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Mineralogical investigations of the phosphatic nodules from Warchha sandstone, salt range with emphasis on replacement process

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ABSTRACT: *Discontinuous layers of phosphatic nodules are present within the upper part of Warchha Sandstone from Warrala area, in the east, to Katha Road Section in the west. The genesis of these phosphatic nodules, especially in Warchha sandstone, poses a big question mark. The interest in these phosphatic nodules is further increased, when they are found to be significantly radioactive. Along the strike, extension of the strata containing these phosphatic nodules is up to 35 km. Samples were collected from various localities including Nawabi Kas, Warrala, Malot, Karuli, Simbal, Gahi, Matin and Nurpur. These samples were studied petrographically and on the average the* P_2O_5 *content is more than 19.5%, which qualifies them to be called "phosphorites". The radioactivity measured through Gamma spectrometer is up to 600 ppm* eU_3O_8*, while chemical analyses show concentration of* U_3O_8 *up to 787 ppm in one of the samples. The petrographic study, with especial emphasis on replacement process, indicates hydroxyl apatite replacing calcite.*

INTRODUCTION

Warchha Sandstone is a formation belonging to Nilawahan Group of Permian age exposed in the Salt Range. It consists of medium to coarse-grained sandstone, conglomeratic at places and has interbeds of shale. The sandstone is red, purple or shows shades of lighter pink color. The sandstone is arkosic in nature. The upper most shale beds of the formation contain nodules, which are phosphatic and at places calcareous in nature. Usually the phosphatic nodules are uraniferous.

The origin of these phosphatic nodules is less understood and the main purpose of this study is to carry out petrography and replacement studies in order to have a better understanding of their genesis. Although the samples from this area were studied, petrographically, many times but the studies were not focused on replacement processes. This is for the first time that replacement of calcite by hydroxyl apatite is observed and reported from the samples of phosphatic nodules. During the microscopic observations of the thin sections, it was observed that the bulk of phosphorite grains consist of cryptocrystalline collophane (individual crystal diameter smaller than 1 μm) rather than microcrystalline and as a result it appears as brownish, isotropic material in the thin section. The detailed petrography and photomicrographic evidence has been presented and discussed in this paper.

The east-west trending Salt Range extends for approximately 160 km, forming a narrow chain of low lying mountains between the Punjab plains to the south and slopes merging into Potwar Plateau in the north. The eastern limit is defined by River Jehlum; whereas to the west the Range is truncated by River Indus.

GENERAL GEOLOGY OF THE SALT RANGE

The Salt Range is known as "Museum of Geology" and exposes a complete sequence of sedimentary rocks, ranging in age from Pre-Cambrian to Pleistocene. The sedimentary succession has been divided into a number of formations, separated by different unconformities (Table 1).

The oldest rock unit exposed in the area of investigation is the "Salt Range Formation", which is of Pre-Cambrian age. It is overlain by the "Jehlum Group" of early Paleozoic age. Middle Paleozoic is marked by a wide spread unconformity that makes the base of lower Permian in eastern Salt Range. In central Salt Range even early Paleozoic is missing and the upper Paleozoic rocks directly overlie the Pre-Cambrian sequence. Upper Paleozoic is represented by early Permian sediments of Nilawahan Group, which grade upwards into marine deposits of a continental shelf represented by Zaluch Group.

There is a Paraconformity between the rocks of Permian and Triassic rocks. These are successively followed by Mesozoic and Cenozoic formations (Shah, 1977).

TABLE 1. STRATIGRAPHIC COLUMN OF THE SALT RANGE EXPOSED IN THE AREA OF INVESTIGATION

STRATIGRAPHIC COLUMN				
ERA	SYSTEM		UPPER INDUS BASIN	
MESOZOIC	TRIASSIC	UPPER	KINGRIALI FM	
		MIDDLE	TREDIAN FM	
		LOWER	MIANWALI FM	
	PARACONFORMITY			
PALAEOZOIC	PERMIAN	UPPER	ZALUCH GROUP	CHHIDRU FM
				WARGAL LIMESTONE
				AMB FM
		LOWER	NILAWAHAN GROUP	SARDHI FM
				WARCHHA SANDSTONE
				DANDOT FM
				TOBRA FM
	MAJOR UNCONFORMITY			
		MIDDLE	JEHLUM GROUP	BAGHANWALA FM
		LOWER		KHISOR FM
				JUTANA FM
				KUSSAK FM
				KHEWRA FM
	PRE-CAMBRIAN			SALT RANGE FORMATION

LOCATION OF PHOSPHATIC NODULES IN SALT RANGE

The field party of Atomic Energy Minerals Centre, (AEMC) Lahore collected samples from the Salt Range. They reported that phosphatic nodules are mainly present in the eastern Salt Range at Nawabi Kas, Warala village, Malot Area, Karuli Area, Simbal Area, Dhok Hani Bakhsh, Gahi Area, Matin Area, and Nurpur Area Fig. 1 (Aziz Ullah, et al., 2003).

