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ZEOLITIC TUFFS OF KIMOLOS ISLAND, AEGEAN SEA, GREECE AND THEIR INDUSTRIAL POTENTIAL

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ABSTRACT

Tuffaceous rocks and lavas of the Pliocene age exist on Kimolos Island, Aegean Sea, Greece. These tuffaceous rocks have been locally transformed to clinoptilolite and mordenite tuffs. The former are porous and relatively soft, whereas the latter are massive and hard. The diagenetic transformation of volcanic glass to clinoptilolite and mordenite took place in an open hydrological system by circulation of alkaline ground waters. The fluids responsible for mordenite formation had probably higher temperature than that of clinoptilolite due to high heat flow rates originating from the emplacement of lavas in their vicinity.

Even though clinoptilolite and mordenite tuffs have similar chemical analyses, the composition of mordenite exhibits lower variability than that of clinoptilolite.

Regarding cement properties, those cements containing mordenite tuff have a slightly higher strength than that of cements with either Milos pozzolana or clinoptilolite tuff. The higher strength of mordenite cement is probably due to the higher zeolite content of the mordenite tuff and also its higher reactive silica content. In addition, when compared to Milos pozzolana, the zeolite tuffs demand more water to produce paste of the same consistency. This means that when zeolitic cement is used for concrete production, it is likely that a superplasticizer needs to be added in the mixture.

In conclusion, the use of zeolitic tuffs as an additive in cement is promising. However, the full evaluation of these materials demands a thorough examination in areas related to their specialised properties and also extended testing on concrete produced with these materials. © *1997 Elsevier Science Ltd*

Introduction

Kimolos Island is located in Central Aegean Sea, being member of the South Aegean Volcanic Arc (Fig. 1). The substrate of the island is composed of Pliocene lavas and volcaniclastic rocks, locally transformed to bentonite, kaolin, silica polymorphs and zeolites.

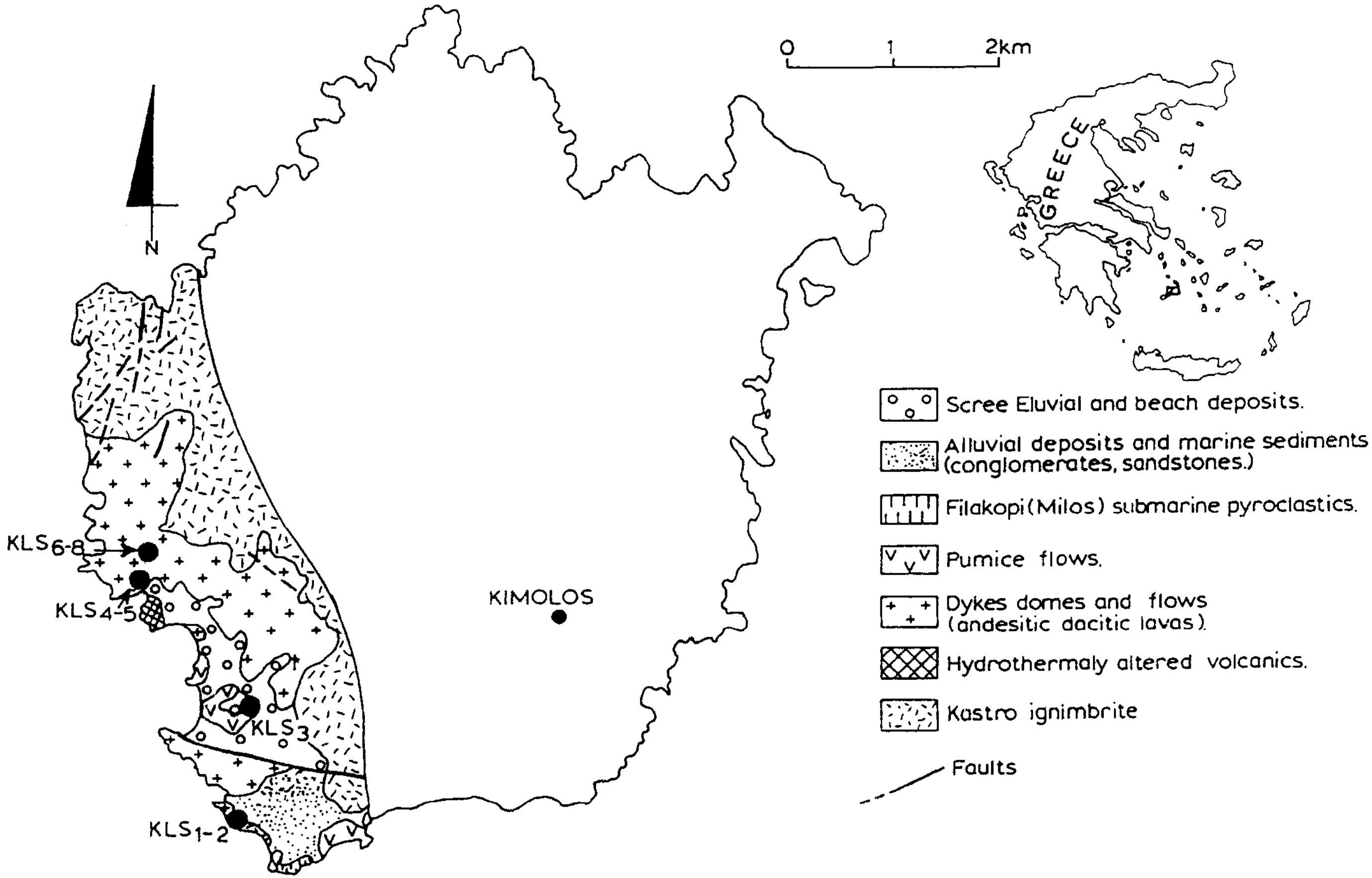

FIG. 1.
Geological map of South-West Kimolos Island, Greece (from Fytikas & Vougioukalakis 1992). Zeolite occurences and sampling sites are indicated as KLSx.

