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ΓΕΩΛΟΓΙΑ. – **The Mineralogy and Geochemistry of Bentonites of the north —east Milos, Aegean Sea, Greece,** *by A. E. Kelepertsis**, διὰ τοῦ Ἀκαδημαϊκοῦ κ. Λουκᾶ Μουσούλου.

ABSTRACT

Fifteen bentonite samples from the NE part of Milos island were analysed to investigate their mineralogy, geochemistry and origin. The mineralogical assemblage of the samples includes montmorillonite, as the main clay mineral, chlorite, and quartz, cristobalite, pyrite, siderite, as secondary accessory minerals.

Field observations, mineralogical and chemical data, suggest that the Milos bentonites were formed by hydrothermal alteration caused as the result of interaction between andesitic-dacitic rocks and circulating heated seawater.

INTRODUCTION

On the island of Milos (Fig. 1) there are many deposits of industrial minerals and a few small occurrences of sulfide-sulfate deposits. Kaolinite and bentonites are the most important between the industrial minerals, and occur in several parts of Milos. All these deposits are very young (Pliocene-Pleistocene) connected with volcanic rocks in an active volcanic arc, the South Aegean volcanic arc (Keller, 1982, Innocenti et al., 1981).

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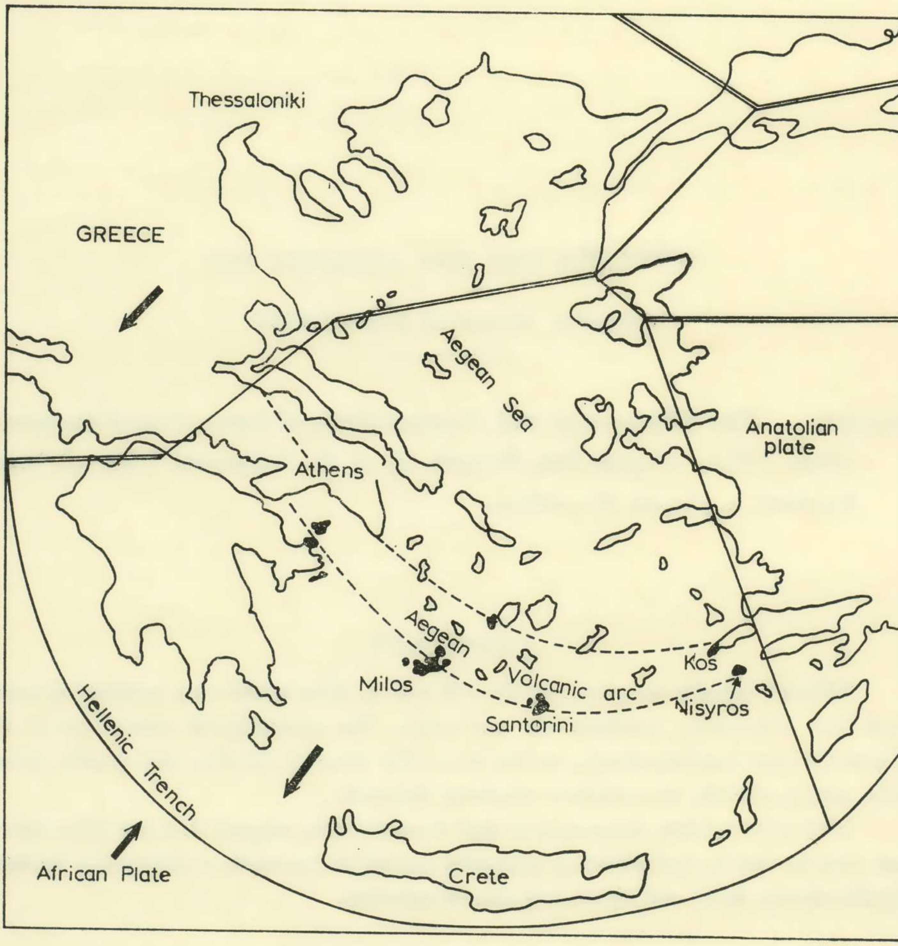

Fig. 1. Map of Greece showing the present Aegean tectonics and the occurrence of Plio-Pleistocene volcanics (Mc Kenzie 1978, Keller 1982).