The occurrence of phosphatic nodules in Warchha Sandstone is not reported so far from Central Salt Range and Western Salt Range but the work is in progress and indications in the parts of central Salt Range are positive (Butt, personal communication).

The localities, with grid references and Topo-sheet numbers along with brief field descriptions are given in Table 2.

DESCRIPTION OF HAND SPECIMENS

The samples of phosphatic nodules were collected, mainly from eastern part of the Salt Range exposed in the upper part (within shale bed) of the Warchha sandstone. The size of the concretions / pellets / nodules usually ranges between 1mm and 15mm. They are generally sub-rounded in shape and have high specific gravity. On the basis of physical appearance, they can be divided into two types:

1. Grayish black in color, with pinkish brown tinge; and
2. Dull red to maroon and blackish gray in color with light gray to whitish material seen in cracks. Some black spots are also seen. These samples give weak effervescence when treated with 10% diluted HCl.

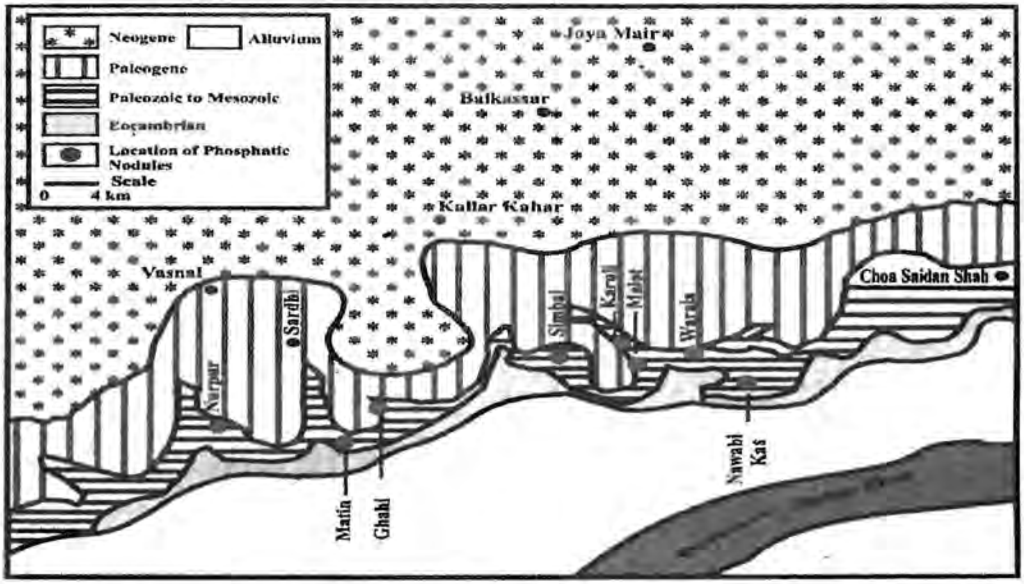

Fig. 1. Location of phosphatic nodules (after Aziz Ullah, et al., 2003).