Zeolitic rocks have been discovered in the northern and northeast part of the island, in association with bentonite deposits (1,2). The reported zeolites are mordenite and, to a lesser extent clinoptilolite. However, recent field work in Kimolos combined with laboratory analysis, revealed that zeolitic rocks are more abundant at the west-southwest part of the island (Fig. 1).

Reports in recent literature describe possible applications of zeolitic tuffs in cement industry (3,4,5,6). It is well known that certain zeolitic rocks exhibit pozzolanic properties, therefore, they may be used for cement production (7,8,9).

The origin of Kimolos zeolitic tuffs and their possible industrial application as a cement additive, is the subject of this study.

Analytical Techniques and Experimental Procedures

Rock samples from Kimolos were mineralogically and chemically analysed by several methods.

X-Ray Diffraction analysis was used to determine the presence and percentage of zeolites in the tuff samples (Athens University).

Microprobe major element analysis on zeolite assemblages was performed in the Department of Geology, at the University of Athens. In addition, several representative tuff samples were chemically analysed by ICP at the Royal Holloway University of London. Silica was measured by spectrophotometry.

After the evaluation of the XRD results, two major zeolite deposits were located (Fig. 1), namely sites KLS_1 (clinoptilolite-rich) and KLS_{5-8} (mordenite-rich). Some 50 kg were taken from each deposit. XRD and Atomic Absorption analyses were carried out at TITAN's R&D laboratory. Those representative samples were used in order to study the effect of the zeolitic tuffs on cement properties.

The bulk samples were prepared and tested as follows:

- The raw materials were crushed in a jaw crusher down to a size of less than 0.5 mm in diameter.
- Clinker and gypsum were co-ground together with raw materials at different percentages in a ball mill for the same period of time (42 min).
- The specific surface (Blaine) and the strength of the final products were determined according to the European regulations (CEN 196-1).
- The water demand and the setting time (initial and final) of the laboratory-prepared cements were determined.

Results

Part A. Geological Evaluation

1. Geology-Mineralogy-Geochemistry of the materials under examination. At the southwest coastline of Kimolos Island, green pumice tuffs exist. Some 2 km to the north, a massive-hard, dull green tuff exists (Fig. 1). The mineralogical analysis of both zeolitic tuff deposits is presented in Table 1.

The results indicate that:

TABLE 1

Semiquantitave Mineralogical Composition of Zeolitic Tuffs(%)

	KLS_1	KLS_2	KLS_3	KLS_4	KLS_5	KLS_6	KLS_7	KLS_8
Minerals	Porous tuff				Massive tuff			
Mordenite	-	-	-	-	70	70	75	75
Clinoptilolite	50	70	40	60	-	-	-	-
Cristobalite	-	-	-	-	20	20	-	10
Opal-CT	40	-	30	25	-	-	10	-
Sanidine	10	20	-	-	10	10	10	15
Albite	-	-	25	-	-	-	-	-
Smectite	-	5	5	5	-	-	-	-
Illite or Mica	-	5	-	10	-	-	5	-

- Porous tuffs are rich in clinoptilolite, whereas massive tuffs are rich in mordenite.
- The mineralogical analyses of the mordenite tuffs indicate that the zeolite content is consistent (70-75%). On the contrary, clinoptilolite tuffs have zeolite content ranging from 40% to 70%.

TABLE 2

Microprobe Analysis of Mordenite and Clinoptilolite Assemblages from Zeolitic Tuffs of Kimolos Island

MORDENITE								
	KLS_6				KLS_7			
	spot no1	spot no2	spot no3	AVERAGE	spot no1	spot no2	spot no 3	AVERAGE
SIO_2	70,70	69,79	71,86	70,78	73,47	71,21	72,45	72,38
Al_2O_3	11,26	10,99	11,41	11,22	11,67	11,06	11,24	11,32
Fe_2O_3	0,15	0,34	0,14	0,21	0,32	0,29	0,17	0,26
MgO	0,29	0,35	0,30	0,31	0,16	0,49	0,42	0,36
CaO	0,60	0,76	0,86	0,74	0,83	0,95	0,85	0,88
Na_2O	3,73	2,83	3,36	3,31	3,09	2,64	3,10	2,94
K_2O	2,72	2,11	2,26	2,36	2,35	2,79	2,00	2,38
BaO	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
TOTAL	89,45	87,17	90,21	88,94	91,89	89,43	90,23	90,52

CLINOPTILOLITE								
	KLS_2				KLS_4			
	spot no1	spot no2	spot no3	AVERAGE	spot no1	spot no2	spot no 3	AVERAGE
SIO_2	72,77	74,02	67,74	71.42	68,42	72,94	66,26	69,21
Al_2O_3	9,76	9,08	11,91	10,25	14,01	9,28	11,93	11,74
Fe_2O_3	1,46	1,60	0,02	1,03	0,28	1,91	0,60	0,93
MgO	0,74	0,66	0,47	0,62	0,94	1,31	0,75	1,00
CaO	0,53	0,63	0,40	0,52	1,74	0,90	1,23	1,29
Na_2O	1,35	1,14	2,26	1,58	1,70	0,52	1,72	1,31
K_2O	3,41	3,54	4,72	3,89	3,37	2,13	2,91	2,80
BaO	0,01	0,00	0,10	0,04	0,18	0,16	0,11	0,15
TOTAL	90,03	90,67	87,62	89.44	90,64	89,15	85,51	88,43

- Quartz is not detected in the analysed samples. Opal-CT accompanies both clinoptilolite and mordenite, whereas cristobalite accompanies only mordenite.
- The feldspar content, either sanidine or albite, is generally low in all the zeolitic tuff analysed samples. By contrast, some porous(pumice) tuffs, approximately 3 Km. east of site KLS2, are mainly composed of K-feldspar.

