ANALYSIS OF INDIAN NATURAL CHROMITE ORE AND ROCKS BY NUCLEAR ANALYTICAL TECHNIQUE

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Received: Jul. 2019 Accepted: Aug. 2019 Published: Sep. 2019

Abstract: A number of Indian chromitites have been studied by using complementary and non-destructive PIXE technique. Thirteen elements including Co, Ni, Cu, Zn, Ga, Zr, Mo, Nb and Pb were established in these chromitites, which may be useful to interpret the various geochemical conditions and the probable cause of their inceptions in chromitite matrix. PIXE technique is a powerful method for fast determination of variable multi elemental analyses. The advantage of this technique is that one can obtain all major and minor elements present at once in pure concentration. The chemical constituents of chromite ores and ultrabasic rocks of Boula, Keonjhar district of Orissa State, India, a part of the Eastern Ghats terrain, were analyzed by using PIXE technique. The present work, thus, establishes the usefulness and versatility of the PIXE technique for research in geo-scientific methodology.

Keywords: PIXE, Nuclear Analytical Technique, Peninsular India, Chromite Ores.

1. Introduction: Multi-elemental analysis of geological samples is of great importance in geological research and mineral prospecting. In geological research, the classification of ore and rock samples is done by studying the presence of elements such as Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K and P. Similar information on trace elements will also be obtained using the analytical techniques. A trace element in the present study is defined as an element which is present in a sample with concentrations less than 1000 ppm. Owing to their low concentrations, it is difficult to get information on trace elements unless a suitable technique is adapted. Many methods are employed to characterize the geological areas in according with potentially interesting findings. Traditional geological survey reveals the areas of potential interest. Areas, thus selected, are investigated in greater detail by drilling. Since, the cost of final drilling is very high, it is essential to extract as much initial information as possible. Small samples at regular depth levels from the drilled core are collected and accurate elemental analysis is performed on these samples. It is therefore important to adapt useful analytical techniques to get more reliable information. A brief description of the various available analytical techniques which are adapted in geo research is given below to get information about the elemental concentrations.

The essential information on the elemental composition of the geological material can be deduced from the use of several analytical methods such as Atomic Absorption Spectrometry (AAS), Instrumental Neutron Activation Analysis (INAA), X-ray Fluorescence (XRF), Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) and Particle Induced X-ray Emission (PIXE) etc [1-4]. Some of these methods are destructive for the reason that the samples cannot be used for further studies; some of the techniques give information on one element only or they require sample preparation before analysis. In contrast, PIXE has some distinctive features of being nondestructive, quick and rapid measurements, allowing multi elemental determination and requiring little or no sample preparation.

PIXE is a non-destructive technique for rapid analysis of a wide range of trace elements with ppm sensitivity. Due to its high sensitivity, it is used in the fields of geology and geophysics for investigating trace elements in geological specimens [5-7]. Use of protons offers a good sensitivity even at lower atomic numbers due to the fact that Bremsstrahlung background caused by protons is very low compared to electron excitation. PIXE technique has rapidly gained acceptance as a valuable analytical tool because of the ever-increasing need for elemental analysis of very small amounts of sample, as in the case of geological materials. In the present work, we estimated the concentrations of trace elements in the Indian Peninsular chromite ores and ultra basic rocks by using PIXE technique.

Chromium (Cr) is a grey, hard metal most commonly found in the trivalent state in nature. Hexavalent (chromium (VI)) compounds are also found in small quantities. Chromite ($FeOCr_2O_3$) is the only ore containing a significant amount of chromium. The ore has not been found in the pure form; its highest grade contains about 55% chromic oxide. Chromium levels in soil vary according to area and the degree of contamination from anthropogenic chromium sources. Tests on soils have shown chromium concentrations ranging from 1 to 1000 mg/kg, with an average concentration ranging from 14 to about 70 mg/kg. Chromium (VI) in soil can be rapidly reduced to chromium (III) by organic matter. As chromium is almost ubiquitous in nature, chromium in the air may originate from wind erosion of shale's, clay and many other kinds of soil. In countries where chromite is mined, production processes may constitute a major source of airborne chromium. In Europe, endpoint production of chromium compounds is probably the most important source of chromium in air.

