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MINERALOGY AND CHEMISTRY OF LIMESTONE RESOURCES OF KHYBER AGENCY, N.W.F.P.

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X-ray diffraction analyses, derivatography, and chemical analyses data for the limestone resources of the Khyber Agency are presented and discussed. The rocks of the area studied range from magnesia to dolomitic limestones and are composed of calcite, dolomite and subordinate amount of quartz and illite. Utilization of these limestone resources for cement, sugar and chemical industries has been suggested.

INTRODUCTION

Shah *et al.* [1] have mapped the geology of the Eastern Khyber Agency. Much geological work have been done on the area by Vicary [2], Hayden [3], Jan [4], Khan [5] and others. The economic geology of the area was reported on by Coulson [6], Gee [7] Heron [8] and others. Limited mineralogical and chemical studies of the Khyber limestone have been conducted. These deposits were studied to determine their possible economic utilization.

Geology of the area. The area extends mostly to the east of the Khyber highway, with a part extending to the southwest. It is bounded by the Peshawar plain in the east, the Bara Valley in the south, the Pak-Afghan border to the north and by the Kabul river in the north-east.

The Khyber Agency area is underlain by a sequence of sedimentary and metamorphic rocks intruded by plutonic and volcanic bodies.

Stratigraphic Sequence

Formation	Lithology	Age
Quaternary deposits	Gravel bed	Pleistocene to Recent
Murree formation	Shale, sandstone, conglomerate, etc	Miocene
Khyber limestone	Limestone, shale and sandstone	Permo-carboniferous
Ali Masjid formation	Limestone, quartzite and shale	Devonian
Shagai limestone	Limestone and dolomite	Devonain-Silurian
Landi Kotal formation	Slates, phyllites, limestone, quartzite etc.	Silurian Ordovician to Cambrian

Landi Kotal formation. Though heterogeneous, the Landi Kotal formation displays almost the same range of lateral lithology throughout most of its outcrops from the vicinity of Jamrud across the border in Afghanistan. It is composed of phyllite and slate with abundant basic igneous dykes and sills. Quartzite beds at this locality are thin and are associated with sandy beds. Thin veins of quartz are also present.

Limestone interbedded with the slate are grey, light grey and buff. It is fine grained to medium grained and recrystalline.

The slates extend eastwards to the Kam Shilman and Loe Shilman valleys. The slate is overlain by about 30.5 m of limestone named Shagai limestone by Shah and Siddiqi [1].

Shagai limestone. The formation is typically exposed 0.8 km northwest of the Shagai Fort. The Shagai limestone is medium to thin bedded, very fine grained, gray, black, brown and greyish yellow. It extends from the Bagiari picket quite close to the eastern end of the Khyber Pass, continuing westwards through the Shagai Fort to the vicinity of Ali Masjid Town. At the Bagiari Picket, only the topmost part of the formation is exposed.

The Ali Masjid area affords excellent exposures of the Shagai limestone, but its apparent thickness has been augmented by repetition. It is entirely thick bedded and grey.

Ali Masjid formation. All the beds between the micritic Shagai limestone and the immensely thick bedded, drusy grey limestone of the Khyber limestone are placed in the Ali Masjid Formation.

The limestone is dark grey, weathering to light grey and thin to medium bedded. It contains quite a few calcite veins. The formation is well exposed near the Ali Masjid Mosque. This section is faulted and may have been thickned by repetition.

Khyber linestone. The Khyber limestone is exposed on either side of the road all the way from Ali Masjid to Landi Kotal. The limestone is predominantly grey and weathers to shades of grey and occasionally yellow. It is mostly thick bedded or massive, with thin to medium beds appearing especially on weathering. The limestone is almost completely recrystalline.

Exposures of the Khyber limestone are widespread, extending from near Bara Fort to Loe Shilman in a N-S direction and from Ghund Garh to Bazar in an EW direction and are fine to medium grained and highly fossiliferous.

Samples for the present studies were collected from the localities shown in Fig. 1.

RESULTS AND DISCUSSION

Chemical composition. Twelve representative channel samples of the "Khyber limestone" from the Khyber Agency were analysed by conventional as well as instrumental methods. The results of the analyses are summarised in Table 1, while the normative mineral composition are presented in Table 2.

