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GEOLOGY AND GEOCHEMISTRY OF THE EOCENE ZEOLITE-BEARING VOLCANICLASTIC SEDIMENTS OF METAXADES, THRACE, GREECE

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ABSTRACT

The Eocene zeolite-bearing volcaniclastic sediments (Ca-rich clinoptilolite 51 % on average) of Metaxades, Thrace, Greece, are studied in terms of geology and chemical composition. The alternating formations along a vertical profile in the Metaxades main quarry face are: Discrete horizons of zeolite-bearing volcaniclastic tuffs, zeolite-bearing volcaniclastic tuffs including pebbles, zeolite-bearing volcaniclastic tuffs including thin silica-rich layers, and a calc-clayey horizon. A positive correlation is observed between MgO and CaO in the volcaniclastic tuffs including silica-rich layers. Sr, Rb and Ba are the most abundant trace elements in all layers; among them, Sr is found to correlate positively with zeolite. The enrichment of some trace elements is mainly attributed to mineral abundances, mineral chemistry or leaching processes. The zeolite-bearing volcaniclastic sediments of Metaxades represent an inhomogeneous sequence, which was deposited in a shallow marine environment under turbulent to quiet sedimentary conditions.

Key words: *zeolite, Ca-rich clinoptilolite, volcaniclastic sediments, Metaxades, Greece.*

RESUMEN

Los sedimentos eocenos volcanoclásticos con zeolita (51% de media de clinoptilolita rica en Ca) de Metaxades, Tracia, Grecia, se estudian desde el punto de vista geológico y de su composición química. Las formaciones alternantes que se pueden observar en un corte vertical en la cantera principal de Metaxades son: horizontes aislados de *tuffs* volcanoclásticos con zeolita y con delgadas capas ricas en sílice, y un horizonte calco-arcilloso. Se observa una correlación positiva entre MgO y CaO en los *tufss* volcanoclásticos que presentan capas ricas en sílice. El Sr, el Rb y el Ba son los elementos traza más abundantes en todos los horizontes. Entre ellos, el Sr presenta una correlación positiva con la zeolita. El enriquecimiento en algunos elementos traza se atribuye esencialmente a las abundancias de los minerales, la química mineral, o a fenómenos de lixivinción. Los sedimentos volcanoclásticos con zeolita de Metaxades representan una secuencia inhomogénea, que fue depositada en un ambiente marino somero, bajo condiciones desde turbulentas hasta tranquilas.

Palabras clave: *zeolita, clinoptilolita rica en Ca, sedimentos volcanoclásticos, Metaxades, Grecia.*

Introduction

The Metaxades area of Thrace, northeastern Greece, became recently the research subject of many studies due to its significant zeolite deposits (Tsirambides *et al.*, 1989; Marantos *et al.*, 1989; Tsolis-Katagas and Katagas, 1990; Tsirambides, 1991; Tsirambides *et al.*, 1993; Filippidis, 1993; Savin *et al.*, 1993).

However, previous studies are based on a relatively restricted number of samples representative of certain only sites of the zeolite-bearing volcaniclastic formations; hence, some differences in results and interpretations were inevitable (e.g., Tsolis-Katagas and Katagas, 1990; Tsirambides *et al.*, 1993; Savin *et al.*, 1993). Because of the great petrologic and commercial interest of these zeolite-bearing rocks, a detailed investigation has been undertaken.

This study concerns the results from a) a detailed field knowledge through a geological mapping (scale 1:5,000) constructed for the first time, and b) the petrographical observations, mineralogical abundances, mineral chemistry and chemical varia-

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tions (major and trace elements) along a vertical profile of the main quarry face in the Metaxades volcaniclastic sediments.

Geology

The Metaxades upper Eocene zeolite-bearing volcaniclastic sediments belong to the Orestias Tertiary molassic basin of the northeastern Thrace in Greece. This meta-Alpine basin has an elongated shape an extends into Bulgaria. It is dominated by sediments of Eocene to Pleistocene age, deposited uncoformably on the crystalline basement of the Rhodope massif (Fig. 1).

The sedimentary formations occurring in this basin, according to data from Andronopoulos (1977), Tsirambides *et al.* (1993) and Koutles (Ph. D. in progress) are from bottom to surface:

1. Eocene formations consisting of a) breccias-conglomerates (10-15 m thick) which lie unconformably upon the metamorphosed basement. Their composition is phyllitic, gneissic, amphibolitic, quartzitic or andesitic; they display a grading from coarser to finer fragments upwards, b) gray siltstones (≈ 100 m thick) with psammitic and marly interlayers, c) mostly semi-loose sandstones (40-50 m thick) of varying grain-size, including very thin clayey interlayers, d) white to pale gray, yellow or green zeolite-bearing volcaniclastic tuffs (20-25 m of visible thickness) conformably deposited on the sandstones or siltstones; a thin layer of gray marl is descernible on the upper part of the tuffs, e) loose white-yellowish marly limestone (5-10 m thick) and f) limestone (less than 30 m thick) rich in fossils.
2. Oligocene formations of relatively great thickness, unconformably deposited on the Eocene formations. They consist of gray clays, red-yellowish sandstones, white-yellow siltstones and interlayers of marly limestone.
3. Quaternary sediments of varying thickness, deposited over all previous formations.

