A MINERALOGICAL AND CHEMICAL STUDY OF CHAGHI TRAVERTINE

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Chaghi travertines are spring water carbonate deposits of high purity. Small amounts of oxides of iron, magnesium, and silicon have been determined in the rocks which are well within the range of tolerable impurities. An inverse relationship between FeO and MgO content has been observed. X-Ray diffraction and DTA studies prove that the travertines are totally composed of calcite and not aragonite as was reported earlier which gave the name of 'aragonite marble" to this decorative stone.

INTRODUCTION

Spring water carbonate rocks are found as low hills or as terraces, resting upon older volcanic and intrusive rocks or Subrecent to Recent eoline sands or alluvial fans, at various places in Chaghi District. These terrestrial carbonate rocks are dense, translucent having pleasant green shades and take good polish. Thus they make excellent decoration stones and are called "onyx marble." They are also known by the name 'aragonite' or 'aragonite marble' on the presumption that the constitutent carbonate mineral is aragoite.The deposits were discovered in early fifties and are described by Hunting Survey Corporation[1], W. Ahmed [2] and M. Ahmed[3]. One of the major deposits of the Chaghi District namely Mashki Chah has recently been mapped on 1:50,000 scale in the Geological Map series by S.A. Ahmed[4] and Alam and Iqbal[5]. Z. Ahmed[6] and Arthurton *et al.*[7] have called these carbonate rocks of terrestrial origin as travertine which is more accurate petrographic nomenclature. Marbles from Peshawar Division and travertine from Chaghi District have recently been reviewed by Mohsin *et al.*[8].

Regional Geological Setting. Chaghi Hills are a distinct geomorphic feature constituting an independent petrographic province and a tectonic unit of the first order. These hills form a high land in the northern part of Baluchistan and partly lie in Afghanistan. The exposed rocks include sedimentary volcanic and intrusive rocks that span from Cretaceous to Quaternary. The Chaghi massif is about 5,700 Km² in area[9] and is composed of biotite granite, quartz diorite, gabbro and dyke swarm. These are intruded into the rocks of Sinnjrani volcano-sedimentary group consisting of andesite, agglomerate, tuff, shale, and limestone of Cretaceous age. This calcalkaline magmatic complex has been given the name of North Chaghi Arch[1]

Chaghi arched uplift or Chaghi Volcanic Plateau[10] and Chaghi median massif[11].

The Cretaceous volcano-plutonic complex of Chaghi Hills (Fig. 1) as well as the Quaternary volcanism are now interpreted as volcanic arc formed by the subdunction of the leading edge of the Arabian plate beneath the Afghan and Lut blocks of the Eurasian plate[12]. A very wide gap, upto 500 km, exists between the trench along the coast of Makran and the Chaghi Volcanic arc. This gap is twice the width of a typical trench-arc gap and is filled with Tertiary flysch sediments[13].

Travertine deposits are hot spring deposits formed during wanning stage of Quaternary volcanism. The Volcanic cones and vents, which were deeply eroded, provided the sites for spring water carbonate deposition. The deposits may therefore rest upon Pleistocene volcanic ash or even an older alluvium. The terraces of travertine are also
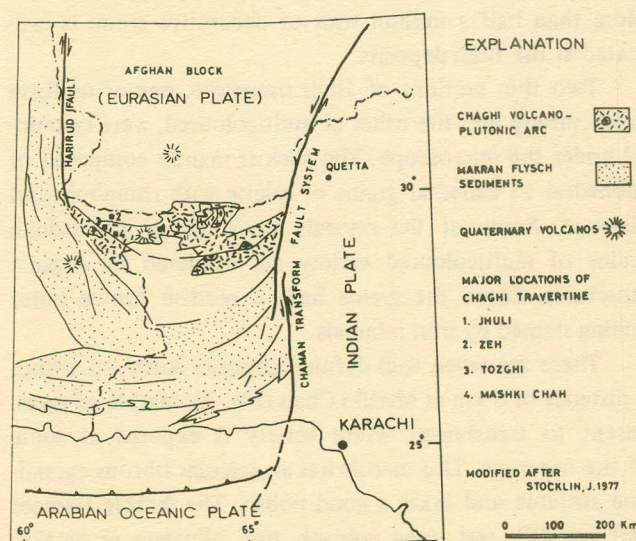

Fig. 1. Tectonic setting of Chaghi volcano – plutonic ore.

lying over Cretaceous andesitic lavas and intrusive dioritic rocks in places where spring water found its way to the bedrock.

