

## GEOCHEMICAL STUDIES OF LAMBIDOGI (HAZARA) PHOSPHATES, PAKISTAN

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Petrological and geochemical data of Lambidogi phosphorites of Hazara (NWFP) have been described and discussed. The early Cambrian phosphorite deposits of Lambidogi (Hazara) occur as discontinuous outcrops and in the form of lenses. These are hosted in the dolomite of the Abbottabad Formation. Texturally Lambidogi phosphorites are of two types - microspherites (finely crystalline anathigenic mud) and oval shaped pelletes ranging in size from 0.2 to 3 mm. Mineralogically these phosphorites have been identified generally as hydroxylapatite and fluorapatite. X-ray diffraction, infrared spectral studies, Differential thermal and thermogravimetric and Chemical analysis have been carried out on Lambidogi phosphorites. These phosphorites are of high grade ( $P_2O_5 = 37.85 \pm 1.20$ ) with low  $SiO_2$  ( $0.89 \pm 0.83$ ) and  $MgO$  ( $0.62 \pm 0.30$ ) contents.  $R_2O_3$  contents ( $Al_2O_3 = 1.93 \pm 0.26$ ;  $Fe_2O_3 = 2.62 \pm 0.09$ ) are also within the desirable limits for using the Lambidogi ore in manufacturing phosphatic fertilizers.

**Key words:** Geochemistry, Phosphorites, Hazara.

### Introduction

The import figures of phosphatic fertilizers for Pakistan are Rs. 1759 million for 1989 in addition to imported natural rock phosphate which amounts to Rs. 72 million for the same year [1]. Rock phosphates of Hazara are the only commercially workable deposits in Pakistan. These deposits were first reported in 1970 at Kakul, Lagarban and Dalola [2]. At present phosphate mining from Kakul and Lagarban deposits of Hazara is partially meeting the demand for indigenous phosphatic fertilizer production. Phosphate deposits, with considerable reserves have been reported recently at Tarnawai and Lambidogi, but these have not been evaluated so far.

The deposits of Lambidogi ( $34^{\circ}15'$ ;  $73^{\circ}20'$ ) are accessible via Mansehra road and are at a distance of about 9.5 km from Abbottabad city. These deposits are located north of Kakul phosphatic horizon. There is no general consensus regarding the extension of Hazara phosphorite deposits, though these have been reported to be exposed within an area of about 155 km<sup>2</sup> [3]. Lambidogi phosphate deposits near Banda Pir Khan village (Fig. 1) are distributed in the form of lenses; although at some places they continue for about 60-70 metres in strike length [3].

Phosphorite deposits of Hazara were first discovered by Latif [2]. Bhatti *et al.* [4] conducted some detailed investigations on phosphate deposits of Kakul - Mirpur. Later on, Hasan *et al.* [3] carried out detailed stratigraphic and petrographic studies of Kakul - Mirpur, Lagarban, Dalola and Sirban Hill deposits. Since 1980, Sarhad Development Authority has been exploiting some of these phosphorite deposits [5] and in 1982 British mining consultants undertook exploration studies of Kakul, Lambidogi, Lagarban and Dalola areas [6] (Fig. 2,3).

Lambidogi phosphorite deposits have been mentioned by Hasan and Ghaznavi [3] as an extension of Kakul deposits.

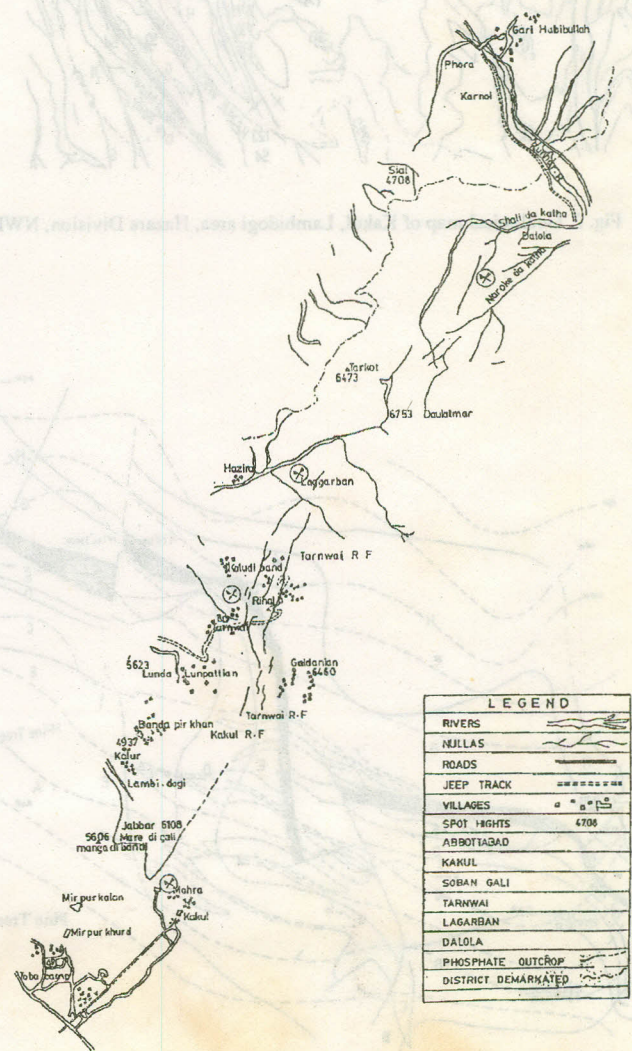


Fig. 1. Location map of Hazara phosphate deposits. (scale 1:5000)