The complete sequence of the above formations is not always present in all sites of the basin. One or more formations may be locally absent due to tectonic activity, erosion or not deposition. In the broader area, two main visible faults and several fractures have been observed.

Figure 2 is a detailed geological map (originally mapped in a scale 1:5,000) of the broader area of Metaxades, covering 15.66 km^2. In the investigated area of Fig. 2, the following formations were recognized:

a) Eocene formations consisting of zeolite-bearing volcaniclastic tuffs, limestones, marly-limestones, sandstones and siltstones, b) Plio-Pleistocene formations and c) Fluvioterrestrial formations.

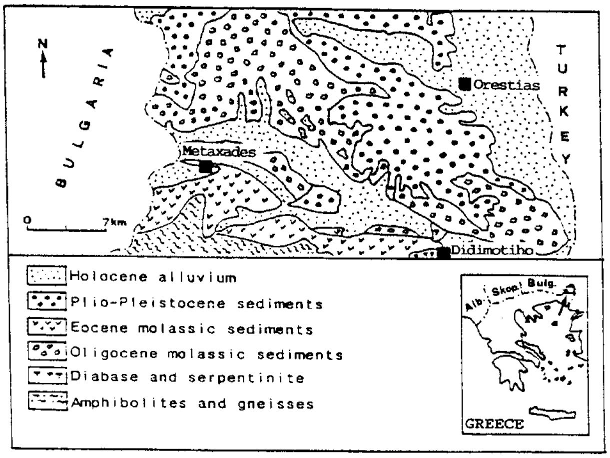

Fig. 1.—Geological map and geographic position of the Metaxades area, Thrace, Greece (from Bornovas and Rondogianni-Tsiambaou, 1983).

Samples and analytical methods

The observations in this study are based on the examination of a complete series of samples taken from a representative stratigraphic column (1T) of total height 13 m, from the eastern site of the main quarry face at Metaxades area (Figs. 2 and 3).

Firstly, the samples were cut and large area polished surfaces of them were macroscopically examined. Thin and polished thin sections were prepared for petrographic observations in transmitted light and for microprobe analysis of the mineral constituents, respectively.

X-ray diffractograms were obtained on randomly oriented samples, using a Philips diffractometer, equipped with a PC-APD diffraction software. The operating conditions were: CuKα radiation, use of monochromator and scanning speed 1° per minute over the interval 2-60° of 2θ.

Electron microprobe analyses were performed by an ARL-SEM with Tracor Northern EDS, TN 5502, ZAF correction. Operating conditions were: accelerating voltage 15 kV, beam current 20 nA and counting time 15 seconds. The minerals used as probe standards were orthoclase, wollastonite, corundum, periclase, albite, chromite, almandine and pyrophanite. Although special care was taken for clinoptilolite analysis by enlarging the electron beam and reducing the beam current and counting time, the volatilization of the alkalies was not avoided (see Tsirambides *et al.*, 1993). Table 1 presents representative analyses of the main mineral constituents.

Bulk rock chemical analyses both for major and trace elements were performed on the profile samples and the results are presented in Table 2. The analytical equipment used was XRF PW 2400 with X-ray spectrometer. Before chemical determinations of trace elements, the powder used for the pelets was heated at 900° C for four hours.

The mineralogical composition of the profile samples was estimated by XRD, using standard mixtures of the minerals (Table 3). Considering the chemical composition of the minerals and their proportions, the chemical composition of the rock samples (Table 2) is in good agreement with their mineralogical composition (Table 3).