Microprobe analyses on either clinoptilolite or mordenite assemblages were performed on zeolite rich samples (Table 1). The analytical results are shown in Table 2.

As shown on the above table:

- Clinoptilolite grains exhibit a greater variability in their major element content compared to mordenite. Similar variation on clinoptilolite major element composition has been reported on Santorini zeolitic tuffs which have also been deposited in a nearshore marine environment (10).
- Kimolos clinoptilolite is of the potassium-rich variety whereas either Ca-rich clinoptilolite or heulandite are absent. Its low calcium content is consistent with the presence of that zeolite type.
- Kimolos mordenite is of a Na-rich variety. Interestingly, K-mordenite that is formed by hydrothermal alteration of tuffs and lavas, is absent.
- A minor amount of barium is present only in clinoptilolite, probably replacing potassium in the lattice of clinoptilolite.
- The sum of Al_2O_3 + Fe_2O_3 is almost equal and constant in both mordenite and clinoptilolite, ranging from 11.28 to 12.67. However, clinoptilolite assemblages are richer in iron and magnesium than those of mordenite. High values of these elements have also been detected in Santorini clinoptilolite tuffs, attributed to the presence of partially altered volcanic glass patches that are merged with clinoptilolite crystals (9).

Major and trace element analysis (ICP) was performed on zeolitic tuff samples. The results are shown in Table 3.

The higher Zr, V and Li content determined in clinoptilolite tuffs, compared to the content of mordenite ones, is attributed to their higher detrital mineral content of the former. Additionally, the higher Fe_2O_3, MgO and TiO_2 content of clinoptilolite tuff leads to the assumption that the original tuff transformed to clinoptilolite had more mafic components than those of the mordenite tuff.

Even though barium is absent from mordenite assemblages (Table 2), barium enrichment in mordenite tuffs (Table 3) is attributed to the presence of small barite veins that occasionally form thin networks in these tuffs.

The bulk samples extracted from the two main zeolite deposits ($KLS_{1\&2}$, and $KLS_{5\text{-}8}$) were mineralogically and chemically analysed, prior to their use for cement production (Table 4).

The comparison of the chemical analyses indicates that clinoptilolite tuff has a higher insoluble residue (RI), Al_2O_3, Fe_2O_3, and K_2O + Na_2O content than the mordenite tuff.

Regarding cement production, clinoptilolite tuff should be added in a lower amount than mordenite tuff, because of its higher insoluble residue. In addition, the absence of detectable SO_3 quantities and very low Cr content in both tuffs is considered an advantage.

TABLE 3

Chemical Analyses of Whole Rock Samples (by ICP)

	Clinoptilolite-rich tuff samples			Mordenite-rich tuff samples			
	Major element analysis (%)						
	KLS_1	**KLS_2**	**KLS_4**	**KLS_5**	**KLS_6**	**KLS_7**	**KLS_8**
SiO_2	72,14	63,55	69,52	70,48	70,17	69,85	70,49
Al_2O_3	11,03	15,35	11,72	10,97	11,23	11,26	11,29
Fe_2O_3	2,95	3,48	1,69	0,69	1,86	1,36	0,84
MgO	1,11	1,3	1,06	0,34	0,64	0,6	0,68
CaO	0,84	1,29	1,25	1,42	1,46	0,24	1,74
Na_2O	2,66	1,8	1,83	2	1,49	2,78	1,37
K_2O	3,37	7,65	2,31	3,85	3,84	3,34	1,9
TiO_2	0,27	0,32	0,22	0,08	0,09	0,08	0,08
P_2O_5	0,05	0,08	0,04	0,03	0,04	0,02	0,04
MnO	0,07	0,04	0,02	0,02	0,02	0,02	0,02
LOI	6,13	5,07	9,77	9,97	9,78	9,6	11,73
TOTAL	100,62	99,93	99,43	99,85	100,62	99,15	100,18
	Trace elements analysis (ppm)						
Ba	299	202	255	1104	497	117	1058
Cr	5	6	4	3	3	4	4
Cu	1	22	4	2	3	2	2
Li	16	58	15	6	5	6	8
Sr	179	105	449	131	93	43	196
V	27	35	16	5	10	5	5
Zn	66	158	35	39	57	69	49
Zr	154	178	149	87	94	87	102

TABLE 4

Chemical and Mineralogical Analysis of Bulk Zeolitic Tuff Samples

	MORDENITE TUFF	CLINOPTILOLITE TUFF
Minerals Identified*	Ca-mordenite, mordenite, high sanidine, illite	K-clinoptilolite, sanidine, albite, illite, smectite
LOI	10,97	7,12
RI	71,85	75,92
SiO_2	68,80	62,70
Al_2O_3	11,72	15,26
Fe_2O_3	1,28	3,24
CaO	1,13	2,11
MgO	0,51	1,01
SO_3	-	-
K_2O	3,20	5,97
Na_2O	3,37	2,47

2. *Genesis of Zeolites*

2.1. Field observations & laboratory results. Mordenite exists in the south, massive tuff outcrop (sampling sites KLS_{5-8}, Fig. 1). On the other hand, clinoptilolite exists in the southwest, porous tuff outcrop (sampling sites $KLS_{1\&2}$). Another clinoptilolite tuff outcrop of minor size exists in between (sampling site KLS_3).

The porous tuffs contain irregular and well rounded fragments of chert and lavas up to 50 cm. Clinoptilolite is accompanied by sanidine, cristobalite, or opal-CT and minor amounts of illite and smectite. Na-feldspars in the form of albite are not so common (Table 1).

