XRF and AAS Studies of the Distribution of Major and Trace Elements in Cis- Indus Range Rock Samples

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Summary: Analytical investigations on geological samples collected from the cis-indus range rock samples were done by using XRF and AAS technique. Infrared studies were also carried out on these samples for their structure speculation, which mainly indicated the calcite nature of the mineral.

The gravimetric analysis indicated mainly the presence of carbonates and hence the carbonaceous nature of these rocks. The major, minor and trace elements as determined by employing X-ray fluorescence (wd) and atomic absorption spectroscopic studies were Ca, Sr, Mn, Fe, Na, Pb and Zn. The maximum concentrations in these rock samples were found for Ca, which lied in the range of 21-29%. Zinc concentrations were found to be minimum, and were nearly 0.0001% in all samples.

Introduction

Chemical investigations of rocks and minerals are of great significance because of their value in industrial processes [1]. Many classical and instrumenttal procedures are widely used in determineing the analytical concentrations of various elements or their compounds in such samples [2].

In the present work, rock samples were selected from the area of Dawal (Cis-Indus Salt Range, Pakistan) for chemical investigations. Basically, salt range has been divided into two regions, i.e. (i) Cis-Indus salt range and (ii) Trans-Indus Salt range. The Salt Range is bound in the east by the Jhelum Fault and in the west by the Kalabagh Fault (Kalabagh Fault and the Jhelum Fault are the geological boundaries of the Salt Range). In actual we see the continuity of the Salt Range across the Kalabagh Fault, and this is known as the Trans Indus salt range., while the area lying to the east of Kalabagh Fault is known as Cis Indus Salt Range. Geologically speaking, Cis Indus Salt Range is a museum of rocks containing rocks as old as 550 million years to recent times. So one can get the whole rock record that is available on earth's surface. Most of the elements like Pb, Zn and Mn etc. that have been analyzed are present in the sandstone rock, while the elements like Ca, Sr, Fe and Na are present in the limestone and both of these are present in abundance in the area under investigation. The sampling was carried out in the eastern part of the Cis Indus Range of the Jhelum district.

The major elements namely, Si, Ca, Mg, Fe and P were estimated in oxide forms by using gravimetric method. The major and trace elements were determined by XRF and AAS techniques. Qualitative analysis was done by IR, which showed the presence of calcite as a major constituent.

Results and Discussions

Gravimetry

In gravimetric analysis, the major elements namely Mg, Si, Fe, Al, Ca and P were estimated as oxides. The most abundant oxide was found to be CaO, as indicated from the results given in Table-1. This reveals the carbonate nature of these rock samples.

The moisture content was also determined by drying the samples at 100°C. At this temperature, hygroscopic water (H_2O) was lost. Loss on ignition was determined by igniting the samples at 1000°C. Since the samples were found to be of carbonaceous nature, thus an appreciable loss in weight was observed which was mainly due to the evolution of carbon dioxide.

X-ray fluorescence spectroscopic method

The qualitative and quantitative analysis of samples was done by XRF, which reveals the presence of Ca, Mg, Si, Al, Na, and K. From the

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Table-1:Percent Wieght (%) of Different Oxides Determined Gravimetrically

Sample No	SiO_2	CaO	MgO	Al_2O_3	Fe_2O_3	P_2O_5	Loss on Heating	Loss on Ignition
1	2.00	40.0	0.55	0.10	0.10	6.25	2.6	45
2	1.50	46.0	0.05	0.20	0.05	5.00	2.8	43
3	3.30	47.0	0.45	0.10	0.03	5.50	0.6	44
4	6.80	40.0	0.45	0.10	0.05	5.20	1.0	44
5	6.05	44.0	0.40	0.10	0.10	5.90	0.6	41
6	1.10	48.5	0.55	0.30	0.05	5.10	0.2	41
7	4.00	46.5	0.40	0.15	0.20	5.10	2.0	41
8	3.40	50.0	0.55	0.15	0.55	2.05	1.0	41
9	1.40	21.5	0.50	0.20	0.10	2.25	0.3	46
10	1.20	45.0	0.40	0.20	0.20	6.15	1.5	45
11	2.60	45.0	0.50	0.25	0.20	7.75	0.9	41
12	3.90	45.5	0.80	0.20	0.20	4.40	1.0	40
13	1.40	50.5	0.80	0.20	0.20	4.00	1.2	40
14	1.20	29.0	0.85	0.30	0.10	4.40	1.6	41
15	6.60	44.0	0.70	0.50	0.10	4.10	1.4	41
16	1.50	45.0	0.70	0.40	0.10	2.80	2.0	46
17	2.70	45.0	0.55	0.30	0.05	2.40	0.2	46
18	1.10	46.0	0.60	0.30	0.15	2.35	0.7	46
19	2.90	46.0	0.60	0.40	0.15	2.25	0.8	46