The largest producers of chromium ore are South Africa (44%), India (18%), Kazakhstan (16%), Zimbabwe (5%), Finland (4%), Iran (4%) and Brazil (2%) with several other countries producing the rest, which is less than 10% of the world production [8]. In India, Chromite deposits are found in association with basic and ultrabasic rocks like dunite, pyroxenite, amphibolite and their altered masses. The Peninsular Indian chromites contribute to the entire Indian Chromium production and are distributed in the States of Orissa, Karnataka, Andhra Pradesh and Tamil Nadu. Geologically, the chromite formations are restricted to the Eastern Ghats, Iron Ore Series and Green Schist's of the Peninsular India. The present area of investigation, Boula is a part of the Eastern Ghats terrains, where chromium enriched chromite is associated with pyroxenites.

The industrial development in the world mostly depends on the utility of chromium metal as an important component with Fe and Mn. Chromium is the chief mineral in the production of Chromium metal which is the primary component in the manufacture of stainless steels, and high tech machinery. It is useful in metallurgical refractory and chemical industries based on certain specification of ore. Chromite mineralogy is very interesting area of study, because of the isomorphous mixtures of spinal group. In view of its importance the estimation of the amount of chromium present in Chromite ore and the rock samples along with the minor and trace elements is of greater importance. This forms the backdrop of this research paper.

2. Materials and Methods:

2.1. Sample collection and Preparation:

2.1.1. Study Area: The chromite ore and rock samples have been procured from various chromite mines of Boula in Keonjhar District of Orissa of Eastern India. Boula area is mostly a hilly county made up of chains of low ridges and their foot hills with the northeastern spurs and separated by broad rivers like Salandhi, which flow in the South-Eastern direction. The highest elevation is Δ1343, Phyljora Huli. Apart from the River Salandhi and Bintkholi stream, all the other rivulets remain dry for most part of the year.

2.1.2. Ore Samples: About 200g of chromite ore is crushed into granules in a stainless steel mortar with hard strokes. The strongly magnetic material has been separated as magnetite. Observing the granular shape, size and color under the microscope, the chromium grains are separated. Heavy liquids like tetrabromo ethane used for more clear separation of gangue form the ore mass. The granules are washed with water, decanted and dried at room temperature and powdered to -230 microns. Then the powder is ground in an agate mortar for about 45 minutes each to a mesh size of -400 microns.

2.1.3. Rock Samples: About 200g of fresh rock sample was taken and washed thoroughly under water flow and dried in an oven. The sample was crushed into small chips through -170 microns of mesh. The powder thus obtained was subjected to coning and quartering till the powder was finally ground in an agate mortar for easy digestion. This powder was used in the following analytical work.

Contamination during sample preparation is a serious source of error in geochemical analysis. It usually occurs during grinding and crushing and may create cross contamination. In the present work, the cross contamination is eliminated by careful cleaning and by pre-contaminating the apparatus with the sample to be crushed or ground. Contamination during grinding process is eliminated by carrying out the grinding in agate. The cleaned, processed and separated ore and rock samples were then made into pellets by the following procedure. Small amounts (~150 mg) of ore and rock from each sample were crushed, finely powdered and thoroughly mixed with the binding material (such as boric acid etc) in the ratio 1:1 by weight. 150 mg of high purity (99.9997%) graphite powder was mixed with the samples in order to monitor the beam current. These solid mixtures were thoroughly ground, homogenized and pressed into pellets. A hydraulic press was used to compress the resulting mixture into a pellet of 13 mm diameter and about 1.5mm thickness. The pellets were then used as targets. The prepared targets were placed over the target ladder. The collimated beam was made to fall on the samples and the emitted respective characteristic X-rays were collected using Si (Li) detector which is maintained at liquid nitrogen temperature.