Geology of the Deposits. A number of travertine occurrences are known in Chaghi District, of which the main localities are Mashki Chah, Juhli and Zard Kan, where good quality decorative stone is available in adequate quantity. Other known deposits are Butak, Patkok, Tozghi and Zeh. Zard Kan depoist is a travertine terrace inclined at 10° to 18° towards east resting partly upon syenodiorite and partly on volcanic tuff. The weathered marble is brown but freshly broken surface is yellow, pale green grayish white and white. The decorative stone is dense, fine grained textured and takes smooth polish. Few thin layers of calcareous tuffa are interbedded, but they do not impair the general quality. Under the microscope the rock is seen to be composed of anhedral calcite grains showing well developed rhombohedral cleavage. Frequent reddish brown patches in the slide are due to the presence of an opaque mineral such as haematite.

At Juhli, six deposits are within a radius of 2 km. The deposits are isolated terraces or low mounds with inclination ranging from 2 to 10° in various directions. The marble beds are pale to dep green separated by well defnined thin layers of pale yellow or reddish coloured calcareous tuffa. At some places hematite and calcite have replaced the translucent travertine. In the haematite rich layers, vugs are frequently found to be present and are believed to hae formed due to upward pressure of gases released by the decomposition of carbonaceous matter[11]. Freshly broken surface of some layers is translucent uniform green and the variety is known as "uniform green" or "jade." Other varieties are known as dark green and multicoloured onyx marbles. More than half a million tons of decorative stone is estimated at the Juhli deposits.

Two thin sections of Jhuli travertine, one of uniform green variety and the other of multicoloured, were examined under the microscope. The rock is mainly composed of subhedral to anhedral grains of calcite with rhombohedral cleavage. Some of the crystals are strained. The calcite grains of multicoloured variety are bordered by organic structures. Often the grains have a reddish brown outer zoning stained by iron minerals.

There are seven well defnied deposits scattered within a distance of 8 km at Mashki Chah (Fig. 2). Marble of transparent to translucent white variety is exposed at some of the outcrops. This marble has an acicular fibrous cyrstalline structue and takes a good polish. The marble terraces and low hills rest upon volcanic tuff, alluviam or on Sinjrani andesitic flows. These are, by far, the most important

