

PRELIMINARY RESULTS ON CLINOPTILOLITE-CONTAINING VOLCANICLASTIC SEDIMENTS FROM METAXADES, NE GREECE

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ABSTRACT

Clinoptilolite-containing volcaniclastic sediments from Metaxades (NE Greece) have been investigated. The powdered samples were subjected to chemical treatments and were separated into different grain-size fractions. Qualitative and quantitative determination of all mineral phases was based on XRD analyses. The dominant size fraction is the 20-2 μm (medium + fine silt) with clinoptilolite being most abundant in the 2-0.2 μm fraction. The minerals present are: Quartz, K-feldspar, plagioclase, mica, clinoptilolite, α - and β - cristobalite, illite, smectite, mixed-layer illite/smectite and carbonates. No heulandite was observed. According to the semi-quantitative method the clinoptilolite content varies from 17 to 41% (average 30%) but with the more reliable method of heavy liquid, the clinoptilolite content varies from 59 to 72% (average 69%). From the geological observations (based on three shafts and one outcrop), our analytical data and the assumption of continuity of the layers between the three shafts and the outcrop, the estimated geological inferred reserves of clinoptilolite are at least 10 million tons. Much more has to be done to establish if we have proved or measured reserves, before we start thinking about exploitation of the clinoptilolite in these volcaniclastic sediments.

ΣΥΝΟΨΗ

Ερευνήθηκαν κλινοπτιλολιθοφόρα ηφαιστειοκλαστικά ιζήματα από τους Μεταξάδες (ΒΑ Ελλάδα). Το περιεχόμενο σε κλινοπτιλόλιθο παρουσιάζει μέση τιμή 30% με την ημιποσοτική μέθοδο και 69% με τη μέθοδο βαρέων διαλυμάτων. Οι ορυκτές φάσεις είναι χαλασίτης, κλινοπτιλόλιθος, κρυσταλίτης, κρυσταλίτης, α - και β -χριστοβαλίτης, ιλλίτης/σμεκτίτης, μικτός ιλλίτης/σμεκτίτης και ανθρακικές ενώσεις. Δεν παρατηρήθηκε ηουλανδίτης. Τα εκτιμώμενα γεωλογικά δυνατά αποθέματα κλινοπτιλόλιθου είναι τουλάχιστο 10 εκατομμύρια τόνου. Για τον προσδιορισμό των βέβαιων αποθεμάτων απαιτούνται επιπλέον ερευνητικές εργασίες.

1. INTRODUCTION

In recent years considerable deposits of zeolite-bearing sedimentary rocks have been reported in various parts of the world. More and more attention has been paid to this specific group of minerals because of their large field of industrial and agricultural application (Sand and Mumpton, 1978; Gottardi and Galli, 1985).

Zeolites occur in rocks of many types and in a wide variety of geological environments. Clinoptilolite has proved to be one of the main zeolites in many sediments. The formation of clinoptilolite in a saline, alkaline lake (clo-

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Προκαταρκτικά αποτελέσματα σε κλινοπτιλολιθοφόρα ηφαιστειοκλαστικά ιζήματα των Μεταξάδων, ΒΑ Ελλάδα.
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sed hydrological system) is very usual. It can be formed in hydrologic open systems by the percolation of meteoric water in tuffs and tuffaceous sediments. It may also be formed by the processes of burial diagenesis or metamorphism of sediments containing volcanic debris. Deep sea occurrences as alteration product of terrestrial or submarine volcanic sediments are quite common (Sand and Mumpton, 1978; Gottardi and Galli, 1985).

Zeolitic sedimentary rocks show a widespread distribution in the Rhodope Massif, covering several hundred square kilometers (Aleksiev and Djourova, 1975, 1977, 1986; Kosiaris et al., 1987; Skarpelis and Marantos, 1987). They are of an Oligocene age and were formed by alteration of pyroclastic volcanic glass under marine conditions. This paper reports on clinoptilolite-containing volcanoclastic sediments in southeastern Rhodope, in Greek territory.

2. GEOLOGIC SETTING

The general area in which the zeoliferous volcanoclastic sediments occur belongs geotectonically to the Rhodope Massif (Dimitrov, 1959; Kronberg et al., 1970) which is mainly composed of metamorphic rocks. More exactly the studied area is located near the Greek-Bulgarian border at the southern side of an elongated molassic basin of Oligocene age which extends into Bulgaria (Fig. 1).

