

*Full Length Research Paper*

# **Geochemistry of phosphorite deposits around Hirapur-Mardeora area in Chhatarpur and Sagar Districts, Madhya Pradesh, India**

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The Hirapur-Mardeora phosphorite deposits are found to occur in Bijawar group of Gangau iron formations over the basement of Bundelkhand granite complex in the Archean period. There are four distinct units of phosphorites which include shale-phosphorite, secondary-phosphorite, ironstone-phosphorite and quartz-breccia phosphorite. Chemical analysis of 24 representative samples of these different units was carried out for qualitative and quantitative determination of their major and trace element concentration, geochemical behaviour and inter-element relationship. The study reveals that these elements were precipitated by direct, inorganic, syngenetic, and authigenic processes in the primary phosphorites and by epigenetic, leaching, remobilization and reprecipitation in the cavities, voids, fractures and fissure fillings in the secondary phosphorites during diagenesis. The phosphogenic processes might have taken place during the slight reduction of fairly oxidising conditions under tropical to arid climate in shallow water marine environment of the basin.

**Key words:** Hirapur-Mardeora, phosphorite, geochemistry, Chhatarpur and Sagar districts, diagenesis.

## **INTRODUCTION**

Phosphorites today are regarded as one of the most important economic minerals used. Nearly 90% of total world phosphate output is utilised for the manufacture of a number of fertilizers like superphosphate, triple super-phosphate, diammonium-phosphate and monoammonium-phosphate which are essential for agro industries all over the globe. Agricultural resources, followed closely and intimately by energy, are the most basic of all the resources available to man and today soil phosphorus deficiency was identified as a major constraint preventing upland soils from being used to produce adequate food for the growing populations of developing countries in tropical and sub-tropical regions (Buresh et al., 1997). Phosphorite deposits of Hirapur-Mardeora with an average of 26.40% P<sub>2</sub>O<sub>5</sub> content can be proved as a suitable phosphorus rich alternative to the currently available

synthetic fertilizers.

The previous investigators concentrate on different aspects of Bijawar group of rocks include geology (Dubey, 1952); petrography (Krishnan, 1942, 1968); petrography, geochemistry, classification and origin (Israili, 1978); structure (Pant, 1980); uranium mineralisation (Mahadevan, 1986); Bijawar and Vindhyan tectonics of Central India (Misra, 1987). In the present study, an attempt was made to interpret the data of advance nature to ascertain the geochemical behaviour, inter-element relationship of major and trace elements and environment of depositional basin. The present study indicated that within the interpreted and inferred basinal conditions, the chemistry of basinal waters and subsequently post depositional alterations played significant roles in producing different varieties of phosphorite in different proterozoic basins. The original composition of the sedimentational water was of prime importance. Conceding the fact that, some of the trace elements and as well as that of the major mobile elements were either

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introduced into the apatitic mud or left the indurated apatite. The concentration or depletion of major and trace elements was dependent primarily on such factors like their mobility with respect to apatite associated assemblage of elements, type and intensity of weathering and the effects of secondary processes. Various elements, both major and trace which combine to form phosphorite of a particular composition changed their character in course of geological history. In spite of such addition or subtractions of the primary elements, they left some traces of their presence in the original sediments and these have been used for making significant interpretations about various palaeo-environmental condition (Saigal and Banerjee, 1987).

The inter-correlation of elements brings out three major associations such as apatitic-phosphorite, ferruginous clayey phosphorite and weathered (leached) aluminous phosphorite. Each element association reflects a grouping of elements – (a) structurally substituted in major mineral apatite, (b) adsorbed onto the mineral surface or (c) existing as discrete minerals derived from apatite by weathering. The variations in major and trace elements abundance are indication of a change in environmental condition of deposition. The concentration and kind of element adsorbed or entering into the crystal structure depend on a number of factors, such as pH, Eh, nature and structure of the adsorbant, availability and concentration of ions, rate of nodule growth, nature and rate of sedimentation and various other parameters. Because such varied factors have complex interactive elements in nodules, they can occur in several chemical associations as weakly adsorbed, strongly adsorbed or in the structure of carbonate or oxides.

## GEOLOGICAL SETTING

The proterozoic phosphorite deposits of Hirapur-Mardeora area in Sagar and Chhatarpur districts of Madhya Pradesh (Lat. 24°19'N and 24°23'N and Long. 79°9'E and 79°14'E) belongs to the gangau ferruginous and phosphatic formations of the Bijawar group of rocks (Mathur and Mani, 1978; Banerjee et al., 1982). The megascopic, microscopic, scanning and X-Ray studies of the phosphatic rocks of the study area revealed that there are two distinct types of phosphorites, viz., primary and secondary. Mineralogically, the primary phosphorites being associated with shales, ironstones and quartz-breccia are mainly composed of collophane (a carbonate fluorapatite phase), whereas the secondary phosphorites contain crandallite (calc-aluminium phosphate).

According to Krishnan (1942, 1968) and Dubey (1952), the quartzites and sandstones and sometimes conglomerates form the basal member of the series resting unconformably on the Bundelkhand gneissic complex. Siliceous-limestones and hornstone-breccia are also associated with the quartzites. These are rather irregularly distributed and are less than 60 m in thickness.

They are overlain in turn by ferruginous sandstone containing pockets of hematite. The rocks are either horizontal or have a south easterly dips, though at few places in the south, they were subjected to crushing and disturbances before the Vindhyan were deposited. In the Hirapur-Bassia area, the Bundelkhand granites are either directly overlain by Bajna dolomite or juxtaposed against the 'Gangau Ferruginous Formations' made up of conglomeratic-breccia and shales. There is no tillite in the vicinity of the phosphorite horizon, but it has been recorded in the adjacent regions (Mathur and Mani, 1978).

Stratigraphic succession of the study area is given in Table 1. The authors have also prepared the geological cross-section from the geological map (Figure 1) along the profile line A-B across the phosphorite beds, just to show more clearly the geological sequence of rock units of the study area (Figure 2).

## MATERIALS AND METHODS

Careful and systematic sampling was done in the area. 24 representative samples were collected from different lithologic units such as shale phosphorites (06), secondary phosphorites (05), ironstone phosphorites (06), and quartz-breccia phosphorites (07). The samples were crushed in a steel mortar to a coarser fractions and it was further crushed in porcelain mortar till it became medium to fine grained. Finally, the material was finely powdered up to 300 to 400 mesh sizes in an agate mortar which was then transferred into polythene bags, numbered and packed properly for geochemical analysis. Two types of solution 'A' and 'B' were prepared and kept in a 250 ml plastic bottle for the determination of major oxides by adopting the procedure followed by Shapiro and Brannock (1962). Solution 'A' was used for the determination of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> and solution 'B' for the determination of TiO<sub>2</sub>, MnO, CaO, MgO, Fe<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, K<sub>2</sub>O and P<sub>2</sub>O<sub>5</sub>. The oxides like, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, MnO, total iron and P<sub>2</sub>O<sub>5</sub> were determined by Beckman DU-2 Spectrophotometer using various wave-lengths following USGS standards (AGV-1, BCR-1 and GSP-1) for each major oxides. CaO and MgO were analysed by titration method with ethylenediaminetetraacetic acid (EDTA) using Erichrome Black indicator-I. FeO was also analysed by titration method using potassium dichromate solution, whereas both Na<sub>2</sub>O and K<sub>2</sub>O were determined with the help of flame photometer. CO<sub>2</sub> was determined volumetrically in a series of 250 ml beakers, of which 0.5 gm of calcium carbonate (CaCO<sub>3</sub>) was used as standard and 0.5 gm of the powdered sample was added to it. 25 ml of hydrochloric acid (HCL, 0.5 N) was added to each beaker and allowed to remain overnight. The remaining acid in the beaker was titrated with sodium hydroxide (NaOH, 0.35 N) and bromophenol blue was used as an indicator, which gave yellow to blue end point and then the calculation of CO<sub>2</sub> in percent was made. The trace elements were determined adopting the procedure followed by Naqvi and Husain (1972) by using X-ray fluorescence (XRF) techniques except U<sub>3</sub>O<sub>8</sub> which was determined with the help of atomic absorption spectrophotometer. An attempt was also made to determine the content of organic matter, sulphate, Y, Zr and Sr but their presence were almost negligible.