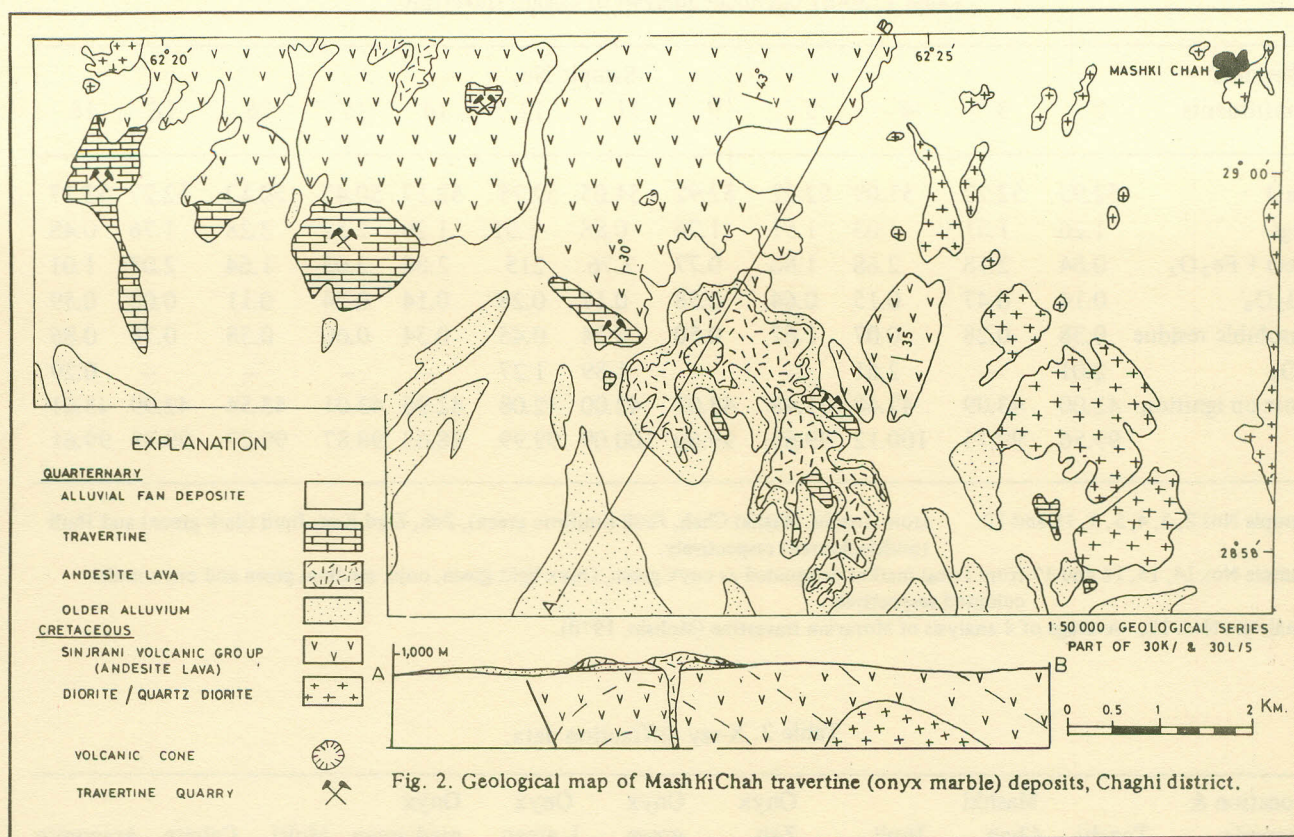deposits containing over on million tons of marketable reserves.

Chemical Analysis. There are two groups of samples namely field smaples collected from the qurries and the market samples obtained from the marble dealers in Karachi. Although more than one sample was collected from each of the localities, only the representative samples were analysed due to limited laboratory facilities at our disposal. The original sample numbers, however, have been retained and these appear in the chemical, differential thermal and X-ray analyses.

A number of chemical analyses for the essential components of travertine have been carried out and are summarized in Table 1. The analyses show a high carbonate content which reflect the purity of the marble. The next significant constituent is iron oxide which is in the range of 1-3 per cent. The analyses carried out during the present sutdy show the total iron oxide content which is responsible for imparting various coloս.s to the onyx marble. Ferrous oxide in the rock imparts green shades while ferric oxide when hydrated gives a yellowish brown colour to the rock. Manganese and cobalt, if present only in traces, may also colour the rock. It is observed that marbles of Tozghi and Zard Kan which are white or greyish white in colour have less than one per cent iron oxide. In contrast to that, dark green variety from Jhuli contains as high an amount of iron oxide as 3.76 per cent. The travertines of light green shades have an intermediate quantity of iron oxide.

It may be noted that Chaghi travertines in general have a higher iron content when compared to the Moravian travertines, deposited from cold water springs, during the middle Pliestocene interglacial period[15]. Sulphur has been dtermined in a few samples (Jhuli and Tozghi) and is probably in pyrite grains. Magnesium oxide is invariably present and is always more than one per cent which is significantly higher when compared with Moravian travertines. On the other hand alumina and slicia are low in travertines from Chaghi when compared with those from Moravia.

Attempt has been made to bring out relationships between the constituents. Due to insufficient number of analysis, clear relationships have not been observed between iron oxide, alumina and silica (insoluble matter). However, an inverse relationship between FeO and MgO has been observed (Fig. 3). Presence of impurities increase the solubility of carbonates and it appears that high content of FeO in the spring water keeps magnesium carbonate in solution while $CaCO_3$ is precipitated.