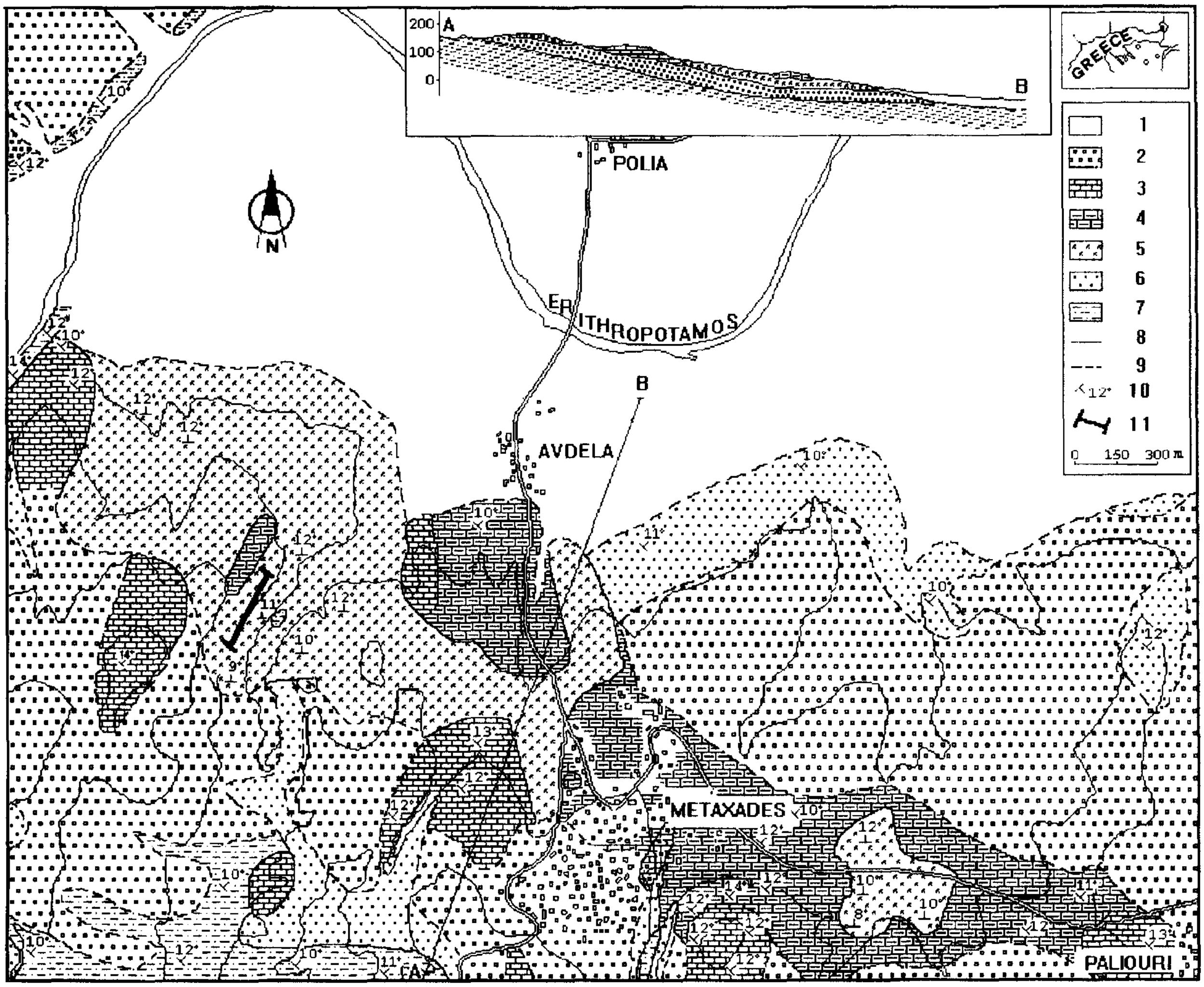

Fig. 2.—Detailed geological map of the Metaxades area.
1: Holocene fluvio-terrestrial formations, 2: Plio-Pleistocene formations, 3: limestones, 4: marly-limestones, 5: volcaniclastic tuffs, 6: sandstones, 7: siltstones, 8: geologic boundary, 9: geologic boundary probable or covered, 10: strike and dip of beds, 11: Metaxades main quarry.

Petrography

The white to pale gray volcaniclastic sediments of Metaxades display earthy streak and conchoidal fracture. Detailed observations showed that the lower part of the section studied, presents a massive to poorly bedded structure and poorly sorted components of the unwelded and coarse grained deposits, lacking internal structures or laminations. On the other hand, cross-bedding predominates at the intermediate part of the section. The volcaniclastic sediments here are fine-grained and may be divided in planar- and trough cross-bedded. The laminated upper layers consist mainly of non-volcanogenic components, especially of silt and clay size clastic grains. Manganese dendrites are noticed through the whole section.

The main lithologies present and alternating in layers along the studied profile are (Fig. 4): a) Discrete horizons of zeolite-bearing volcaniclastic tuffs (samples 1T11, 1T18, 1T34, 1T64, 1T73, 1T109), having a total thickness of 7 m. b) Layers of volcaniclastic tuffs including small pebbles (1 cm on average but sometimes reaching 7 cm) from the surrounding rocks (samples 1T5, 1T51, 1T82, 1T90, 1T98). Total thickness 2.5 m. The sample 1T5 was taken just below an eroded thin layer of limestone occurring at the top of the profile, containing thus a significant content of calcite. c) Zeolite-bearing volcaniclastic tuffs including thin silica-rich layers (samples 1T41, 1T59, 1T67, 1T75, 1T85, 1T95, 1T101), comprising 2 m of total thickness. d) A calc-clayey horizon (sample 1T23) of total thick-

Fig. 3.—View of the main quarry face at Metaxades and location of the studied vertical profile 1T.

ness 1.5 m, included in a discrete horizon of volcaniclastic tuff.

