

Precambrian Phosphorites in the Bijawar Rocks of Hirapur-Bassia Areas, Sagar District, Madhya Pradesh, $India^{1,2}$

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The Preeambrian phosphorites of Bijawar Group of rocks show characteristics of a epicontinental sea with restricted and very shallow marine environment of formation along some shoals, which existed during the iron-rich Precambrian times. These phosphorite deposits located in the Hirapur-Bassia areas show extensive leaching of carbonate and phosphate minerals during episodes of weathering. X-ray diffraction studies indicated that carbonate-flourapatite is the major apatitic phase in these phosphorites while crandallite developed on the surface outcrops. There is a general tendency for the depletion of $CO₂$ in these apatites leading to formation of flourapatite. This CO₂ is an indicator of hidden weathering in the rocks. Major and trace element determinations of phosphorite have been used to indicate various correlation factors responsible for the concentration of elements in these Precambrian leached phosphorites.

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The paper is a contribution to the aims and objectives of IGCP Project 156

 2 The paper is dedicated to Prof. Dr. R.C. Misra, who as a teacher and guide had been a source of inspiration to the senior author for the last two decades

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INTRODUCTION

The Bijawar Group of rocks constitute a well defined, though poorly studied rock entity, and is named after the township of Bijawar, where they define the eastern Bijawar Basin. The name Bijawar was given to the early Precambrian sediments resting over the primordial Bundelkhand granite massif and underlying the Upper Proterozoic Vindhyan Group of sandstones (Medlicott, 1859). Mathur (1960) and Mathur and Mani (1978) carried out geological mapping of the type Bijawar basin and the stratigraphic succession of the area after these authors is given below:

VINDHYAN GROUP (Upper Proterozoic)

SEMRI FORMATION

-- Unconformity

BIJAWAR GROUP

Gangau Ferruginous Formation Tillite and Shale Bajna Dolomite Ferruginous conglomerate and breccia

Amronia Quartzite Dargawan Traps Malhera Breccia

BUNDELKHAND GRANITE and GNEISSES

Our present interest lies in the Gangau Ferruginous Formation of the above scheme which contains reddishbrown phosphorite in its lower parts, bordering the granitic rocks of Bundelkhand massif. In the Hirapur-Bassia areas, Bundelkhand granites are either directly overlain by Bajna Dolomite or come in direct contact of Gangau Ferruginous Formation containing conglomerates, breccia and shales (Fig. 2). There is no 'tillite' in the vicinity of the phosphorite horizon, but has been recorded in the adjacent regions (Mathur and Mani, 1978). Open synclinaI and anticlinal structures are prominent in the shales and the Gangau Formation is locally bounded by a synformal structure in the Bassia area $(Fig. 1)$. Some preliminary information about this deposit is contained in the review by Pant (1980). Similar phosphorites also occur at Sonrai in the Lalitpur district, west of Hirapur, where copper, lead-zinc and uranium minerals are intimately associated with the secondary phosphate horizons.

Authors shared responsibilities for different tasks, viz. Banerjee for geological mapping, sampling, geological and geochemical interpretations, mineralogy, overall synthesis and writing, Khan for the major and trace element analyses by AAS and other techniques, and Srivastava and Saigal for X-ray diffraction studies.

PETROLOGICAL CHARACTERS

Since, only the underlying carbonates and the top phosphorites are of direct relevence to the present paper, the litho-characteristics of only these two rock types have been described. The fine grained Bajna Dolomites are of two types, namely: (a) brown ferruginous dolomite and (b) grey dolomitic limestone. The first type grades into overlying Gangau Formation. Their composition vary from cherty, shaly dolomite to pure dolomite rock. The Gangau Formation on the other hand are composed of ferruginous breccia, conglomerate and reddish brown slates and shales. The ferruginous sandstone and ferruginous shale occur as intercalations within the ferruginous conglomerate and breccia with abundant apatite grains in the groundmass. Based on the nature of occurrence in the area, four categories of phosphorites have been recognized:

Type I: Ferruginous, shaly, laminated pho sphorite Type II: Massively bedded, ferruginous phosphorite Type III: Brecciated/Conglomeratic, ferruginous phosphorite Type IV: Veins/Pore filling type, remobilized, secondary, crystalline apatitic, phosphorite.