## RESULTS

The major- and trace element concentrations are listed in

**Table 1.** Stratigraphic succession of the Hirapur-Mardeora area.

Lower Vindhayan system	Semri group (Late/Upper Precambrian) .....Unconformity.....	
	II	
Bijawar group  (Early to middle Precambrian)	Gangue  Ferruginous and phosphatic formations	Quartz-breccia phosphorites Ironstone-phosphorites Shale-phosphorites, at places weathered/ leached formed secondary phosphorites
Cuddapah system	I	
	Non-phosphatic formations .....Unconformity.....	
Archean -	Bundelkhand complex	

Tables 2 and 3 respectively. The average concentrations of CaO (34.35 wt.%) had the highest among the major oxides followed by P<sub>2</sub>O<sub>5</sub> (26.40 wt.%), SiO<sub>2</sub> (21.05 wt.%), Fe<sub>2</sub>O<sub>3</sub> (9.76 wt.%), Al<sub>2</sub>O<sub>3</sub> (4.19 wt.%), CO<sub>2</sub> (1.38 wt.%) and the concentrations of remaining oxides are less than 1 wt.%. In between trace elements Zn (233.19 ppm) has the highest average concentration followed by Cr (210.50 ppm), Ni (197.05 ppm), Cd (177.53 ppm), Cu (138.17 ppm), Co (115.50 ppm) and the concentration of others are less than 100 ppm. Average Concentration of U<sub>3</sub>O<sub>8</sub> (0.07 ppm) is much less when compared to other elements.

## DISCUSSION

### Major elements geochemistry

The high P<sub>2</sub>O<sub>5</sub> and CaO values indicate high apatite content, and strong positive correlation of P<sub>2</sub>O<sub>5</sub> and CaO (Figure 3a) might be the result of diagenetic phosphatization in which CO<sub>2</sub> might be removed by PO<sub>4</sub> before the precipitation of phosphorite during high oxidising conditions of the basinal water which gave rise to carbonate fluorapatite as an end product (Ames, 1959) or it may be due to the increase and decrease of pH as described by Krumbein and Garrels (1952) and Nathan and Sass (1981). According to Banerjee (1979), there are many evidences for the co-precipitation of carbonate in rhythmic alternation of calc-phosphate and silica saturation cycles and as differentiation is prominent between day and night formed phosphate-calcium layers and this differentiation is diagenetically controlled, and shows sympathetic relation between the two. CaO/P<sub>2</sub>O<sub>5</sub> ratios is much lower than the values derived for the most reactive phosphate rock which shows the extent of its carbonate substitution as interpreted for Ogun phosphate rock by Adesanwo et al. (2009). The upwelling of deep ocean

currents to the shelf deliver dissolved phosphate and CO<sub>2</sub> to coastal shallower waters, diffusion of phosphorous into bottom water accompanied by change in alkalinity due to CO<sub>2</sub>, which loss lead to the formation of grains and nodules and phosphatization of coprolites (Kholodov, 2003). Random and linear but progressive positive relationship of CO<sub>2</sub> and Na<sub>2</sub>O with P<sub>2</sub>O<sub>5</sub> (Figure 3b and c) reflects that during phosphatization the CO<sub>3</sub> content might have replaced by PO<sub>4</sub> within the basin and this reaction is partly balanced by Ca<sup>+2</sup> and Na<sup>+1</sup> and controlled by crystallographic control on the degree of carbonate substitution (Adler et al., 1963; Youssef, 1965; McClellan, 1980; Manheim and Gulbrandsen, 1979), but one other cause for such a relationship between these two oxides might be the mild weathering of these phosphorites. Al<sub>2</sub>O<sub>3</sub> shows a weak negative relationship with P<sub>2</sub>O<sub>5</sub> which might be due to the mutual ionic substitution between Al<sup>+3</sup> and Ca<sup>+2</sup> in the apatite lattice under high alkaline conditions of the basinal waters or the Al<sub>2</sub>O<sub>3</sub> may be adsorbed in hydrous aluminium-silicates, ferruginous and clay minerals which is high in P<sub>2</sub>O<sub>5</sub> content (Figure 3d). The irregular distribution of crandalite CaAl<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>(OH)5•(H<sub>2</sub>O) particularly in secondary phosphorite samples indicated the hidden leaching/ weathering of ore in which small amount of Ca<sup>+2</sup> was replaced by Al<sup>+3</sup> during remobilization and recrystallization by means of the ground water circulation and sea-waves tides and currents in the Bijawar basin. K<sub>2</sub>O shows a progressive random but negative relationship with P<sub>2</sub>O<sub>5</sub> in primary phosphorite samples and weak positive and linear relationship in secondary phosphorite samples (Figure 3e). The negative relationship indicated the presence of minor amount of K<sub>2</sub>O in the outside of the apatite crystal lattice (Cook, 1972), and on the other hand, the positive correlation in secondary phosphorites may be due to solution, reprecipitation, leaching and/ weathering of ore in an alkaline, marine, shallow water conditions of the Bijawar basin. The weak relationship of