Mineralogy

The XRD analyses showed that more or less all lithological layers contain the same minerals, but in varying amounts (Table 3). The mineralogical phases identified by different methods, are zeolite (clinoptilolite), quartz, feldspars, ± cristobalite, ± mica/clays, ± calcite, ± amphibole, ± epidote, ± opaques. According to Tsirambides *et al.* (1993), the clays are consisted mainly of smectite and according to Filippidis (1993), the opaques are consisted of ilmenite and moissanite. Clinoptilolite, cristobalite and smectite account for the diagenetic phases (Tsirambides *et al.,* 1993; Savin *et al.,* 1993).

The chemical composition of each mineral phase displays some differences in the various lithological layers (Table 1). The calc-clayey horizon is extremely fine grained and consequently it was impossible to be microprobe analysed.

Zeolite, which represents the 51 % on average in the volcaniclastic tuffs, is clinoptilolite according to its thermal stability (Boles and Surdam, 1979; Tsirambides *et al.,* 1993; Filippidis, 1993). It appears as tiny crystals and without any zoning. The Si/Al ratio values of clinoptilolite from all samples are > 4.7 and in agreement with different authors classification (Mumpton, 1960; Mason and Sand, 1960; Alietti, 1972; Boles, 1972; Alietti *et al.,* 1977). The Si, Al, Ca and Mg values are more or less similar with those presented by Tsirambides *et al.* (1993), while the values of Na and K are much lower, due to volatilization during the microprobe analysis. Tsirambides *et al.* (1993) give average values of 0.95 and 1.08 per unit cell, for Na and K, respectively, for the Ca-rich Metaxades clinoptilolite. Among the zeolite-bearing volcaniclastic tuffs, the clinoptilolite of the discrete ones is the richest in calcium. In very low concentrations, iron (Fe_2O_3) was detected in the cli-

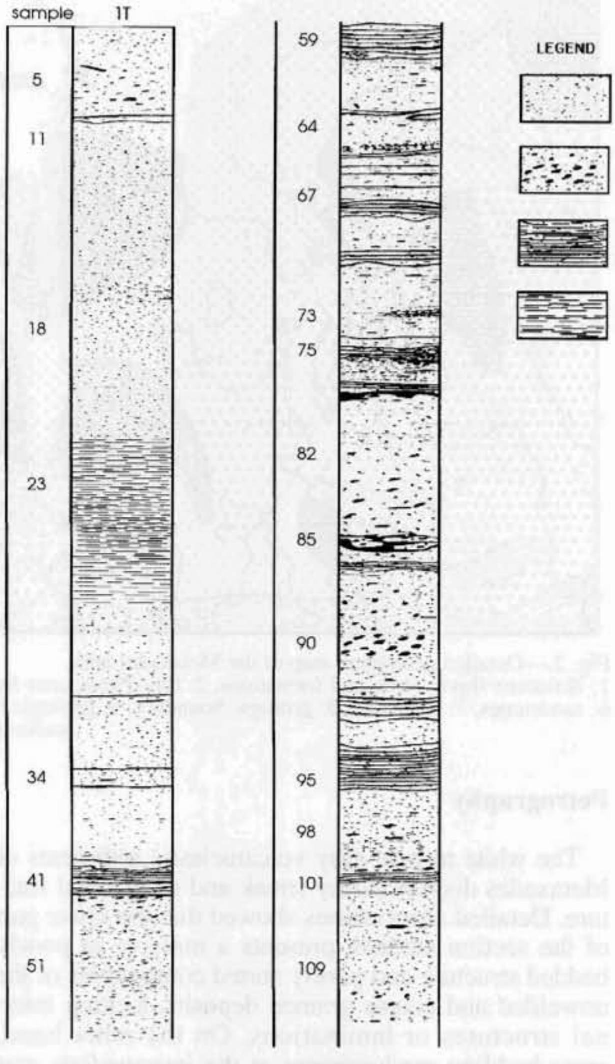

Fig. 4.—Graphical presentation of the vertical profile 1T (total height 13 m) at the Metaxades main quarry face, illustrating the petrographical sequence of the various layers and the sample locations.
1: Discrete zeolite-bearing volcaniclastic tuffs (DZT), 2: Zeolite-bearing volcaniclastic tuffs including pebbles (ZTP), 3: Zeolite-bearing volcaniclastic tuffs including thin silica-rich layers (ZTS), 4: Calc-clayey horizon (CCH).

noptilolite from the discrete volcaniclastic tuffs including pebbles.

Sanidine displays no chemical differences in the three categories of volcaniclastic tuffs, while plagioclase is albite in the discrete volcaniclastic tuffs and sodic oligoclase in the other two categories, displaying considerable contents of potassium in all samples (Table 1).

Biotite displays a relatively high Mg/(Mg+Fe^{2+}) ratio. In the discrete volcaniclastic tuffs this ratio shows a large variation and in some cases biotite reaches the field of phlogopite; in this second case part of potassium is replaced by calcium as in margarite.

Amphibole is tschermakitic hornblende both in the discrete volcaniclastic tuffs and in those containing silica-rich layers, displaying small differences in calcium and sodium contents (Table 1).