In the present paper, samples of bentonites from six (6) active quarries were studied for their mineral identification and as well as for their major element contents. An attempt also was made to interpret the origin of the bentonites.

GEOLOGICAL SETTING

The island of Milos as well the neighbouring islands of Kimolos, Poliegos and Antimilos are known for their kaolin and bentonite deposits, most of which are under active exploitation.

This group of islands belong to the South Aegean volcanic arc (Fig. 1) which is characterized by recent volcanism showing a solfataric activity, while the islands of Nisyros and Santorini belonging to the same arc are at present volcanogenetically active.

The geological structure of Milos consists of mainly Pliocene-Pleistocene volcanic rocks. Metamorphic rocks and Neogene deposits appear sporadically only in the southern part of Milos. Figure 2, is a map of Milos showing the geology and the investigated bentonite occurrences. The volcanics of the island belong to a calc-alcaline suite and range from basalts to thyolite with a predominance of andesites and dacites. Most authors (Keller, 1982, Barton et al., 1983) believe in a mantle derived parental magma with contamination by continental crust. Some ignimbrites belong to the early stage of volcanism, which was followed by the extrusion of andesitic and dacitic lava flows and domes. During the last stage pyroclastics and rhyolitic lavas were formed of 0.48 m.y. age (Fytikas et al., 1976). The final volcanic stage was followed by phreatomagmatic eruptions and solfataric activities.

The bentonites studied are connected with the alteration of andesitic and dacitic lavas as well as pyroclastic flows consisting of andesitic-dacitic lava fragements. In the same area near the bentonite deposits there are large barite bodies (Picridou and Kastanas mines). According to Hauck (1984) the top zones of the barite bodies are overlaying by silicified tuffs, while kaolinitic zones form the footwall.

ANALYTICAL METHODS

Sample collection and preparation.

Fifteen samples were collected from six bentonite mines at the area of Aspro Chorio and Kavos of NE Milos (Fig. 3). The samples were taken along

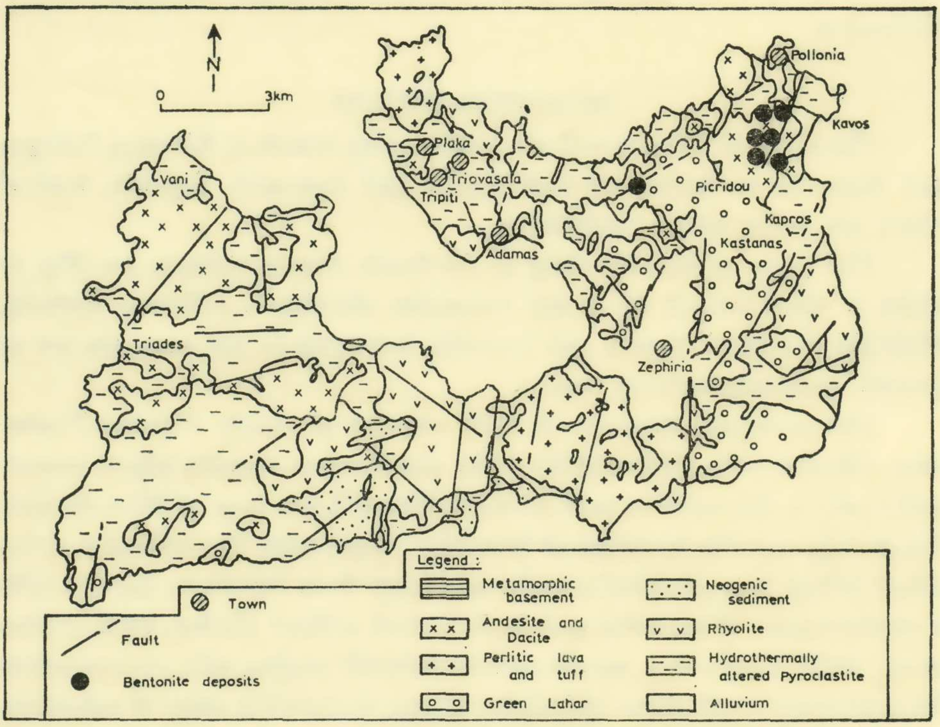

Fig. 2. Map of Milos island showing the geology and the locations of samples studied (Fyticas 1976, Hauck 1984).

