals. The external PIXE technique helps a lot in determining the chemistry of gem minerals, as it is non-destructive type of the analysis and it aids in full characterization. Preliminary XRD patterns on powdered gemstones are also studied. A typical XRD spectrum of the present investigation is shown in Fig.8, where the data (2θ, d, h k l values and intensities of Al_2SiO_5 (Mullite)) show similarity with JCPDS-ICDD, PDF-2, Sets 1-42 database, as presented in Table.4. Aluminium and silicon are major compositional elements of moonstone gems and it is confirmed by XRD studies.

Table 4: X-ray Diffraction Analysis of Moonstone Gem

2-Theta	d(nm)	I(v)	(h k l)	Theta	1/(2d)	2pi/d
13.807	0.5366	9	(1 1 0)	6.253	0.00932	0.11709
19.386	0.4575	1	(1 0 1)	9.693	0.01093	0.13734
23.15	0.3839	12	(0 2 0)	11.575	0.01302	0.16367
26.072	0.3415	100	(1 2 0)	13.036	0.01464	0.18399
27.893	0.3196	34	(0 2 1)	13.947	0.01564	0.1966
30.961	0.2886	8	(0 0 2)	15.48	0.01733	0.21771
33.408	0.268	20	(2 2 0)	16.704	0.01866	0.23445
35.279	0.2542	27	(1 1 2)	17.64	0.01967	0.24717
36.962	0.243	4	(2 2 1)	18.481	0.02058	0.25857
37.105	0.2421	28	(1 3 0)	18.552	0.02065	0.25953
39.33	0.2289	4	(3 0 1)	19.665	0.02184	0.27449
40.913	0.2204	46	(1 2 2)	20.457	0.02269	0.28508
41.128	0.2193	3	(3 1 1)	20.564	0.0228	0.28651
42.781	0.2112	19	(2 3 0)	21.391	0.02367	0.2975
45.701	0.19836	2	(2 3 1)	22.851	0.02521	0.31676
48.61	0.18715	4	(4 0 0)	24.305	0.02672	0.33573
49.02	0.18568	2	(1 4 0)	24.51	0.02693	0.33839
51.09	0.17863	4	(3 3 0)	25.545	0.02799	0.35174
53.649	0.1707	14	(3 3 1)	26.824	0.02929	0.36808
54.508	0.16821	6	(4 2 0)	27.254	0.02972	0.37353
57.629	0.15982	26	(0 4 2)	28.815	0.03129	0.39314
58.752	0.15703	2	(4 0 2)	29.376	0.03184	0.40013
59.058	0.15629	7	(2 2 3)	29.529	0.03199	0.40202
60.898	0.152	31	(3 3 2)	30.449	0.03289	0.41337
62.042	0.14947	2	(3 1 3)	31.021	0.03345	0.42036
64.213	0.14493	2	(5 0 1)	32.106	0.0345	0.43353
65.687	0.14203	10	(2 5 0)	32.844	0.0352	0.44238
67.911	0.13791	2	(2 5 1)	33.956	0.03626	0.4556
69.53	0.13509	3	(0 2 4)	34.765	0.03701	0.46511
70.571	0.13335	20	(1 5 2)	35.285	0.0375	0.47118
71.012	0.13263	8	(2 1 4)	35.506	0.0377	0.47374
72.07	0.13094	3	(5 1 2)	36.035	0.03819	0.47985
74.051	0.12792	80	(0 6 0)	37.025	0.03909	0.49118
75.303	0.1261	5	(5 3 1)	37.652	0.03965	0.49827
78.674	0.12152	3	(4 4 2)	39.337	0.04115	0.51705
80.572	0.11913	3	(2 3 4)	40.286	0.04197	0.52742
83.802	0.11534	3	(0 4 4)	41.901	0.04335	0.54475
85.026	0.11399	6	(1 4 4)	42.513	0.04386	0.55121
87.238	0.11166	3	(3 6 1)	43.619	0.04478	0.56271
88.948	0.10995	3	(4 4 3)	44.474	0.04548	0.57146