In Type-I phosphorite, microgranular apatite grains occur within the ferru-

Fig. 1. Lithological distribution map of Bassia phosphorite production area in Hirapur-Bassia sector. Location map in the inset

Fig. 2, Schematic/diagrammatic cross section across the phosphorite deposits in Hirapur-Bassia-Mardeora area. Scale approximate

ginous shaly matrix either as dispersed matter or as well developed microlaminations. Visual estimates of micaclay mineral abundance in thin sections gives an inverse relationship with the quantity of apatite grains. Recrystallized coarse (0.02-0.15 mm) apatitic veins tation of the apatites; traverse through the shales (Fig. 3), mostly in a random manner or along secondary surfaces.

The Type-If phosphorites are massive, hard and compact, very fine grained, with thin laminations of coarse-grained quartz. Apatite is randomly distributed in the micaeeous groundmass and occur as small crystallites (0.02-0. 05 mm). Interstitial subhedral to anhedral elongated polyerystalline quartz (0. 01- 0. 02 *am)* show dissolution features on their margins. Subrounded to subangular fragments of ferruginous shaly phosphorite sometimes occur embedded in this type of ore, suggesting a later origin of this type of phosphorite. The void filling type of secondary apatite riddled with disseminated ferruginous matter occur with well defined rims of magnetite (Fig. 4). Such apatite are usually large $(0.05-0.25 \text{ mm})$ and show successive growth layers. Pore filling episode shows the following stages of evo lution :

(a) Apatite crystals growing outward with long axes normal to the confining wall have ferruginous inclusions along successive layerings. Some of them show curved twin planes (Fig. 5). Possibly some of the ferruginous layers were pre-existing which were removed during dissolution process and precipi-

(b) Overgrowths of clear apatite on the pre-exisitng clouded apatite grains indicate authigenic precipitation;

(c) Precipitation of quartz in the remaining voids of the pore spaces;

(d) Iron oxide (magnetite/goethite) forming in the late stages of diagentie alterations.

The Type-III phosphorites contain ferruginous cement and occur in association of conglomeratic and brecciated quartzites. More or less equant apatite crystallites (0.01 mm) in a shaly groundmass contain profuse ironoxide disseminations.

The Type-IV phosphorite occur as lateritie cover with well developed reniform surfaces. Large, perfectly crystalline prismatic apatite grains $(0.05-0.25 \text{ mm})$ radiate into the voids and pores (Fig. 4). The microcrystalline groundmass is stained reddish brown by the secondary iron-oxides. A more detailed petrological description is given by Banerjee (1982).

Fig. 3. Photomicrograph of Type-I phosphorite showing recrystallized coarse grained apatite crystals occurring within randomly oriented secondary veinlets in a predominantly areno-argillaceous groundmass. (X-nicols)

Fig. 4. Photomicrograph of void-filling type phosphorite with well developed apatite crystallites growing in size towards the open void spaces. Dark magnetite layers occur normal to the growth direction of the apatite crystallites. $(X\text{-nicols})$

Fig. 5. Photomicrograph showing curved twin planes of apatite crystallites and their growth along the cavity margins. Secondary magnetite fills the remaining void spaces and also permeates into the twin planes of the apatite. (X-nicols)

Characteristic x-ray diffraction patterns cially those from the top, weathered shown in Fig. 6A and B reveal that profiles, show positional shifts in the stituent, while quartz is the major an ideal earbonate-flourapatite and a gangue. There is, however, a general number of secondary peaks remain sup-

MINERALOGY **prevalence** of carbonate-poor (CO₂: 0. 10-2.85%) flourapatites. The diffraction pattern of the bulk samples, especarbonate-flourapatite is the major con- diffraction peaks from those known from