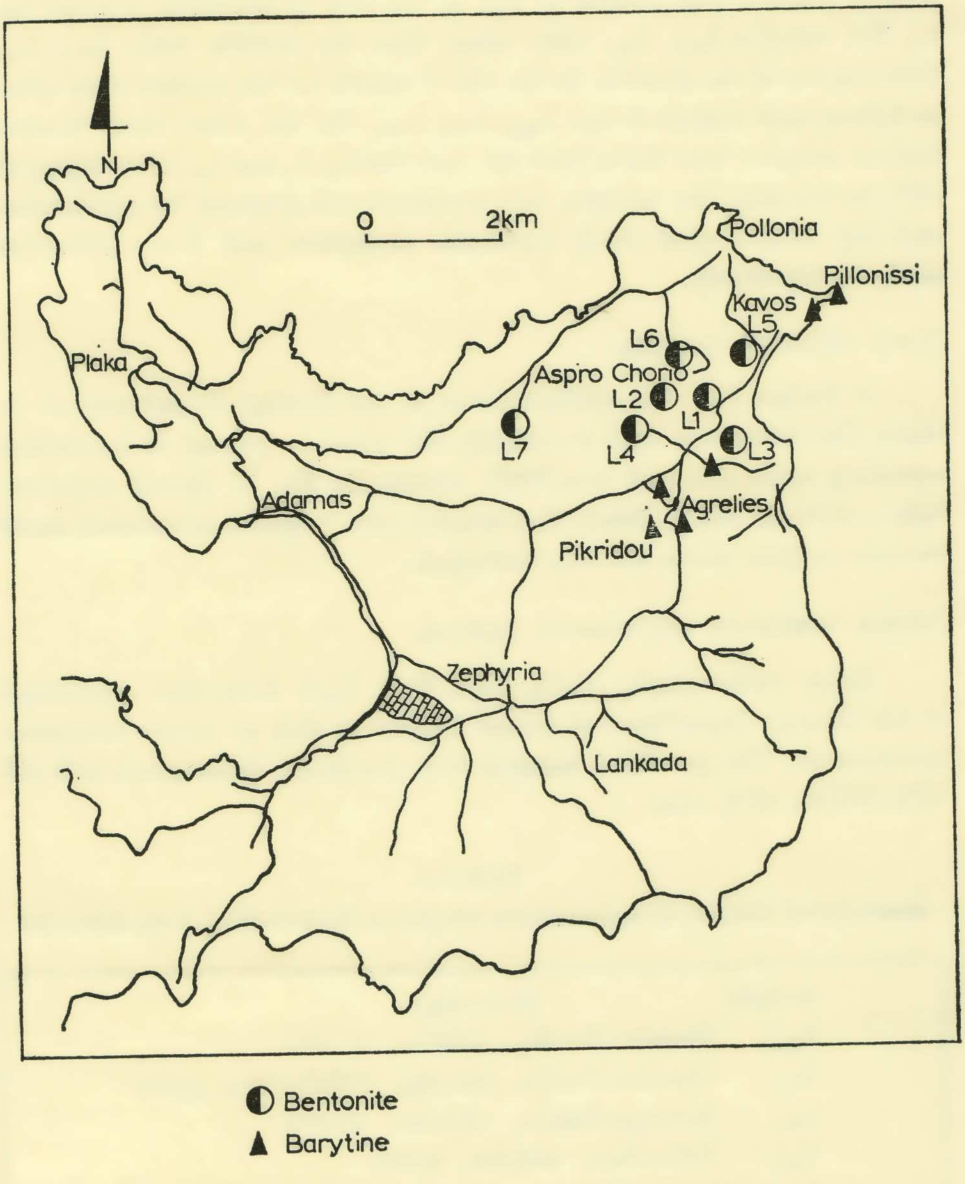

Fig. 3. Map of eastern Milos showing the locations of bentonites studied.

vertical sections from bottom to top, in the sites of bentonite quarries L_1, L_7. The samples L_{1-1}, L_{7-1} were taken from the bottom while L_{1-3}, L_{7-3} from the top of the quarries. In the site of quarry Lσ the samples were taken as follows from bottom to top: L_{6-3}, L_{6-2}, L_{6-1}. On the other hand, random surface samples were taken from the quarries L_4, L_3 and L_2. After drying at 30°C for 2-3 days, the samples were powdered and prepared for geochemical and clay mineralogical study by atomic absorption and X-ray diffraction analysis respectively.