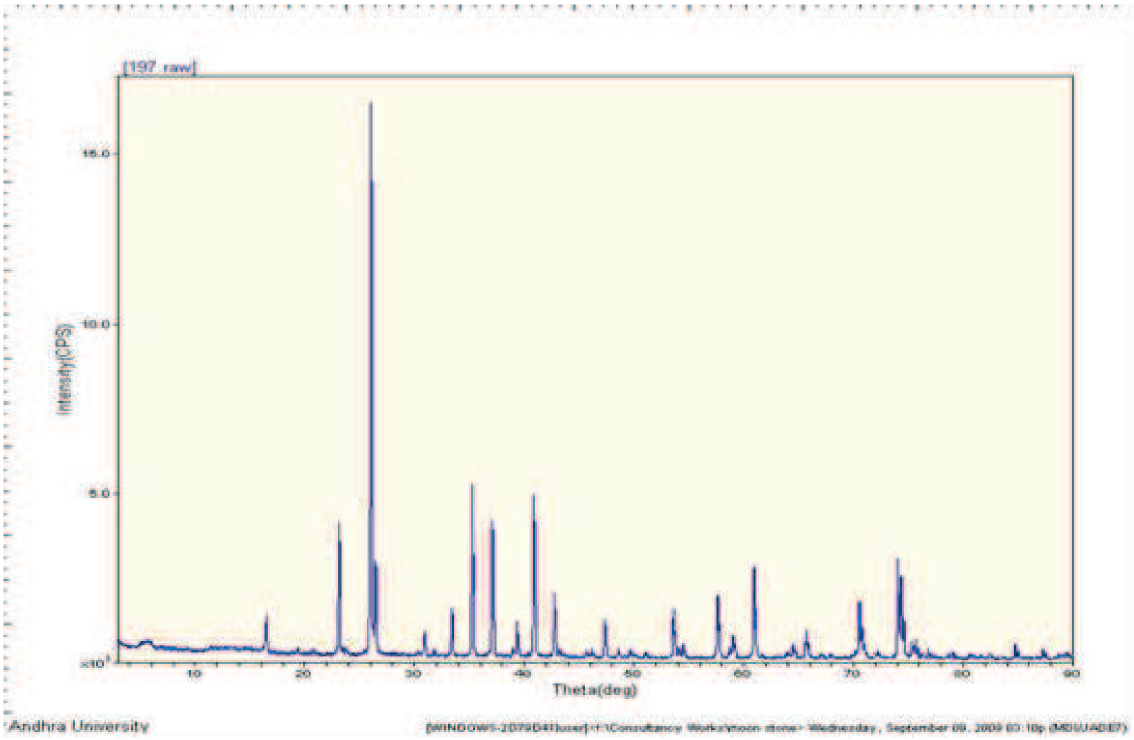

Fig. 8: X-ray Diffraction Spectrum of the Eastern India Moonstone Gem

The results of the External PIXE analysis of moonstone, suggest that owing to natural origin, the trace element content varies depending on the local geological surroundings leading to large deviations in trace element composition. Thus PIXE, with external milli and micro beams is increasingly used for multi elemental analysis in geological problems, where the determination of the major and trace elements composition phases and their inclusions [34,35]. On the other hand, external PIXE data are obtained in a much faster and more direct way.

4. Conclusion: For the first time moonstone gems from Eastern Ghats of Andhra Pradesh, India were analyzed with a complementary and non-destructive external beam PIXE technique. Thirteen elements, including the trace elements Co, Ni, Ga, Ba, Zn and Pb, were measured in these moonstones, and the results from this analysis may be useful in interpreting the various geochemical conditions of these gemstones and the probable cause of their inceptions in moonstones. The crystal structure and the lattice parameters of moonstones were estimated using XRD studies, trace and minor elements were determined using external PIXE, and major compositional elements were confirmed by XRD studies.

The complementary, accelerator-based technique of external beam PIXE analyses was used to characterize natural moonstone gems. These gems are mainly used for scientific and technological applications but are also used commercially. The moonstones were identified by their elemental concentrations, and several elements and their concentrations were determined from these samples. Trace element levels in gemstone affect their color as well as beauty and thus market values. Importantly, these findings supported the preliminary XRD studies. In the present study, adularia moonstone was found to be more prevalent than albite moonstone. Because the external PIXE technique is non-destructive and aids in full characterization of minerals, it can identify and determine the chemistry of the minerals present in moonstones.

Thus the external PIXE technique with a 3MV pelletron accelerator was used for characterization of natural and semi precious gemstones. The study concludes that the technique can determine the elemental concentrations of the gem minerals and variations can be summarized with the color and nature of the mineral group.