TABLE 2. THE LOCALITIES, WITH GRID REFERENCES, TOPO-SHEET NUMBERS, AND BRIEF FIELD DESCRIPTIONS

Area / Vicinity	Locality	Grid Reference	Topo Sheet No.	Remarks
Nawabi Kas	Western flank of Nawabi Kas, 2km from Warala village	973453	43 – D/14	It is the eastern most locality of phosphatic nodules in the Salt Range. They occur in upper most shale beds of Warchha Sandstone. Nodules are grayish black with pinkish tinge. The sp. Gravity is high. Radioactivity ranges up to 700 cps
Warala Village	NE of Sagar Nala	944449 to 946457	43 – D/14	Almost similar in shape and appearance
Malot Area	500m SW of Malot Village	924449 to 924448	43 – D/14	The phosphatic nodules occur within the two upper most shale beds of Warchha Sandstone. They are pinkish brown to grayish black in color with high sp. Gravity and radioactivity ranges up to 800 cps.
Karuli Area	1) East of Karuli Village; 2) Near school at Karuli; 3) Karuli Village	907451 905447 898441	43 – D/14	Phosphatic nodules are found in upper most shale and second shale bed (from top) of Warchha Sandstone. They are dull red to blackish red in color. The radioactivity ranges from 400-600 cps. Some nodules give effervescence when diluted HCl is poured upon them.
Simbal Area	South of Simbal village	879452	43 – D/10	They occur in the upper shale bed of Warchha Sandstone. They are reddish black to dark maroon in color and commonly associated with caliches. Radioactivity up to 400 cps has been recorded
Gahi Area	SW of Dhok Hani Bakhash	838400	43 – D/10	Similar lithology as described in Simbal area
Matin Area	South of Matin Kalan	821384	43 – D/10	There are two horizons of phosphatic nodules. The nodules of older horizon are pink in color with black specks. The radioactivity ranges up to 600 cps. The nodules of younger horizon are black in color and radioactivity ranges from 100 to 200 cps.

Nurpur Area	2km south of Nurpur	734394 to737394	43 – D/10	They occur within the upper shale bed of Warchha Sandstone associated with the pedogenic carbonate nodules. The color varies from pinkish brown to blackish gray, with high sp. Gravity. The radioactivity ranges from 800 to 2200 cps

MICROSCOPIC OBSERVATIONS

Thin sections were prepared from the rock samples containing these nodules. Minerals identified in the thin sections, under polarizing microscope (Olympus BX50), and their approximate percentages ranges, through visual estimations are shown in Table 3.

TABLE 3. MINERALS IDENTIFIED IN THE ROCK SAMPLE AND THEIR APPROXIMATE PERCENTAGES

S.No.	Mineral Identified	Approximate Percentage
1	Collophane / Hydroxyl Apatite	40% to 70%
2	Hematite / Magnetite	5% to 41%
3	Calcite	0% to 30%
4	Barite	0% to 25%
5	Clay	0% to 8%
6	Feldspar + Quartz	Usually in accessory amount

Collophane

It is the most dominant constituent and appears as an isotropic to sub-isotropic material showing weak birefringence. It is amorphous to cryptocrystalline in nature. It occurs in the form of pellets (<2 mm) and some times as nodules (>2 mm), measuring up to 15mm. Under the microscope they are of light yellowish brown color, (Plates 1 & 2) with hematitic staining at places. Clay is often seen to be associated / intermixed with collophane. In most of the samples collophane pellets / nodules are seen to have converted into a fibrous / spherulitic to radiating material, which was also reported earlier (Zafar & Rashid, 2002; Sultan, 2003). The hydroxyl apatite generally appears on the margins of collophane, (Plates 3, 4, & 5) indicating isomorphic replacement / transition between two species of phosphate. No skeletal phosphate is seen in these nodular samples.

Hematite / Magnetite

Hematite occurs in crack fillings (Plate 2) as well as on the margins of the collophane, (Plate 6) forming thin parallel bands with the rosette-shaped / fibrous hydroxyl apatite. Sometimes it also occurs in massive form and is of reddish color. It is generally an alteration product of magnetite, whose remnants are often observed. Staining effect is observed in almost every thin section. In one of the samples, it is observed that the hematite has replaced calcite in the first phase and hydroxyl apatite has replaced the hematite in the second phase (Plate 4).

Magnetite occurs in these samples as opaque and typically cryptocrystalline material. It can be recognized by its steel gray, metallic luster in reflected light. Generally it is present along the margins of barite and calcite filling in the cracks.