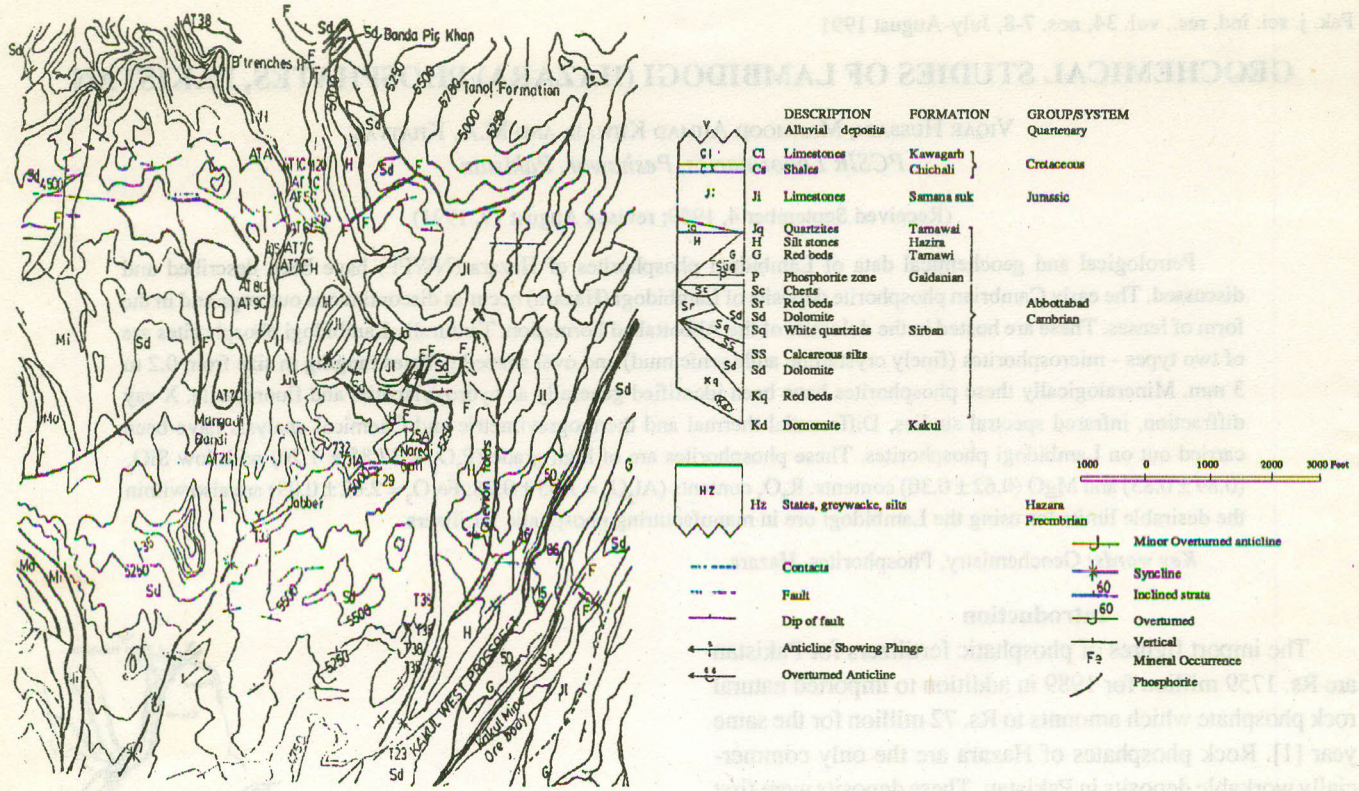


Fig. 2. Geological map of Kakul, Lambidogi area, Hazara Division, NWFP (After British Mining Consultants and Sarhad Development Authority, 1977).