Table-2: Percentage Wieght of Elements Determined by XRF

Sample No	Si	Ca	Mg	Al	Fe	Na	K
1	0.330	39.430	0.415	0.035	0.015	0.015	0.005
2	0.480	39.235	0.400	0.040	0.015	0.015	0.005
3	0.595	39.130	0.385	0.050	0.015	0.015	0.005
4	0.415	39.240	0.400	0.045	0.015	0.015	0.005
5	0.500	39.165	0.410	0.050	0.015	0.015	0.005
6	0.800	38.990	0.460	0.075	0.015	0.015	0.010
7	0.280	39.520	0.365	0.045	0.015	0.015	0.010
8	1.055	38.430	0.430	0.080	0.015	0.015	0.015
9	0.515	39.250	0.405	0.060	0.015	0.015	0.010
10	0.570	39.065	0.465	0.090	0.015	0.015	0.015
11	0.680	39.090	0.440	0.090	0.015	0.015	0.015
12	0.450	39.235	0.550	0.080	0.015	0.015	0.010
13	0.350	39.430	0.470	0.060	0.015	0.015	0.005
14	1.065	38.510	0.565	0.125	0.015	0.015	0.015
15	1.250	38.275	0.580	0.200	0.015	0.015	0.030
16	0.650	39.035	0.530	0.110	0.015	0.015	0.010
17	0.550	39.210	0.490	0.090	0.015	0.015	0.015
18	0.550	39.200	0.450	0.080	0.015	0.015	0.010
19	1.090	36.880	0.435	0.115	0.015	0.015	0.020

The above values fall within a standard deviation of ± 2.0% for triplicate measurements

results given in Table-2, it was obtained that calcium was abundant in all the rock samples, which confirms the carbonaceous nature of these rocks. The concentration of CaO found was in well agreement with the literature values for carbonaceous rocks [6].

Atomic absorption spectroscopic method

AAS was used to determine major and minor elements. The results in %age concentration are given in Table-3.

Among the major elements analyzed in this study, Ca was abundantly found in all the rock samples. The very high percentage of Ca in the provided rock samples is attributed to the presence of carbonaceous rocks. This was also confirmed by XRF and gravimetric methods.

Magnesium concentration in all samples was high but was lower than what is required for the dolomitization of calcite rocks.

Mutual interference between Ca and Mg can be avoided by adding $LnCl_3$ or KCl to solutions as a releasing agent. The presence of 0.5% potassium in solution was found to be useful in lowering the Mg interference on Ca and removing the Ca interference on Mg. Potassium was also useful as an ionization suppressant in Sr determinations. Ca, Mg, Mn and Sr are almost totally restricted to the soluble fraction. These elements are present in calcite and dolomite; Mn is concentrated principally in dolomite, while Sr is present in greater amounts in calcite.[7].

Infrared spectroscopic method

Infrared spectroscopy is useful in the identification of minerals. It was rather difficult to

Table-3:Percentage Wieght of Elements Determined by AAS

Sample No	Ca	Mg	Fe	Zn	Cr	Pb	Sr	Mn	Na
1	29.30	0.07	0.010	0.0005	0.0007	0.045	0.165	18.40	0.030
2	22.85	0.07	0.010	0.0010	0.0005	0.075	0.180	22.80	0.050
3	27.00	0.07	0.007	0.0007	0.0007	0.050	0.175	24.30	0.040
4	22.30	0.07	0.010	0.0010	0.0010	0.050	0.215	21.20	0.045
5	22.90	0.07	0.001	0.0015	0.0001	0.020	0.145	22.45	0.095
6	24.35	0.07	0.001	0.0020	0.0005	0.030	0.195	19.90	0.050
7	28.80	0.07	0.015	0.0008	0.0007	0.080	0.175	26.80	0.055
8	22.50	0.07	0.050	0.0030	0.0001	0.030	0.225	19.60	0.065
9	22.10	0.07	0.010	0.0008	0.0001	0.035	0.210	20.10	0.090
10	25.70	0.07	0.050	0.0003	0.0001	0.045	0.195	21.35	0.050
11	25.30	0.07	0.007	0.0001	0.0010	0.010	0.170	22.00	0.090
12	20.90	0.07	0.010	0.0001	0.0010	0.010	0.235	17.95	0.065
13	24.00	0.07	0.005	0.0001	0.0010	0.070	0.160	19.20	0.045
14	27.20	0.07	0.005	0.0001	0.0001	0.070	0.195	17.10	0.045
15	32.85	0.07	0.007	0.0001	0.0007	0.070	0.220	15.45	0.045
16	31.35	0.07	0.003	0.0001	0.0007	0.080	0.245	20.35	0.040
17	26.80	0.07	0.003	0.0001	0.0007	0.060	0.230	15.40	0.035
18	27.80	0.07	0.005	0.0001	0.0007	0.070	0.250	20.55	0.065
19	20.30	0.07	0.005	0.0001	0.0007	0.050	0.240	18.65	0.095

The above values fall within a Standard deviation of ± 2.0% for triplicate measurements

assign the bands because rocks are not simple compounds but complex mixture of minerals. The basic layout of all the spectra was nearly similar, which indicated the same chemical composition of rocks.