TABLE 4. APPROXIMATE MODAL COMPOSITION OF THE PHOSPHORITES

Field Data			Petrographic Analyses							
S. No	Sample No	Field Location with NGR/ Toposheet No.	Collophane + Hydroxyl Apatite	Iron Oxides	Calcite	Barite	Feldspar	Quartz	Clay	Rock Name Assigned
1	WNW-74/02	Nawabi Kas 973453 43 D/14	63	13	2	20	0	Acc.	2	Phosphorite
2	WRM-51/02	Malot area 923448 43 D/14	40	27	0	8	11	12	2	Phosphorite
3	WK-26/02	Karuli (East Area) 907451 43 D/14	62	12	8	18	0	Acc.	0	Phosphorite
4	WR-35/02	Simbal Area 879452 43 D/14	70	12	0	10	0	Acc.	8	Phosphorite
5	WR-37/02	Simbal Area 879452 43 D/14	45	41	2	12	0	0	0	Phosphorite
6	WR-40/02	Gahi area 838400 43 D/10	65	18	2	0	15	0	0	Phosphorite
7	GH -N-2	Gahi area 838400 43 D/10	70	6	20	0	0	Acc.	4	Phosphorite
8	GH -N-4	Gahi area 838400 43 D/10	67	5	24	0	0	Acc.	4	Phosphorite
9	GH -N-5	Gahi area 838400 43 D/10	57	6	12	25	0	Acc.	0	Phosphorite
10	WR-43/02	Matin area 821384 43 D/10	67	25	0	8	0	0	0	Phosphorite
11	WR-45/02	Matin area 821384 43 D/10	58	17	20	0	0	Acc.	5	Phosphorite
12	WRN- 52/02	South of Nurpur 734394 43 D/10	64	10	12	10	0	Acc.	4	Phosphorite
13	WRN-53/02	South of Nurpur 735394 43 D/10	66	22	8	0	0	Acc.	4	Phosphorite
14	WRN-54/02	South of Nurpur 737394 43 D/10	47	23	30	0	0	Acc.	0	Phosphorite

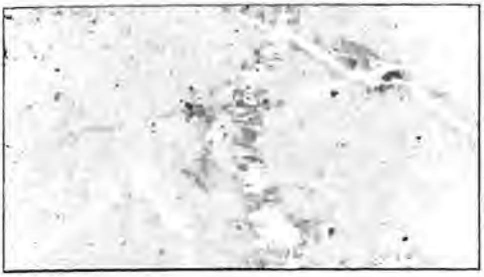

Plate 1. Thin section of the sample taken from Nurpur area. Cross cutting cracks / veins filled by calcite and barite in collophane. Hematitic / limonitic staining is also visible. Cross polar view, magnification 100 times.

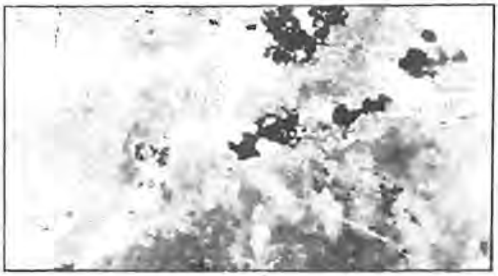

Plate 2. Thin section of the sample taken from Malot area (Salt Range). Collophane concretions, hematite replacing calcite in cracks. Cross polar view, magnification 100 times.

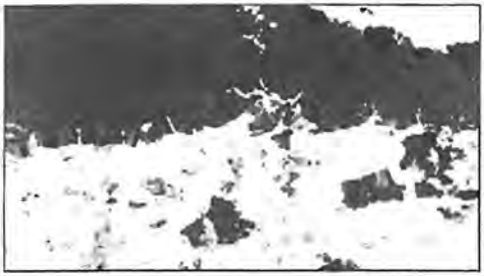

Plate 3. Thin section of Phosphatic nodule from Warchha Sandstone. Pressure dissolution of hydroxyl apatite into calcite. One of the margins of collophane concretion has no hydroxyl apatite (top right corner). Cross-polar view, magnification 100 times.

Plate 4. Thin section made from sample taken from Gahi area. Replacement phenomena; first hematite has replaced calcite and later rosette-shaped hydroxyl apatite is seen replacing hematite; cross polar view, magnification 100 times.

Plate 5. Photomicrograph taken, from the thin section of phosphatic nodule, from Warchha sandstone, Salt Range. Replacement of calcite by hydroxyl apatite is clearly visible. Collophane concretion is also visible. Cross-polar view, magnification 100 times.

Plate 6. Thin section of the sample taken from Nurpur area. Hematite band seen along the collophane concretion. The upper portion is occupied by barite, which has filled the crack. Cross polar view, magnification 100 times.