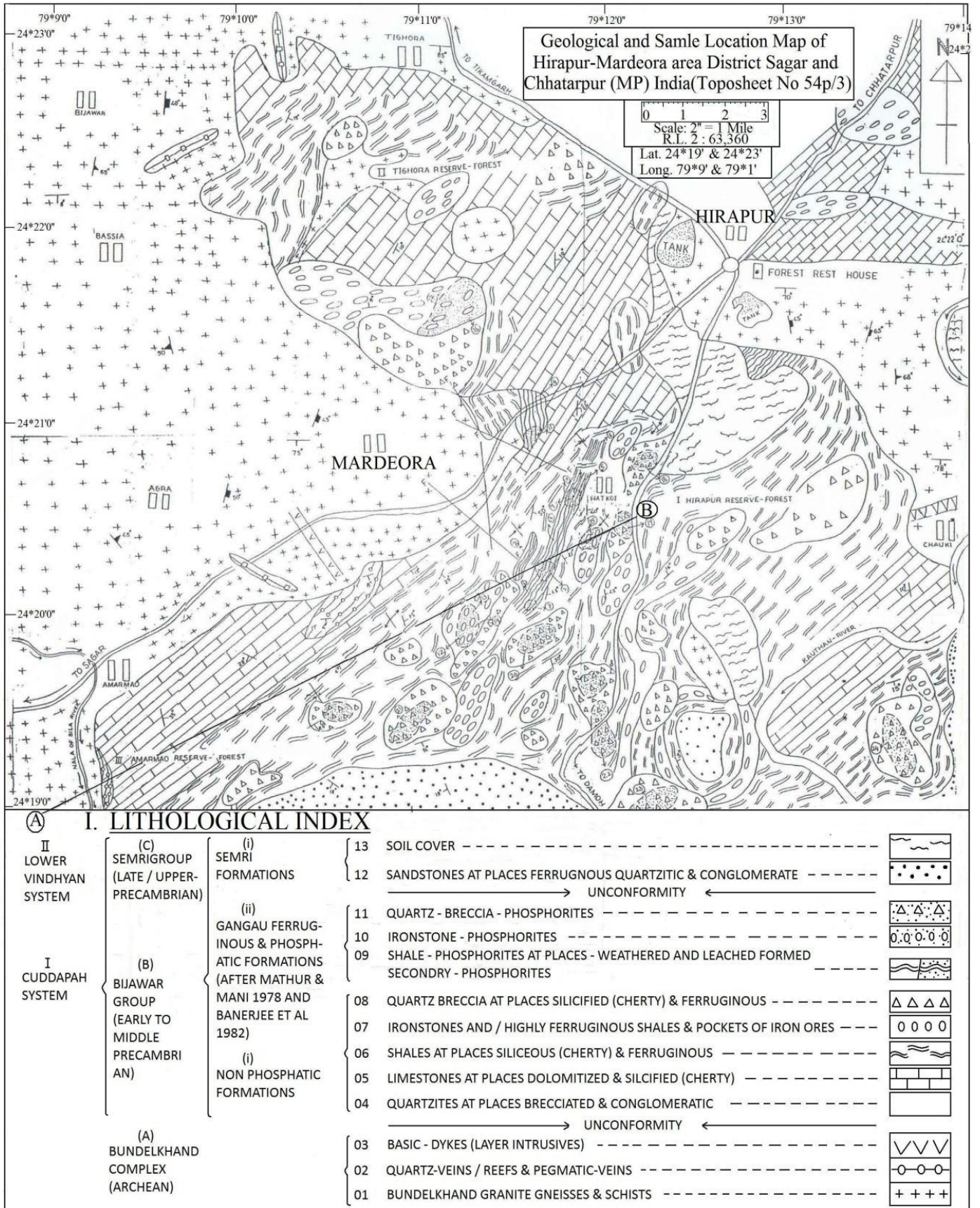
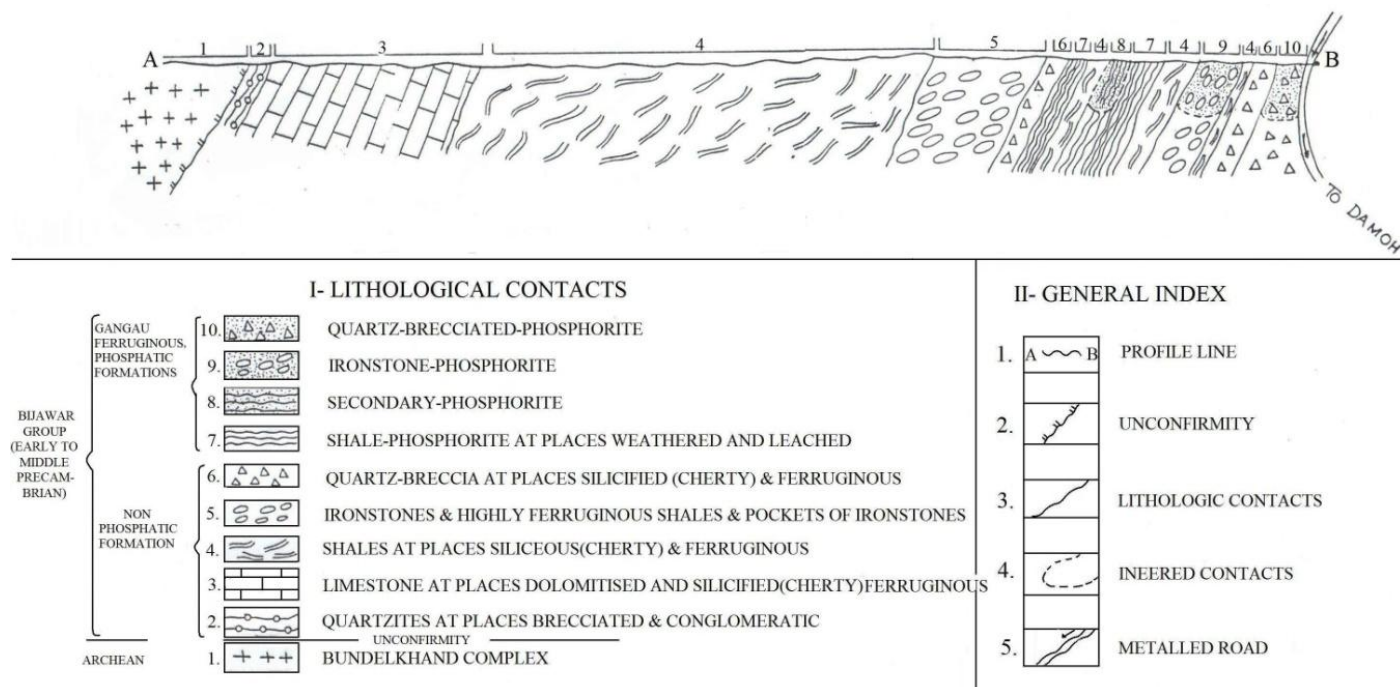


Figure 1. Geological and sample location map of Hirapur-Mardeora area, district Sagar and Chhatarpur, Madhya Pradesh, India.



**Figure 2.** Diagrammatic cross-section along the line A-B across the phosphorite deposits, Hirapur-Mardeora area, district Sagar and Chhatarpur, Madhya Pradesh, India.

**Table 2.** Major elements distribution (wt.%) in phosphate bearing rocks of Bijawar group around Hirapur-Mardeora area.