Norms have been calculated on the assumption that phosphorus is present in apatite, $Ca_5(PO_4)_3(OH)$. Magnesium is located in dolomite, $CaMg(CO_3)_2$. Left over lime after forming apatite and dolomite forms calcite, $CaCO_3$. The potash and soda are present as muscovite, $K_2Al_4(Si_6Al_2)O_{20}(OH)_4$ and paragonite $Na_2Al_4(Si_6Al_2)O_{20}(OH_4)$ respectivley. Soda is reported as excess Na_2O because SiO_2 or Al_2O_3 is insufficient to form paragonite. A small amount of iron (FeO) is present in the form of siderite ($FeCO_3$). The silica left over after forming muscovite is reported as quartz (SiO_2). Left over alumina is reported as excess Al_2O_3. Iron in the form of Fe_2O_3 is reported as excess which may be due to pyrite, nearly always present in limestone.

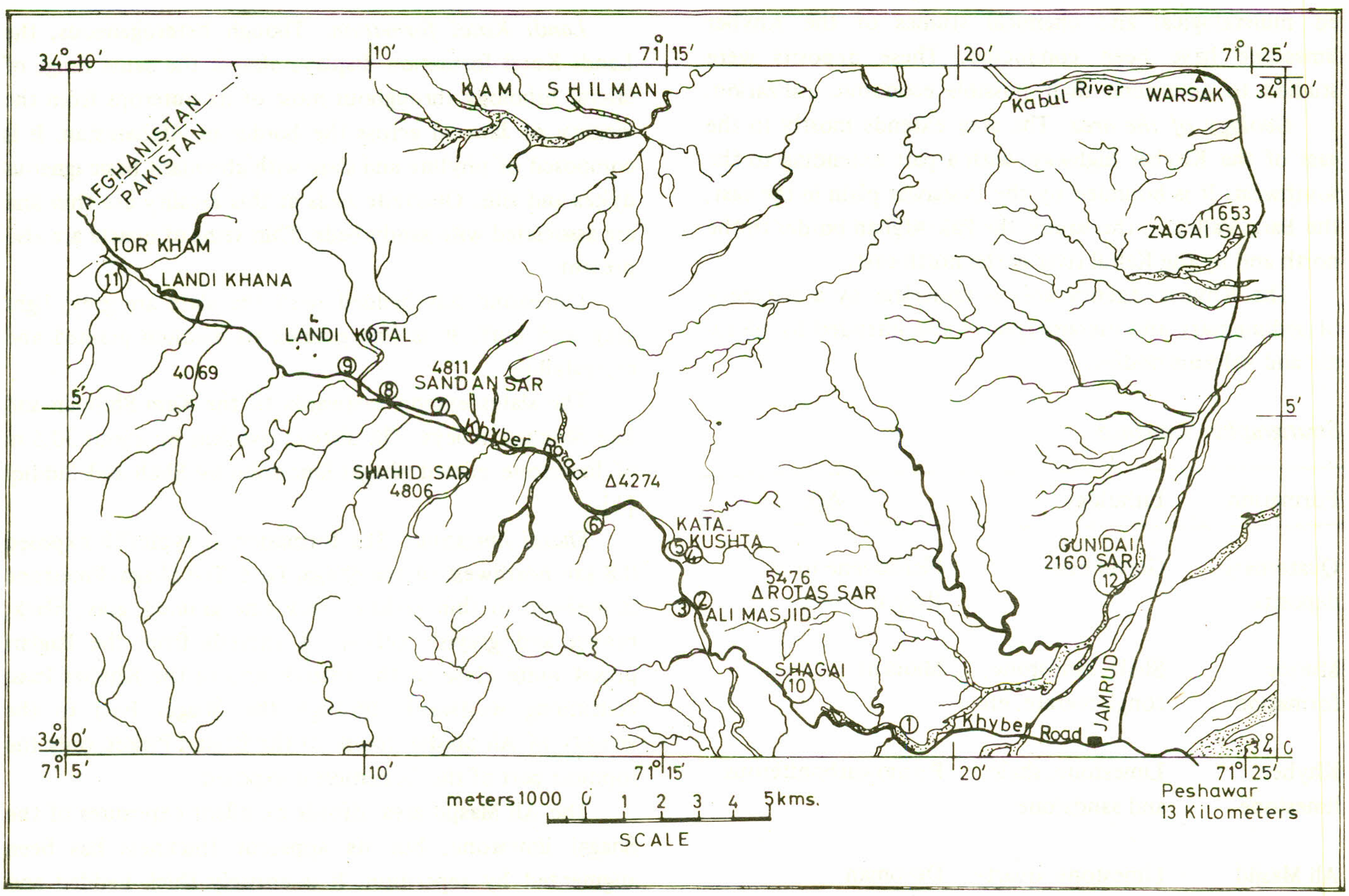

Fig. 1.