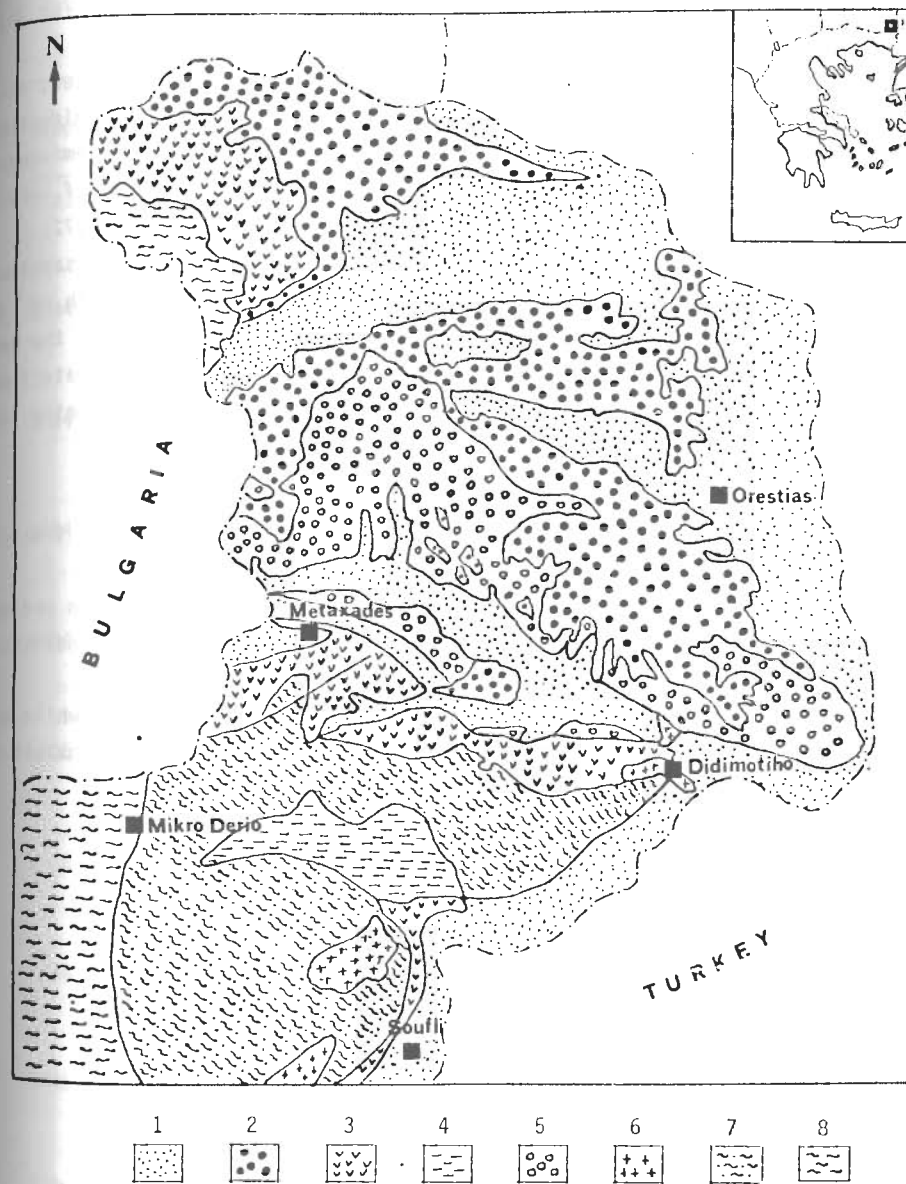
The zeolitic sediments are connected with an acidic (rhyolitic-dacitic) pyroclastic volcanism of the Upper Eocene - Lower Oligocene.

The altered volcanoclastic sediments of Metaxades are generally white to pale gray with shades of yellow, brown, pink or green with a dull or earthy luster. The volcanoclastic sediments present conchoidal fracture and generally resemble well-sorted siltstones to the unaided eye. Clinoptilolite occurs mainly as lath-shaped crystals of different size.

3. ANALYTICAL TECHNIQUES

Nine samples were ground in a mechanic tungsten mortar to reduce grain size and to homogenize them. Ten grams of each powdered sample were subjected to the following chemical treatments (Jackson, 1974) to remove the non-silicate phases; 1N sodium acetate buffer solution (pH = 5) for carbonate removal; 30% H₂O₂ for organic matter and Mn-oxides removal; and a 1M NaHCO₃ - 0.3M Na-citrate solution, with periodic addition of 1g increments (up to 3g) of Na₂S₂O₄ during digestion in a water-bath at 75-80°C (removal of free Fe-oxides and interlayer Fe and Al hydroxides).