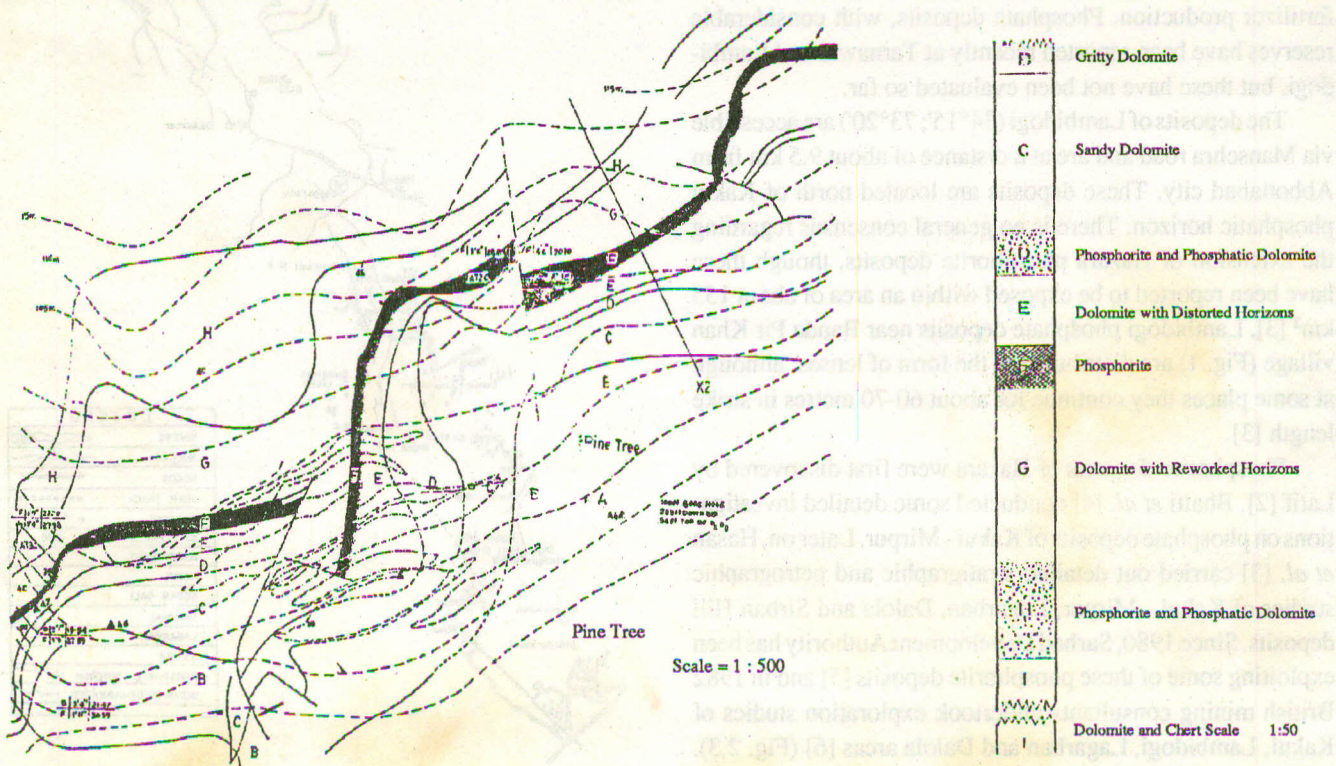


Fig. 3. Group of trenches in Lambidogi area, Hazara Division, NWFP (After British Mining Consultants and Sarhad Development Authority, 1977).

However, the detailed studies on geochemistry and economic potential of Lambidogi deposits were still lacking. In the present work, attempts have been made to discuss the geochemistry, petrogenesis and grade of Lambidogi Phosphate deposits.

*Stratigraphy.* Rocks exposed in the Hazara area range in age from Precambrian to Recent and have been mapped by Calkin and Matin [7] and Latif [2].

Lockhart Limestone .....	Paleocene
Kawagarh Formation .....	Late Cretaceous
Lumshiwai Formation .....	Early Cretaceous
Chichali Formation .....	Late Jurassic
Samana Suk Formation .....	Middle Jurassic
.....unconformity.....	
Hazara Formation .....	Early Cambrian
(Phosphorite bearing)	
Abbottabad Formation .....	Early Cambrian
Tanawal Formation .....	Precambrian
Hazara Formation .....	Precambrian

Most of the Hazara phosphorites are generally hosted in the Abbottabad Formation, which consists of a sequence of cherty dolomite in the upper part, quartzose sandstone in the middle part and limestone and dolomitic limestone in the lower part [3].

Kakul and Lambidogi phosphorites are hosted in Galadian member of Abbottabad Formation. Phosphorite occurs in association with phosphatic dolomite and dolomite with distorted horizons of chert [6].

#### Materials and Methods

Fifteen samples of phosphorites and host rocks were collected from trenches of Lambidogi phosphate deposit along the strike length of 400 metres. 1 gm of the representative samples in triplicate were subjected to chemical analysis. X-Ray diffraction studies were undertaken to ascertain the mineralogical composition of Lambidogi phosphorites.

*Sample preparation.* Both the acid and fusion decomposition procedures were employed [8,9]. In the acid decomposition the powdered phosphate rock was treated with HCl (Conc.) followed by HCl (Conc.) and HNO<sub>3</sub> (1 : 4) mixture and treatment with HClO<sub>4</sub> (70 - 72%). In the fusion method, the samples under study were fused in platinum crucibles using anhydrous sodium carbonate as flux, followed by digestion with concentrated hydrochloric acid. For magnesium and potassium contents, known standard procedures were employed for sample preparation [8].

*Chemical analysis.* P<sub>2</sub>O<sub>5</sub> was determined by (i) spectrophotometric method using vanadomolybdate reagent and meas-

uring the intensity of the resulting yellow-coloured complex at 450 nm on EPMA Model LS-7 Spectrophotometer and (ii) gravimetric method, first separating as phosphomolybdate followed by precipitation as magnesium ammonium phosphate hexahydrate using magnesia mixture [8 - 10]. Calcium content was determined volumetrically with standard KMnO<sub>4</sub> solution, after first precipitating as calcium oxalate. Iron was determined by Zimmermann-Reinhardt volumetric method, aluminium by gravimetric method precipitating as AlPO<sub>4</sub>. Flame photometric methods was used for the estimation of potassium contents. For magnesium content determination, phosphate ore sample was dissolved in HCl (2 : 1) and HNO<sub>3</sub> (Conc.) mixture, followed by heating with H<sub>2</sub>SO<sub>4</sub> (1 : 1) till evaporation of fumes of H<sub>2</sub>SO<sub>4</sub>. After treating the residue with 95% alcohol, calcium sulphate was removed by filtration and in the filtrate magnesium was determined gravimetrically by precipitating with diammonium hydrogen phosphate and weighing as Mg<sub>2</sub>P<sub>2</sub>O<sub>7</sub> [8 - 10].