Table 1. Chemical analyses of Khyber limestone

Sample No. Composition (%)	FS-1	FS-2	FS-3	FS-4	FS-5	FS-6	FS-7	FS-8	FS-9	FS-10	FS-11	FS-12
CaO	51.37	51.66	49.36	41.78	55.01	55.44	49.07	49.81	55.01	55.42	52.87	51.44
MgO	2.64	2.40	4.11	10.71	–	0.05	3.78	3.57	Traces	0.27	0.54	3.85
Fe_2O_3	–	0.03	–	0.14	–	–	0.15	0.03	–	0.04	–	0.11
FeO	0.05	0.09	0.10	0.14	0.06	0.10	0.14	0.15	0.07	0.06	0.06	0.10
SiO_2	2.93	2.47	1.84	1.80	1.32	0.67	3.00	2.40	0.80	0.93	1.22	0.27
Al_2O_3	0.40	0.31	0.65	0.29	0.69	0.45	0.25	0.66	0.25	0.08	1.83	0.03
MnO	–	–	Traces	Traces	Traces	Traces	–	–	–	–	–	0.04
TiO_2	–	–	–	–	–	–	–	–	–	–	–	–
Cr_2O_3	–	–	–	–	–	–	–	–	–	–	–	–
P_2O_5	0.04	0.01	0.15	0.32	0.08	0.04	0.12	0.05	0.10	0.03	0.05	0.03
Na_2O	0.14	0.17	0.30	0.31	0.31	0.33	0.38	0.40	0.38	0.22	0.22	0.23
K_2O	0.06	0.08	0.20	0.08	0.02	0.03	0.07	0.20	0.07	–	0.03	–
Moisture	0.09	0.05	0.03	0.10	0.03	0.02	0.03	0.04	0.04	0.03	0.05	0.03
Loss on ignition	42.40	42.68	42.90	44.60	42.69	43.07	42.78	42.68	43.31	42.84	42.95	43.81
Total	100.12	99.95	99.64	100.27	100.21	100.20	99.77	99.99	100.03	99.92	99.82	99.94

Table 2. Normative mineral composition of Khyber limestone

Normative minerals	FS-1	FS-2	FS-3	FS-4	FS-5	FS-6	FS-7	FS-8	FS-9	FS-10	FS-11	FS-12
Calcite	85.04	85.93	77.58	47.08	98.05	98.78	77.89	79.90	98.00	98.23	92.94	82.28
Dolomite	12.14	11.04	18.90	49.26	Nil	Nil	17.38	16.42	Nil	1.23	4.52	17.70
Siderite	0.08	0.14	0.16	0.22	0.09	0.16	0.22	0.24	0.11	0.10	0.10	0.16
Apatite	0.09	Nil	0.28	0.75	0.18	0.09	0.28	0.12	0.23	Nil	0.12	.07
Muscovite	0.51	0.68	1.70	0.78	0.16	0.25	0.58	1.70	0.58	Nil	0.17	Nil
Paragonite	–	–	–	–	–	–	–	–	–	–	–	–
Quartz	2.70	2.16	1.07	1.44	1.20	0.55	2.73	1.63	0.53	0.93	1.14	0.27
Excess Fe_2O_3	–	0.03	–	0.14	–	–	0.15	0.05	Nil	0.04	–	0.11
Excess Al_2O_3	0.20	0.05	–	–	0.62	0.35	0.02	–	0.02	0.08	1.76	0.03
Excess Na_2O	0.14	0.17	0.30	0.31	0.31	0.33	0.38	0.40	0.38	0.22	0.22	0.23
Total	100.48	100.44	99.90	99.82	100.56	100.41	99.47	100.30	99.79	100.79	100.97	100.85

The calcite content of the samples varies between 47.8 and 98.78% whereas dolomite content varies from nil to 49.00%. The siderite content of the sample is between 0.08 and 0.24%.