TABLE 5. RADIOMETRIC AND CHEMICAL ANALYSES SHOWING U_3O_8 AND P_2O_5

CHEMICAL ANALYSES				
Sr No	Sample No	eU_3O_8 (cps) Radiometric	U_3O_8 (ppm) Chemical	P_2O_5 (%)
1	WNW-74/02	450	479	21.07
2	WRM-51/02	450	522	18.59
3	WK-26/02	300	526	21.92
4	WR-35/02	600	469	22.98
5	WR-37/02	150	411	21.51
6	WR-40/02	400	430	13.37
7	GH -N-2	200	426	20.66
8	GH -N-4	175	452	22.73
9	GH -N-5	180	495	22.93
10	WR-43/02	375	569	16.56
11	WR-45/02	275	606	19.56
12	WRN-52/02	400	483	20.53
13	WRN-53/02	600	787	22.35
14	WRN-54/02	450	454	24.39

Calcite

It generally occurs as cementing material and as filling of cracks, which are "septarian" in character. In most of the thin sections it occurs as cryptocrystalline / very fine-grained aggregates, which usually do not show any cleavage. However in some thin sections the calcite crystals are seen, which are comparatively large and are elongated. Such calcite is present in quite low percentages. Hematitic staining over calcite can also be seen in few thin sections, indicating that hematite had entered the rock at a later stage, in solution form.

Barite

It occurs mainly as crack filling material (Plates 1 & 6)). Sometimes it is visible with naked eye in hand specimen. Barite is usually in the form of inter-grown crystals forming rosettes or platy aggregates and concretionary masses. They were identified due to their birefringence, interference figure and form.

CHEMICAL ANALYSES

The samples were also analyzed in the Chemistry Division, of the AEMC, for determining percentages of P_2O_5 and U_3O_8 content. The analyses show that the nodular samples, from Warchha Sandstone, contain uranium up to 787 ppm with an average of 508 ppm (Table 5) and P_2O_5 content is present up to 24.39% at the maximum with an average of 21%. On the basis of the chemical composition, these are named as "*phosphorites*" (Pettijohn, 1975).

PHOSPHATIZATION OF CALCIUM CARBONATE

Replacement of calcium carbonates by phosphate minerals is described as phosphatization. The conditions in which the phosphatization of calcium carbonate can occur were first defined by Ames (1959). He passed a basic solution of sodium phosphate and sodium hydroxide, through a tube packed with fragments of calcite. In order to determine its composition, he checked the composition of the solution from the bottom of the tube and studied samples of the sediment in the tube, from time to time.

$$3Na_3PO_4 + NaOH + 5CaCO_3 \longrightarrow Ca_5(PO_4)_3OH + 5Na_2CO_3$$

Calcite

Hydroxyl Apatite

He concluded that the original calcite was replaced and perfectly pseudo-morphed by apatite and that the apatite contained a few percent of carbonates substituting for phosphate in its crystal structure.

According to Ames, phosphatization of calcite would occur in PO_4^{3-} concentrates as low as 0.1 ppm. It is generally known that in areas of oceanic upwelling, the PO_4^{3-} content is usually 0.3–0.8 ppm, which is more than adequate to cause replacement of calcite by apatite. In reducing environments, immediately below the seawater-sediment interface, it is common to find 1ppm PO_4^{3-} in solution because of the decay of phosphate-containing organic tissues in such environment. It certainly seems possible that a significant amount of Phosphorites have been produced by very early diagenetic replacement just below the seafloor.

ORIGIN OF PHOSPHORITES

Phosphorites are chemical / biochemical rocks rather than terrigenous detrital rocks and nearly all phosphorites are of marine origin. They contain at least 19.5% P_2O_5 by laboratory chemical analyses. Kazakov (1937) determined that P_2O_5 content of marine waters is at maximum between 30-500 m depth. At depths less than 30m, the phosphorous is consumed by phytoplankton during photosynthesis. At depths greater than 500m, the content of carbon dioxide in the water is so great that the water can not become saturated with respect to apatite because, like calcite, it is soluble in acid. The ancient phosphorites (Phosphoria Fm) formed in fairly shallow waters confirm this fact. The modern deposits of phosphorites are also located in shallow marine depths.

According to Pettijohn (1975), environment where phosphatic nodules can form include: transgressive and regressive shelf and shore zones; and intra-tidal channels, where through current and wave reworking of sediments, phosphorites can be formed.

Diagenetic phosphate can precipitate in sandstone in the form of nodules and cement. Once formed these phosphatic nodules are very resistant to weathering and can easily be reworked into succeeding beds and may form concentrates.