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References

1. Kasipathi c. 1997. Mineral Resources of Visakhapatnam District, Andhra Pradesh. *Visakha Science. Journal, (A.P.Akad. Sci Publ.),* **1**, 39.
2. Kasipathi C. 1999. Precious & semi-precious stone occurrences with Eastern Ghats formations, Visakhapatnam District, A.P. *The Indian Mineralogy* **33**, 23.
3. Joseph D., Lal M., Shinde P. S. & Padlia B. D. 2000. Characterization of some selected gemstones (rubies and sapphires) by Energy Dispersive X-ray Fluorescence (EDXRF). *X-ray Spectrometry* **29,** 147-150.
4. Naasu K.1978. The origins of color in minerals. American Mineralogist. **63**, 219 – 229.
5. Johansson T. B., Akselsson R. & Johansson S. A. E. 1970. X-ray analysis: Elemental trace analysis at the 10–12 g level. *Nuclear Instruments and Methods in Physics Research B* **84 (1)**, 141 – 143.
6. Rogers P. S. Z., Duffy C. J., Benjamin T. M. & Maggiore C. J. 1984. Geochemical applications of nuclear microprobes. *Nucl. Inst. and Meth. in Physics Research B* **3,** 671.
7. Benjamin T. M., Duffy C. J., Maggiore C. J., Rogers P. S. Z., Woolum D. S., Burnett D. S & Murrell M. T. 1984. Microprobe analyses of rare earth element fractionation in meteoritic minerals. *Nuclear Instruments and Methods in Physics Research B* **3**, 677 – 680.
8. Sie S. H., Ryan C. G., Cousens D. R. & Griffin W. L. 1989. Application of the proton microprobe in mineral exploration and processing. *Nuclear Instruments and Methods in Physics Research B* **40/41**, 690-697.
9. Jime´Nez-Reyes M., Tenorio D., Esparza-Lopez J. R., Cruz-Jime´Nez R L., Mandujano C. & Elizalde S. 2001. Neutron activation analysis of obsidians from quarries of the central quaternary Trans-Mexican 505 Volcanic Axis. *Journal of Radio analytical and Nuclear Chemistr ,* **250,** 465–471.

10. Tenorio D., Almaza´ n-Torres M. G., Monroy-Guzma´ n F., Rodri´Guez-Garci´a N. L. & Longoria Luis C. 2005. Characterization of ceramics from the archaeological site of San Miguel Ixtapan, Mexico State, Mexico, using NAA, SEM, XRD and PIXE techniques., *Journal of Radio analytical and Nuclear Chemistry* **250,** 465 – 478.
11. Ryan S. R., Fischbeck H. J. & Chesnut K. 1985. Correlation of archaeological ceramics and clays using an external-beam PIXE analysis of the major elemental constituents.. *Nuclear Instruments and Methods in Physics Research B* **10/11,** 645 - 649.
12. Maenhaut W., Vandenhaute J & Duflou H 1987**.** Applications of PIXE to biological and biomedical samples at the university of Kent. *Nuclear Instruments and Methods in Physics Research B* **22**, 138.
13. Uda M., Tsunokami T., Murai R., Maeda K., Harigai I., Nakayama Y., Yoshimura S., Kikuchi T., Sakurai K. & Sasa Y. 1993. Quantitative analysis of ancient Egyptian pigments by external PIXE. *Nuclear Instruments and Methods in Physics Research B* **75,** 476
14. Venkateswara Rao R., Mary Anupama P., Guru Mahesh D., Iqbal A. W., Ramakrishna Y. & Venkateswarulu P. 2010. Estimation of trace elements in various parts of human teeth using external beam PIXE. *International Journal of Physics and Applications* **2,** 123-134.
15. Arai N., Sakamoto W. & Maeda K. 1996**.** An attempt to analyze fish otolith by in- air PIXE. *Nuclear Instruments and Methods in Physics Research* B **(109/110),** 341-344.
16. Bhulokareddy S., Venkateswarulu P., Bhaskararao K., Seshagirirao V., Ramachandrarao K., Ramakrishna Y. & Nagaraju G. J. 2001. Trace elemenental analysis in the whole blood samples of Diabetes and Rheumatoid patients using PIXE technique. *Andhra Pradesh Akademy Science Publications* **5**(3), 185-189.
17. Nagaraju G. J., John Charles M., Bhuloka Reddy S., Sarita P., Seetharami Reddy B., Rama Lakshmi P. V. B. & Vijayan V. 2005**.** Trace elemental analysis in cancer afflicted tissues of pennies and testis by PIXE. *Nuclear Instruments and Methods in Physics Research B* **229,** 457-464.
18. Rautray T. R., Vijayan V. & Panigrahi S. 2007. Analysis of Indian pigment gallstones. *nuclear instruments and methods in physics research B* **255**, 409 -415.
19. Chanda S. C., Manna A., Vijayan V., Pranaba K Nayak., Ashok M. & Acharya H. N. 2007**.** PIXE and XRD analysis of nano crystals of Fe, Ni and Fe_2O_3. *Materials Letters* **61,** 5059-5062.
20. Mohapatra A., Rautray T. R., Patra A. K., Vijayan V. & Mohanty R.K. 2008. Elemental composition in mud crab Scylla serrata from Mahanadhi estuary, India: in situ irradiation analysis by external PIXE. *Food and Chemical Toxicology* **47** (1), 119–123.
21. Rautray T. R, Vijayan V., Sudarshan M. & Panigrahi S. 2009**.** Analysis of blood and tissue in gall bladder cancer. *Nuclear Instruments and Methods in Physics Research B* **267,** 2878–2883.
22. Olabanji S. O., Haque A. M. I., Znadolin S., Ajayi R. T., Buoso M. C., Ceccato D., Cherubini R., Zafiropools D. & Moschini G. 1996. Applications of PIXE, PIGE, SEM and EDAX techniques to the study of geological samples. *Nuclear Instruments and Methods in Physics Research B* **109/110**, 262.