Geochemistry

Table 2 shows the concentrations of major and trace elements along the studied 1T profile. Element abundances for all varieties of volcaniclastic tuffs are mostly similar and comparable to values given by Alexiev and Djourova (1988) for the southeastern Bulgarian zeoliferous volcaniclastic rocks of north-eastern Rhodope. Among the oxide values, considerable differences are observed mainly for SiO_2, Al_2O_3 and CaO (Fig. 5) in the layer of the calc-clayey horizon (sample 1T23) and in the uppermost part of the profile (sample 1T5) which although belonging to the variety of volcaniclastic tuffs including pebbles, displays the highest proportion of calcite (Table 3).

Among the trace elements, Sr, Rb and Ba are the most abundant in nearly all the samples of the sequence. The trace elements Zr, Y, Zn, Nb, Pb and Ga show some minor concentrations while the rest (Cu, Ni, Co, Sc, Cr, V) are near or below detection limit (Table 2).

Discussion and conclusions

Considerable work has been done and published on the formation and occurrence of zeolites by reaction of silisic volcanic glass with pore water. Much attention has been focused on the alteration of ash

Table 1.—**Representative chemical analyses of the main mineral constituents in the different layers of the 1T vertical profile of Metaxades main quarry face**

	Clinoptilolite			Sanidine			Plagioclase			Biotite			Amphibole	
	1T41	1T18	1T90	1T41	1T18	1T90	1T41	1T18	1T90	1T41	1T18	1T90	1T41	1T18
SiO_2	70.43	68.65	69.66	67.46	66.27	67.67	63.19	65.57	67.91	36.60	44.07	41.87	44.45	43.01
TiO_2	—	—	—	—	—	—	—	—	—	2.97	0.27	2.24	0.36	0.57
Al_2O_3	11.50	12.44	12.30	18.01	18.32	17.89	20.14	21.25	21.28	13.25	15.33	15.46	15.56	14.52
Fe_2O_3	—	0.21	—	—	—	—	—	—	—	—	—	—	—	—
FeO	—	—	—	—	0.31	—	5.43	—	—	21.06	16.88	16.59	12.30	12.74
MnO	—	—	0.38	—	—	—	—	—	—	0.10	—	0.13	0.08	0.29
MgO	0.30	0.57	0.51	—	—	—	—	2.41	—	13.73	12.43	13.15	11.28	11.65
CaO	4.23	5.21	3.75	—	—	—	2.64	0.41	2.52	—	0.35	0.40	10.34	11.78
Na_2O	0.03	0.02	0.11	3.43	3.59	3.45	7.66	9.09	7.20	0.38	0.04	0.03	2.01	1.62
K_2O	0.65	—	0.53	11.22	11.50	11.02	1.01	1.15	1.10	8.66	7.66	7.01	0.37	0.71
Total	87.13	87.10	87.24	100.35	99.98	100.03	100.06	99.87	100.01	96.74	97.02	96.87	96.75	96.89
							structural formula on the basis of:							
	72[0]			32[0]						22[0]			23[0]	
Si	30.440	29.770	30.100	12.180	12.050	12.211	11.398	11.510	11.822	5.548	6.313	6.023	6.400	6.290
Ti	—	—	—	—	—	—	-	—	—	0.339	0.029	0.042	0.040	0.060
Al	5.856	6.360	6.265	3.832	3.925	3.805	4.281	4.397	4.366	2.367	2.588	2.620	2.640	2.510
Fe^{3+}	—	0.069	—	—	—	—	—	—	—	—	—	—	0.660	0.500
Fe^{2+}	—	—	—	—	0.048	—	0.819	—	—	2.670	2.022	1.996	0.830	1.060
Mn	—	—	0.139	—	—	—	—	—	—	0.012	—	0.016	0.010	0.040
Mg	0.196	0.367	0.329	—	—	—	—	0.629	—	3.101	2.654	2.819	2.420	2.540
Ca	1.958	2.422	1.736	—	—	—	0.510	0.078	0.470	—	0.053	0.062	1.600	1.850
Na	0.025	0.017	0.092	1.201	1.264	1.207	2.680	3.093	2.431	0.112	0.012	0.009	0.560	0.460
K	0.357	—	0.292	2.584	2.666	2.537	0.232	0.257	0.245	1.674	1.399	1.287	0.070	0.130

Table 2.—**Bulk rock chemical analyses along the 1T vertical profile of Metaxades main quarry face**