The residues were separated into four size fractions by gravity or centrifugation and stored in an oven overnight at about 100°C. Subsequently, oriented mounts on glass slides of each size fraction were prepared for mineralogical



Σχ. 1. Πετρογραφικό σκαρίφημα της περιοχής Μεταξάδων, ΒΑ Ελλάδα.

Fig.1. Petrographic sketch map of the Metaxades area, NE Greece (from Bornovas and Rondogianni-Tsiambaou, I.G.M.E., 1983).

1. Holocene (alluvium) deposits, 2. Plio-Pleistocene sediments,
3. Eocene molassic formations, 4. Eocene-Oligocene molassic formations,
5. Oligocene molassic formations, 6. Diabases-Serpentinites,
7. Schistes, 8. Amphibolites. Scale 1:350,000.

analysis by X-ray diffraction techniques. Glycolated, heated (at 550°C for 2h) and randomly oriented samples were also examined.

X-ray diffraction traces were taken with a Philips diffractometer, Ni-filtered CuK α radiation, using fluorite as internal standard. The scanning speed was 1/1° per minute over the interval 2 - 40° of 2 θ . Qualitative and semi-quantitative determination of all mineral phases was based on the methods of Schultz (1964), Perry and Hower (1970), Reynolds and Hower (1970) and Boles (1972).

For quantitative purposes an alternative method was used. Three samples were well grinded and 20g of eachone were treated by a heavy liquid with sp. g. = 2.3 (tetrabrom-aethan: sp. g. = 2.96 plus ethanol: sp. g. = 0.79). Thus, the heavier mineral phases (i.e. quartz, feldspars, phyllosilicates and carbonates) were separated from the zeolite present (sp. g. = 2.0-2.2). X-ray diffractometry insured the reliability of the method.

4. GRAIN SIZE DISTRIBUTION

Grain size distributions of the analysed samples after chemical treatments are given in Table 1. From these data it is apparent that:

The average amount of the sum carbonates + organic matter + iron and manganese oxides (COI) in the zeoliferous samples is low (less than 14%) indicating an environment of high-Eh (Degens, 1967).

The dominant size fraction is the 20-2 μ m (medium + fine silt) while the finer fraction (less than 0.2 μ m) consists less than 10% of the total (except in sample 2/86).

Table 1. Grain size distribution of the analysed samples of the clinoptilolite-containing volcanoclastic sediments, Metaxades, NE Greece.

Sample	Weight* (g)	COI (%)	Silicates (%)	Grain size (μ m)			
				>20 (%)	20-2 (%)	2-0.2 (%)	<0.2 (%)
1/83	8.6	14	86	17.4	46.6	26.7	9.3
1/84	6.6	34	66	56.1	24.2	13.6	6.1
2/84	9.5	5	95	33.7	41.1	18.9	6.3
3/84	9.4	6	94	25.5	44.7	23.4	6.4
4/84	9.3	7	93	23.6	48.4	21.5	6.5
1/85	9.6	4	96	22.9	44.8	22.9	9.4
1/86	8.8	12	88	72.7	17.0	8.0	2.3
2/86	9.5	5	95	22.1	32.6	13.7	31.6
5/86	9.6	4	96	17.7	47.9	27.1	7.3

*After chemical treatments.

COI = Carbonates + Organics + Iron and Manganese oxides.

Table 2. Semi-quantitative mineralogical analysis of the clinoptilolite-containing volcanoclastic sediments, Metaxades, NE Greece.