The muscovite (or illite) is present in all samples and the amount varies between nil and 1.70%. The quartz content of the samples varies between 0.53 and 2.73%.

Derivatography. MOM Derivatograph was employed for simultaneous differential thermal analysis (DTA), thermogravimetry (TG) and derivative thermogravimetry (DTG) for all samples.

The temperature of 1 g sample in a platinum crucible was increased at a uniform rate (10°/min.) in an electric furnace. 1 g of Al_2O_3 in a similar crucible was used as reference material. Derivatogram (the DTA, TG and DTG curves) was recorded on a photographic chart. Derivatograms of some samples are shown in Fig. 2. The calcite and dolomite composition of the samples has been determined by projecting the minimum points between the peaks of the DTG curve on the TG curve and presented in Table 3. The percent composition of calcite and dolomite are comparable to that of calcite and dolomite in Table 2. Endothermic peak in DTA curve caused by the decomposition of calcite $CaCO_3 \rightarrow CaO + CO_2$ appeared at 930° and endothermic peaks in dolomite CaMG $(CO_3)_2$ appeared at 800 and 930° due to the liberation of CO_2 from $MgCO_3$ and $CaCO_3$ respectively.

Table 3. Composition of calcite and dolomite in Khyber limestone

Sample No.	Calcite (%)	Dolomite (%)	Total
FS- 1	83.50	13.20	96.70
FS- 2	85.00	11.50	96.50
FS- 3	77.50	19.00	96.50
FS- 4	48.00	49.00	97.00
FS- 5	97.00	Nil	97.00
FS- 6	98.00	Nil	98.00
FS- 7	78.00	18.00	96.00
FS- 8	79.00	16.00	95.00
FS- 9	98.00	Nil	98.00
FS-10	98.50	Nil	98.50
FS-11	93.00	4.00	97.00
FS-12	82.50	17.00	99.50

X-ray Diffraction Analysis. X-ray powder diffraction data of some of the samples are given in Table 4A. The Seifert X-ray unit with a Debye-Scherrer Camera (dia. 11.4 cm) was used. The samples were irradiated to Ni-filter Cu K radiation for 5 hr at 35 KV and 19mA. Paste of the sample was made with a drop of collodion and moulded to a tiny cylinder of dia 0.5 cm and length 1 cm approximately. Reflections 3.04, 2.29 and 2.10°A are present in the sample FS-3 only. Reflections for quartz (3.36, 4.25 and 1.82°A) are present in all the samples except FS-7, FS-8 and FS-9. The summary of the minerals identified in each sample is given in Table 4B.

All the samples were treated with 1:1 HCl solution. The acid insoluble fractions were studied by X-ray powder diffraction. Spacings and relative intensities of a few samples are given in Table 5A and the results are summarized in Table 5B. Reflections for quartz (3.36, 4.25 and 1.82°A) are present in all samples. Reflections for illite (9.82, 4.92, 4.46 and 3.35°A) are present in all samples except FS-3, FS-4, FS-9 and FS-11. Some weak reflections for feldspar (albite) (3.78, 3.49, 3.19 and 2.97°A) are seen in samples FS-5 and FS-8 only.

CONCLUSIONS

The results obtained indicate that the magnesia contents of the limestone samples except FS-3, are within the recommended limits of British Standard Specification for cement manufacturing. Due to shortage of water in the area cement factory based on dry method manufacturing is recommended.

The samples having 3-2 % MgO may be used in sugar refining, paper industry and for the manufacture of precipitated calcium carbonate.