Sample	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	MnO	CaO	MgO	Fe <sub>2</sub> O <sub>3</sub>	FeO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	CO <sub>2</sub>
1	22.10	6.70	0.45	0.12	29.91	0.32	10.32	1.63	2.10	1.05	22.95	1.08
2	17.98	5.10	0.02	0.14	35.92	0.39	9.85	0.85	2.39	1.21	25.05	2.10
3	16.32	5.00	0.95	0.39	32.21	0.95	11.65	1.05	2.65	1.78	23.10	2.85
4	33.05	7.09	0.41	0.20	23.81	0.20	12.71	0.05	1.05	0.83	16.95	0.89
5	31.23	6.98	Tr	0.03	26.08	1.03	10.09	0.23	1.87	1.01	18.00	1.81
6	39.07	10.01	0.66	0.19	22.27	0.69	9.83	Tr	1.21	Tr	14.79	0.93
7	4.29	1.54	1.00	Tr	43.00	0.20	14.08	0.29	0.25	0.27	32.10	1.32
8	2.81	1.74	Tr	Tr	49.41	0.24	8.17	Tr	0.19	0.33	35.76	1.81
9	2.01	5.09	0.02	0.01	48.17	Tr	1.12	Tr	0.07	0.13	42.80	1.32
10	3.04	6.83	Tr	0.39	44.92	0.41	3.01	0.03	0.24	0.14	40.30	0.79
11	2.05	6.24	0.04	Tr	40.42	Tr	7.32	0.21	0.89	0.53	39.21	1.01
12	20.83	2.95	0.03	0.02	35.02	1.01	11.32	0.21	0.24	0.21	27.48	1.23
13	23.01	1.29	0.25	0.13	32.19	0.09	15.17	0.48	0.31	0.74	25.99	2.03
14	22.31	0.98	Tr	Tr	33.02	0.39	16.01	0.31	0.21	0.71	26.73	1.04
15	17.98	1.32	0.04	0.11	37.59	0.12	10.00	0.41	0.31	Tr	29.70	1.53
16	21.19	2.00	0.50	0.10	36.00	1.60	9.27	0.38	0.25	0.48	28.50	1.03
17	20.54	3.16	0.50	0.10	36.00	1.25	10.88	0.38	0.25	0.52	26.96	0.95
18	41.32	6.19	0.43	0.13	17.95	0.92	14.01	0.11	0.31	1.12	15.32	2.01
19	29.70	2.41	Tr	Tr	33.19	1.01	8.35	0.12	0.43	1.01	23.70	1.02
20	23.10	2.93	0.40	0.09	36.32	0.39	8.10	0.19	0.21	1.11	26.56	1.03
21	18.45	1.23	Tr	Tr	40.98	0.92	7.32	0.01	0.52	1.32	28.30	2.01
22	40.16	5.40	0.50	0.10	27.00	0.74	6.66	0.19	0.19	1.58	18.23	0.59
23	33.50	6.97	0.77	Tr	26.00	0.80	10.08	0.29	0.25	2.45	17.85	Tr
24	19.25	1.39	0.19	0.12	36.98	0.65	8.98	0.21	0.31	2.39	27.35	1.35

Tr, trace.

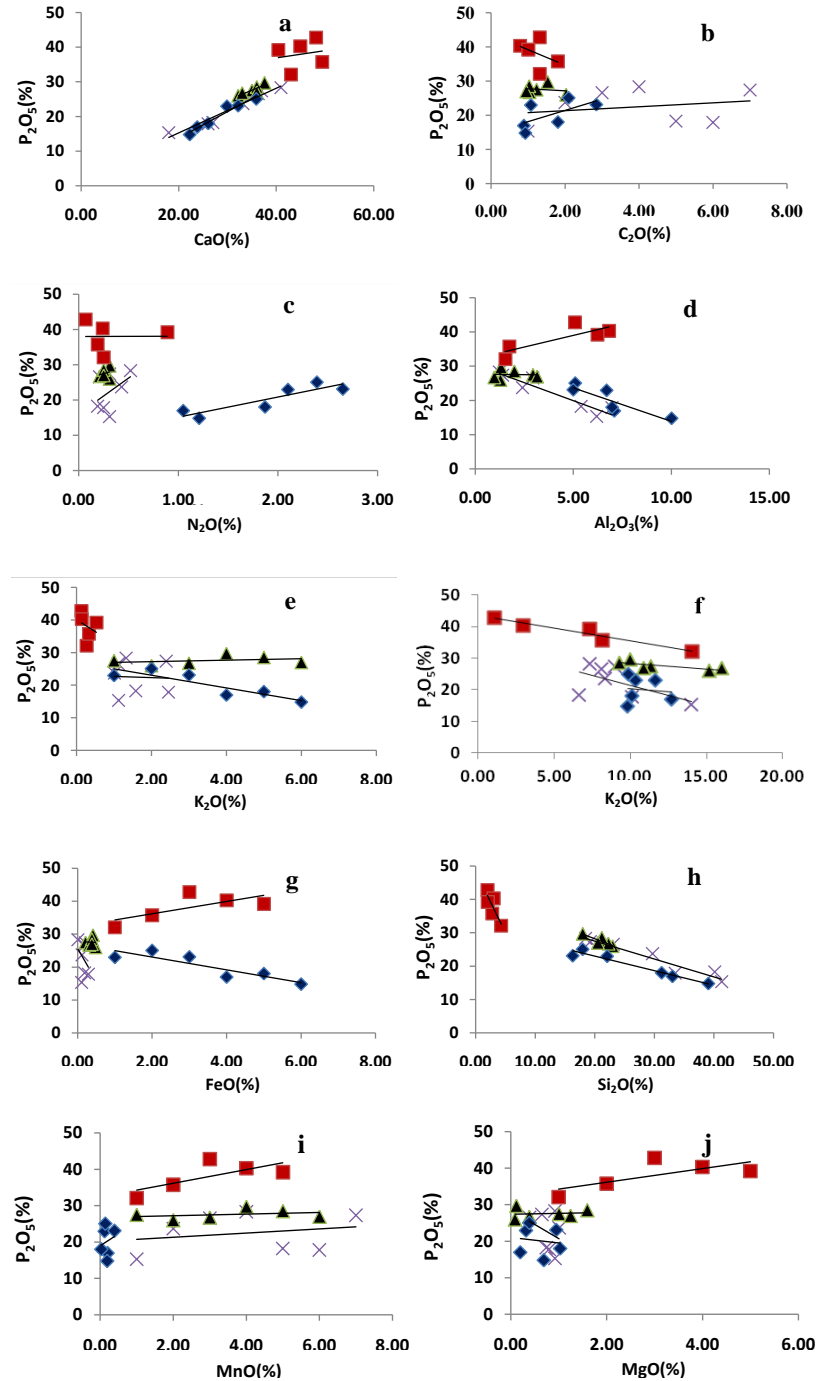
**Table 3.** Trace elements distribution (ppm) in phosphate bearing rocks of Bijawar group around Hiraapur-Mardeora area.

Sample	Ni	V	Cr	Cu	Ga	Pb	Co	Zn	Cd	U <sub>3</sub> O <sub>8</sub>
1	10	169	Tr	104	5	ND	Tr	308	ND	0.102
2	152	141	215	37	11	9	ND	550	101	0.105
3	47	155	25	Tr	15	37	24	104	Tr	0.035
4	92	172	82	68	22	Tr	29	Tr	179	0.005
5	9	98	58	19	Tr	Tr	113	141	42	0.006
6	69	132	39	Tr	18	5	49	225	Tr	0.005
7	ND	Tr	300	295	ND	Tr	502	409	110	0.083
8	159	ND	149	ND	Tr	17	195	187	113	0.101
9	15	4	Tr	Tr	290	5	22	Tr	205	0.138
10	5	Tr	38	59	9	ND	53	635	596	0.130
11	Tr	25	ND	15	18	12	Tr	20	610	0.110
12	50	Tr	76	170	9	ND	161	260	Tr	0.063
13	310	15	152	192	ND	ND	130	Tr	198	0.049
14	1129	29	280	Tr	Tr	12	141	ND	125	0.050
15	112	75	Tr	180	2	Tr	ND	178	230	0.069
16	508	Tr	305	160	25	22	11	210	210	0.061
17	603	101	692	145	38	4	Tr	Tr	109	0.053
18	48	Tr	210	185	ND	Tr	25	200	113	0.003
19	39	41	ND	154	ND	ND	119	110	165	0.069
20	300	ND	300	112	4	ND	109	59	Tr	0.071
21	361	ND	265	305	Tr	12	Tr	Tr	120	0.103
22	Tr	105	195	Tr	9	4	Tr	Tr	110	0.051
23	111	9	408	145	18	2	165	135	8	0.040
24	9	48	Tr	142	29	Tr	Tr	ND	29	0.097