	1T5	1T11	1T18	1T23	1T34	1T41	1T51	1T59	1T64	1T67	1T73	1T75	1T82	1T85	1T90	1T95	1T98	1T101	1T109
Charac-teriz.	ZTP	DZT	DZT	CCH	DZT	ZTS	ZTP	ZTS	DZT	ZTS	DZT	ZTS	ZTP	ZTS	ZTP	ZTS	ZTP	ZTS	DZT
SiO_2	33.83	69.18	67.54	56.14	64.38	67.60	65.82	67.29	68.68	71.69	67.25	62.35	64.37	65.42	70.57	63.18	62.53	67.32	63.67
TiO_2	0.07	0.09	0.13	0.33	0.08	0.17	0.09	0.07	0.09	0.06	0.09	0.06	0.10	0.07	0.17	0.07	0.10	0.06	0.09
Al_2O_3	6.97	11.26	11.82	8.52	11.86	10.76	11.58	10.88	11.81	10.82	11.54	9.03	11.35	10.58	10.46	10.45	11.15	10.24	10.83
Fe_2O_3	1.76	0.47	0.91	2.52	0.95	0.94	0.48	0.47	0.74	0.31	0.60	0.83	0.73	0.38	1.55	0.33	0.99	0.22	0.53
MnO	0.46	0.03	0.03	0.16	0.03	0.03	0.02	0.03	0.01	0.01	0.02	1.46	0.10	0.01	0.12	0.01	0.03	0.01	0.04
MgO	0.58	0.74	0.57	1.28	0.81	0.93	0.64	0.53	0.57	0.32	0.60	0.45	0.50	0.45	0.54	0.45	0.55	0.44	0.43
CaO	26.73	2.46	2.24	12.43	2.94	3.51	3.20	2.18	2.76	1.28	2.94	6.07	3.42	2.34	2.57	2.27	3.20	2.85	2.74
Na_2O	0.98	1.40	2.18	0.65	0.93	0.96	0.86	0.66	1.16	0.50	1.08	0.52	1.31	0.84	1.70	0.73	1.21	1.02	1.48
K_2O	1.30	2.27	3.30	3.08	2.37	2.51	3.00	4.33	3.19	6.54	3.12	3.63	2.98	3.56	2.63	3.52	2.73	2.25	2.68
P_2O_5	0.01	0.00	0.01	0.05	0.01	0.02	0.08	0.02	0.01	0.01	0.02	0.01	0.01	0.13	0.15	0.01	0.01	0.01	0.01
LOI	27.00	10.35	9.75	13.67	13.72	10.69	13.75	11.60	10.21	7.36	11.52	13.91	13.39	15.03	8.77	17.13	15.58	14.45	16.46
Total	99.68	98.26	98.47	98.84	98.06	98.12	99.51	98.05	99.23	98.90	98.77	98.32	98.26	98.80	99.24	98.14	98.08	98.85	98.96
Trace elements in ppm																			
Nb(4)*	14	26	18	8	30	22	29	29	28	30	29	25	25	28	18	32	28	28	24
Zr(7)	43	76	69	69	70	78	70	67	70	70	72	58	71	66	71	68	84	65	67
Y(2)	38	21	16	33	27	54	36	28	40	43	29	80	36	22	38	28	24	25	27
Sr(11)	698	1,051	823	575	1,556	1,285	1,484	1,053	1,273	521	1,412	953	1,282	1,151	748	1,166	1,409	1,497	1,245
Rb(7)	59	137	158	203	197	196	236	277	223	324	233	241	218	259	165	264	221	218	213
Pb(10)	29	34	37	26	50	30	42	29	45	21	43	51	46	24	36	25	48	25	44
Ga(4)	11	17	17	13	22	18	20	19	19	18	19	17	19	19	16	20	20	19	18
Zn(7)	55	27	34	81	41	42	28	32	29	20	27	46	36	24	36	26	47	23	30
Cu(5)	8	8	10	44	14	23	8	10	10	5	8	9	9	9	12	10	11	10	11
Ni(17)	bdl	bdl	bdl	61	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Co(13)	bdl	bdl	18	15	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Ba(13)	1,605	724	1,735	365	215	183	164	85	106	43	96	73	97	59	104	63	108	94	110
Sc(4)	bdl	bdl	4	13	5	5	4	4	bdl	bdl	4	4	5	4	4	bdl	5	7	bdl
Cr(14)	bdl	bdl	bdl	80	bdl	19	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	23	bdl	bdl	bdl	bdl
V(9)	9	bdl	10	85	bdl	20	bdl	bdl	bdl	bdl	bdl	9	9	bdl	24	bdl	13	bdl	bdl

* Detection limit. bdl: below detection limit. DZT, ZTP, ZTS, CCH: for abbreviations see Fig. 4.

Table 3.—**Mineral abundances (semi-quantitative) along the 1T vertical profile of Metaxades main quarry face, determined by XRD**

Sample	Zeolite	Quartz	Cristobalite	Calcite	Plagioclase	Sanidine	Mica + Clays
1T5	17	tr	0	50	12	17	4
1T11	37	5	24	0	7	14	13
1T18	39	8	tr	0	24	22	7
1T23	9	19	5	24	7	0	36
1T34	60	3	10	0	8	8	11
1T41	42	4	11	tr	9	0	34
1T51	66	3	10	0	6	6	9
1T59	55	6	22	0	4	0	13
1T64	59	4	11	0	8	7	11
1T67	34	12	34	0	4	16	0
1T73	61	4	17	0	6	0	12
1T75	44	6	26	9	5	10	0
1T82	46	4	16	tr	9	19	6
1T85	49	5	20	0	5	8	13
1T90	37	7	13	tr	12	11	20
1T95	51	7	31	0	11	0	0
1T98	75	7	0	0	11	7	0
1T101	60	5	28	0	7	0	0
1T109	49	5	9	0	12	10	15

tr=trace; 0=not detected.