*Thermal analysis.* Thermogravimetric (TGA) and differential thermal (DTA) analysis were carried out in an open crucible (ceramic) under atmospheric pressure at a heating rate of 10°/min on MOM derivatograph (Paulic Paulik Erdey) type thermobalance with automatic recording on photographic chart [11].

*Infrared spectra.* All spectra were recorded on a Hitachi Model - 270-50 infrared spectrophotometer in the range 4000-250 cm<sup>-1</sup> using KBr disc technique.

#### Results and Discussion

*Petrography.* Thin section data reveal that apatite occurs generally as pellets and microspherite in Lambidogi phosphorites (Fig. 4). Other minerals identified in phosphorite thin sections occurring in small quantities include iron, quartz and calcite in matrix and some opaque minerals are irregularly distributed throughout (Fig. 5,6).

Microscopically, most of the phosphate grains in these phosphorites occur in pelletal forms. The authigenically formed microspherite and pellets are mineralogically hydroxylapatite and fluorapatite. The oval, spherical and elliptical shaped pellets are the aggregates of finely precipitated cryptocrystalline phosphorite mud [12] (Fig. 4,6). Generally, pellets are dark brown in colour in plane polarized light and show isotropic behaviour in cross nicols. Sometimes, the margins of pellets show anisotropic behaviour which may be due to recrystallized nature (Fig. 7). The brown colouring of the pellets may be due to irregular patches of iron oxide (Fig. 6). These pellets vary widely in their size (0.2 - 3mm) and show the inclusions of clay, siliceous and opaque minerals, which are not identified optically (Fig. 8). Some apatite pellets show fractured character (Fig. 4) while others are seen in discrete

form (Fig. 7). In dolomitic phosphorite thin sections, medium to coarse grains of dolomite and calcite with perfect sets of cleavage are common (Fig. 9).

Absence of detrital grains like quartz in thin sections of the phosphorites suggest that Lambidogi phosphorites are primary marine sediments [13]. These sediments were precipitated as microphosphite or phosphorite mud which were subsequently modified into pellets during later

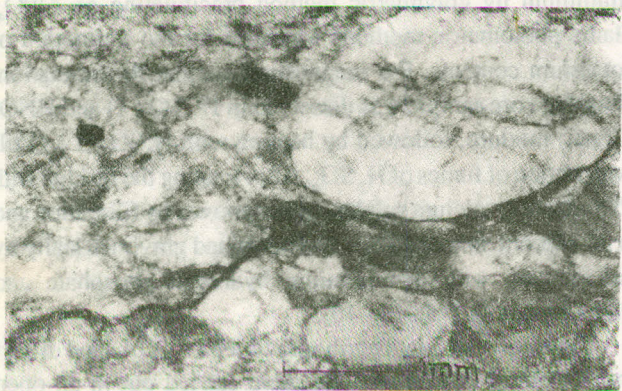


Fig. 4. Apatite occurring as oval shaped pellets and microcrystalline phosphorite mud (CP x 25).

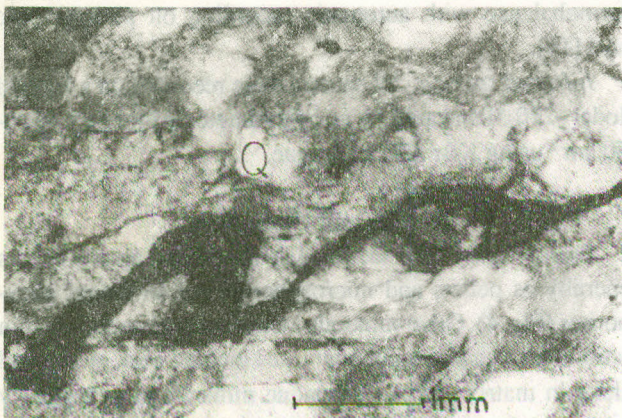


Fig. 5. Sample of phosphorite showing intracrysts of quartz (Q) along with some gangue minerals in matrix (CP x 25).

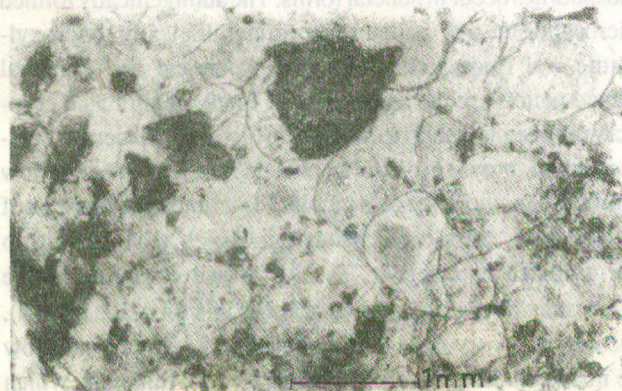


Fig. 6. Sample of phosphorite showing apatite pellets varying in size and shape (CP x 25).

processes e.g. diagenesis [12]. According to Riggs [12] these pellets are considered to be allochemical phosphorites which are produced by the physico-chemical or biochemical formation of phosphate within the area of deposition and are subsequently transported within the depositional basin as clastic constituents.