Tr, trace; ND, not detected.

of Fe<sub>2</sub>O<sub>3</sub> and FeO with P<sub>2</sub>O<sub>5</sub> particularly in primary rocks (Figure 3f and g) may be due to non-deposition of Fe<sub>2</sub>O<sub>3</sub> and FeO content with P<sub>2</sub>O<sub>5</sub> at the time of phosphatization. On the other hand, the stronger negative relationship of Fe<sub>2</sub>O<sub>3</sub> in secondary phosphorites (Figure 3f) may be due to leaching and mild weathering of iron from the ores and reprecipitation along with P<sub>2</sub>O<sub>5</sub> in the pore spaces, cavities/ voids, veins etc. in highly oxidising marine environment or due to the presence of different sources of phosphorous, as in the case of other phosphorite deposits (O'Brien et al., 1990; Baioumi, 2007). The absence of pyrite in these phosphatic rocks of the study area clearly indicates a high oxidising environment. The total iron content may be due to the upwelling currents observed in the shallower parts of the basin where phosphatization was in progress as described by Holland (1973) that, during early proterozoic, at least the disposal and concentration of phosphorous in marine sediments was supposed to be controlled largely by the distribution of iron and the periodic upwellings of reducing iron-rich ocean waters. Conversely, a progressive negative relationship of SiO<sub>2</sub> with P<sub>2</sub>O<sub>5</sub> might be due to the replacement of (PO<sub>4</sub>)<sup>-3</sup> trivalent anions by similar equidimensional anions such as divalent (SO<sub>4</sub>)<sup>-2</sup> and tetravalent (SiO<sub>4</sub>)<sup>-4</sup> (Krishnan, 1942;

Betekhtin, 1959; Manheim et al., 1980), which reflect that in the study area, the (PO<sub>4</sub>)<sup>-3</sup> has been mutually substituted by (SiO<sub>4</sub>)<sup>-4</sup> before the final precipitation of phosphorites in the depositional environment (Figure 3h) and this is the considerable factor which lead to lowering the phosphorite grade (Awadalla, 2010). Besides this, the ionic radii and charges of silicon and phosphorous are very close to each other and they helped in the replacement of the apatite lattices. The high content of SiO<sub>2</sub> in few phosphorite samples may be due to silicification of ores by diagenetic process in the sedimentary basin as described by Banerjee et al. (1982) for the phosphatic rocks of the Hiraapur area in Sagar district. The precipitation took place in the marine, in shallower conditions of the basin which is a well known fact for all older phosphorites. Weak negative relationship of MnO with P<sub>2</sub>O<sub>5</sub> in all the samples (Figure 3i) suggest its non-affinity with P<sub>2</sub>O<sub>5</sub> and minor occurrences of Mn in the outside of apatite lattices as found earlier in the phosphatic stromatolites from jhamarkotra and other areas that P<sub>2</sub>O<sub>5</sub> and Mn shows antipathetic relationship and such a relationship indicates that neither Mn has any direct affinity with phosphates nor it occurs in apatite structure (Banerjee et al., 1984; Banerjee and Saigal, 1988). MgO is having a random and weak negative



**Figure 3.** Scatter plots showing mutual relationship of CaO, CO<sub>2</sub>, Na<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, Fe<sub>2</sub>O<sub>3</sub>, FeO, SiO<sub>2</sub>, MnO and MgO Vs P<sub>2</sub>O<sub>5</sub> in the phosphorites of Hirapur-Mardeora area.

relationship in primary phosphorite and merely positive relationship in the secondary phosphorites (Figure 3j) which may be the result of the substitution of Mg<sup>+2</sup> by Ca<sup>+2</sup> in the apatite that may decrease the crystallite size of the apatite by the increase in size of Mg ions or it may be due to the precipitation in the marine and shallower

parts of the basin as the inhibiting effect of Mg on the crystallization of apatite is evident weather it is in solution or in the original carbonate. These experimental results suggest a pathway for the genesis of apatite and indicated conditions for its formation, which could prevail within the sediments in shallower water, during a very

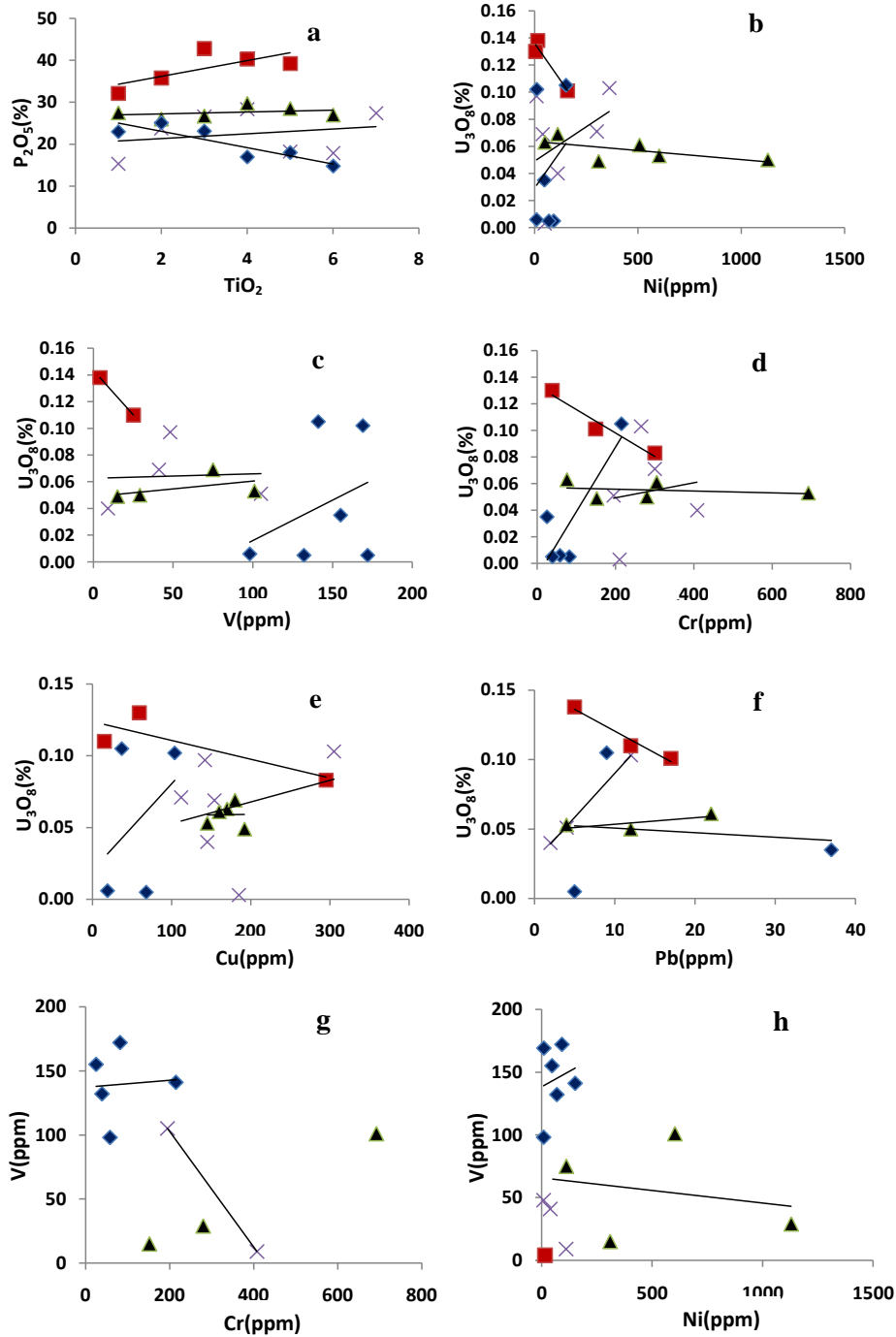
early diagenetic stage (Morse, 1979; Lucas, 1984). Poor relationship between Mg and P also indicates that Mg may not have been incorporated into the apatite structure as described by the quaternary phosphorites of southeast coast of India by Rao et al. (2002). Low MgO value indicates very little or no dolomitization has occurred in the area. Like MnO and MgO, the  $\text{TiO}_2$  also shows a weak and linear negative relationship with  $\text{P}_2\text{O}_5$  in all phosphorite types in the study area (Figure 4a). Goldschmidt (1954) reports that under some conditions,  $\text{TiO}_2$  is absorbed by clay minerals. The antipathetic relationship shown by 'detrital trace elements' is an inverse correlation with  $\text{P}_2\text{O}_5$  content and such a relationship is clearly exhibited by  $\text{TiO}_2$ , which is located predominantly in detrital rutile, ilmenite and leucoxene (Cook, 1972).