X-ray diffraction analysis.

A Philips PW 1010 diffractometer at the Geology Department of Athens University was used to identify the minerals present in bentonites, operating under standard conditions, namely Cu Ka, Ni filtered radiation; tube conditions 36KV, 24mA. The samples were prepared as air-dried smear mounts on glass plates and run untreated.

Atomic absorption spectrometer analysis.

Major oxides (Al_2O_3, Fe_2O_3, MgO, CaO, $N_{a2}O$, K_2O) were determined at the Geology Department of Athens University with an atomic absorption spectrometer. The powdered samples were previously decomposed with HF 40%/$HCLO_4$ 60% acid.

TABLE 1

Mineralogical analyses of representative samples as determined by-X-ray diffraction

Sample	Mineralogy
L_{1-3}	Montmorillonite, chlorite, quartz
L_{2-1}	Montmorillonite, chlorite, cristobalirte, pyrite
L_{2-2}	Montmorillonite, chloiite, quartz
L_{3-1}	Orthoclase, siderite, pyrite
L_{4-3}	Montmorillonite, chlorite, quartz, siderite
L_{6-1}	Montmorillonite quartz

MINERALOGY

Table 1 shows that all the samples analysed consist of the clay mineral montmorillonite. On the other hand, the sample L_3-$_1$ consists of a different

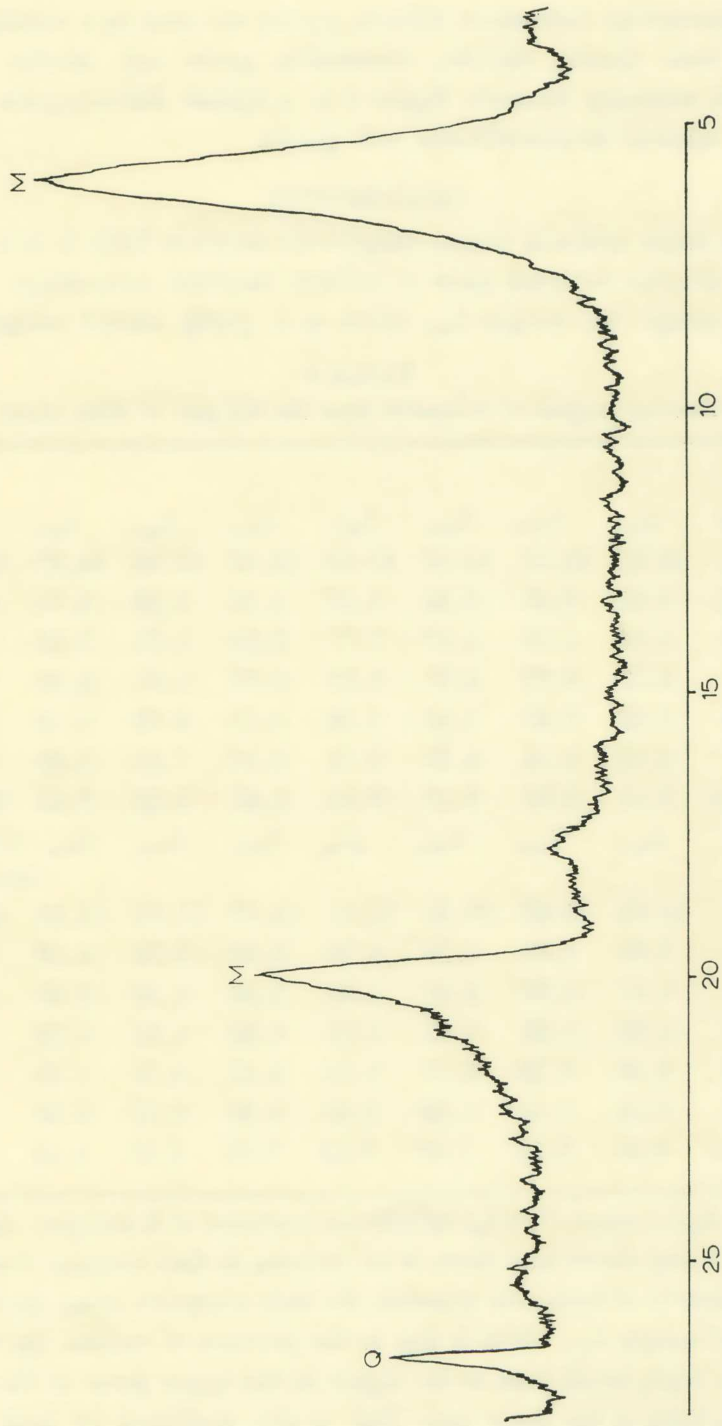

Fig. 4. Whole-rock XRD traces of sample L_{1-3} bentonite (M=montmorillonite, Q=quartz).