X-Ray Diffraction. X-ray powdered diffraction data has been obtained to identify the minerals present in the

Fig. 2. Geological map of MashKiChah travertine (onyx marble) deposits, Chaghi district.

EXPLANATION

QUARTERNARY
ALLUVIAL FAN DEPOSITE

TRAVERTINE

ANDESITE LAVA

OLDER ALLUVIUM
CRETACEOUS
SINJRANI VOLCANIC GROUP
(ANDESITE LAVA)

DIORITE / QUARTZ DIORITE

VOLCANIC CONE

TRAVERTINE QUARRY

1:50 000 GEOLOGICAL SERIES
PART OF 30K/ & 30L/5

rock. Powedered samples of travertine to a fineness of 200 mesh were mounted as cylinders around glass fibres in a Debye-Scherrer Powder Camera of 11.46 cm diameter. Each sample was run for 5 hours and reflections were recorded on a film. The diffraction pattern of eight samples have been carefully studied and the data is presented in Table 2. The d values of travertine samples have been compared with standard samples and all the lines on the films are found to be chractersitic of rhombohedral lattice of calcite. Diffraction due to orthorhombic aragonite lattice have not been observed in any single film.

Diffractometry of acetic acid insoluble residue of three samples, one each from Jhuli, Zeh and Tozghi was undertaken. We, however, did not succeed in detecting lines other than those of calcite on the x-ray films. It appears as if the carbonate was not completely dissolved and the residue still cotained sufficient calcite to mask other minerals present.

Goldsmith *et al.* [16] have shown a correlation between X-ray spacing and Mg substitution in calcite. The shift in the line of the strongest reflection of calcite sample from that of pure mineral is proportional to the amount of Mg present in the sample. For pure calcite reflection 112, referred to the true unit rhombohedral cell, is d=2.036 A°. Mg content can be calculated from the graph prepared by Goldsmith *et al.* [16] .

where $\Delta d = d \text{ (standard)} - d \text{ (sample)}$

The shift in the strongest line on the film of the analysed samples are calculated and is around 0.03A° which when plotted on Goldsmith's graph gives somewhat high $MgCO_3$ content. The calibration curve presented by Goldsmith for the determination of Mg content in calcite itself has a confidence interval. Moreover the measurements of diffraction lines on the film are done by visual methods which are not very accurate. However, it is clearly observed that all travertine samples show a consistent amount of magnesium in their chamical analysis and at the same time a shift in their d values.

Differential Thermal Analysis. Thermal behavior of eight travertine samples were studied by standard D.T.A. technique. All the samples recorded characteristic curve of calcite where an assymetric endothermic peak occurs around 900°C due to dissociation of carbonate. The reaction in pure calcite begins at 900°C reaches to peak at 1000°C and rapidly ends at slightly higher temperature. However, in a sedimentary calcite rock the reaction starts at an earlier temperature and takes a longer period to complete and ends at a temperature lower than 1000°C.

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Table 1. Short chemical analysis of chaghi travertine.

Chemical constituents	Sample No. 2	3	4	5	9	11	12	14	15	16	18	18
CaO	52.93	52.22	51.09	52.22	52.92	51.05	52.75	52.17	50.47	50.12	52.27	53.37
MgO	1.26	1.51	1.03	1.51	1.76	0.88	1.01	1.26	2.52	3.28	1.76	0.48
$FeO + Fe_2O_3$	0.84	2.18	2.68	1.86	0.77	3.76	215	2.86	2.03	1.64	2.07	1.01
Al_2O_3	0.14	0.47	0.15	0.64	0.58	0.17	0.28	0.14	0.24	0.11	0.08	0.59
Insoluble residue	0.38	0.28	0.07	1.62	0.50	0.34	0.45	0.34	0.60	0.58	0.76	0.86
SO_3	2.01	–	2.61	–	–	1.89	1.27	–	–	–	–	0.29
Loss on ignition	42.00	43.09	42.48	41.48	43.07	42.00	42.08	42.96	43.01	43.54	42.99	43.01
	99.56	99.75	100.12	99.69	99.60	100.09	99.99	98.63	98.87	99.27	99.93	99.61

Sample Nos 2, 3, 4, 5, 9, 11 and 12 from Tozghi, Mashki Chah, Jhuli (uniform green), Zeh, Zard Kan, Jhuli (dark green) and Jhuli (multicoloured) respectively.