### Trace elements geochemistry

The higher concentration of nickel may be due to adsorption by ferric oxides, ferruginous and clay minerals and on the surfaces of apatites or during early diagenesis may have been incorporated with the crystal structure of apatite (Altschuler, 1980; Jarvis et al., 1994), and low uranium content can be interpreted to the fact that they are deposited in a shallow marine condition under arid climate. The negative relationship between nickel and uranium (Figure 4b) may be due to mutual ionic substitution during high oxidising, marine conditions of the basin before the precipitation of apatites (Debrabant and Paquet, 1975; Lucas et al., 1978). The weaker negative correlation between uranium and vanadium (Figure 4c) indicates that perhaps there was not a proper mutual substitution of these elements in the apatite crystal lattices during the inorganic processes of the phosphorites. The antipathetic relationship of Cr with  $\text{U}_3\text{O}_8$  (Figure 4d) may be due to adsorption of Cr by U in the gangue of phosphorites like other trace elements. It also indicates the incomplete mutual substitution of these two elements in the apatite crystal lattices (Howard and Hough, 1979). Uranium and copper are associated with phosphatic shales, secondary phosphorite, ironstones and quartz-breccia but not with limestones. On the other hand, there is no bio-hermal limestone and iron and copper sulphide mineralization in these sediments. Thus, the progressive positive relationship between uranium and copper (Figure 4e) in the samples of phosphatic shales, ironstones and quartz-breccia indicated the formations of these rocks during the fair oxidisation to slight reduction of shallow marine conditions of the proterozoic basin. It may be suggested that during the geochemical environment of the basin, there might be mutual substitution, though on minor scale of  $\text{Ca}^{+2}$  by  $\text{Cu}^{+2}$  and of  $\text{P}^{+5}$  by  $\text{U}^{+6}$  in the apatite crystal lattices. The progressive weaker negative relationship between U and Cu in the samples of secondary phosphorites may be due to leaching and lateritization generated by groundwater

action. The weathering, remobilization and redeposition of these phosphorites were perhaps responsible for the enrichment of secondary uranium (Verma, 1980; Al-Bassam et al., 1983). Progressive weak positive correlation between uranium and lead in the primary phosphorite samples (shale, ironstone and quartz-breccia) and negative correlation in the secondary phosphorite samples (Figure 4f) supports the depositional environment accompanied by sedimentary processes during phosphatization as seen in between uranium and copper (Howard and Hough, 1979). The negative correlation between V and Cr in the primary phosphorite samples of shales and quartz-breccia perhaps indicates that  $\text{Cr}^{+6}$  may be replaced by  $\text{V}^{+5}$  during highly oxidising conditions of the basinal-sea waters, and on the other hand, a positive relationship between the two elements in ironstone phosphorites (Figure 4g) supported the affinity of Cr with Fe in the ironstone and other phosphorites. These elements may be adsorbed in the iron-oxide, ferruginous and clayey fine grained minerals during phosphatization processes. In the secondary phosphorite samples, the absence of any relationship between these two elements may be due to weathering and/leaching of the ore by groundwater action (Gulbrandsen, 1966; Bliskovskiy, 1969; Banerjee et al., 1984; Saigal and Banerjee, 1987). Negative correlation of V with Ni and Co in all phosphorite samples (Figure 4h and 5a) supports the occurrence of these elements in the marine environment and adsorption by the gangue constituents of the phosphorites (Krauskopf, 1955; Gulbrandsen, 1966). The natural affinity of Cr for the group of elements like V-Ni-Cr-Zn is considered to be typical of organic matter (Saigal and Banerjee, 1987). The progressive positive relationship between Ni and Cr (Figure 5b) supports the elements association group in the phosphorite samples suggested by Saigal and Banerjee (1987). The weaker progressive positive relationship between Ni and Cu supported the trace elements group associations in these marine sediments (Figure 5c). It was also suggested that these elements in the phosphorites may occur as 'trapped ions' (Krauskopf, 1955; Gulbrandsen, 1966; Saigal and Banerjee, 1987). The weaker and/or poor positive relationship between Ni and Co (Figure 5d) supported that the Co's ionic radii differ from those of phosphorus and it is not so easy to accommodate Co in the apatite structure. The weaker relationship between these elements also indicates the adsorption by means of higher contents of iron and clay and elemental group associations in these phosphorites. This relationship also indicated the formation of phosphatic sediments in the 'red bed' environments (Gulbrandsen, 1966; Saigal and Banerjee, 1987; Boyle, 1984). The progressive positive relationship between Ni and Cd (Figure 5e) supported the affinity with iron in the Gangau-Ferruginous formations which form distinct group of elements during oxidization to reducing marine and shallower conditions of the proterozoic basins