mineral assemblage (orthoclase, siderite, pyrite) and may be a weakly altered volcanic rock. Quartz, chlorite, cristobalite, pyrite and siderite are also present as accessory minerals. Figure 4 is a typical diffractogram showing the clay mineral montmorillonite and quartz.

GEOCHEMISTRY

The major oxides in various samples are shown in Table 2. It is obvious that all samples analysed show a uniform chemical composition approximatelly, except the sample L_{3-1} which is a partly altered volcanic rock.

TABLE 2

Chemical analyses of bentonites from the NE part of Milos island

oxide sample	L_{1-1}	L_{1-2}	L_{1-3}	L_{2-1}	L_{2-2}	L_{3-1}	L_{4-2}	L_{4-3}
Al_2O_3	12.83	13.57	14.17	15.10	14.47	16.65	14.95	13.81
Fe_2O_3	4.69	6.75	6.23	4.58	4.24	3.36	4.50	6.23
MgO	1.58	3.05	3.18	2.87	2.90	1.91	2.52	2.60
CaO	2.29	0.99	0.88	0.85	0.67	1.61	0.39	0.48
Na_2O	0.66	0.67	0.58	0.36	0.16	0.62	0.16	0.42
K_2O	0.52	0.31	0.25	0.71	0.39	7.81	0.60	0.34
H_2O+	7.41	8.83	9.19	9.14	8.61	5.82	9.41	10.90
	L_{4-4}	L_{6-1}	L_{6-2}	$_6L_{-3}$	L_{7-1}	L_{7-2}	L_{7-3}	Average bentonite
Al_2O_3	14.64	15.02	15.30	14.11	13.59	13.93	14.19	14.26
Fe_2O_3	4.90	3.85	4.20	4.20	5.06	5.20	4.19	4.91
MgO	1.81	3.96	3.10	3.91	3.56	3.30	2.55	2.92
CaO	0.60	1.26	1.13	1.05	1.33	1.13	4.09	1.37
Na_2O	0.36	0.78	0.67	0.84	0.67	0.80	1.35	0.60
K_2O	0.34	0.14	1.06	0.60	0.90	0.37	0.26	0.48
H_2O+	9.95	9.93	7.39	9.32	8.84	8.88	6.41	9.50

The high K_2O content (7.81%) reflects the existence of K-feldspar. Inspection of Table 2 also shows that there is an increase in CaO contents from top to deeper horizons of bentonite quarries, the only exception being the high CaO content of sample L_{7-3} which is due to the presence of calcite. On the other hand, the Al_2O_3 levels tend to be higher at the upper parts of the quarries L_1, L_7, L_6 than in the lower ones. This is also confirmed by field observations which revealed that kaolinitic zones form the top horizons of bentonite formations. The above data suggest that there was a vertical change in the physicochemical conditions of the fluids which caused the alteration of andesitic and dacitic lavas.

ORIGIN OF BENTONITES

It is known from previous studies that there is a high enthalpy geothermal field on Milos island (Fyticas and Marinelli 1976). The heat flow was responsible for intense hydrothermal activity which caused widespread bentonization and alunitization, kaolitization and the formation of various hydrothermal mineral deposits (bentonite, kaolinite, sulphur, barite, galena, alunite and manganese oxides), according to studies of Hauck (1988) and Kelepertsis (1989). Fumaroles (up to 102°C), submarine gas leakage (>50°C), thermal springs (up to 75°C) and hot grounds (up to 100° C) are some present surface thermal manifestations. The physicochemical conditions at these sites of the surface thermal manifestations are favorable for the formation of recent minerals such as alunogen, alunite, natroalunite, gypsum, sulphur, quartz, cristobalite and kaolinite (Kelepertsis, 1989). Alunite, natroalunite, quartz, cristobalite and kaolinite form the important kaolin deposits encountered on Milos island. Based on the observed vertical zoning of clay minerals at the sites of bentonite quarries as well as the chemical data it is proposed that the bentonites were formed by the alteration of volcanic rocks at depth, under alkaline conditions. This conclusion was also supported by Hauck (1988) who based on chemical data (sulfur isotope ratios and geochemical compositions of sulfide and sulfate deposits) proposed a metallogenic model of continous interaction between andesitic tuffs and circulating seawater heated to a temperature of about 260° C at a relatively shallow depth.