2.2. The details of PIXE Experiment: The present PIXE experiment was performed using a 3 MV Pelletron accelerator at the Institute of Physics, Bhubaneswar in Orissa of India. This accelerator has been regularly used for carrying out material analysis using the PIXE technique [9-10]. A 3 MeV proton beam was used to excite the samples. The samples were suspended on an aluminium sample holder. Then the target holder was loaded into the PIXE chamber and the irradiation was carried out in vacuum conditions. A collimated proton beam of 4 mm diameter was made to fall on the target. The beam current was kept at 20 nA. The targets on the aluminium holder were positioned in the scattering chamber at an angle of 45° with respect to the proton beam. With respect to that beam, an energy dispersive Si (Li) detector (with 160 KeV FWHM resolutions at 5.9 KeV) recorded the characteristic X-ray spectra at 90°. For each sample, the total charge collected and the average beam current were noted. The spectra were gathered for a sufficiently long time in order to obtain good statistics. Spectra were recorded by using a Canberra series MCA. In the present study, PIXE technique was adapted to analyze the chromite ore and rock samples belonging to Boula in Keonjhar district of Orissa, India. The concentrations of different elements were estimated in each sample using GUPIX software package. The estimated concentration of chromite and other trace elements is furnished in tables 1, 2 and3.

2.3 Data Analysis: The collected data were analyzed with the GUPIX software package [11-12]. The relationship between characteristic X-ray yield Y (Z) for an element of atomic number Z and its concentration C_z in a given target matrix is

$$Y(Z) = HY1(Z)\, C_z Q \epsilon_z t_z,$$

Where Y1 (Z) is the computed Yield from the database per steradian per unit concentration and per unit integrated beam charge; Q the beam charge; ϵ_z the intrinsic efficiency of the Si (Li) X-ray detector; and t_z the transmission of the X-rays through any absorber placed between the detector and the specimen. The instrumental constant H is the product of the geometric solid angle of the X-ray detector and any systematic normalization factor present in the charge integration system. The instrumental constant H was measured using 3 MeV protons and a wide range of pure single-element standards emitting both K and L X-rays in the energy region 3–26 KeV. Thus the X-ray yield (Y) is converted to elemental concentration via a defined standardization technique involving H value, the theoretical yield, detection efficiency and filter transmission values.

3. Results and Discussion: The chromite ore and ultrabasic rock samples collected from different parts of Boula were irradiated with the 3MeV proton beam obtained from tandem type Pelletron accelerator at IOP, Bhubaneswar, India. From the emitted characteristic x-rays, elemental concentrations in the samples were calculated. The estimated major elemental concentrations are provided in table 1 and the concentration values are specified in percentage. The measured minor and trace elemental concentrations of chromite ore and ultrabasic rocks are presented in table 2 and table 3 respectively along with their standard deviation. The elemental concentrations in table 2 and table 3 are given in μg/g (ppm) except for the elements Ti, V, Mn, Co and Ni and their concentration is specified in terms of percentage. In the above mentioned tables, the experimental errors in each of the measured concentrations are also given along with the concentrations. Errors in 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 subtraction. It can be seen from tables numbered 1, 2 and 3 that the results are consistent within the permissible errors.

The range of concentration of Ti was found in these samples between 0.013% and 0.96%, whereas Mn is between 0.0078% and 0.36% (tables 2 and 3).On the other hand, the range of concentration for the element Ni is quite large, which is in between 0.41% and 2.56%. Further–more, the concentrations of trace elements (tables 2 and 3) show interesting behavior with large variation except for the elements Cu and Pb, which are present in some 10's of ppm (range:14-73ppm and 12-78ppm respectively)in these samples.

In the literature [13-14], it is reported that the average values of nickel (Ni) in igneous rocks of the Proterozoic period are above 200 ppm. It is found that the concentration of nickel (Ni) in our samples shows the higher values than the previous researcher literature values for the rocks of igneous origin. It indicates that our samples are of igneous origin belonging to the Proterozoic period. Another important geochemical parameter is that the concentration of zirconium (Zr) can be used as an effective indicator of the province considered as less prone to weathering, and is believed to be neither affected by transportation during weathering nor by any other specific later geochemical event of less significance [3]. Furthermore, it is immobile, highly stable and rarely decomposes in nature. So the concentration of Zr in ores may represent the constituent of source rock or solution from which it is generated. In these samples, the content of Zr is rather high with a significantly large variation, leading to the situation that there may be many geological events responsible for their natural and the consequent formations.