Infrared spectroscopy is extremely sensitive to short range ordering. The inorganic groups have strong and usually simple absorption spectra. A strong absorption within one of these bands implies that a given functional anion group (e.g. carbonate) is present. The wave number of this strong absorption peak or that of smaller peaks elsewhere in the spectrum indicated as to which metal cation the group is bonded, for example, calcium in calcium carbonate or magnesium in magnesium carbonate. Intermediate values for the principle absorption may be considered diagnostic of solid solutions. Carbonates show strong spectral peaks in the 1450-1410 cm^{-1} range, medium strength between 880-800 cm^{-1} and relatively weak absorption in the range of 760-700 cm^{-1}. The diagnostic peak is weak and varies from 714-710 cm^{-1} in calcite. The present infrared investigations revealed the carbonate nature of these rocks mainly as calcite.

The characteristic absorption band of carbonate at 1580-1420 cm^{-1} was quite broad in almost all samples indicating that the nature of these rock samples is carbonaceous including impurities. However, in sample numbers 8 to 19, the region became refined ranging from 1543-1405 cm^{-1}, which indicated the crystallization of these carbonate rocks.

A medium strength band appeared at 873 cm^{-1} in all the samples and a second sharp absorption band was also obtained at 712 cm^{-1} which confirmed the carbonaceous nature of such rock samples. The 700 cm^{-1} band is characteristic for identification even in a mixture of these rocks because magnesite, calcite and aragonite absorb at 748, 711 and 700 cm^{-1}, respectively [8].

The spectra of sample number 15 to 18 were more refined, and characteristic band at 1430 cm^{-1} was narrow, which indicated that these samples are becoming crystalline i.e. limestone is in the process of metamorphism towards marble.

Few samples were also ignited at 800°C and were then analyzed by IR spectroscopy. The spectra of these samples clearly showed that the characteristic peaks at 712 cm^{-1} and 873 cm^{-1} disappeared at 800°C which are the characteristic peaks for carbonates (calcite group), thus confirming the presence of carbonaceous nature of these rocks.

Geochemistry

It is now generally agreed that the elemental composition of carbonates depends first on the concentration and ionic composition of natural solutions, mineralogy and carbonate spectral components (such as type of allochems, micrite, spar and dolomite), and secondly on their diagenetic history. Recent shallow-marine to hypersaline-marine carbonates are dominated by metastable aragonite and Mg-calcite, with or without dolomite, whereas most older carbonate rocks contain calcite and/or dolomite [9].

The stable calcite is restricted to meteoric and subsurface waters, or deep marine environments. The

Table-4:IR Absorption Brands in Rock Samples (cm^{-1})

Sample No	$\nu_{(3)}$	$\nu_{(2)}$	$\nu_{(4)}$
1	1582 - 1433 (b)	873 (s)	712 (s)
2	- 1408(b)	873 (s)	711 (s), 798 (sh)
3	1595 - 1423(b)	873 (s)	711 (s), 799 (sh)
4	1593 - 1412 (b)	873 (s)	712(s)
5	1577 - 1420(b)	873 (s)	712(s)
6	1518 - 1405(b)	873 (s)	712 (s), 799 (sh)
7	1591 - 1435(b)	873 (s)	712 (s)
8	1506 - 1405(b)	873 (s)	711 (s), 792(sh)
9	1543 - 1438(b)	873 (s)	712(s), 799(sh)
10	1581 - 1423(b)	873 (s)	712(s), 798(sh)
11	1339(b)	873 (s)	712(s), 799(sh)
12	1421(b)	873 (s)	712(s), 780(sh)
13	1437(b)	873 (s)	712(s), 784(sh)
14	1423(b)	873 (s)	712(s), 798(sh)
15	1422(b)	873 (s)	712(s), 798(sh
16	1427(b)	873 (s)	712(s)
17	1447(b)	873 (s)	711(s)
18	1413(b)	873 (s)	712(s)
19	1427(b)	873 (s)	713(s)

$\nu_{(2)}$ = Wagging vibration of CO_3^- ion, $\nu_{(3)}$ = Rocking vibration of CO_3^{-2} ion