Fig. 6. A A typical X-ray diffractogram of bulk phosphorite showing prominent apatite peaks. B A X-ray diffractogram of phosphorite concentrate after apatite peaks are removed by computer stripping technique. The remnant peaks show the presence of crandallite

pressed due to overlapping by the predominant apatite peaks in most phosphorites. Using a computer programme, all apatite peaks were stripped-off from the diffraction patterns, which resulted in the enhancement of the suppressed peaks. The residual pattern (Pig. 6B) is comparable to crandallite (ASTM file no. $16-162$) - an aluminous phosphate, which seem to have formed by variable substitutions in the apatite structure along the apatite \rightarrow crandalite \rightarrow millisite weathering series. The lattice parameters were calculated from the observed diffraction patterns and by referring to hexagonal axes with the equation:

 $a^{O} = \sqrt{1.3333 \text{ d}^{2} (h^{2} + k^{2} + hk)}$

for (210) , (310) , (320) and (410) planes and c^0 = 1. d for (004) and (002) planes. Lattice dimensions of the apatite (carbonate-flourapatite) crystallite vary between 9.29 Å - 9.379 Å for a_0 and 6.880 Å for c_0 , whereas for crandallite a_0 is recorded as 7.83 Å and c_0 as 9.67 Å. $CO₂$ was determined by the peak-pair method of Gulbrandsen (1970), which varies from 0. 10 to 2.85%.

The summary of axes in the unit cell of apatite shows no significant difference between the mean length in the unleached and weathered phosphorites, which varies from 9.29 \AA in weathered phosphorites, to 9.37 Å in massive unleached phosphorites. $CO₂-a₀$ plots show a wide scatter and random correlation suggesting extensive leaching dur- the samples with variable $\rm P_2$ $\rm O_5$ con ing weathering.

CHEMICAL COMPOSITION

Spectrophotometric determination of major elements were carried out using the U.S. Bureau of Analytical Standards $BCR₁$ and $GSP₁$ and B.A.S. Standards (U.K.) the Thomas Phosphate 31-A. Trace elements were determined by atomic absorption and x-ray floureseence techniques. Table 1 depicts the

major elements and recalculated molar percentages of average Hirapur apatites. The observed charge imbalancing is due to the unaccounted flourine content which was not determined during the present work. Higher concentration of P_2 O_5 is noticed in the weathered phosphorites (Type IV). Silica show gradual decrease with increasing P2 05, while Ca increases simultaneously. However, the total Si values have not been considered for any interpretations, whose distribution in the rock is controlled by both diagenetic and secondary quartz. Similarly, the primary association of iron with phosphorite is not established with certainity. Na content is fairly high compared to any known phosphorite types from India. All trace elements show low concentrations with few exceptions. The intercorrelation of elements define three major associations such as: (1) apatitic phosphorite, (2) ferruginous-clayey phosphorite and (3) 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. Most elements actually- exist in more than one association. The element distribution pattern in the apatite structure indicate a positive correlation of CaO and P_2 O₅ (Fig. 7A). To establish the inter-element relationships, linear or otherwise, all tents have been plotted. The major element regression plots of CaO - P_2 O₅, P_2 O₅ - CO₂ and CaO - Na₂O are given in Fig. 7A-C. Since, the range of values of minor elements are of less significance, the comparison of major elements has been deemed to be possible between different petrological and chemical types. Comparison of less-weathered phosphorites with the weathered ones and variations in the composition of their contained carbonate-apatite as reflected by the normalised structural concentration values can be taken as the measure of the chemical ingradients

Fig. 7A-C. Regression plots showing: A Positive correlation of CaO and P205 . B Crude linear relationship of P_2O_5 and CO_2 . C Negative correlation of CaO and Na_2O