Table.1: Major elements determined (values are in percentage) in chromitites by PIXE.

S.No	CR1	CR2	CR3	CR4	CR5	CR6	CR7	CR8	CR9	CR10
Chromium	19.96	14.95	23.88	16.51	12.78	13.72	17.92	31.88	15.90	18.32
Iron	8.45	12.32	10.42	21.38	14.36	19.28	24.45	15.35	6.40	11.31

Note: CR1 to CR10 represent chromitite samples from Boula (FACOR) mines of Keonjhar District, Orissa from south to north of the mining district.

Table .2: Distribution of minor and trace elemental concentrations in chromite ores–by PIXE method (values are in ppm) & (* = concentrations are in percentage)

S.No.	Ti*	V*	Mn*	Ni*	Cu	Zn	Ga	Zr	Nb	Mo	Pb
CR1	0.96	0.45	0.36	0.41	46 ± 3.86	919 ± 39.51	778 ± 32.67	48 ± 3.79	38 ± 3.11	16 ± 1.40	73 ± 5.69
CR2	0.95	0.32	0.32	1.53	18 ± 1.51	940 ± 40.42	724 ± 30.40	34 ± 2.68	10 ± 0.82	11 ± 0.96	48 ± 3.74
CR3	0.88	0.42	0.24	0.62	34 ± 2.85	382 ± 16.42	516 ± 21.67	41 ± 3.23	6 ± 0.49	08 ± 0.70	21 ± 1.63
CR4	0.51	0.38	0.18	1.43	28 ± 2.35	906 ± 38.95	638 ± 26.79	26 ± 2.05	18 ± 1.47	12 ± 1.05	33 ± 2.57
CR5	0.78	0.36	0.21	0.96	31 ± 2.60	328 ± 14.10	580 ± 24.36	18 ± 1.42	22 ± 1.80	07 ± 0.61	70 ± 5.46
CR6	0.72	0.28	0.26	0.52	22 ± 1.84	248 ± 10.66	732 ± 30.74	16 ± 1.26	28 ± 2.29	05 ± 0.52	54 ± 4.21
CR7	0.92	0.45	0.33	0.56	40 ± 3.36	882 ± 37.92	542 ± 22.68	8 ± 0.63	9 ± 1.38	09 ± 0.79	18 ± 1.40
CR8	0.88	0.35	0.31	0.63	37 ± 3.10	661 ± 28.42	328 ± 13.77	30 ± 2.37	14 ± 1.14	08 ± 0.70	46 ± 3.58
CR9	0.90	0.40	0.22	0.48	25 ± 2.10	761 ± 32.72	676 ± 28.39	19 ± 1.50	11 ± 0.9	08 ± 0.70	51 ± 3.97
CR10	0.32	0.31	0.13	1.76	15 ± 1.26	309 ± 13.28	346 ± 14.53	21 ± 1.65	17 ± 1.39	09 ± 0.79	14 ± 1.09

Table 3: Distribution of minor and trace elements in ultrabasic rocks–by PIXE method

S.No.	Ti*	V*	Mn*	Co*	Ni*	Cu	Zn	Ga	Zr
CR1	0.18	0.080	0.27	0.01518	1.79	69.3 ± 3.95	77.8 ± 5.83	40.7 ± 2.8	240 ± 16.56
CR2	0.34	0.024	0.014	0.0088	1.53	34 ± 1.93	41 ± 3.07	21 ± 1.44	18 ± 1.24
CR3	0.41	0.029	0.018	0.0096	0.86	40 ± 2.28	24 ± 1.80	28 ± 1.93	32 ± 2.20
CR4	0.017	0.004	0.031	0.0036	1.43	27 ± 1.53	15 ± 1.12	11 ± 0.7	16 ± 1.60
CR5	0.30	0.030	0.01612	0.0132	1.96	73 ± 4.16	28 ± 2.10	30 ± 2.07	22 ± 1.51
CR6	0.14	0.014	0.0986	0.0086	0.52	28 ± 1.59	14 ± 1.05	24 ± 1.65	11 ± 0.75
CR7	0.013	0.0014	0.0094	0.0025	2.56	16 ± 0.92	24 ± 1.80	8 ± 0.55	9 ± 0.62
CR8	0.48	0.0229	0.10	0.0071	0.63	31 ± 1.77	8 ± 0.60	18 ± 1.24	14 ± 0.92
CR9	0.011	0.0026	0.015	0.0122	2.04	19 ± 1.08	6 ± 0.45	10 ± 0.6	19 ± 1.31
CR10	0.44	0.0014	0.0078	0.0092	1.76	12 ± 0.68	10 ± 0.75	6 ± 0.41	4 ± 0.27