23. Dutta R. K., Sudarshan M., Bhattacharya S. N., Chakravorthy V. & Chintalapudi S. N. 1998. Quantitative multielemental analysis of titaniferous magnetites. *Nuclear Instruments and Methods in Physics Research B* **104**, 403.
24. Olabanji S. O., Ige O. A., Mazzoli C., Ceccato D., Akintunde J. A., De Poli M. & Moschini G. 2005. Accelerator-based analytical technique in the evaluation of some Nigeria's natural minerals: fluorite, tourmaline and topaz. *Nuclear Instruments and Methods in Physics Research B* **240**, 350–355.
25. Mando P. A. 1994. Advantages and limitations of external beams in applications to arts and archaeology, geology and environmental problems. *Nuclear Instruments and Methods in Physics Research B* **85**, 815.
26. Mohanty A. K., Das S. K., Vijayan V., Senagupta D. & Saha S. K. 2003. Geochemical studies of monazite sands of chhatrapur beach deposit of Orissa, India by PIXE and EDXRF method. *Nuclear Instruments and Methods in Physics Research B* **211**, 145–154.
27. Nayak P. K. & Vijayan V. 2006. Complementory PIGE, PIXE, EDXRF and g-ray spectroscopic investigation on natural chromites. *Nuclear Instruments and Methods in Physics Research B* **245,** 505 -510.
28. Dev B. N. 1999. Materials modifications in heavy ion interactions with single crystals and their ion beam characterization. *Nuclear Instruments and Methods in Physics Research B* **156**, 258.
29. Rout B, Ghose S. K., Mahapatra D. P., Dev B. N., Bhakru H. & Haberl A. W. 2001**.** Status of ion micro beam facility at the Institute of Physics,Bhubaneswar, India. *Nuclear Instruments and Methods in Physics Research B* **181** 110-115.
30. Chiari M., Migliori A. & Mando P. A. 2002. Measurement of low currents in an external beam set-up *Nuclear Instruments and Methods in Physics Research B* **188**, 162–165.
31. Campbell J. L., Hopmann T. L, Maxwell J. A. & Nezedly Z. 2000**.** The Guelph PIXE software package III: Alternative proton database. *Nuclear Instruments and Methods in physics research B* **170,** 193-204
32. Maxwell J. A., Campbell J. L. & Teesdale W. J. 1989. The Guelph PIXE software Package. *Nuclear Instruments and Methods in Physics Research B* **43**, 218.
33. Maxwell J. A., Campbell J. L.& Teesdale W. J. 1995. The Guelph PIXE software package II. *Nuclear Instruments and Methods in Physics Research B* **95**, 407–421.
34. Macarthur J. D., Ma X.-P., Palmer G. R., Anderson A. J. & Clark A. H. 1990. Below-surface analysis of inclusions with PIXE and PIGE. *Nuclear Instruments and Methods in Physics Research B* **45**, 322-326.
35. Campbell J. L., Maxwell J. A., Teesdale W. J., Wang J. X. & Cab L. J. 1990. Micro-PIXE as a complement to electron probe microanalysis in mineralogy. *Nuclear Instruments and Methods in Physics Research B* '**44**, 347 -356.

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