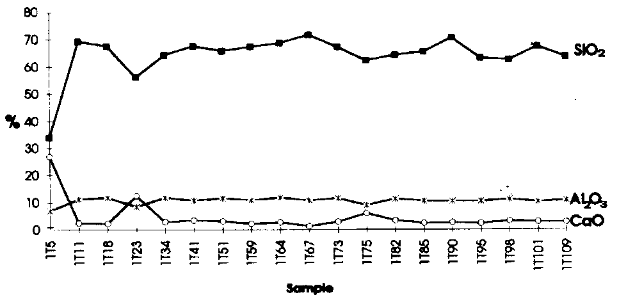

Fig. 5.—The variation of SiO_2, Al_2O_3 and CaO through the 1T vertical profile of Metaxades main quarry face.

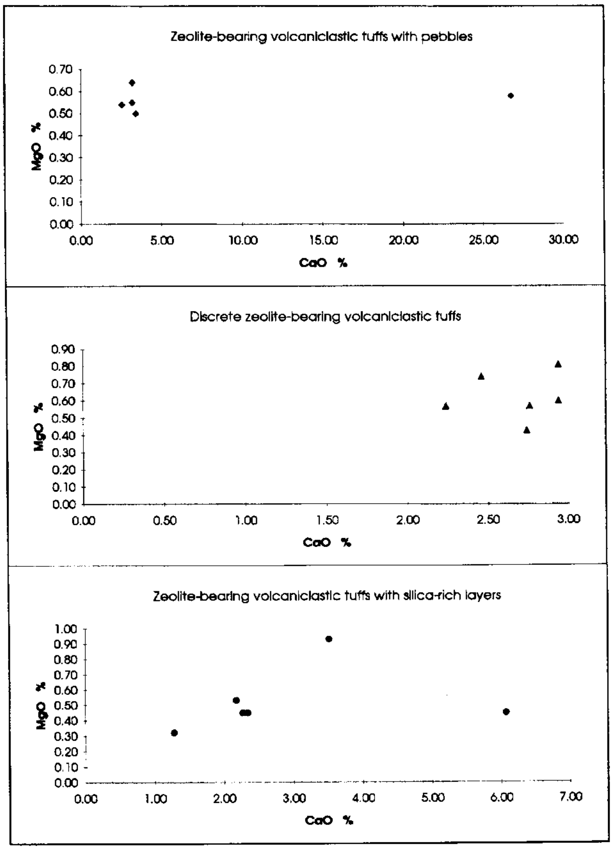

Fig. 6.—MgO vs CaO along the 1T vertical profile of Metaxades main quarry face.

layers in various geologic environments (e. g., Boles and Coombs, 1975; Ogihara and Iijima, 1989, 1990). The zeolite-bearing volcaniclastic sediments of Metaxades are considered to be the alteration products of volcanic material (rhyo-dacitic in composition) in a depositional environment of low salinity (Tsirambides *et al.*, 1993). In their study, Tsirambides *et al.* (1993) concluded that the mineralogical differences they observed among samples taken from the Metaxades area, reflect differences especially in original rock composition and to a less extent in the fluid chemistry. Clinoptilolite was formed largely from the replacement of volcanic glass. Tiny clinoptilolite crystals are abundant as interstitial cement and polycrystalline pseudomorphs of glass shards. Savin *et al.* (1993) concluded from oxygen isotope data that the formation of the diagenetic phases of cristobalite and smectite took place under different temperature conditions, less than 60° C and less than 45° C, respectively. Since both these minerals are closely associated with clinoptilolite, we consider that probably this significant zeolite was formed under such low temperatures.

The massive and/or graded bedding, observed in the lower part of the vertical profile studied, could be attributed to high energy pyroclastic flows which transported on land and deposited in the shallow sea large quantities of clastic material with variable grain size. Probably, the trough cross-bedding, observed mainly in the intermediate part of the profile, is the result of riple marks transport downwards in the Metaxades basin by means of pyroclastic flows. The upper layers of the section, consisted mainly of non-volcanogenic components, were most probably created under quiet sedimentary conditions.