(* = concentrations are in percentage & Values are in ppm)

We would further like to bring the attention of the readers towards the fact that a significant number of geologists consider chromite deposits as the product of magmatic differentiation of basalt melts [15] which are segregated at the beginning of the process, due to fractional crystallization of dry magmas or at the end of the process segregated from residual melt enriched with volatiles that reduces the crystallization temperature of chromites. Hence, in order to understand the probability of this differentiation process that may lead to association of various trace metals with major elements, a series of inter-elemental correlation has been attempted from the results of the concentrations of various elements and only the outstanding and the extra ordinary correlations have been plotted and considered for further understanding and discussion. It is observed that there are excellent correlations and some similar behavior pattern between Fe-Co (Fig.1) and Cr-Ni (Fig.3) and there is no specific relation between Fe-Ni (Fig.2) and Cr-Co (Fig.4), in other words in terms of geology the elements of iron and chromium follow the sympathetic relation with cobalt and nickel where as iron and chromium elements follow the antipathetic relation with nickel and cobalt respectively. It may be possible that there is a simultaneous precipitation in case of former two groups of elements and simultaneous differentiation in the latter groups of elements with that of the source solution.

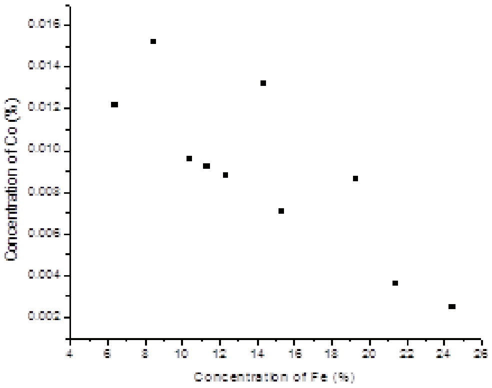

Fig.1: Variation of Co with respect to Fe

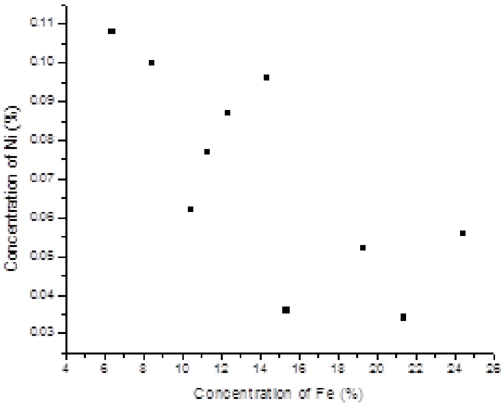

Fig.2: Variation of Ni with respect to Fe

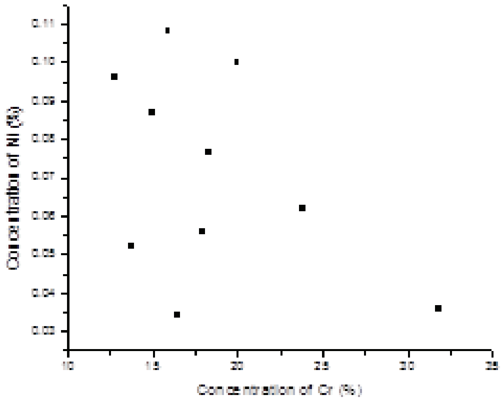

Fig 3: Variation of Ni with respect to Cr

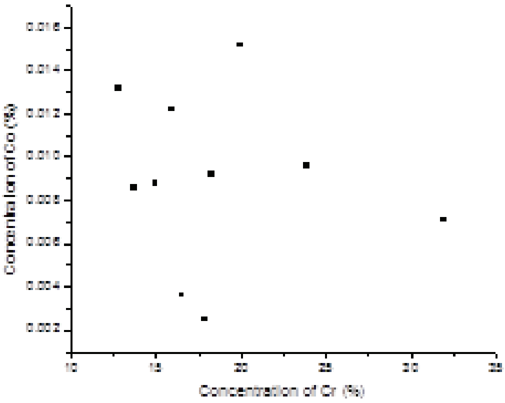

Fig.4: Variation of Co with respect to Cr

To compare the elemental concentration profile between chromite ore and rock samples, the ranges and the mean elemental concentrations have been determined from each set of these samples. The mean minor and trace elemental concentrations of the chromite ore and rock samples are summarized in Fig.5. The minor element concentrations were found to be very similar between the chromite ore and rock samples, except for Zn and Ga. The concentrations of Zn and Ga are comparatively high in Chromite ore samples than the Rock samples whereas Co is low in chromite ore samples. It is clear from Table2 and Fig.5, the concentration of elements Mo, Nb and Pb are observed only