The hydroxyl and fluorapatitic composition of Lambidogi phosphorites is itself an evidence that apatite was precipi-

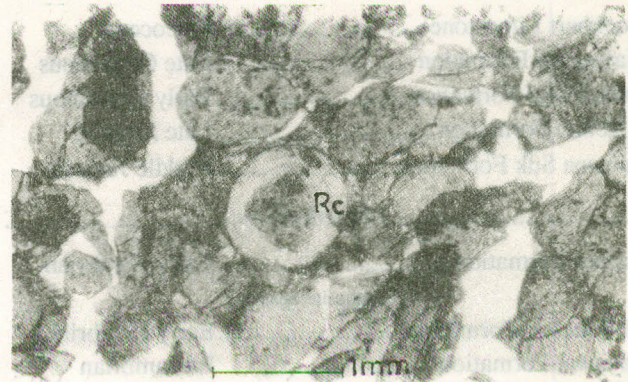


Fig. 7. Apatite pellets with recrystallized (Rc) margin showing anisotropic behaviour.

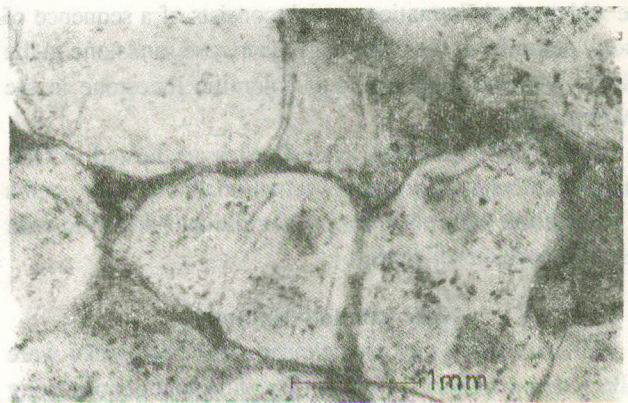


Fig. 8. Apatite pellets of varying size showing inclusions of clay and opaque minerals (CP x 25).

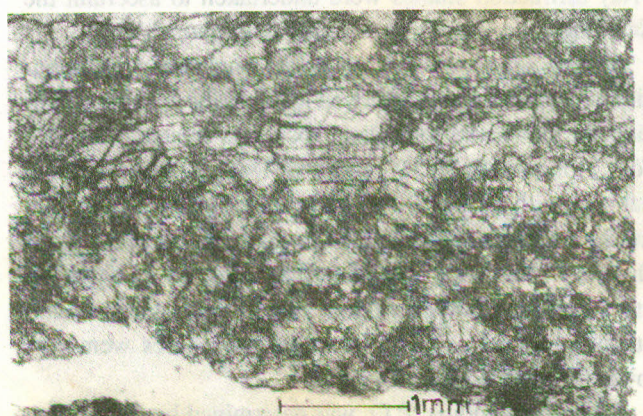


Fig. 9. Carbonate grains with perfect sets of cleavage (CP x 25).

tated directly [14]. The rounded nature of apatite pellets suggests that adequate reworking of these pellets took place within the area of deposition. The fractured nature of some pellets suggests that shallow marine conditions with periodic disturbances by strom (tide) generated waves [14] prevailed in Hazara basin at the time of deposition of Lambidogi phosphorites.

The chemical values of  $P_2O_5$  and CaO described in Table 1 show strongly negative behaviour with each other. The negative relationship between these oxides suggests that apatite besides precipitating directly, was also formed by replacing calcium ions. According to Ames [15] fluorapatite is the end member product of diagenetic replacement in which dissolved phosphate ions substitute for carbonate in calcareous materials.

**Mineralogy.** X-ray powder diffraction studies of the two Lambidogi phosphorite samples were carried out with X-ray diffractometer. The hydroxylapatite (2.79, 3.40, 2.69 Å) is the major constituent. Second most important apatite mineral present in these samples is fluorapatite (2.79, 2.71, 1.84 Å) (Fig. 10). Accessory minerals include quartz, calcite and pyrite.

**Infrared spectral studies.** Infrared spectral studies were carried out on the samples LDP-1,4 and LDD-6,7. The spectra are described in Table 2 and Fig. 11. Samples LDP-1,4 showed spectral characteristic different from samples LDD-6,7. Characteristic absorption bands in the 2000-400 $cm^{-1}$  range were observed for the phosphorite concentrates [16]. Medium intensity absorption bands around 575-600 $cm^{-1}$  assigned to (P-O) bending mode were observed at 573 $cm^{-1}$ , 603 $cm^{-1}$  and 570 $cm^{-1}$ , 602 $cm^{-1}$  for samples LDP-1 and LDP-4, respectively. Weak intensity absorption bands around 1040-1044 $cm^{-1}$  and 1090-1100 $cm^{-1}$  assigned to (P-O) weak modes were also observed for LDP-1 and LDP-4 samples at 1044 $cm^{-1}$ , 109 $cm^{-1}$  and 1042 $cm^{-1}$ , 1094  $cm^{-1}$ , respectively. According to Banerjee *et al.* [16], the strong  $CO_2$  absorption

TABLE 1. CHEMICAL COMPOSITION OF LAMBIDOGI PHOSPHATE DEPOSITS.