of the depositional waters at the time of the phosphorite formation. Those elements which indicate negative correlation e.g. most of the plots of Na_2O with respect of CaO suggest that only very small part of Na₂O has substituted in the apatite structure, while the rest of it occurs in association of other minerals. This random distribution pattern also reflects varying degree of weathering at different locations. There is consistent decrease in the overall trace-element concentrations in the more weathered phosphorites except for Mn, which tend to be fairly high in weathered profiles (Table 2). Such a distribution pattern of trace elements indirectly suggest a positive correlation of various elements with CaO and $P₂O₅$ - the essential constituents of the carbonate-flourapatite. Trace elements like U and Th show positive interelement correlation along the entire profile (Fig. 8) from weathered to least weathered phosphorites. The CaO/ Th, U correlation is represented by a curve which shows that the increase of U and Th with gradual decrease of CaO is a product of apatite-calcite leaching/ weathering near to the surface. Since the depth of weathering is not uniform, the distribution pattern of U and Th with respect to CaO and P_2 O₅ also varies in the same proportion. Therefore, it can be assumed that both U and Th have no strong correlation either with the apatites nor with the crandallites, but have been concentrated in the rocks as a result of leaching. Figure 8 depicts the absolute abundance of U with progressive leaching within the deposit. The ratio of Th/U varies from 0.23 to 0.42 with a mean of 0. 32 and this is considered significantly higher that the worldwide average of 0. I0 (Wedepohl, 1969). It is nowever pos sible that Th may have some crude affinity for the crandallite in the shaly phosphatic horizons. This type of relationship can be interpreted to be due to variability in the depths of leaching, and thus, suggest that most of U and Th in these rocks have formed by the process of secondary enrichment. $CO₂$

Fig. 8. Graphic presentation of absolute abundance of uranium with progressive leaching within the phosphorite deposit of Hirapur-Bassia area

Fig. 9. Schematic diagram of the distribution pattern of phosphorite in a weathering/leaching profile at Hirapur-Bassia area (scale arbitrary)

shows a weak and crude linear relationship (Fig. 7B) with P_2O_5 in most apatites, but in more weathered rocks the $CO₂$ content is higher, possibly due to secondary vein-filling calcites, and in this, the plots deviate significantly from linearity. This near random correlation also indicates variable leaching.

DISCUSSION

The dolomitic limestone bottom at Bassia is abruptly followed by sandy apatitie phosphorite and then by sandy clayey ferruginous phosphorite layers, each one of these show transition into other phosphorite types depending upon

degree and intensity of weathering (Fig. 9) basin was not protected from the onsleaching, collapse and recementation. The bottom-most part of the phosphorite unit appears to have formed by the phosphatization of carbonates, although the sharp boundaries between the two does not convincingly prove such an interpretation.

The chemistry shows that these carbonate-flourapatites are poor in $CO₂$ content. In more weathered phosphorites, mineral phases of crandallite are more prominent, inspite of the presence of a dominant apatite phase. In carbonate-flourapatites, 4% CO₂ is considered normal concentration, consequently the low $CO₂$ values (Table 1) of the Hirapur-Bassia apatites is due to the processes of decarbonation, caused by the dissolution and reprecipitation. The early illite-montmorillonite assemblage seem to have transformed into muscovite, which accounts for most of the K and A1 present in these phosphorites. A part of K seem to have been derived from the potassic minerals of the cratonic mass of Bundelkhand granitic complex which also provided land derived phosphorus through weathering of the terrestrial cover. As mentioned earlier, trace element content is low in the shaly and lateritic phosphorites compared to massive bedded phosphorites. Most trace elements seem to have leached out of the system during prolonged episodes of weathering and leaching. The irregular distribution of crandallite is also due to differential weathering of shaly apatitic phosphorites. The carbonate flourapatite \rightarrow crandallite (Ca) transformation in these phosphorites appear to be in their early stages, compared to phosphorites of the Sonrai area of the western Bijawar basin, where minerals of more advanced weathering stages \rightarrow millisite \rightarrow wavellite are also recorded. It is possible that the paragenetic sequence would have been the same as those identified in the Sonrai area, West Senegal, parts of Florida, Rumjungle area in Australia and parts of USSR, provided the Hirapur-Bassia

