

A STUDY OF PAKISTANI GYPSUM BY X-RAY POWDER DIFFRACTION

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The Patala Formation of Palaeocene age, exposed at the Gandhala Nala area, Eastern Salt Range, Punjab, Pakistan, displays perfect crystals of gypsum. These crystals have been analysed by X-ray diffraction, scanning electron microscopy and wet chemical method. X-ray diffraction data are in good agreement with the reported values of ASTM. The chemical analysis of the samples indicates that the composition of the crystals is also close to theoretical for the compound $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Thus, the deposit provides a source of relatively high purity gypsum crystals and may be used as standard (reference) sample in local industries.

Key words: Gypsum, X-ray diffraction, Analysis.

Introduction

Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) which has a composition of 79.0% calcium sulfate and 21.0% water, is used as commercial and generic term for all calcium sulfate materials. It is widely distributed in nature and occurs in three major varieties: the transparent crystalline is called selenite, the massive is called alabaster while the fibrous, silky variety is known as stain spar. Gypsum reserves and resources are common throughout the world. More than eight countries produce gypsum and very few are without any resources. It has both industrial and technical applications and has set new records of consumption in chemical, agricultural and ceramic industries [1,2].

The present work is undertaken to study the geological, structural and chemical variations in Pakistani gypsum crystals which belong to Patala Formation and may be used in local industrial consumption.

Experimental

X-ray diffraction measurements. Gypsum crystals were ground in a mortar and pestle. Later, the pellets of powder were made and dried at 60°C for 1 hr. in order to remove excess humidity absorbed in the material.

X-ray diffraction study. JEOL diffractometer was calibrated with the standard quartz sample and spectrum was collected with Cu radiation using Ni filter and scintillation detector. The powder pattern was scanned from 4° to $146^\circ 2\theta$ with 40kV and 20mA at a scan speed of $2^\circ/\text{minute}$.

For chemical composition, atomic absorption spectrophotometer equipped with flame atomizer was used. Scanning Electron Microscopy (SEM) was also employed to see the nature (morphology) of gypsum crystals.

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Results and Discussion

Geological occurrence. Figure 1 illustrates the location map of Patala Formation, where the gypsum crystals are exposed at the Gandhala area. The Patala Formation is 20 to 27 meter thick in the Eastern Salt Range and displays thickening towards west and has been reported as 90 meter thick at Patala Nala. The Formation consists of dominantly black shales with subordinate marls and occasional limestones. The basal part displays yellowish brown sandstones. The Formation, exposed at Gandhala area displays native sulfur, pyrite and several thin coaly horizons but only one or two coal seams are economically exploited in Eastern and Central Salt Range.

Wynne [3] called the Patala Formation as Hill Limestones and later on, he [4] renamed it Nummulitic Formation due to the presence of Nummulitic fossils. Cotter [5] called these beds as the unit 4 of Nummulitic series of Middlemiss [6]. Davies [7] called those shales as the upper Ranikot beds. Davies and Pinfold [8] named this Formation as Tarkhobi shales and Eamest [9] retained this nomenclature. However, Latif [10] called these as Kuzagali shales.

Fatmi [11] reported that the Patala shale displayed selenite crystals and marcasite nodules at many places. Ibrahim [12] stated that the Patala Formation conformably overlaid the Lockhart Limestones throughout its extent, but in the Eastern Salt Range, the Lockhart limestone was not developed and the formation conformably overlaid the yellowish brown sandstones of Palaeocene age. He also reported that the formation is conformably overlaid by the Nammal Formation.

Microscopic investigation. Figure 2 shows a SEM-micrograph of gypsum crystal. It is observed that the crystal is laminated. The plane of lamination is 040 and is closed packed plane in monoclinic cell.