According to the chemical results obtained along the vertical profile, the variations observed for SiO_2, Al_2O_3 and CaO (Table 2) are due mainly to the high contents of calcite (50 % and 24 %) in the top layer of the volcaniclastic tuffs with pebbles (1T5) and in the calc-clayey horizon (1T23) (Table 3). Among major element oxides, a positive correlation was observed between MgO and CaO only in the volcaniclastic tuffs including silica-rich layers (Fig. 6) with the exception of sample 1T75 which contains the highest percentage of calcite (9 %). Furthermore, Sr was found to correlate positively with CaO in the discrete volcaniclastic tuffs and the volcaniclastic tuffs including thin silica-rich layers, with a small deviation of the sample 1T75 (Fig. 7).

A correlation between mineral abundances and element concentrations (Tables 2 and 3) showed that Sr correlates positively only with clinoptilolite (Fig. 8) while it does not show any affinity with calcite. Rb does not show any correlation either with sanidine or clays and clinoptilolite. No correlation was also observed between Ba and sanidine, plagioclase, clinoptilolite or clays. Consequently, the enrichment of Rb and Ba in certain layers could be attributed either to their leaching through the volcaniclastic sequence, or to their varying contents in a certain mineral phase present in the different layers.

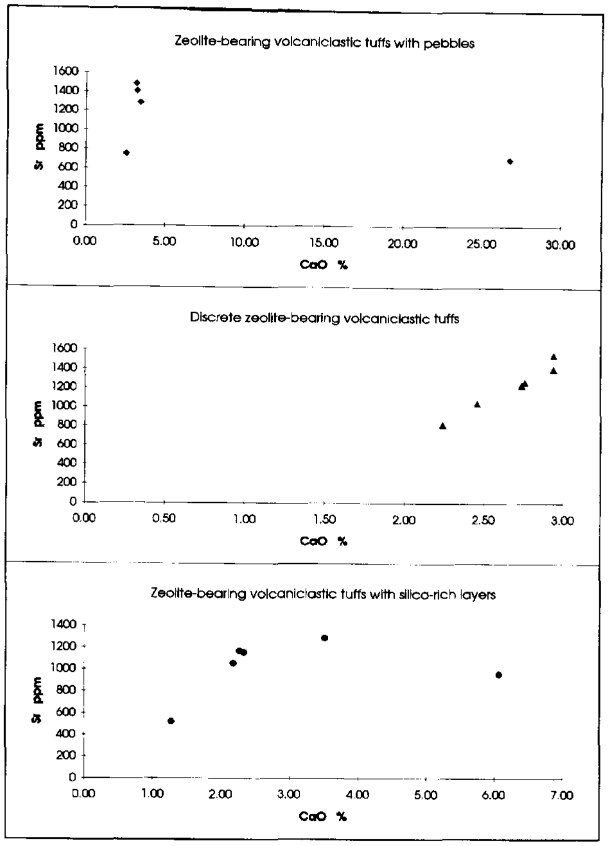

Fig. 7.—Sr vs CaO along the 1T vertical profile of Metaxades main quarry face.

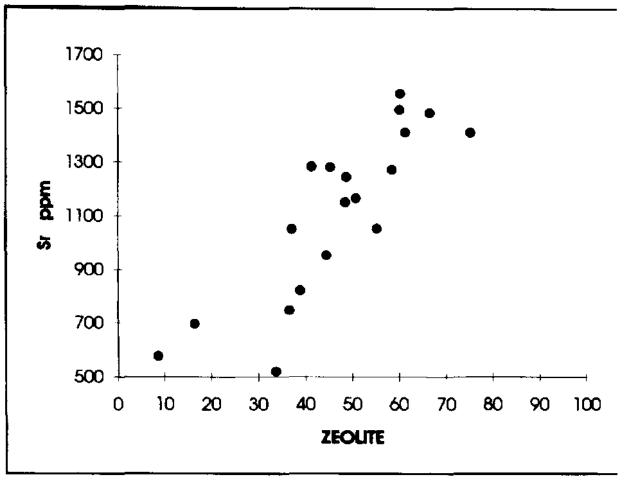

Fig. 8.—Sr vs zeolite abundance along the 1T vertical profile of Metaxades main quarry face.

Among the trace elements with minor concentrations, some of them such as Y, Zn, Cu, Ni, Cr and V, show an enrichment in certain layers and especially in the calc-clayey horizon. This enrichment could possibly be assigned to different mineralogy of this horizon.

In summary, according to the data of the present study, it results that the Ca-rich clinoptilolite-containing volcaniclastic tuffs of Metaxades area, which are considered to be the alteration products of volcanic material in a depositional environment of low salinity (Tsirambides *et al.,* 1993), do not represent a homogeneous sequence but alternate with tuffs including pebbles from the surrounding rocks, tuffs including silica-rich layers, and a calc-clayey horizon. This lithological inhomogeneity is reflected both in the mineralogical composition and well as in the chemistry of the minerals present in the different formations. Furthermore, varying concentrations of certain trace elements in each mineral phase in the different layers as well as leaching processes, seem to be responsible for the enrichment of these elements in certain layers. The zeolite-rich volcaniclastic sediments of Metaxades represent an inhomogeneous sequence of constituents, which were deposited in a shallow marine environment under turbulent to quiet sedimentary conditions.

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