The massive rich in mordenite tuffs that exist north of the clinoptilolite tuff (site 2, Fig. 1) are harder. Usually, mordenite is accompanied by minor amounts of sanidine and cristobalite. The Si/Al ratio is high in mordenite, ranging from 6.3 to 6.6 (Table 2). These ratio values are characteristic for mordenite varieties of sedimentary origin (11).

Both zeolitic tuffs have an acidic composition, as indicated by their high silica and (Na + K)/Ca ratio, and low iron, calcium and magnesium concentrations. High barium concentration values are attributed to the presence of barite crystals. High levels of SiO_2 have been measured in opal-CT or cristobalite rich samples.

Generally, the zeolite content of the mordenitic tuffs is higher than that of the clinoptilolite ones (Table 1). Clinoptilolite and mordenite have replaced bubble wall shards and long tubular shards. They have also filled vugs and fissures forming euhedral tabular and thread-like crystals, respectively. However, thread-like mordenite crystals are not so common in mordenite tuffs. This indicates that most of mordenite exists as a direct glass replacement.

Continental evaporites or their moulds, characteristic of a saline-alkaline lake deposit (12) are absent from the zeolite paragenesis of Kimolos. In some areas located at the SW part of the island, kaolinite and/or alunite covering bentonitic and zeolitic tuffs, point to the latest stage of the hydrothermal alteration of the volcanic rocks. Even though there exist cherty or barite veins that cut the zeolitic rocks, there is no gradual alteration of the tuffs related to the walls of the veins. This indicates that the late hydrothermal fluids circulating through the faults or fissures of the tuffs had no significant contribution to the genesis of the zeolites on Kimolos Island.

Therefore, it is apparent that the formation of zeolites is not associated with:
a) saline-alkaline lake waters,
b) hydrothermal fluids.

In addition, the shallow marine depositional environment of the tuffs, together with their young age and thin overburden, exclude the genesis of zeolite:
a) by depositing in a deep sea environment,
b) by burial diagenesis of the volcaniclastic rocks.

2.2. Formation of Clinoptilolite and Mordenite. Usually, the formation of bentonites and sedimentary zeolites takes place in alkaline environments. Kimolos tuffs, transformed into zeolites and bentonites, are of a shallow marine to nearshore origin as resulted from sedimentological and paleontological data (1, 2).

Tables 2, 3 and 4 show that clinoptilolite and mordenite formed in porous and massive tuffs respectively, have quite similar major element composition. However, pumice (porous) tuffs host the potassium-rich clinoptilolite variety, whereas massive tuffs host the Ca and Na-rich mordenite varieties. The relationship between porosity and mobility of certain cations (Ca^{2+}, Na^+, K^+) during zeolitization is not apparent.

The depositional and diagenetic environment of Kimolos zeolitic tuffs was balanced by the circulation of highly alkaline solutions, originated from the adjacent sea. That circulation of marine waters through the tuffaceous rocks define an open hydrological system of zeolite formation (13, 14).

The presence of K-rich clinoptilolite (Tables 2 and 3) also confirms the formation of Kimolos zeolites in an open hydrological system. The absence of both, Ca-clinoptilolite and K-rich mordenite is also in accordance with that type of zeolite formation. Usually, Ca-clinoptilolite is not formed in open hydrological systems at low temperatures (13). Additionally, K-mordenite occurs in hydrothermally altered tuffs and lavas (15).

The co-existence of adjacent tuff deposits, having a diverse zeolite mineralogy is rather puzzling, because the tuffaceous rocks are of the same age and also of a similar chemical character (Tables 2 and 3).

In some cases, mordenite is known to form at higher temperatures than clinoptilolite (16). Therefore, one factor that might have played a role in the transformation of volcanic glass, or early clinoptilolite to mordenite, was the higher heat flow rates in the northern tuff outcrop caused by the extrusion of andesitic-dacitic lavas (Fig. 1). Similar mordenite formation has been reported to occur in zeolitic tuffs of Northern Greece (16).

Fytikas and Vougioukalakis (17) assume that the first tuffs deposited on the island have an age of about 3.5 M.y (Pliocene-Pleistocene). The transformation of the volcanic glass of the tuffs to zeolites, silica polymorphs and smectite had probably started immediately after their deposition in nearshore environment by the circulation of alkaline ground waters.

Part B. Industrial Applications

Due to their unique properties, zeolites can be used in a wide variety of applications such as in nuclear and metallurgical waste treatment, aquaculture, odour control, animal feed, gas purification, construction (lightweight aggregates), paper production (as filler), and more. The main properties of zeolites are in the areas of:

- ion exchange
- liquid adsorption/desorption
- gas adsorption

Most of the forementioned applications utilize the ion exchange capability of the zeolite minerals in order to produce materials with highly specialized properties. For example, it is possible by specialized techniques to saturate the crystal lattice of clinoptilolite with radioactive strontium and cesium. Afterwards, this material can be stored indefinately.

Regarding cement, the chemical composition and the lattice structure of these materials make them suitable for use in the cement industry. Natural zeolites are hydrated aluminosilicate minerals containing alkaline and alkaline-earth metals, formed by the alteration of volcanic ash which is mainly an amorphous, silicious material. They are considered as materials with high pozzolanic activity for their open structure and chemistry.

The structure of the zeolite minerals is characterized by a large number of channels and cavities which exhibit a high surface area. In addition, they are capable of absorbing more lime than ordinary tuffs and some other glassy mixtures, because the amount of dissolved SiO_2 of zeolites is 3 to 7 times higher than that of other pozzolanas (4). This results in the formation of higher amounts of hydration products which are responsible for strength development.