The microscopic results suggest that gypsum crystals of Patala Formation contain selenite form of gypsum crystals

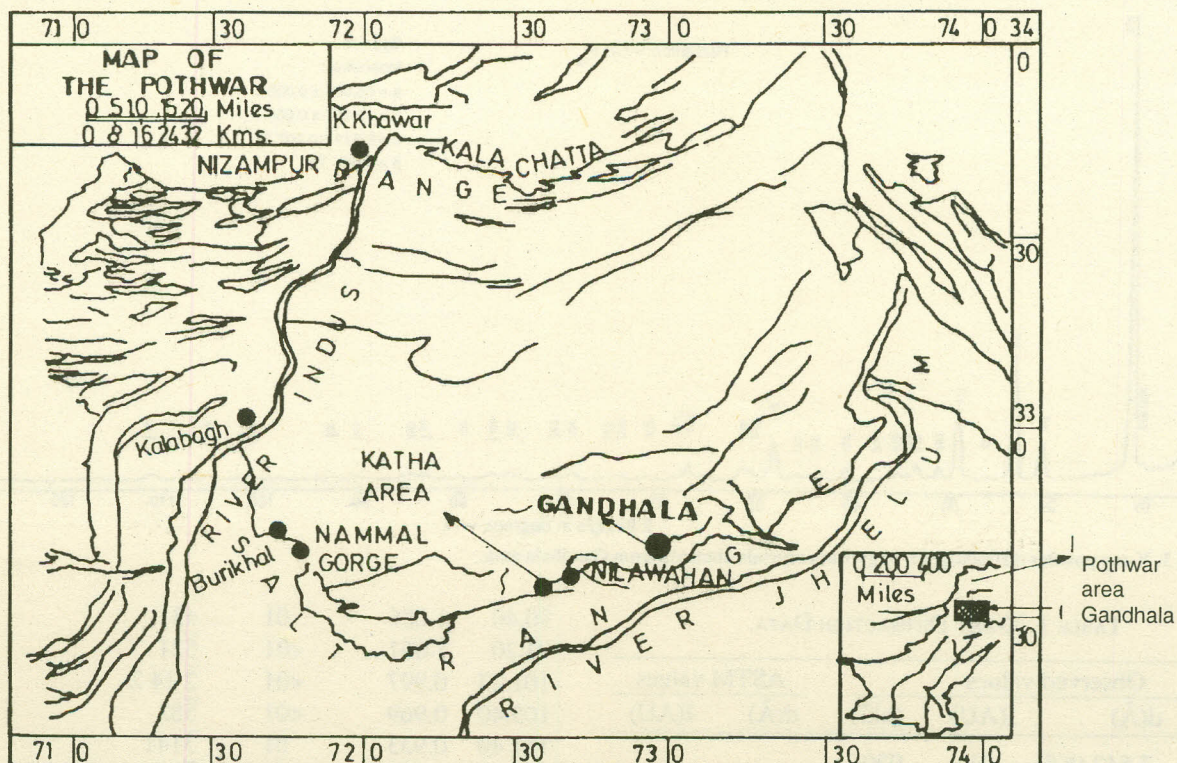


Fig. 1. Location map of Gandhala area.

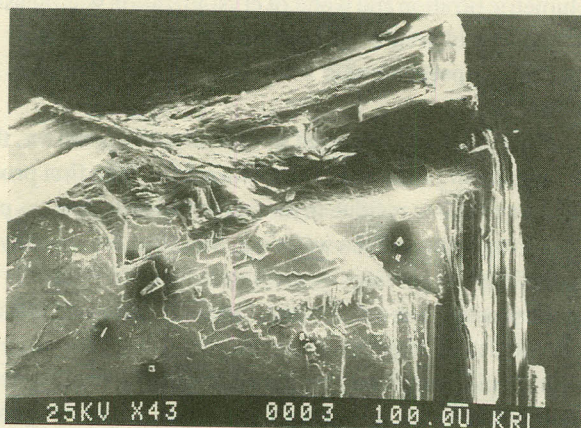


Fig. 2. SEM-micrograph of gypsum crystal.

[11] that have crystallized in the monoclinic system in the form of almost $3.0 \mu\text{m}$ thick sheets and show a perfect and easy cleavage parallel to the plane of crystallization. Therefore, Patala Formation may be called as standard shale for containing clear and clean gypsum crystals of selenite form and a length of 4cm.

X-ray diffraction study. Figure 3 shows the X-ray diffractogram of gypsum powder sample. To obtain precise X-ray data, four diffraction scans of a sample were recorded. The means of peak position 2θ and their corresponding intensities were measured. For intensity measurements the strongest

peak was taken as 100 and relative intensities of other peaks were calculated by normalizing with the strongest peak.