$\nu_{(4)}$ = Unsym. Stretching of CO_3^- ion, b=Broad, s=Sharp, sh=Shoulder

Table-5: Molar Ratios of Different Elements

Sample No.	Mg/Ca	Mn/Ca	Sr/Ca	Na/Ca
1	0.002	0.627	0.005	0.001
2	0.003	0.997	0.007	0.002
3	0.002	0.900	0.006	0.001
4	0.003	0.960	0.010	0.002
5	0.003	0.985	0.006	0.004
6	0.003	0.812	0.007	0.002
7	0.002	0.940	0.006	0.001
8	0.003	0.870	0.010	0.002
9	0.003	0.910	0.009	0.004
10	0.003	0.839	0.007	0.001
11	0.003	0.870	0.006	0.003
12	0.003	0.860	0.010	0.003
13	0.003	0.800	0.006	0.001
14	0.002	0.772	0.007	0.001
15	0.002	0.475	0.006	0.001
16	0.002	0.650	0.007	0.001
17	0.004	0.915	0.013	0.002
18	0.002	0.740	0.010	0.002
19	0.003	0.925	0.010	0.004

transformation of metastable aragonite and Mg-calcite to stable calcite is mostly a wet dissolution and precipitation process, which takes place largely under the influence of meteoric water. During this process, the trace element content of the solid phase is systematically partitioned through a liquid phase into the precipitate. The course of these changes provides valuable information on the original mineralogy and the chemical characteristics of depositional and diagenetic solutions. In this study the molar ratios of each element with respect to Ca are used to find wide variation in the amount of carbonates in the samples [10].

Strontium and sodium

The molar ratio of Sr/Ca is much higher in the limestones than in the dolomites, and varies according to the samples. Strontium increases from flats, through supratidal-dune complex and bar shoal, to sub tidal faces. Similarly it increases progressively from sub tidal to supratidal channels. This increase of Sr is the inverse of the dolomitisation from sub tidal to flats.[11].

The variation of Na/Ca ratio is similar in all samples. It is related to salinity variation in the deposition and diagenetic solutions. Sodium increases from sub tidal environment to dune complex, due to increase in salinity following partial evaporation of seawater. Sodium, not balanced by chloride, occurs in relatively equal amounts in recent limestone samples here.

Magnesium and manganese

The molar ratio of Mg/Ca in the limestone is less than 0.2, so these are approximately ideal calcites with little unreplaced dolomite.

Manganese and calcium

The molar ratio Mn/Ca shows similar trend. It is much lower in the limestone samples. Mn/Ca ratio increases with dolomitization but its low value indicates the presence of calcite. In modern limestones, the amount of Mn increases from shallow marine through brackish to fresh water. Manganese has a strong dependence on carbonate mineralogy.

Experimental

All the chemicals used in the present work were procured from E. Merck and were of analytical grade having a purity of >99%. The chemicals were used as such without any further purification. The rock samples were crushed, ground and stored in appropriate glass containers in a dessicator. These were later subjected to gravimetric, X-ray fluorescence, Infrared and AAS analysis.

Gravimetry

The classical procedures for the determination of Ca, Mg, Al, Fe, Si and P were done as described in the literature [3]. These elements were determined in their oxide forms. Loss on ignition was also determined.

X-ray fluorescence

The major and minor elements were estimated by using the WD-XRFspectrometer PW- 1606, Philips. The samples used for such studies were initially fused with borate salt followed by casting of the mold to form a disc.

Atomic absorption spectroscopy

The solutions were prepared by dissolving 1.0 gram of powdered sample in 50 mL of 5% nitric acid. The solution was heated to boiling to ensure complete dissolution of metal ions. The volume was later made up to 100 mL with distilled water. No preconcentration or separation procedures were adopted in this case. No spiking was necessary in these cases. Standard solutions of metal ions were prepared by dissolving appropriate amounts of their nitrate salts in distilled water. Dilutions were done to obtain desired concentrations. These were then run on AAS to obtain a calibration curve for obtaining the concentrations of unknown metal ions in solution [4,5].

The trace elements were determined by using the atomic absorption spectrophotometer model, Shimadzu, AA- 670. This instrument has a built-in facility of automatic background correction. The wavelengths (in nm) used for analysis in AAS were as follows: Ca (422.7), Sr (460.7), Mn (279.5), Fe (248.3), Na (589.0), Pb (217) and Zn (213.9).

Infrared spectrophotometry

IR studies were carried on Infrared Spectrophotometer, Shimadzu, model IR-460. All the samples were mixed with appropriate amounts of KBr and pressed in a hydraulic press at high pressure for the formation of a disc. The spectra were scanned in full wavelength range of the instrument. Peak position and % transmittance of the peaks were recorded and printed by data processor accessory connected with the instrument.

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