Sample Nos 14, 15, 16 and 17 from Local market designated as onyx green, Onyx light green, onyx medium green and onyx multicoloured respectively.

Analysies Nos. 18, Average of 4 analysis of Moravian travertine (Mohsin, 1970).

Table 2. X-ray diffraction data.

Location & sapmle numbers	Tozghi 2	Mashki Chah 3	Jhuli 4	Onyx Zeh 5	Onyx green 14	Onyx l. green 15	Onyx med.green 16	Multi coloured 17	Calcite	Aragonite	
	3.92	3.78	3.74	3.78	3.76	3.81	3.97	3.80	3.86	4.21	
	2.00 S	2.99 S	2.99 S	2.99 S	2.99 S	2.99 S	3.02 S	2.99 S	3.03 S	3.39	S
	–	–	2.86	–	–	–	2.74	–	2.84	3.27	M
	2.50	2.46	–	2.48	2.47	2.45	–	2.46	2.49 M	2.87	
	2.29 M	2.25 M	2.26 M	2.26 M	2.26 M	2.26 M	2.63 M	2.26 M	2.28 M	2.73	
	1.01 M	2.05 M	2.07 M	2.04 M	2.08 M	2.07 M	2.11	2.06 M	2.09 M	2.70	M
	1.91 M	1.88 M	1.91 M	1.90 M	2.90 M	1.89 M	1.93 M	1.98 M	1.92 M	2.48	M
	1.88 M	1.86 M	1.86 M	1.86	1.86 M	1.86 M	1.89 M	1.90 M	1.91 M	2.40	
	1.81	1.79	1.78	1.78	1.77	1.78	1.81	1.86	1.87	2.37	
	–	1.59	1.59	1.59	1.60	1.54	1.52	1.59	1.58	2.34	M
	1.52	1.51	1.52	1.51	1.52	1.51	1.51	1.51	1..52	2.32	
	1.47	1.46	1.47	1.46	1.46	1.45	–	1.43	1.42	2.18	
	1.47	1.43	1.47	1.43	1.33	1.40	1.35	1.41	1.35	2.10	M
	1.34	1.33	1.29	1.33	1.29	1.28	1.30	1.33	1.33	1.97	M
	1.24	1.22	1.23	1.23	1.23	1.23	1.24	1.23	1.23	1.88	M
	–	–	1.18	1.17	1.17	1.17	1.19	1.17	1.17	1.87	
	–	1.14	1.16	1.14	1.14	–	1.15	1.15	1.14	1.81	
	1.05	1.08	1.04	1.04	1.04	–	1.04	1.04	1.04	1.75	
	1.04	1.00	1.01	1.03	1.01	1.00	1.01	1.00	1.01	1.72	
	0.97	0.98	0.96	0.96	0.96	0.96	–	0.98	0.98	1.69	

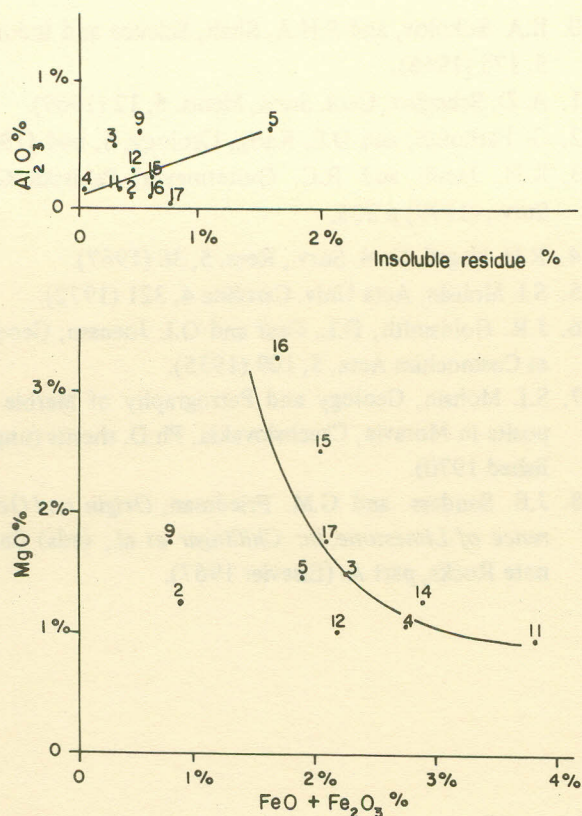Note: Intensity in marked as S (strong) and M(medium) against d values A?.