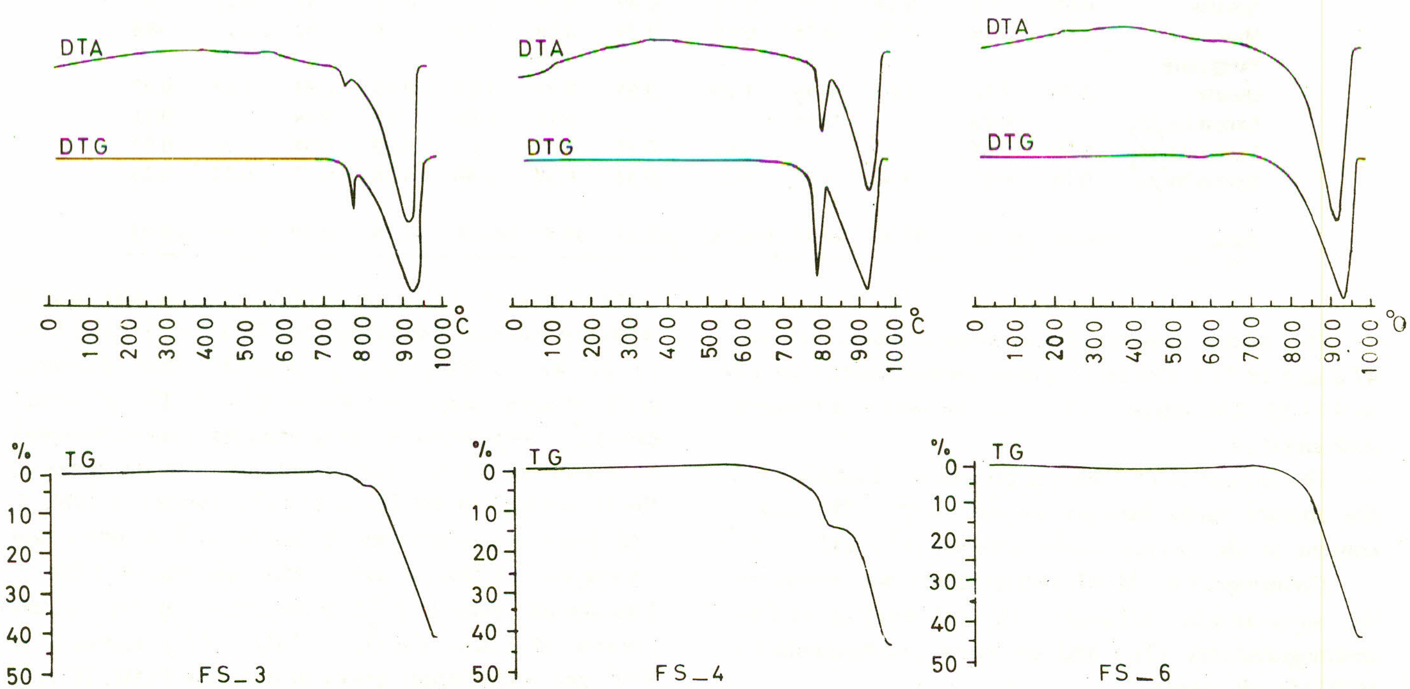

Fig. 2.

Table 4A. X-ray powder data of Khyber limestone

FS-1		FS-3		FS-4		FS-5		FS-8	
d (A)	I	d (A)	I	d (A)	I	d (A)	I	d (A)	I
–	–	4.04	5	–	–	–	–	–	–
3.86	30	3.70	30	3.86	10	3.85	10	3.83	20
3.36	20	3.36	10	3.31	5	–	–	–	–
–	–	3.17	5	–	–	–	–	–	–
3.02	100	3.20	30	3.02	100	3.02	100	3.01	100
2.84	10	2.88	100	–	–	–	–	2.83	10
2.49	50	2.67	30	–	–	–	–	–	–
–	–	2.62	30	2.49	20	2.48	30	–	–
2.28	60	2.39	40	–	–	2.27	35	2.46	30
–	–	2.28	5	2.28	20	2.08	35	–	–
2.10	60	2.20	50	2.09	20	–	–	2.27	40
–	–	2.03	5	–	–	–	–	2.08	35
–	–	2.01	40	1.91	30	1.91	50	–	–
1.92	80	1.91	10	1.87	30	1.86	50	–	–
1.87	80	1.84	10	–	–	–	–	1.91	50
–	–	1.79	80	1.61	5	–	–	1.85	50
1.62	5	–	–	1.60	15	1.60	10	–	–
1.61	20	–	–	1.51	10	1.51	10	–	–
–	–	1.56	10	–	–	–	–	1.61	10
1.54	30	1.54	70	–	–	1.47	5	1.59	10
1.47	5	1.46	10	1.44	5	1.44	5	1.50	10
1.44	40	1.43	5	1.42	5	1.41	5	–	–
1.42	40	–	–					1.46	5
1.36	5	1.38	15					1.43	15
1.34	10	1.33	5					1.41	10
1.30	15	1.30	5					1.35	5
–	–	1.27	5					1.33	5
1.23	10	1.23	5					1.29	10
1.18	20	–	–						
1.15	20	–	–						