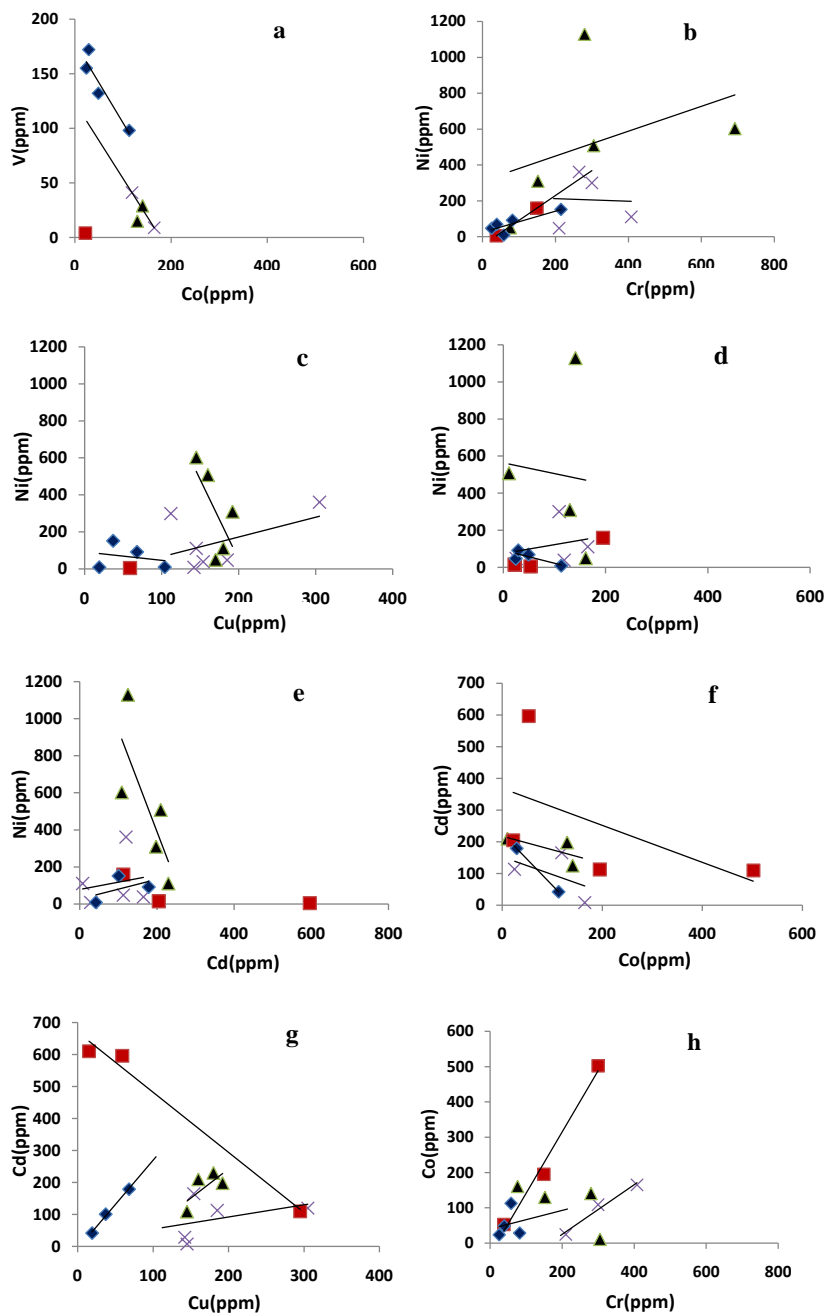




**Figure 4.** Scatter plots showing mutual relationship between TiO<sub>2</sub> and P<sub>2</sub>O<sub>5</sub> as well as between trace elements in the phosphorites of Hirapur-Mardeora area.

(Gulbrandsen, 1966; Saigal and Banerjee, 1987). The negative correlation between Cd and Co (Figure 5f) indicated that, due to difference in ionic radii, Co could not be replaced in the apatite crystal lattices. Cd might have been found in the apatite site or both elements might have been adsorbed in the gangue minerals of the phosphorites (Saigal and Banerjee, 1987). Cd and Cu

show strong positive relationship in the shale-phosphorite samples but they have weaker negative correlation in the ironstones, quartz-breccia and secondary phosphorite samples (Figure 5g). It may be possible that both the trace elements were replaced in the apatite crystal lattice on a minor scale and the remaining contents were adsorbed by the crypto to micro-crystalline masses of



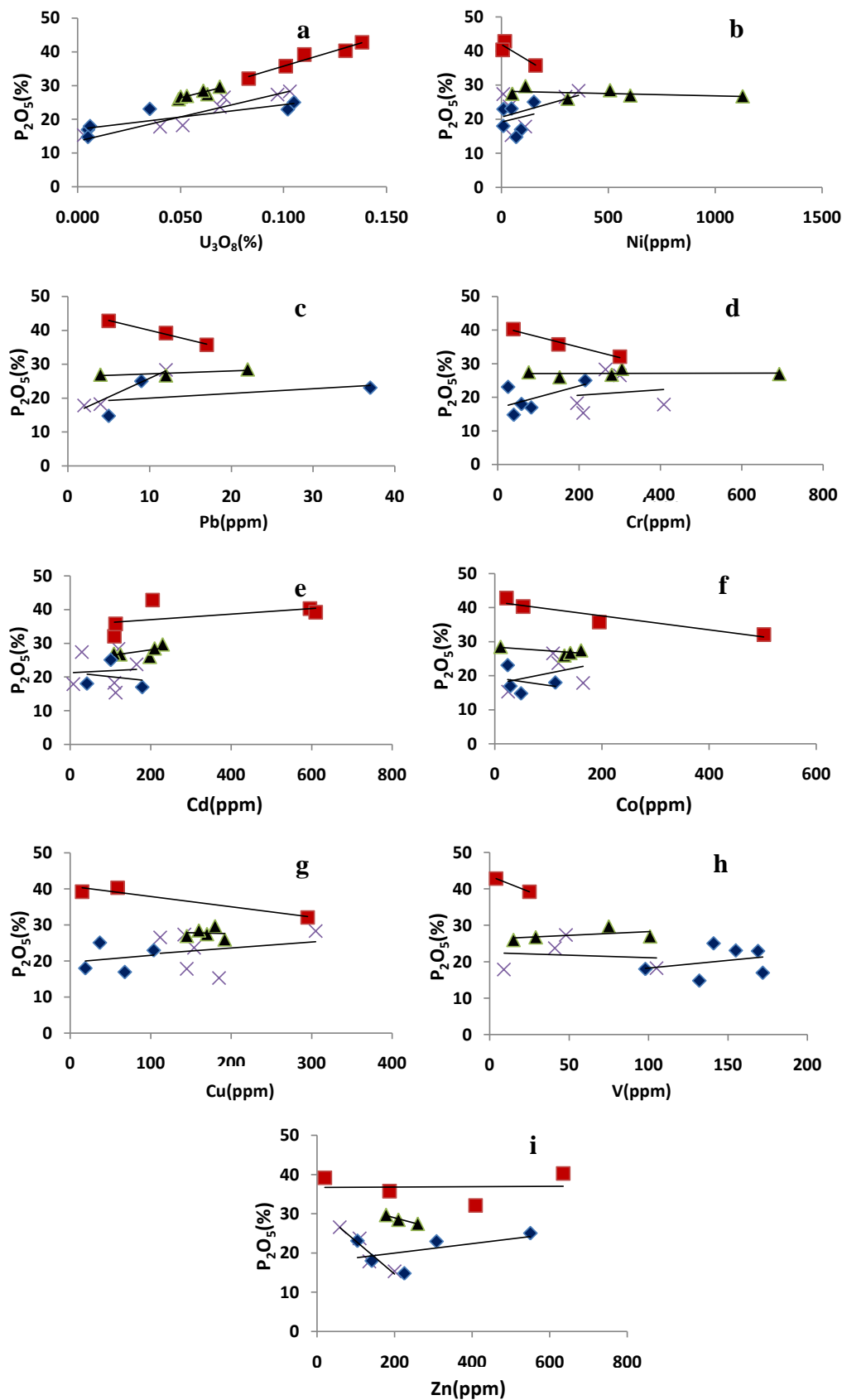
**Figure 5.** Scatter plots between trace elements in the phosphorites of Hirapur-Mardeora area.

phosphatic, ferruginous and clayey minerals. The iron-oxide and hydrated iron-oxide may play an important role during highly oxidising conditions of the basin (Saigal and Banerjee, 1987). Co and Cr show progressive positive relationship in the samples of phosphatic shales, quartz-breccia and remobilised rock types, but a weaker or random relationship exists in the ironstone-phosphorites (Figure 5h). The geochemistry and other features of this relationship are also similar to those of the trace elements

discussed previously.