Fig. 3. Relationship of chemical constituents of travertine (number are described in Table 1)

The dissociation of carbonate in Chaghi travertine samples begins at 700°C, or evern earlier, reaches to peak around 900°C and ends up rapidly at 930°-950°C. The DTA curve of calcite is affected by absolute grain size of a rock and its heterogenity. In general the fineness of grain and pressence of only one grain size in a rock results in a narrow peak and at lower temperature than the standard. The characters of DTA curves of Chaghi travertine fairly well resemble those of Moravian travertine in which the reaction begins at 700°C and attains the peak at 930°C[17].

An endothermic peak between 400°C and 500°C which results due to the conversion of orthorhombic aragonite to trigonal calcite has not been observed on any of the thermogram.

It is conclusively shown here that the Chaghi travertines are totally-composed of calcite. Neither the X-ray diffraction pattern nor the DTA curves record a presence of an aragonite phase in any of the samples studied. The rock was reported as despoists of aragonite marble by Hunting Survey Corporation in 1960 and is continually being so named by all mining and export organizations. The practice should stop and the decorative stone should be called by its petrographic name "travertine" or by a commercial name

"onyx marble" in allusion to its green colour.

Deposition of Travertine. Calcium bicarbonate is abundant in spring water of calcareous formations which may be transformed to carbonate due to a change of carbon dioxide partial pressure and cause the precipitation of poorly soluble calcium carbonate giveing rise to tuffa or travertine deposits. During early or middle Pleistocene thermal springs were active, and coming through calcareous members of Sinjarani volcanic group were carrying calcium bicarobnate.

The change in physico-chemical conditions of water may be caused purely by inorganic processes or may be influenced by organisms as algae and bacteria.

The criteria for distinguishing inorganic from organic precipitation, accordig to Sanders & Friedman[18] is that calcium carboate crystallizes outside the tissues of living organim or within them. Algal activity may have played an important role in changing the chemical environment, but as precipitation takes place outside the living tissues, such an origin should be considered inorganic. The carbonate precipitation has taken place in pools or irregular topography. If any aragonite was deposited it readily inverted to calcite, which is more stable polymorph at surface temperature and pressure condition. After subsequent erosion they formed terraces of flat or gentle dipping beds. The Chaghi Arc continues to be tectonically active and thermal spring are alive. Present day deposition of the travertine, caught at various stages ot compaction and diagenesis, can be seen at several places in Chaghi district.
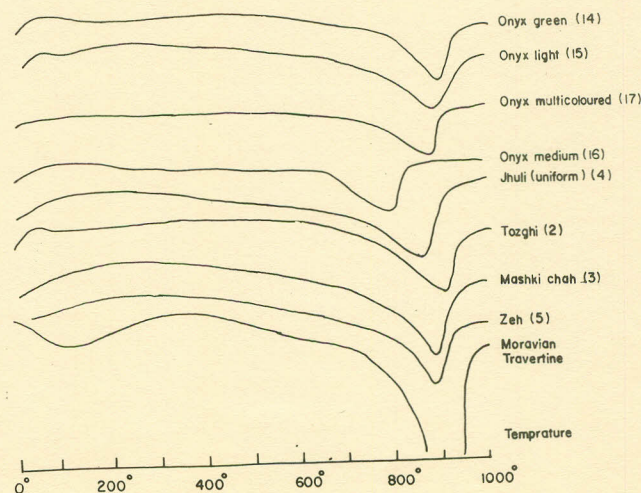
Fig. 4. DTA curves of Chaghi travertines

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