Sample	Fraction (μ m)	Q (%)	Ksp (%)	Pl (%)	M (%)	Cpt (%)	α -Cr (%)	β -Cr (%)	I (%)	I+I/S (%)	I/S (%)	S (%)
1/83	>20	19	8	12	-	23	38	-	-	-	-	-
	20-2	19	9	8	-	23	41	-	-	-	-	-
	2-0.2	23	14	19	-	16	28	-	-	-	-	-
	<0.2	-	-	-	-	13	87	-	-	-	-	tr
1/84	>20	57	tr	15	-	-	4	24	-	-	-	-
	20-2	55	tr	22	18	-	5	-	-	-	-	-
	2-0.2	62	-	16	-	-	-	-	-	22	-	-
	<0.2	4	-	-	-	-	-	-	9	-	87	-
2/84	>20	53	18	19	-	tr	5	5	-	-	-	-
	20-2	16	20	19	-	24	8	13	-	-	-	-
	2-0.2	4	-	4	-	84	4	4	-	-	-	-
	<0.2	-	-	-	-	45	-	-	-	-	-	55
3/84	>20	8	6	33	-	25	28	-	-	-	-	-
	20-2	11	5	13	-	36	35	-	-	-	-	-
	2-0.2	20	10	6	-	30	34	-	-	-	-	-
	<0.2	-	-	-	-	13	70	-	-	-	-	17
4/84	>20	42	12	22	tr	11	13	tr	-	-	-	-
	20-2	19	9	15	-	29	23	5	-	-	-	-
	2-0.2	5	tr	3	-	76	13	3	-	-	-	-
	<0.2	-	-	-	-	38	34	-	-	-	-	28
1/85	>20	45	9	25	-	10	11	-	-	-	-	-
	20-2	17	6	18	-	37	18	4	-	-	-	-
	2-0.2	7	-	3	-	90	tr	-	-	-	-	tr
	<0.2	-	-	-	-	23	6	-	-	-	-	71
1/86	>20	47	16	19	13	-	5	-	-	-	-	-
	20-2	46	18	22	11	-	3	-	-	-	-	-
	2-0.2	45	-	45	-	-	-	-	-	10	-	-
	<0.2	8	-	-	-	-	-	-	13	-	79	-
2/86	>20	11	17	46	-	22	4	tr	-	-	-	-
	20-2	12	7	13	-	41	19	8	-	-	-	-
	2-0.2	4	-	5	-	68	18	-	-	5	-	-
	<0.2	-	-	-	-	3	3	-	-	-	-	94
5/86	>20	22	17	15	-	10	12	24	-	-	-	-
	20-2	20	12	13	-	26	19	10	-	-	-	-
	2-0.2	14	7	5	-	59	15	-	-	-	-	-
	<0.2	5	-	tr	-	33	23	-	-	-	-	39

Q = quartz, Ksp = potassium feldspar, Pl = plagioclase, M = mica, Cpt = clinoptilolite, α -Cr = α -cristobalite, β -Cr = β -cristobalite, I = illite, I/S = mixed-layer illite/smectite, S = smectite, tr = trace (<3 %).

5. MINERALOGICAL RESULTS

Mineralogical results taken from X-ray diffraction analyses are given in Tables 2, 3 and 4.

The minerals present according to the semi-quantitative method are: Quartz, K-feldspar, plagioclase, mica, clinoptilolite, α - and β -cristobalite, illite, smectite and mixed-layer illite/smectite. No heulandite, which is the Ca-rich member of the group seven ($T_{10}O_{20}$ unit), was observed. The technique of Boles (1972) was used for distinction of clinoptilolite from heulandite.

Table 3. Average distribution of the minerals (%) of the clinoptilolite-containing volcanoclastic sediments, (free of CO₂, see table 1), Metaxades, NE Greece.

Sample	Q	Ksp	Pl	M	Cpt	α -Cr	β -Cr	I	I+I/S	I/S	S
1/83	18	9	11	-	20	2	-	-	-	-	tr
1/84	54	tr	16	5	-	3	14	tr	3	5	-
2/84	25	14	15	-	29	6	8	-	-	-	3
3/84	12	6	16	-	31	35	-	-	-	-	tr
4/84	21	7	13	tr	36	20	3	-	-	-	tr
1/85	20	5	15	-	42	11	tr	-	-	-	7
1/86	47	15	22	12	-	4	-	tr	tr	tr	-
2/86	7	6	15	-	29	10	3	-	tr	-	30
5/86	17	11	10	-	33	17	9	-	-	-	3

Q = quartz, Ksp = potassium feldspar, Pl = plagioclase, M = mica, Cpt = clinoptilolite, α -Cr = α -cristobalite, β -Cr = β -cristobalite, I = illite, I/S = mixed-layer illite/smectite, S = smectite, tr = trace (<3 %).

The clinoptilolite is most abundant in the 2-0.2 μ m fraction with the highest value (90%) shown in sample 1/85 (Table 2). The β -cristobalite is abundant in the two coarsest fractions, being completely absent from the finest (less than 0.2 μ m) fraction. Most of the smectite is present as a separate phase and appears mainly in the finest fraction with the highest value (94%) in sample 2/86 (Table 2). The clay minerals are appearing only in the two finest fractions.

According to the semi-quantitative method the clinoptilolite content in the zeoliferous samples varies from 17 to 41% (average 30%, Tables 1&3). It is important to note that with the more reliable method of heavy liquid, the clinoptilolite content in the zeoliferous samples is much higher, varying from 66 to 72% (average 69%, see Table 4).

The semi-quantitative method is more applicable to clay minerals and the-

Table 4. Clinoptilolite content in the volcanoclastic sediments, Metaxades, NE Greece. Heavy liquid method.