Presence of gypsum and lateritic clays is reported in the lower part of Sardhai Formation at the contact with Warchha Sandstone, especially in the eastern Salt Range at Salloi and Takwan areas. It indicates evaporatic conditions, which may have prevailed for short intervals during regression. Sardhai Formation, having a lower transitional contact with the Warchha Sandstone, also contains phosphatic nodules and concretionary layers, which are sometimes uraniferous (Naseem ud Din et al., 2001). Such phosphatic nodules are also reported to be present at the base of the sandstone unit of Chhidru Formation of Late Permian age (Shah, 1977).

It is quite possible that the shale beds, containing phosphatic nodules, which are considered to be the part of Warchha Sandstone, are actually part of overlying Sardhai Formation or vice versa. Alternatively, the nodules originally belonging to older Formations could have been reworked and subsequently incorporated in the Warchha Sandstone.

URANIUM IN PHOSPHORITES

Sediments of phosphatic composition, which are of marine origin, contain uranium ranging from some 10ppm to about 300 ppm. However, locally it may be up to several thousands ppm U, as in Cabinda, Angola, In contrast to marine phosphorites, all continental phosphatic rocks are low in uranium, rarely exceeding 20 ppm uranium (Dahlkamp, 1993).

Uraniferous marine phosphorites constitute large uranium resources, but their low average grade and difficult metallurgical extraction exclude them form being a primary uranium source. It is, however, recovered as a byproduct of phosphate.

The most important source of uranium in phosphorites is in Morocco, which has the largest deposits of phosphorites, reported to be over 6 million tons of uranium, with an average grade of 120 ppm. USA, Egypt, Jordan, Syria, Angola and Russia have also significant resources of uranium in phosphorites.

Bedded phosphorites formed at the margin of continental shelf (e.g., Phosphoria Formation, Idaho, USA) generally have higher uranium contents (average 100 to 200 ppm U, max. 6500 ppm U) than phosphorites of shallow marine near-shore deposition (e.g., Bone Valley Formation, Florida, average 20 to 80 ppm U). The latter, however, may achieve secondary enrichments of up to 500 ppm U by reworking. In both cases it is assumed that uranium was more or less synsedimentary, extracted from sea-water and incorporated into apatite grains by substituting calcium (Dahlkamp, 1993).

According to McConnell (1938) that VO_4, As_2O_4, SiO_2, SO_4 and CO_3 may be substituted for the equivalent amounts of PO_4 and minor amounts of Mg, Mn, Sr, Pb, Na, U, Ce, and Y may substitute for Ca. The presence of uranium in these phosphorites seems to be the result of such substitution.

The presence of appreciable amount of chemical uranium ranging from 411 to 787 ppm in all the samples from Warchha Sandstone indicates the strong association of uranium and phosphate and indicates its marine origin. However, absence of any visible uranium mineral in the samples indicates that uranium is present in adsorbed form, either with collophane or barite. Radioactive grains separated through autoradiography from one of the samples from Warchha sandstone, were earlier identified as radio-barite, through XRD, (personal communication with Mr. Khalid Mehmood, XRD expert at AEMC) thus indicating the association of uranium in adsorbed form with barite.

CONCLUSIONS

Although further work is required but on the basis of above discussion it can be concluded that:

1. The phenomenon of hydroxyl apatite replacing calcite has not been confirmed / reported earlier in the Permian rocks of Pakistan. The evidence of this phenomenon, duly supported by the photo-micrographs has been confirmed in phosphorites of Permian rocks of Salt Range, through this study.
2. Warchha Sandstone is reported to be of fluviatile in nature (Shah, 1977). However, in the Eastern Salt Range, there is possibly a facies change and the upper part of the formation represents the marginal facies, deposited by the transgressive-regressive action of the

receding sea. It can, therefore be inferred that these nodules were formed at shallow marine to shoreline margins, by to and fro motion of the receding sea. However no evidence of any fossil has been observed in these samples.

3. Although, the samples of phosphatic nodules, from Warchha Sandstone contain uranium, which has been confirmed by chemical analyses, but no uranium mineral has been identified / observed in these thin sections. Thus, indicating presence of uranium in adsorbed form, either with collophane or barite.
4. Chemical analyses of the samples from Salt Range show uranium but according to previous studies (Arif et al., 2003; Sultan, 2003), of the samples from the Salt Range vicinity, it is mostly in U^{+4} forms, which is not easily leachable and hampers economical extraction of uranium from these nodules.
5. The sporadic distribution of the phosphatic nodules, within the shale bed of Warchha Sandstone, further restricts the chances of an economical uranium deposits.

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