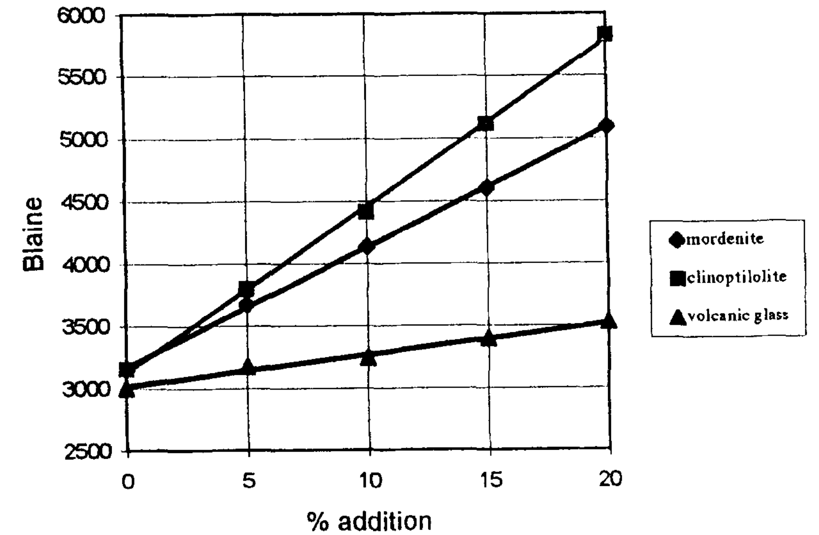

FIG. 2.
The effect of tuff and pozzolana addition on Blaine (fineness: cm^2/g) (Mordenite: mordenite-rich tuff, Kimolos Island; Clinoptilolite: clinoptilolite-rich tuff, Kimolos Island; Volcanic glass: volcanic glass-rich tuff (pozzolana), Milos Island).

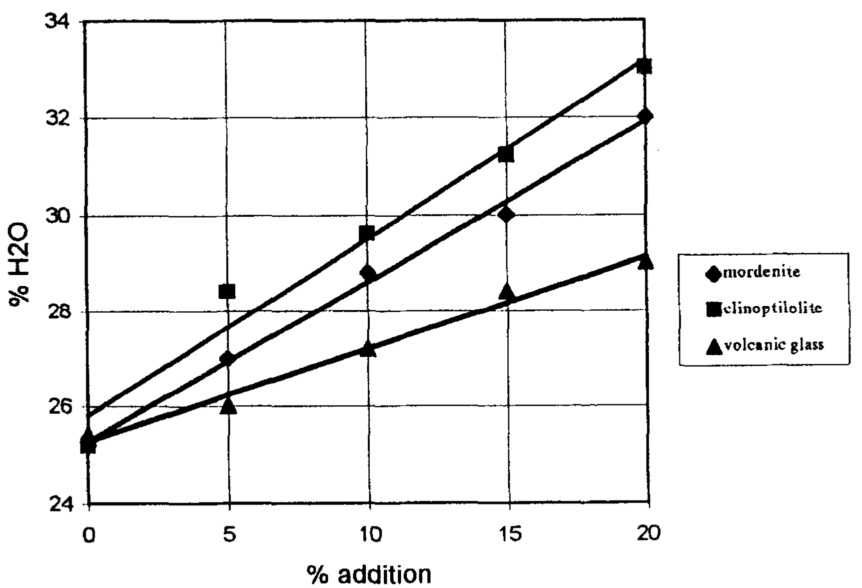

FIG. 3.
Effect of pozzolana and tuff addition on water demand.

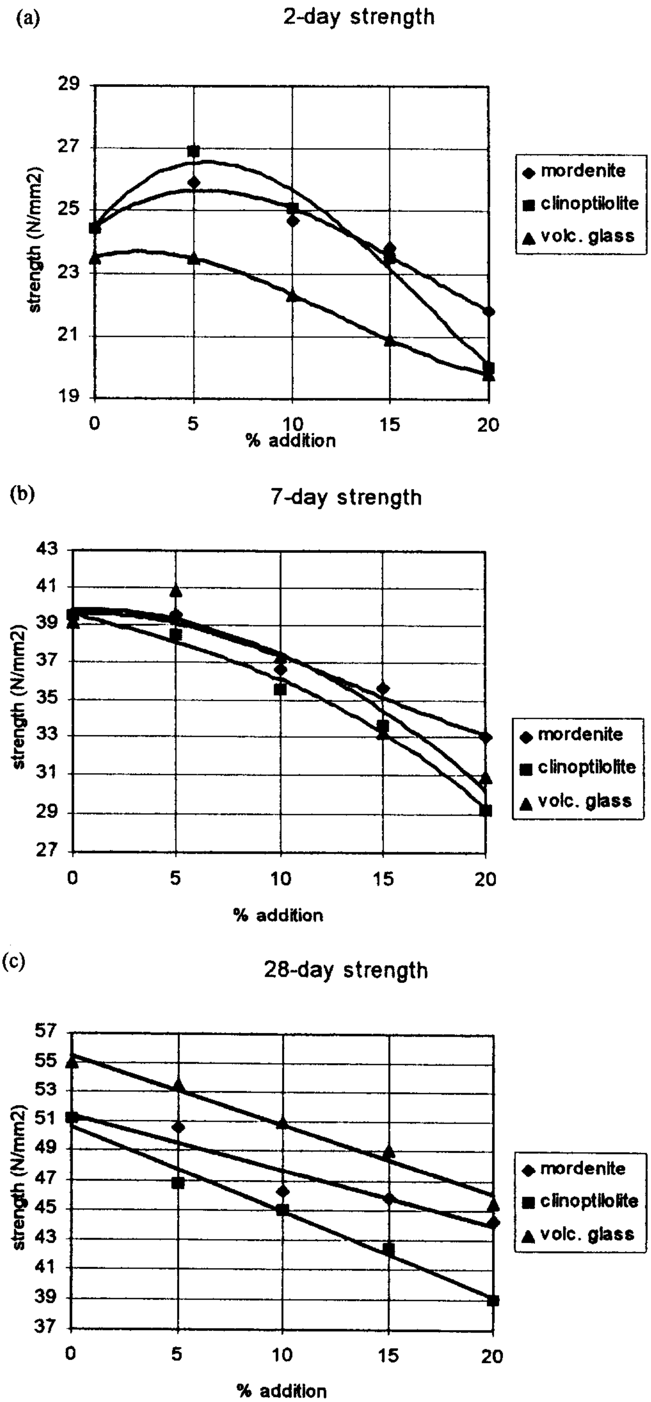

FIG. 4a, b, c.