laught of weathering for a considerable time after they were lithified and uplifted. It is worth recalling that Mathur and Mani (1978) recorded glacial tillites in the adjacent non-phosphatic area, apparently overriding the Gangau Formation and possibly marking the unconformity over which the Lower Vindhyan sandstones were deposited. It can therefore be visualized that towards the closing phases of Gangau sedimentation, warmer climates changed to cooler ones which helped in protecting the basic carbonate-flourapatitic character of the Hirapur-Bassia phosphorite. It is therefore possible that the weathering was not prominent during the Precambrian times but was initiated vigourously during the subsequent periods. During the last phases of evolution of Bijawar rocks, land conditions prevailed with local fluvial influences and groundwater circulation through the exposed rock masses. The ferruginous crust, so common in such environments, were formed locally, but the sandstoneshales developed more extensive ferruginous coatings which also filled the intergranular spaces. This phase is associated with recrystallised aluminocalcic phosphatic cement which occur as rugs and cavity fillings within the alumino-phosphate rich phosphorites. There is gradual decrease in the detrital quartz content from the bottom to the top, and cement is more prominent in the surficial shales and phosphorites. In such places where the leaching was more intense, it induced numerous dissolution features leading to the formation of pseudo-breccia by the removal of cement, collapse and recementation by circulating groundwater containing dissolved iron.

It is significant to note that various mineral transformations noted above have not disrupted any of the primary stratification or the microtextures, which suggest that these transformation reactions were apparently isovolumetric due to leaching by permanent groundwater which received its supply through

 α 0 @ O~ **i** @ O~ f~

I::q

Samples B-1 to C-3 along a vertical profile.
1. Analyst: Dr. F.K. Bhargava/Dr. F.K. Cheria, Atomic Mineral Div., New Delhi.
2. Analyst: H.T. Millard Jr., R.B. Vaughn, S.W. Laster, and B.A. Keaton at USGS in Denver.

3. Thorium values are listed as "less than" the values shown.

5-12: Analysis by A.A.S. at Delhi University.

13-19: Analysis by X.R.F. at University of McQuarie and University of Keele.

the wet tropical rainfall, a condition that could very well be imagined to have existed in the central part of India where the Upper Bijawars are now exposed, at least from the Tertiary times, if not earlier.

The intensity of weathering is dependent on the mineral association and the most common effect is the loss of $CO₂$ in the carbonate flourapatite struc ture. As long as the carbonate is present in the rock it protects the associated apatite, halting the mineral transformation beyond the flourapatite stage (Lueas et al., 1980). Therefore, the apatites like those of Hirapur-Bassia area with low $CO₂$ contents could be safely interpreted to have evolved through the processes of weathering. With prolonged period of weathering, when carbonate was almost completely leached out, other associated minerals were attacked which released additional cations like Al and Fe. In the argillaceous host rocks, these released cations combined with available phosphates and formed crandallite, while in the alumina-poor detrital rocks, flourapatite remained the dominant phase and developed magnetite-goethite coatings. That iron was not readily available at the time of early phosphate sedimentation, is evident from the fact that no iron-phosphate has formed in the sequence. However, in the voidfilling type remobilized and recrystallized phosphorites, it seems that some of these voids and fissures were occupied by ferruginous laminations which have been systematically leached and isovolumetrieally replaeed by crystalline apatite grains, growing from the margins towards the centre of the void spaces (Fig. 4). Such features suggest that small quantity of iron was possibly introduced into the system subsequent to primary phosphate sedimentation, possibly at late diagenetic stages, on the sediment-water interface and was subsequently leached out during early stages of weathering. Widespread ferruginous coatings of all the rocks in the area is due to regional ferruginization process, which seem to have accompanied the regional silicification as the last stages of the geological activity in the region. It is also possible that some Fe was introduced in the sediments through epigenetic processes.

To summarize, the phosphorites of Hirapur-Bassia originated along restricted shoals in littoral basins of the intracratonic sea which fringed the margins of the Bundelkhand granitic craton. The shallow nature of the basin has been interpreted on the basis of occassional rippled sandy surfaces, current cross-laminations, horizontal and wavy laminations in the silty layers and primary parallel laminations and raindrop-imprints on the ferruginous shales. The environment was highly oxidizing, as evident from the abundance of hydrated and non-hydrated iron oxides, inspire of the fact that the basin had a restricted circulation. This also explains an observed fact that the organic matter contribution to the phosphate precipitation was negligible and the water depth of the sedimentation basin was extremely shallow, with occassional subaerial exposures. It is possible, such a shallow oxidizing basin was also responsible for higher concentration of Na in the phosphate rocks.

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