Sample	Q + Ksp + Pl + Cr + M + Clays + C		Cpt	
	g	%	g	%
4/84	6.1	30	13.9	70
1/85	6.7	34	13.3	66
3/86	5.5	28	14.5	72

Q = quartz, Ksp = potassium feldspar, Pl = plagioclase, Cr = cristobalite, M = mica, Clays = illite + mixed layer illite/smectite + smectite, C = carbonates, Cpt = clinoptilolite.

therefore we believe that the heavy liquid method is more reliable for the examined zeolitic sediments.

6. INFERRED RESERVES

The geological observations are based on three shafts and one outcrop in the investigated area (Figs. 2, 3 and 4). The shafts have the following dimensions (length/depth): Shaft A = 430m/15m, shaft B = 55m/10m and shaft C = ~500m/~15m.

Thirteen samples have been selected from two shafts (Fig. 4), nine of them have been treated chemically and three of them with heavy liquid. X-ray diffraction analyses were performed to estimate the total amount of clinoptilolite in the samples. From the geological observations and the analytical data the total thickness of the layers containing clinoptilolite is estimated to be about 7m with average content of this zeolite 30% (with the semi-quantitative method, Tables 1&3) and 69% (with the heavy liquid method, see Table 4). Assuming continuity of the layers between the three shafts and the outcrop, the estimated geological inferred reserves of clinoptilolite in the volcanoclastic sediments of Metaxades are at least 10 million tons.

There is a great confusion about the definition of concepts such as "reserves", "resources", "mineral endowments" and "mineral potential". Geological surveys, bureaux of mines, development sectors and even policy-makers in different countries adopt different classification systems and degrees of certainty about the economic feasibility of exploiting the minerals (Van Rensburg and Bambrick, 1978). Therefore a word of warning should be sounded about exploitation in the investigated area. Much more has to be done, e.g. we need drill holes, detailed sampling and measurements and by far greater number of analyses to estab-

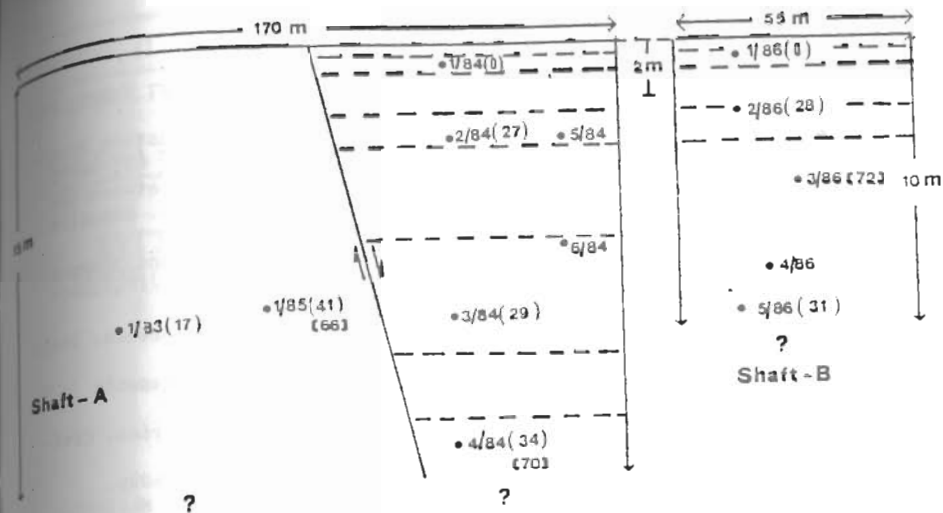


Σχ. 2. Κεντρικό τμήμα τριανσέρας Α, Μεταξάδες, ΒΑ Ελλάδα.
Fig.2. Central part of shaft A, Metaxades, NE Greece.



Σχ. 3. Ζεολιθοφόρα στρώματα τριανσέρας Α (λεπτομέρεια Σχ.2).
Fig.3. Zeoliferous layers of shaft A (detail of Fig.2).

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Σχ. 4. Σχηματική απεικόνιση της θέσης των δειγμάτων σε δύο τριανσέρες (Α και Β), Μεταξάδες, ΒΑ Ελλάδα. (41) = μέση σύσταση (%) σε κλινοκτιλόλιθο με την ημιποσοτική μέθοδο, [66] = μέση σύσταση (%) σε κλινοκτιλόλιθο με τη μέθοδο βαρέων διαλυμάτων.

Fig. 4. Schematic presentation of the sample position in two shafts (A and B), Metaxades, NE Greece. (41) = average composition (%) in clinoptilolite with the semi-quantitative method, [66] = average composition (%) in clinoptilolite with the heavy liquid method.

Wish if we have "proved" or "measured" reserves in the area, before we start thinking about exploitation of the clinoptilolite in these volcanoclastic sediments.

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