Laboratory cement strength vs. percentage of volcanic glass and zeolitic tuff addition.

TABLE 5

Physical Characteristics of Blended Cements

A/A					SET. TIME (min)		STRENGTH (N/mm2		
Mordenite tuff	min	%tuff	Blaine	%H20	INIT.	FIN.	2-day	7-day	28-day
2164	42	0	3150	25,2	105	145	24,4	39,4	51,2
2165	42	5	3670	27,0	100	135	25,9	39,5	50,6
2166	42	10	4130	28,8	95	130	24,7	36,6	46,2
2167	42	15	4600	30,0	90	125	23,8	35,6	45,8
2168	42	20	5090	32,0	85	120	21,8	33,0	44,3
Clinoptilolite tuff									
2164	42	0	3150	25,2	105	145	24,4	39,4	51,2
2169	42	5	3790	28,4	105	140	26,9	38,4	46,7
2170	42	10	4410	29,6	100	130	25,1	35,5	45,0
2171	42	15	5110	31,2	100	130	23,5	33,6	42,4
2172	42	20	5820	33,0	90	125	20,0	29,2	39,0
Milos pozzolana									
2696	42	0	3000	25,4	135	165	23,5	39,1	55,0
2733	42	5	3170	26	145	185	23,5	40,8	53,5
2734	42	10	3240	27,2	155	195	22,3	37,2	50,9
2735	42	15	3390	28,4	160	205	20,9	33,2	49,0
2736	42	20	3520	29	170	210	19,8	30,9	45,4

Even though the silicious amorphous phase of raw materials is considered highly reactive, it has been demonstrated that zeolites are more reactive materials than the parent amorphous phase from which they are derived.

At present, zeolitic tuffs are locally used as pozzolanic materials for cement production. Their use is common practice in countries such as former Yugoslavia and China. The latter, which is one of the major cement producers, uses large quantities of zeolitic tuffs for the production of zeolite cement. Its annual cement output exceeds the 200,000,000 tones. A large portion of this -about 45,000,000 tones- is blended with natural zeolite for the production of zeolite cement.

Test Results of Laboratory Cements. The properties of the two types of zeolitic cement—one with mordenite and the other with clinoptilolite—were compared to those of cement produced with and without the addition of Milos pozzolana, which is widely used in Greece. The test results are summarized in the Table 5.

The effect of the pozzolana and tuff addition on the cement properties is shown in Figures 2 to 4.

As shown in Figure 2, the clinoptilolite tuff is the softest and thus the easiest to grind. Even though Milos pozzolana is a pumice tuff containing a large portion of a glassy material (volcanic glass) while the zeolitic tuffs of a crystalline material, the energy consumption required for the grinding of the former is higher than that of the latter.

The effect of the above materials on the water demand (or consistency) of cement is presented in Figure 3.

TABLE 6

Percentage of Strength Change vs. Milos Pozzolana and Zeolitic Tuff Addition

% strength change			
% addition	mordenite		
	2-day	7-day	28-day
0	0,0	0,0	0,0
5	6,2	0,3	-1,2
10	1,2	-7,1	-6,3
15	-2,5	-9,6	-10,6
20	-10,7	-16,2	-13,5
	clinoptilolite		
0	0,0	0,0	0,0
5	10,3	-2,5	-8,8
10	2,9	-9,9	-12,1
15	-3,7	-14,7	-17,2
20	-18,0	-25,9	-23,8
	volcanic glass		
0	0,0	0,0	0,0
5	0,0	4,4	-2,7
10	-5,1	-4,9	-7,5
15	-11,1	-15,1	-10,9
20	-15,7	-20,9	-17,5

The addition of zeolite tuffs or Milos pozzolana in cement increases the water demand (Fig. 3). However, it is not clear which raw material is responsible for the highest water demand because the specific surface (Blaine) of the produced blended cements ranges from 3,000 to 6,000 cm2/g.

As expected, clinoptilolite cement has the highest specific surface and the highest water demand, whereas, Milos pozzolana has the lowest. It is possible though that the highest water demand of the clinoptilolite cement is due not only to its specific surface but also to clinoptilolite's porous structure which is similar to that of pumiceous tuff.

The cements that were produced by co-grinding clinker, gypsum, and tuff/volcanic glass were used for the production of mortar bars and strength measurements according to European Regulations (CEN 196-1). The results of the measurements are shown in Figures 4a-4c.

These results indicate that the addition of small quantities(-5%) of these materials to cement improves early strength. On the contrary, when more than 10% is added, a significant reduction is observed on the 28-day strength in all blended cement samples. In general, cement containing mordenite tuff and Milos pozzolana yields better results than cement with clinoptilolite.

The percentage of the strength change of the blended cements with respect to the control sample (cement with clinker and gypsum) is summarized in Table 6, and presented in Figures 5a to 5c.