	LDP (1)	LDP (2)	LDP (3)	LDP (4)	LDP (5)	LDD (6)	LDD (7)
Moisture	0.10	0.17	0.08	0.15	0.25	0.05	0.16
Loss on ignition	1.77	1.72	1.95	2.62	1.45	40.00	20.00
Silica	2.20	1.07	0.73	0.01	0.44	4.64	24.89
$P_2O_5$	36.20	39.00	37.26	39.03	37.78	11.02	16.69
CaO	53.80	52.99	55.42	52.88	54.32	25.48	24.34
MgO	0.46	0.41	0.38	0.71	1.13	13.28	8.24
$Fe_2O_3$	2.66	2.65	2.74	2.51	2.55	2.03	3.14
$Al_2O_3$	2.36	1.86	1.69	1.97	1.77	2.32	2.09
$K_2O$	0.42	0.36	0.31	0.24	0.20	0.42	0.34
Total:	99.97	100.23	100.56	100.12	99.89	99.84	99.89

doublets in the 1410 and 1450  $cm^{-1}$  range is characteristic of phosphorite concentrates. Whereas this doublet was not observed for sample LDD-6 and LDD-7, a strong doublet was observed at 1458 · 1434 $cm^{-1}$  and 1456 $cm^{-1}$ , 1434 $cm^{-1}$  for samples LDP-1 and LDP-4, respectively. However, a weak absorption singlet was observed at 1440 $cm^{-1}$  for LDD-6 and at 1448 $cm^{-1}$  for LDD-7 samples.

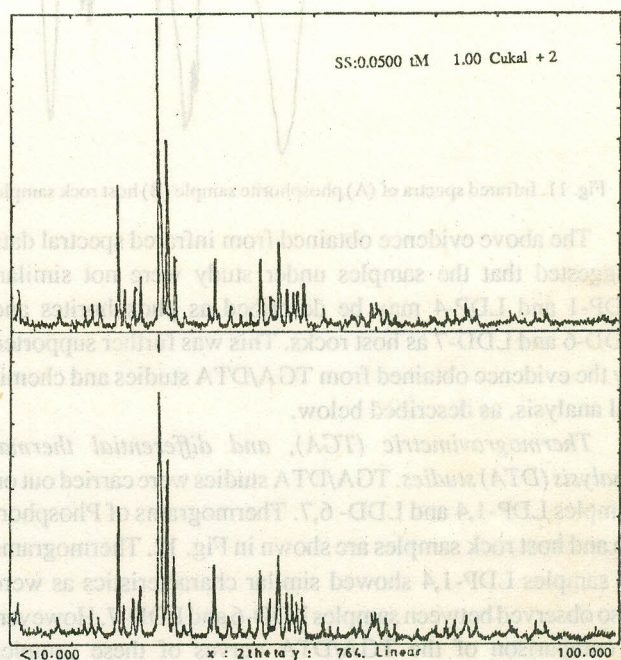


Fig. 10. X-Ray diffractograms of Lambidogi phosphorite samples.

TABLE 2. INFRARED SPECTRA ( $WNCm^{-1}$ ) OF LAMBIDOGI PHOSPHATES.

Sample (LDP-1)	Sample (LDP-4)	Sample (LDD-6)	Sample (LDD-7)
292(665.5)*	2360(78.7)	2924(73.2)	2928(68.9)
1458(54.1)	1456(58.8)	2540(78.3)	2532(74.6)
1434(55.8)	1434(61.7)	1828(75.2)	1448(11.1)
1095(14.8)	1094(21.4)	1440(3.4)	1092(15.4)
1044(5.3)	1042(7.9)	1096(53.3)	1060(17.5)
864(67.6)	964(53.6)	1048(55.5)	880(37.1)
603(32.8)	866(73.1)	880(30.0)	798(60.5)
573(36.5)	688(94.7)	728(63.5)	780(64.9)
474(85.4)	656(88.6)	472(76.2)	728(64.9)
—	602(36.7)	370(12.7)	694(82.9)
—	570(41.5)	322(45.2)	600(65.3)
—	472(88.3)	264(41.8)	572(65.3)
—	440(91.9)	—	516(59.1)
—	332(39.5)	—	470(43.1)
—	276(33.6)	—	372(19.1)
—	—	—	320(41.1)
—	—	—	262(42.9)

\*Figures in parenthesis are percent absorbance.