#### Relationship between $P_2O_5$ and trace elements

The strong sympathetic correlation of  $P_2O_5$  with  $U_3O_8$  in all four types of phosphorite samples (Figure 6a) indicates co-precipitation of phosphorus and uranium in the sedimentary environment in which the Eh and pH of



**Figure 6.** Scatter plots showing mutual relationship of  $U_3O_8$ , Ni, Pb, Cr, Cd, Co, Cu, V, and Zn Vs  $P_2O_5$  in the phosphorites of Hirapur-Mardeora area.

the basinal waters were very close to each other for their precipitation (Elliot, 1968; Nathan and Shillony, 1976; Viqar, 1981). The occurrence of uraniferous phosphatic rocks in the ferruginated zone indicates the oxidising conditions of the basin (Mckelvey and Carlswell, 1956). This relationship also indicates high oxidising conditions due to absence of organic matter, micro-organisms and pyrite. The positive relationship between Ni and  $P_2O_5$  in primary phosphorites (Figure 6b) might be due to minor adsorption of Ni by large bodies cryptocrystalline masses of iron, clay and phosphatic materials, as such, the relationship was found earlier in the phosphatic rocks of Jammu and Kashmir (Khan and Khaki, 2008), but random or negative correlation between Pb and  $P_2O_5$  (Figure 6c) may be due to mutual divalent ionic substitution of  $Ca^{+2}$  by  $Pb^{+2}$  in the apatite lattices as ionic radii and charges of both are very close and similar (Howard and Hough, 1979). The bright red colour of the phosphorites may be due to the presence of  $Cr_2O_3$ . The negative correlation of  $P_2O_5$  with Cr (Figure 6d) supported the chemical affinity with V-Ni-Cr-Zn associations in the clay minerals. The mild weathering of ores might have redistributed within the sediments packages. The very high concentrations of iron and phosphate may entrap some Cr. On a minor scale,  $Cr^{+6}$  might have been replaced by  $p^{+5}$  in the sedimentary basin at the time of diagenesis (Minguzzi, 1941; Heinrich, 1958; Frohlick, 1960; Prevot and Lucas, 1980; Saigal and Banerjee, 1987), whereas  $P_2O_5$  shows positive as well as negative relationship with Cd in primary and also in secondary phosphorite (Figure 6e). In the primary phosphorites, the presence of Cd may be due to its adsorption by apatite, clay and iron bearing minerals. On the other hand, in case of secondary phosphorites, the weak negative correlation between the two may be due to weathering of the ores in which the Cd metal might have been redistributed within the sediments group or partly losing during diagenesis processes. The similar and/close ionic radii of Cd and Ca may help in ionic substitution in the apatite lattice (Krauskopf, 1955; Gulbrandsen, 1966; Saigal and Bannerjee, 1987). Like Cd, the Co also shows a more or less similar behaviour with  $P_2O_5$  in all four types of phosphorites (Figure 6f). Co may be present on the crystal surfaces of apatite, clay and iron bearing minerals, during diagenesis of these sediments (Saigal and Banerjee, 1987; Banerjee and Saigal, 1988) while  $P_2O_5$  shows positive correlation with Cu in primary phosphorites and negative in the secondary phosphorites (Figure 6g). Cu might have been replaced on a minor scale by Ca in apatite lattice or it may be present as adsorptive element. This relationship also indicates a common source of Cu and  $P_2O_5$ . Conversely, a negative relationship may be due to leaching/mild weathering of the ore in which part of Cu might have been lost during diagenesis (Cruft, 1966; Al-Bassam et al., 1983; Saigal and Banerjee, 1987; Singh and Subramanian, 1988). The relationship of  $P_2O_5$  with both V and Zn is strongly

negative (Figure 6h and i) which supports the mutual pentavalent ionic substitution of  $P_2O_5$  by  $V^{+5}$  or  $Zn^{+5}$  in the apatite lattices. The presence of V and Zn in the phosphorites may be due to chemical affinity with  $P_2O_5$  and adsorption by clay minerals (Cook, 1972; Banerjee and Saigal, 1988).

Most of the major and trace elements are inter-related to each other and with  $P_2O_5$  directly or indirectly in the carbonate, silicate and phosphate bearing rocks. The presence or absence of certain elements in the rocks is much helpful and most significant to know the palaeoclimates and nature of deposition of the sediments in the area. The variations in major and trace elements abundance are indication of a change in environmental condition of deposition (Mahadevan, 1986). The concentration and kind of element adsorbed or entering into the crystal structure depend on a number of factors such as pH, Eh, nature and structure of the adsorbant, availability and concentration of ions (Krauskopf, 1967), rate of nodule growth and rate of sedimentation and various other parameters (Cronan, 1969; Ghosh, 1975; Glasby, 1977; Roy, 1981).

## Conclusions

The abundance, distribution and inter element relationship of major and trace elements in the primary and secondary phosphorites reveal that these elements were precipitated by direct, inorganic, syngenetic and authigenetic processes in the primary phosphorites and epigenetic weathering, remobilization and reprecipitation in the voids and cavities fillings in the secondary phosphorites. The phosphatization was taken place in the fairly oxidising to slightly reducing environment, tropical to arid climate, saline sea-basinal waters, shallow marine environmental conditions and epicontinental sea shoals along continental margin in the Bijawar basin. The random distributions and poor correlations among the constituents may be due to mild leaching of the deposit. The study reveals that most of the phosphorites are in primary state while secondary phosphorites were mostly derived from the primary ones through eustatic sea level changes, actions of sea waves, tides, currents and groundwater as most of chemical constituents have same trend of distributions and relationships as that of the primary phosphorites. The formation of epigenetic secondary phosphorites was mainly due to lateritization as indicate by the concentration trends of each element. There are innumerable cases of adsorption, adsorption and partial replacement of certain minor elements out and inside the crystal lattices of apatite. The narrow and wide variations in the concentrations of certain elements attribute possibly to the mild leaching of the syngenetic phosphorites. The formation of crandallite (calcium aluminium phosphate) in the epigenetic ore samples may be due to ionic substitution of  $Ca^{+2}$  by  $Al^{+3}$  inside the

crystal lattice of apatite. It is apparent that the transferred concentrations or leaching of certain minor elements from the primary phosphorites to the secondary ones may be largely dependent on the absorption and adsorption capabilities of the secondary or primary minerals.

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