Table 6 and Figures 5a, b, c indicate that:

- In the early age (second and seventh day) and up to 10% pozzolana addition, the strength change of mordenite cement has intermediate values between those with clinoptilolite and volcanic glass.
- The strength change of mordenite cement in the early age improves when compared to the rest of the blended cements, for pozzolanic material addition exceeding 10 percent.
- In the late age (28 days), the strength change of mordenite cement is less than that of both clinoptilolite cement and Milos pozzolana cement regardless the percentage of zeolitic tuff and volcanic glass addition. The second best pozzolanic additive is Milos volcanic glass.

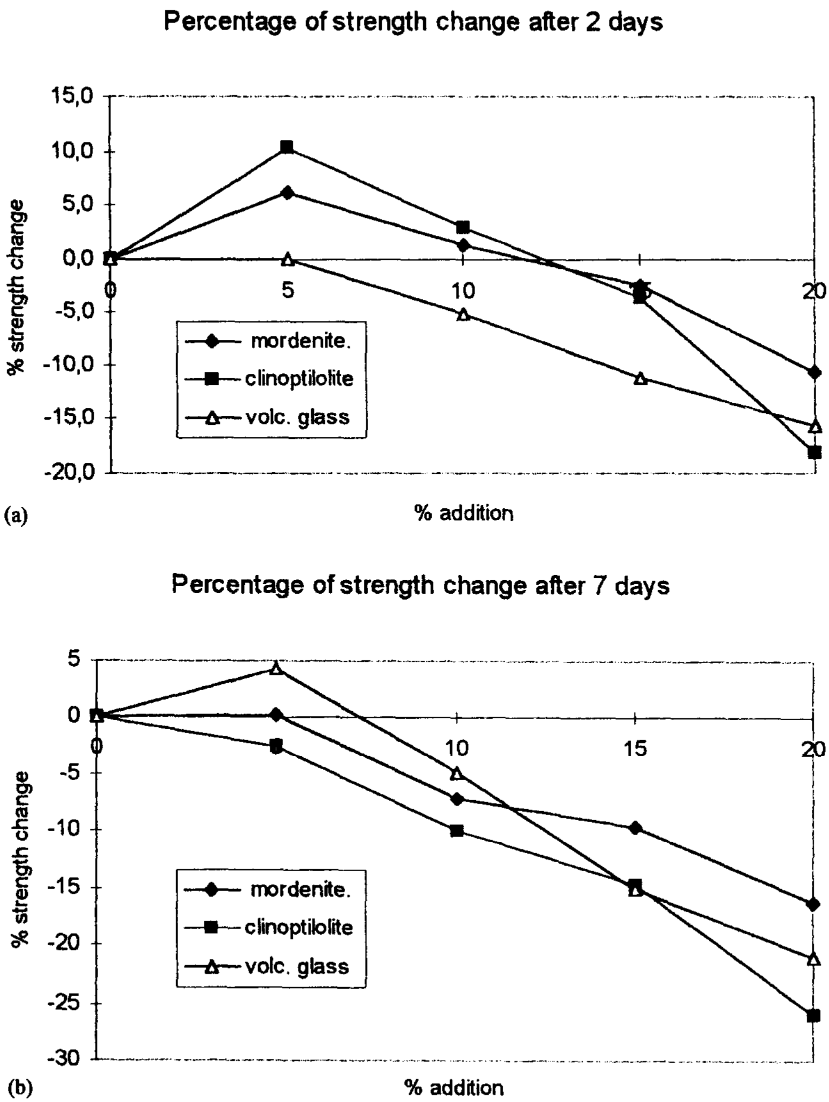

FIG. 5.

(a) Percentage of the 2-day strength change vs. % addition. (b) Percentage of the 7-day strength change vs. % addition.

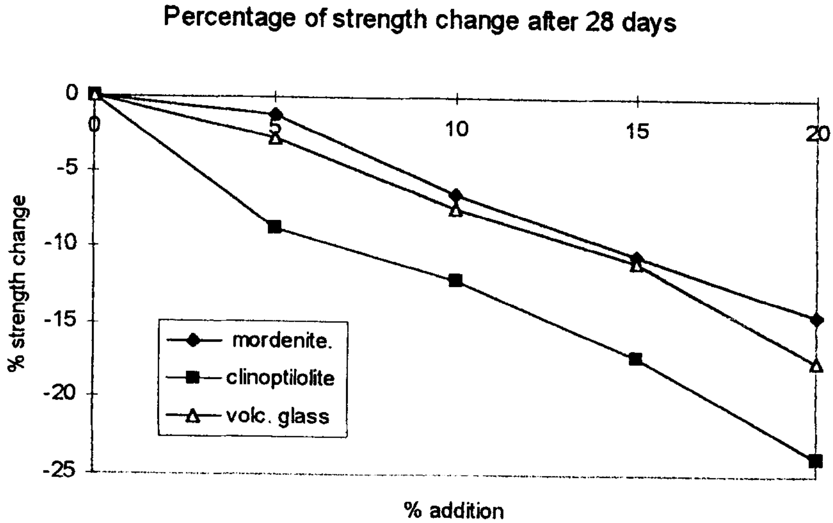

FIG. 5c.
Percentage of the 28-day strength change vs. % addition.

In an attempt to explain the strength results, the reactive silica content of the above materials was determined according to CEN 196-2/and10,13. The strength of the cement is mainly due to the formation of hydrated products among which C-S-H is the most important. C-S-H is formed either from the direct hydration of $C_3S(3CaO.SiO_2)$ and $C_2S(2CaO.SiO_2)$ or from the reaction between $Ca(OH)_2$ and reactive silica. The $Ca(OH)_2$ forms during the hydration of C_3S and C_2S while the reactive silica is contained in the pozzolanic materials.

As shown in Table 7 and its respective Figure 6, there is a good correlation between the reactive silica content of raw materials and the compressive strength of cement. The cements that were used for this compoarison had the same zeolite and Milos pozzolana content (20%).