Table 1 compares the X-ray data with the ASTM file No. 6-0046. In general, all the reflections upto $d=1.480 \text{ \AA}$ were well matched with the ASTM values. However, in addition to the values reported in ASTM, our sample has produced 8 more reflections for the gypsum phase. It is observed that relative intensities of some reflections are 3 to 10 times lower than the reported values. These discrepancies may be due to the presence of preferred orientations of crystallites and hydration of sample in high-humidity atmosphere.

The lattice parameters of monoclinic cell are calculated and refined by using least-squares fit by a computer programme [13]. Thus, the lattice parameter of gypsum crystal are: $a=5.665 \pm 0.003 \text{ \AA}$; $b=15.127 \pm 0.008 \text{ \AA}$; $c=6.511 \pm 0.007 \text{ \AA}$, $\beta=118^\circ 15' 20'' + 3'$; cell volume = 494.37 \AA^3 and the space group as $I 2/a$. It is interesting to note that the cell dimensions are in excellent agreement with the reported values of ASTM file No. 6-0046.

Chemical analysis. Gypsum samples were collected from Eastern Salt Ranges of Gandhala area, Pakistan. To get a better statistics, at least five samples were analyzed. All the samples were ground to fine powder and dissolved in a mixture of hydrochloric and nitric acid. The solution so obtained was subjected to atomic absorption spectrophotometer using standard addition technique [14]. Sulfate ions were determined by

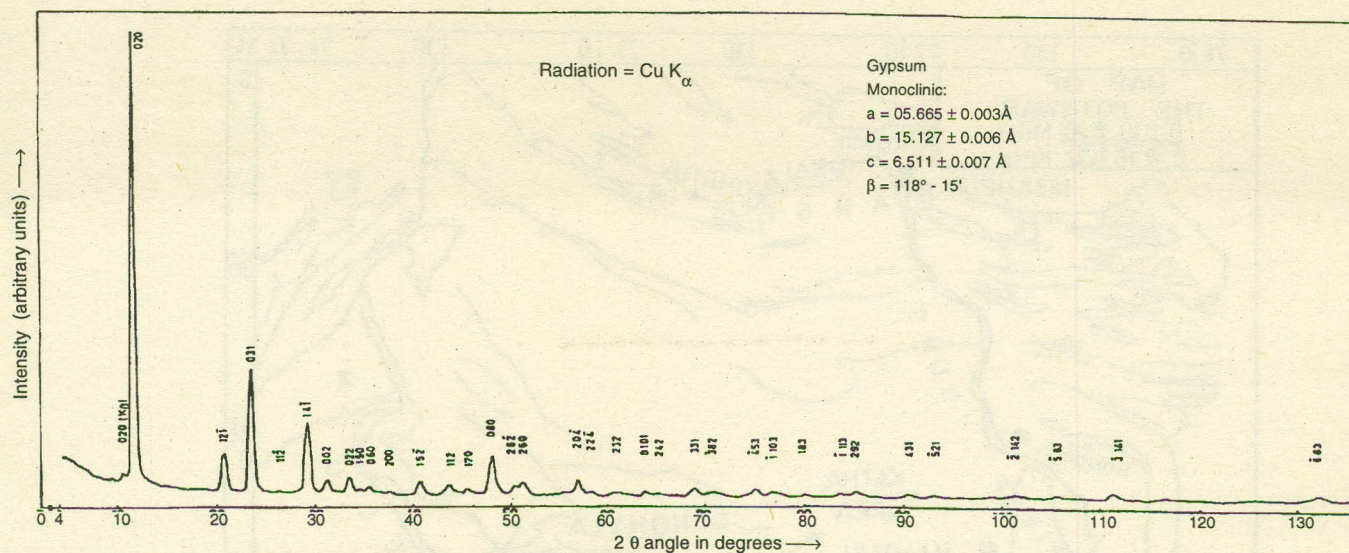


Fig. 3. X-ray powder diffractogram of gypsum crystals obtained from Gandhala area.

TABLE 1. X-RAY DIFFRACTION DATA.