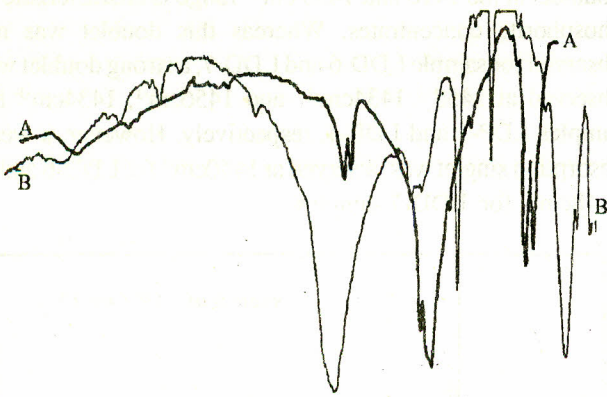


Fig. 11. Infrared spectra of (A) phosphorite sample (B) host rock sample.

The above evidence obtained from infrared spectral data suggested that the samples under study were not similar. LDP-1 and LDP-4 may be described as phosphorites and LDD-6 and LDD-7 as host rocks. This was further supported by the evidence obtained from TGA/DTA studies and chemical analysis, as described below.

**Thermogravimetric (TGA), and differential thermal analysis (DTA) studies.** TGA/DTA studies were carried out on samples LDP-1,4 and LDD-6,7. Thermograms of Phosphorite and host rock samples are shown in Fig. 12. Thermograms of samples LDP-1,4 showed similar characteristics as were also observed between samples LDD-6 and LDD-7. However, a comparison of the TGA/DTA curves of these samples showed significantly different thermal characteristics, indicating the chemical composition of samples LDP-1,4 (Phosphorites) to be different from samples LDD-6,7 (host rocks). Whereas thermograms of all the samples showed a broad endothermic peak around 80-130° (peak temperature 105°) corresponding to the loss of adsorbed water, host rock samples LDD-6,7 also showed two additional characteristic sharp endothermic peaks (not observed for phosphorites samples LDP-1,4) around 660-840° (peak temperature = 770°) and 840-960° (peak temperature = 920°) thought to be due to the decomposition [17] of  $MgCO_3$  and  $CaCO_3$  parts of dolomite structure [18], respectively. Total loss on decomposition for phosphorite samples (LDP-1, LDP-4) and LDD-7, LDD-8 (host rock) were found to be 1.87%, 2.77% and 40.00% and 20.00%, respectively.

**Chemical analyses.** The results of chemical analyses of the seven samples under investigations are described in Table 1. As also evident from TGA, DTA and IR Spectral studies, the analytical data revealed the chemical composition of samples LDP-1,4 to be significantly different from samples LDD-6,7. Samples LDP-2, LDP-3 and LDP-5 were also included in the phosphorites group on the basis of their analytical data which resembled closely with samples LDP-1,4.

High values of loss on ignition were observed for sample LDD-6 (LOI = 40.00%) and samples LDD-7 (LOI = 20.00%) as compared to the phosphorites samples (LDP-1-5) for which LOI was found in 1.45 - 2.62% range. Similarly high silica and MgO contents were observed for the host rock samples as compared to the phosphorites samples (Table 1). However,

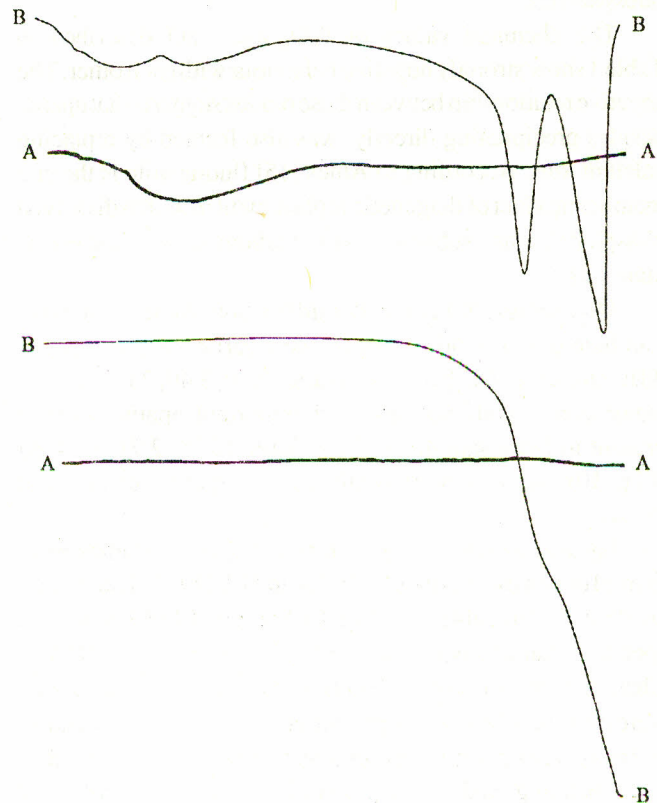


Fig. 12. DTA/TGA thermograms (A) phosphorite sample, (B) host rock sample.

TABLE 3. CHEMICAL COMPOSITION OF SOME STANDARD PHOSPHATES ROCK [19,20].