in Chromite ore samples, which are not observed in the host rocks, viz. pyroxenite, dunite and gabbro. Although the exact cause and mechanism for the presence and absence of these elements in the specific types of chromite ore and rock samples is not established yet, it may be possible that the variation of different factors such as energy, pressure, temperature and gravity etc during the precipitation process or the formation of these chromite ore and rock samples are responsible for aforementioned findings. So, these elements play very important role in order to identify various types of ore and rock samples.

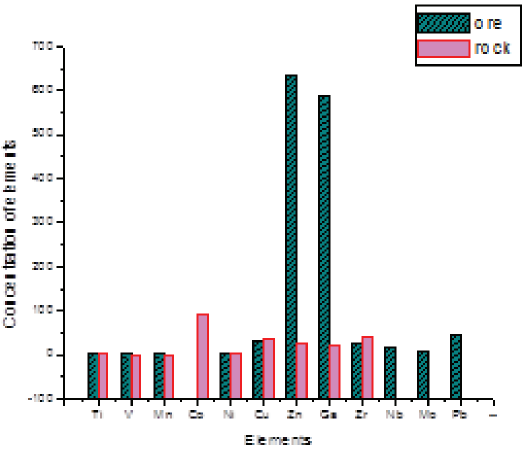

Fig.5: Mean Minor and Trace Elemental Concentration in Chromite Ore and Rock Samples

Conclusions: Thus, a selected number of Indian Peninsular chromitites have been studied by using complimentary and non-destructive PIXE technique. Thirteen elements including Co, Ni, Cu, Zn, Ga, Zr, Mo, Nb and Pb were established in these chromitites, which may be useful to interpret the various geochemical conditions and the probable cause of their inceptions in chromitite matrix. It was found that Ti, Mn and Ni are present in substantial amount with respect to other trace elements. It is interesting to observe that the concentration of nickel indicates the origin of these chromitites in Proterozoic period. Moreover, it is worth mentioning here that the amount of zirconium indicates the effect of many geological events on this specific geological belt. The study advocates the use of PIXE in quantifying trace elements in high-grade ores. However, as the present work is preliminary one, detailed further investigation may lead towards better understanding of the role of trace elements in Proterozoic period.

The accelerator-based nuclear technique of PIXE analyses was used for characterization of some natural chromitites. These minerals are mainly used for scientific and technological applications. Several major, minor and trace elements and their concentrations were determined from these samples. The chromitites are identified by means of their elemental concentrations. Therefore, the PIXE technique helps in determining the chemistry and mineralogy of the chromitites, as it is a non-destructive type of the analyses and it aids in full characterization. Hence the present study advocates the use of PIXE technique, for the characterization of geological materials, especially where a large number of elements are of specific interest.

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