2θ°	Observed values			ASTM values	
	d(Å)	I(AU)	(hkl)	d(Å)	I(AU)
10.60	7.542 (Kβ)	01	020		
11.73	7.544	100	020	7.560	100
20.80	4.270	08	12 $\bar{1}$	4.270	50
23.52	3.782	27	031	3.790	20
27.92	3.195	<01	11 $\bar{2}$	3.160	04
29.23	3.055	16	14 $\bar{1}$	3.059	55
31.30	2.858	02	002	2.867	25
33.57	2.669	03	022	2.679	28
34.64	2.589	01	150	2.591	04
35.63	2.519	01	060	2.530	<1
36.40	2.468	<01	200	2.495	06
40.83	2.210	02	15 $\bar{2}$	2.216	06
43.63	2.074	02	112	2.073	08
45.60	1.989	01	170	1.990	04
18.08	1.892	09	080	1.898	16
50.60	1.804	<01	26 $\bar{2}$	1.812	10
51.40	1.778	01	260	1.778	10
56.92	1.618	02	204	1.621	06
58.43	1.579	<01	224	1.584	02
63.00	1.475	01	232	1.480	<01
63.80	1.459	01	0 10 1		
65.20	1.431	<01	242		
68.50	1.369	02	331		
70.80	1.331	01	382		
75.10	1.265	01	453		
76.95	1.239	<01	1 10 3		
79.97	1.199	<01	183		
83.10	1.162	01	1 11 3		
85.20	1.139	01	292		

(Continue...)

90.40	1.086	01	431
93.20	1.061	<01	521
101.23	0.997	<01	2 14 2
105.40	0.969	<01	583
111.40	0.933	01	3141
132.00	0.844	01	683

volumetric titration and water of crystallization was measured by heat-loss of weight method on analytical balance. It was noted that gypsum sample was free from impurities like Mg, Al and Fe.

Gypsum may be formed in several ways however, there are three main processes of formation [15]. The first process is known as saline residue in the saline deposits. It takes place due to evaporation of sea water e.g. Stassfurt in Germany and Precambrian evaporates of the Salt Ranges in Pakistan. The second process is due to dolomitization of limestone in the sea [15]. The third important process is, due to the action of sulfuric acid, generated by the decomposition of pyrite on calcium carbonate in sedimentary rocks; a similar process concerns formation of good crystals of selenite in many clay deposits.

The gypsum crystals found in the Patala Formation of Salt Ranges, appear to be formed according to the third process of Reid [15] i.e., by the action of sulfuric acid on carbonates; the acid originated from decomposition of pyrite or marcasite present in the Patala Formation. A similar process has been postulated to have occurred in the Piere shales of Canada. The marcasite and pyrite were formed as sedimentary minerals in a very reducing environment which resulted from the presence of abundant organic matter in the Patala Formation; sedimentary sulphide minerals such as marcasite and pyrite are also reported from coral beds in other parts of the world.

According to Krauskopf [16], the formation of marcasite requires slightly acidic conditions, whereas pyrite can form either acidic or weak basic solutions; sulfate minerals require, instead, fairly oxidizing conditions for their origin. Krauskopf found that sulfate minerals generally appear only in sedimentary rocks which are well aerated by exposure to the atmosphere. The marcasite and pyrite minerals, present in the Patala Formation, probably gave rise to sulfates in the zone of weathering due to oxidation and were transported by the subsurface and surface water to react with carbonates for the formation of selenite crystals. He further stated that during the wetting of sulfide ore deposits, the reaction may not go all the way to form sulfates at first and may produce instead native sulfur as a fine powder. This occurrence of native sulfur in Patala shales can occasionally be observed which probably represents the intermediate stage of the conversion of sulfide to sulfate minerals.

The chemical composition of the gypsum obtained from the Patala Formation was calculated in weight% as: CaO=32.13 \pm 0.50; SO₃=47.27 \pm 0.70; H₂O=20.09 \pm 0.25; SiO₂=0.1 \pm 0.02; R₂O₃<0.01; Na₂O=0.044 \pm 0.004; SrO=0.050 \pm 0.02; BaO=0.170 \pm 0.05; K₂O=0.05 \pm 0.005. Our chemical analysis and values of lattice parameters are in good agreement with the work of Cole and Lancucki [17]. Thus, it may be concluded that Patala Formation in the Eastern Salt Ranges of Pakistan may be cited as a shale deposit containing relatively high purity transparent gypsum crystals which can be taken as standard sample for local industrial consumption.

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