In addition to the above materials, the reactive silica and the insoluble residue content of a zeolitic tuff from the area of Pentalofos, Greece were determined. The results, which are summarized in Table 8 and shown in Figure 7, indicate that these two parameters are related.

TABLE 7

Percentage of Reactive Silica vs. Percentage of Strength Change in Blended Cements

MATERIAL	% INSOLUBLE RESIDUE	%REACTIVE SiO2	%Strength change*
Milos white pozzol.	26,6	51,2	-17,5
Milos dark pozzol.	36,2	39,9	-20,7
KimolosClinoptilolite	46,6	31,2	-24,0
Kimolos Mordenite	13,5	60,6	-13,5

* Calculated with respect to the reference sample (clinker/gypsum)

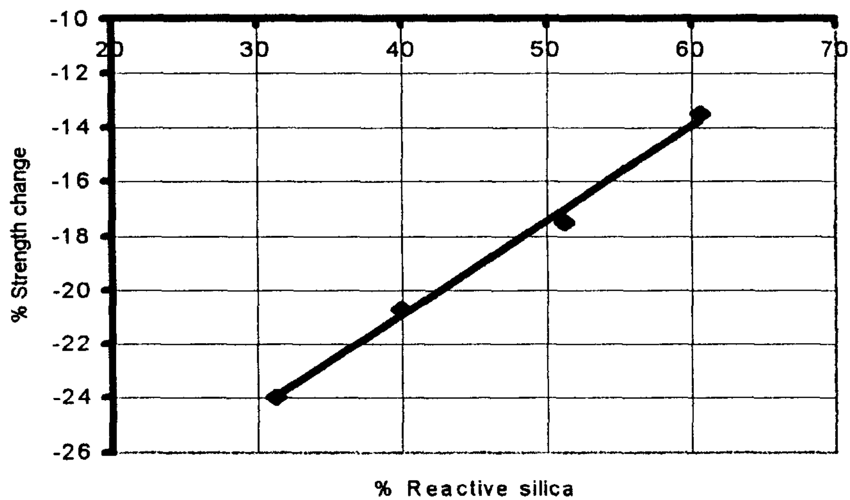

FIG. 6.
Percentage of reactive SiO_2 vs. percentage of strength change.

As expected, the reactive silica content of a pozzolana is inversely proportional to its insoluble residue content. Apparently, the late compressive strength of cement may be related, to a certain degree, to the percentage of the insoluble residue of the added pozzolana. Therefore, a rough estimate of the late strength could be possibly obtained by the quick determination of the insoluble residue of certain natural pozzolanas. However, this assumption requires an extended investigation over a greater number of samples.

Conclusions

Tuffaceous rocks deposited in the west-south west part of Kimolos have been transformed to zeolitic rocks. The diagenetic transformation of volcanic glass to clinoptilolite and mordenite took place in an open hydrological system by circulation of alkaline ground waters. The fluids responsible for mordenite formation had probably higher temperature than that of clinoptilolite due to high heat flow rates originated from the emplacement of lavas in their vicinity.

Even though clinoptilolite and mordenite tuff have similar chemical analyses, the chemical composition of mordenite exhibits a lower variability than that of clinoptilolite.

TABLE 8

Reactive Silica Content vs. Insoluble Residue Content

MATERIAL	% INSOLUBLE RESIDUE	%REACTIVE SiO2
Milos white pozzol.	26,6	51,2
Milos dark pozzol.	36,2	39,9
Pentalofos zeolite	13,1	58,3
KimolosClinoptilolite	46,6	31,2
Kimolos Mordenite	13,5	60,6

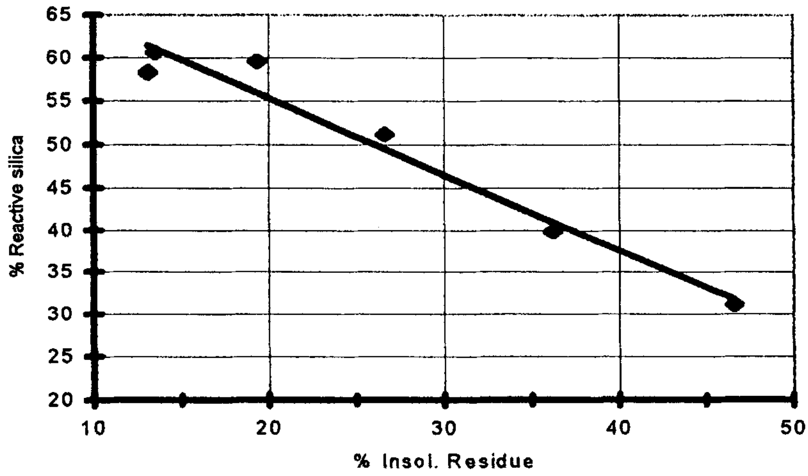

FIG. 7.
Percentage of Reactive Silica vs. Percentage of Insoluble Residue.

Mordenite tuffs are massive while clinoptilolite tuffs are porous. As a result, the latter are softer and easier to grind.

The strength of blended cements containing mordenite tuff is higher than that of cements containing either Milos pozzolana or clinoptilolite tuff. The strength of mordenite cement is higher than that of the clinoptilolite cement probably due to the higher zeolite and reactive silica content of the mordenite tuff.

Furthermore, zeolitic tuffs need more water to produce paste of the same consistency, when compared to Milos pozzolana. This means that when zeolitic cement is used for concrete production, it is likely that a superplasticizer has to be added to control the rheological properties of the mixture.

In conclusion, the usage of zeolitic tuffs as additive in cement production is promising. In order to fully evaluate these materials, their effect on concrete has to be examined. Concrete produced with zeolitic cement containing either clinoptilolite or mordenite from Kimolos Island might have special properties that need to be studied through thorough examination and testing.

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