Table 4B. Summary of the results of X-ray diffraction of Khyber limestone

Mineral Identified	FS-1	FS-2	FS-3	FS-4	FS-5	FS-6	FS-7	FS-8	FS-9	FS-10	FS-11	FS-12
Calcite	++	++	+	++	++	++	++	++	++	++	++	++
Dolomite	–	–	++	–	–	–	–	+	–	–	–	–
Quartz	+	+	+	+	+	+	–	–	–	+	+	+

– No reflection seen + Presence in minor amounts ++ Presence in major amounts

The limestones having higher SiO_2 (> 1 %) or higher Fe_2O_3 (> .035 %) are unsuitable for glass manufacture. Hence, the Khyber limestone is not suitable for this purpose. This limestone may be used for ceramics as having more than 79 % of $CaCO_3$ with permissible amounts of Fe_2O_3 and SiO_2.

However, detailed work is recommended for determining the economic feasibility of these deposits for different industrial purposes. A close interval channel sampling of the carbonate rocks, exposed in the area, will have to be conducted to delineate different zones according to chemical composition. The present work is only a preliminary effort to spotlight the possible industrial uses of the resources available in the area.

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Table 5A. X-ray powder data for limestone (1:1 HCl Treated)

FS-1		FS-3		FS-4		FS-5		FS-6	
d (A)	I	d (A)	I	d (A)	I	d (A)	I	d (A)	I
9.71	5	–	–	–	–	9,82	5	9.82	10
–	–	–	–	–	–	4.92	5	4.92	1
4.46	1	–	–	–	–	4.43	1	4.72	1
4.23	50	4.23	30	4.23	80	4.23	15	4.23	50
3.35	100	3.36	100	3.31	100	3.39	1	3.70	40
2.59	10	3.18	10	2.56	10	3.78	1	3.49	5
2.46	20	–	–	2.46	40	3.49	1	3.35	100
2.32	10	2.42	20	–	–	3.33	100	3.18	5
2.25	2	–	–	2.28	25	3.19	1	2.97	5
–	–	2.28	5	2.23	25	2.97	10	2.84	.5
2.12	15	–	–	2.12	40	2.84	1	2.56	10
2.10	10	–	–	–	–	2.75	1	2.48	30
1.97	10	2.03	2	1.97	30	2.56	10	2.36	5
–	–	1.97	2	–	–	2.46	10	2.28	2
1.82	20	1.93	5	1.81	50	2.28	1	2.22	2
1.66	10	1.82	20	–	–	2.12	10	2.12	30
1.54	20	–	–	1.66	40	1.99	15	1.95	10
1.44	1	1.66	5	1.54	60	1.81	20	1.82	30
1.37	20	1.54	20	1.45	5	1.66	2	1.75	1
1.28	1	–	–	1.41	5	1.54	20	1.66	20
1.24	1	1.37	20	1.37	70	1.49	10	1.54	30
1.22	1			1.28	10	1.45	10	1.49	1
1.19	2			1.25	20	1.37	20	1.45	1
1.18	2			1.22	10	1.25	5	1.40	1
				1.19	20			1.37	40
				1.15	20			1.25	10
								1.22	5
								1.19	10
								1.17	10
								1.15	5

Table 5B. Summary of the results of X-ray diffraction of Khyber limestone (1:1 HCl Treated)

Mineral Identified	FS-1	FS-2	FS-3	FS-4	FS-5	FS-6	FS-7	FS-8	FS-9	FS-10	FS-11	FS-12
Quartz	++	++	++	++	++	++	++	++	++	++	++	++
Illite	+	+	+	–	–	+	++	–	+	–	+	–
Feldspar	–	–	–	–	–	+	–	–	+	–	–	–

– No reflection seen
+ Presence in minor amounts
++ Presence in major amounts

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