	$P_2O_5$	CaO	$SiO_2$	$Al_2O_3$	$Fe_2O_3$	LOI
Florida	33.16	48.14	4.91	1.14	0.70	5.08
Sonegal	36.80	51.51	2.97	1.21	0.67	2.45
Udaipur (India)	36.21	50.26	7.35	1.30	0.73	1.18
Morocco	32.63	50.52	2.34	0.54	0.15	6.86
Algeria	33.78	54.13	1.40	0.41	0.32	—
Jordan (high grade)	34.35	52.65	1.29	0.20	0.20	6.39
Jordan (low grade)	32.75	51.26	4.45	0.35	0.30	8.41
Mirpur (Pakistan)	37.75	51.94	1.74	0.36	1.05	—
Lambidogi (Pakistan)	37.85	53.88	0.89	1.93	2.62	1.90
	$\pm 1.20$	$\pm 1.04$	$\pm 0.83$	$\pm 0.26$	$\pm 0.09$	$\pm 0.44$

both  $P_2O_5$  and CaO contents were higher in phosphorites samples (LDP 1-5) in 36.20 - 39.03% range for  $P_2O_5$  and 55.42 - 52.88% range for CaO, as compared to the host rock samples LDD-6 ( $P_2O_5 = 11.02\%$ ; CaO = 25.48%) and LDD-7 ( $P_2O_5 = 16.69\%$ ; CaO = 24.34%). Analytical data for  $Fe_2O_3$ ,  $Al_2O_3$ ,  $K_2O$  and moisture contents did not show any significant differences between phosphorites and the host rock samples (Table 1).

Average chemical composition of Lambidogi phosphorites (LDP 1-5) appeared to be moisture =  $0.15 \pm 0.07$ ; LOI =  $1.90 \pm 0.44$ ;  $P_2O_5 = 37.85 \pm 1.20$ ; CaO =  $53.88 \pm 1.04$ ;  $SiO_2 = 0.89 \pm 0.83$ ;  $Al_2O_3 = 1.93 \pm 0.26$ ;  $Fe_2O_3 = 2.62 \pm 0.09$ ;  $MgO = 0.62 \pm 0.30$  and  $K_2O = 0.31 \pm 0.09$ . A comparison of the average chemical composition of Lambidogi (Pakistan) deposits (sample LDP 1-5) with some known phosphorite deposits [19,20] of the world is given in Table 3. Compared to the world-wide known phosphate deposits, Lambidogi (Pakistan) deposits appear to be high grade phosphorites with low silica content.  $Fe_2O_3$  and  $Al_2O_3$  contents are comparatively higher but are within the desirable limits [20].

Lambidogi phosphorite deposits, with probable reserves of 1 million tonne [21] are a valuable addition to the existing high grade deposits of Hazara. Further work regarding the commercial exploitation of these deposits is strongly recommended before any mine operations take place.

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#### References

1. *Foreign Trade*, (Federal Bureau of Statistics, Statistics Division, Government of Pakistan, 1989), Vol. 16 (7).
2. M.A. Latif, An Occurrence of Palaeozoic Phosphate Rock in Hazara, West Pakistan, *Inst. Mining and Metall.*, London, 81, 850 (1970).
3. M.T. Hassan and M.I. Ghaznavi, *Phosphate Deposits of Hazara Division, NWFP Pakistan*, (Record of Geological Survey of Pakistan, 1980), Vol. 50.
4. N.A. Bhatti, M.T. Hassan and S.M. Hussain, *Phosphorite Deposits of Kakul-Mirpur Area, Hazara, NWFP, Pakistan* (Information Release Surv., Pakistan, 1972), Vol. 51, pp. 33.
5. Report on Mineral Activities of Sarhad Development Authority in NWFP, S.D.A., Peshawar (1980).
6. *Pakistan Hazara Phosphate Rock Deposits*, British Mining Consultants and Sarhad Development Authority Reports (1982).
7. J.A. Calkin and A.S. Matin, The Geology and Mineral Resources of Gharhi Habibullah Quadrangle and the Kakul Area, Hazara District, Project Report PK 38, US Department Survey (1968), pp. 7.
8. N.H. Furman, *Standard Methods of Chemical Analyses*, (D. Van Nostrand, London, 1963), Vol. 1, 6th ed.
9. P.G. Jeffery, *Chemical Methods of Rock Analysis* (Pergamon Press, Oxford, 1975), 2nd ed.
10. A.I. Vogel, *Quantitative Inorganic Analysis* (Longman Green and Co., London, 1959), 2nd ed.
11. F. Paulik, J. Paulic and L. Erdey, *Z. Anal. Chem.*, 160, 241 (1958).
12. S.R. Riggs, *Economic Geology*, 74, 195 (1979).
13. R.P. Shelden, *Economic Geology*, 59, 1159 (1964).
14. J.M. Bremmer, *Economic Geology*, 77, 221 (1979).
15. L.L. Ames, *Economic Geology*, 54, 829 (1959).
16. D.M. Benerjee, P.C. Basu and N. Srivastava, *Economic Geology*, 75, 1181 (1980).
17. M.A. Khwaja, M. Akif and M.A. Khattak, Proceedings, Seminar, Prospects and Problems of Mineral Based Industries in Pakistan, March, 1989 (In Press).
18. M.A. Qaiser, N.K. Ali and A.H. Khan, *Pak. j. sci. ind. res.*, 2, 23 (1968).
19. Proceeding Technical Conference of ISMA Ltd., New Developments in Phosphate Fertilizer Technology, Hague, Netherland (1976), pp.294.
20. M.A. Khattak, S. Aziz, J. Iqbal and R.A. Shah, International Seminar, Mineral Exploitation Technology, PCSIR Laboratories, Peshawar (1979).