CONCLUSION

The results of the bentonite study of NE Milos are the following:

(a) montmorillonite is the main mineral present, while chlorite, quartz, cristobalite, pyrite and siderite occur as accessory minerals

(b) the chemical data showed that there is an increase of CaO and K_2O contents from the top to the deeper parts of bentonite quarries. On the other hand, Al_2O_3 contents are higher in the upper parts than in the lower parts of the quarries. These vertical variations of CaO, K_2O and Al_2O_3 are well correlated with mineralogical variations of montmorillonite, and kaolinite

(c) field observations in combination with mineralogical and chemical data of bentonites suggest that there was a vertical change in the physico-chemical conditions of the fluids which caused the alteration of andesitic and dacitic lavas and the formation of bentonite at depth and kaolin at top above the bentonite.

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ΠΕΡΙΛΗΨΗ

Ὀρυκτολογική καὶ Γεωχημική ἔρευνα μπεντονιτῶν τῆς Βορειοανατολικῆς Μήλου.

Στὴ μελέτη αὐτὴ ἀναλύθηκαν δέκα πέντε δείγματα πλούσια σὲ μοντμοριλλονίτη ἀπὸ τὸ βορειοανατολικὸ τμῆμα τῆς νήσου Μήλου μὲ σκοπὸ τὴν ὀρυκτολογική, γεωχημικὴ σύσταση καὶ τὴν προέλευση τῶν μπεντονιτῶν. Ἡ ὀρυκτολογικὴ παραγένεση περιλαμβάνει μοντμοριλλονίτη σὰν τὸ ἀργιλικὸ ὀρυκτὸ καὶ χαλαζία, χλωρίτη χριστοβαλίτη, σιδηροπυρίτη, σιδηρίτη σὰν τὰ δευτερογενῆ παραπληρωματικὰ ὀρυκτά. Τὰ χημικὰ δεδομένα τῶν μπεντονιτῶν ἔδειξαν ὅτι ὑπάρχει μιὰ αὔξηση τῶν περιεχομένων CaO καὶ K_2O ἀπὸ τὴν κορυφὴ πρὸς τὰ βαθύτερα μέρη τῶν λατομείων μπεντονίτη. Ἀντίθετα, τὰ περιεχόμενα Al_2O_3 εἶναι ὑψηλότερα στὰ ἀνώτερα μέρη ἀπὸ ὅ,τι στὰ χαμηλότερα μέρη τῶν λατομείων. Οἱ κατακόρυφες αὐτὲς διακυμάνσεις τοῦ CaO, K_2O καὶ Al_2O_3 συσχετίζονται καλὰ μὲ ὀρυκτολογικὲς διακυμάνσεις ὅπως τοῦ μοντμοριλλονίτη καὶ καολινίτη. Ἐπὶ τῇ βάσει ὑπαίθριων παρατηρήσεων, ὀρυκτολογικῶν καὶ χημικῶν δεδομένων προκύπτει τὸ συμπέρασμα ὅτι οἱ μπεντονίτες τῆς Μήλου σχηματίστηκαν ἀπὸ τὴν ὑδροθερμικὴ ἐξαλλοίωση ἀνδεσιτικῶν καὶ δακιτικῶν πετρωμάτων. Ἡ ἐξαλλοίωση αὐτὴ προέκυψε ἀπὸ τὴν ἀλληλοαντίδραση ἀνδεσιτικῶν-δακιτικῶν πετρωμάτων καὶ θερμοῦ θαλάσσιου νεροῦ, κάτω ἀπὸ συνθῆκες ἀλκαλικὲς σὲ σχετικὰ χαμηλὸ βάθος.