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DIAGENESIS AND OIL-GENERATING POTENTIAL OF MIOCENE SEDIMENTS FROM NESTOS DELTA

By
A. TSIRAMBIDES and K. SOLDATOS
Lab. of Mineralogy and Petrology, University of Thessaloniki

Abstract: *Detailed mineralogical investigation is made of Miocene argillaceous sediments taken from onshore drilling cores in Nestos River delta in order to estimate their degree of diagenesis and their oil-generating potential.*

The 20-5, 5-2, 2-0.2 and < 0.2 μm fractions from the 1780 to 3550 meter stratigraphic interval of two wells were analysed. Some mineralogical changes with depth are detectable. The most abundant mixed-layer illite/smectite undergoes a conversion from 10 to about 80% illite layers over this interval. Over the same interval, discrete illite increases from 15 to about 40%, while kaolinite (± little chlorite) decreases from 50 to 5%. The 1M plus $1M_d$ illite polymorphs predominate.

The diagenesis stage may be characterized as early.

The temperatures to which all the examined sediments have been subjected are low (65° to 109° C). Therefore, the dehydration of their mixed-layer clays is low. The low hydrocarbon content of Nestos delta deep sediments is due to the limited presence of fine clastic sediments and to the oil migration to adjacent rocks, because of the intense tectonic activity in the studied area during Neogene and Quaternary.

INTRODUCTION

The diagenesis of argillaceous sediments has been a subject of considerable interest during the past few decades because it might provide an explanation for:

a. The mineralogical differences between ancient and recent sediments (WEAVER, 1959, DUNOYER, 1970, PERRY & HOWER, 1970).

b. The potential of fine grained rocks as sources of gaseous and fluid hydrocarbons (POWERS, 1967, BURST, 1969, PERRY & HOWER, 1972).

The intensity of diagenesis has been proved to be controlled by the tectonics, the initial fabric and composition of the sediments, as well as by the chemical composition of the pore water.

Most of the published evidence concerning the degree of diagenesis is based on X-ray diffractometry of clay-size fractions. In this study the participation of the non-clay minerals has been taken into account, too.

The progressive conversion with increasing depth of smectite into illite through a mixed-layer phase of illite/smectite is the most significant mineralogical change during diagenesis and low grade burial metamorphism. In association with this change are other mineralogical changes as the decomposition of micas, K-feldspars or kaolinite and the formation of chlorite and quartz (DUNOYER, 1964, PERRY & HOWER, 1970, WEAVER & BECK, 1971, HOWER et al., 1976).

The purpose of this study is to examine the mineralogical variations as a function of depth of medium and fine grained sediments from two wells that penetrate the Neogene strata of the Western part of Nestos river delta (Fig. 1), in order to determine their diagenesis stage and their oil-generating potential. These strata belong downwards to Quaternary, Pliocene and Miocene. Lithologically they are characterized by frequent alternations of conglomerates, sandstones, siltstones and clays with exception of the evaporite zone in Upper Miocene-Lower Pliocene (Public Petroleum Corporation, 1977-79, TSIRAMBIDES, 1983). The examined samples come from the Nestos Trough, cover the depth interval from 1780 to 3550 m and their age is Middle and Lower Miocene. Since 1981, a consortium of foreign companies extracts oil and gas from the adjacent Trough of Prinos (Prinos & S. Kavala drilling sites) (Fig. 1).

ANALYTICAL TECHNIQUES

The samples were ground for about 3 minutes in an vibratory mill to reduce grain size and to homogenize them. Twenty grams of each powdered sample were subjected to chemical treatments (JACKSON, 1974) for removal of carbonates, organic matter and Fe & Mn oxides and hydroxides. The residues were separated into five size fractions (>20, 20-5, 5-2, 2-0.2 and <0.2 μm) by gravity or centrifugal acceleration and the suspensions were dried in an oven at 100° C. Complete dryness of them was avoided. Subsequently, oriented glass-slides of the finer two size fractions were prepared for X-ray diffraction study. Also, ethylene glycolated slides and randomly orented samples were used in this study for both qualitative and semiquantitative analyses. X-ray diffractograms were run from 2 to 40° C 2θ using Cukα radiation of a Phillips diffractometer.

The sharpness ratio (SR) of illite, was determined using WEAVER'S (1961) method. The crystallinity index (CI) of illite was obtained according to

KUBLER'S (1966) method. Illite polymorphs were detected using MAXWELL & HOWER'S method (1967). The qualitative and semiquantitative determination of all mineral phases is based on the methods of JOHNS et al (1954), SCHULTZ (1964), PERRY & HOWER (1970) and REYNOLDS & HOWER (1970).

MINERALOGICAL RESULTS AND DISCUSSION

The depth and the grain distribution of the analysed samples are shown in Table 1.

The low content of all the samples in COI (Carbonates + Organics + Iron & Manganese oxides and hydroxides) and mainly in organic matter, speaks of an environment with a high redox potential. Thus the rate of influx of organic matter to the site of deposition was lower than the quantity of oxygen available to oxidize it, a condition that can be met in the turbulent environment of the mouth of a river (here Nestos).

There is an obvious predominance of the >20μm fraction, while the clay size fractions constitute less than 17% of the total sample. The clay content of all samples reveals that they represent shallow water sediments.

The complete mineralogical results are given in Table 2. It is obvious that there are significant mineralogical differences between the fractions of each sample, as well as between similar fractions of different depth.

The dominant non-clay minerals in the two coarsest fractions are quartz and feldaspars (orthoclase and plagioclase). Plagioclase predominates over orthoclase. However, some loss of quartz is evident before 1900m in well 1. Quartz and feldspar traces are noticed in the 2-0.2μm fraction of some samples, too.

The total clay mineral content increases with decreasing grain size in all samples. The dominant clay mineral in the two coarsest fractions is kaolinite. The clay mineral phases in the finest fractions are mixed-layer illite/smectite, discrete illite and kaolinite. Chlorite is very rare. The most abundant mineral in the <0.2μm fraction at all depths is the mixed-layer illite/smectite.

According to OBERLIN & FREULON (1958) the large and well-crystallized kaolinite grains is evidence for terrestrial origin. The kaolinite reflections in all diffractograms appear very thin and sharp confirming thus the presence of well-crystallized kaolinite of terrigenous origin.

A significant decrease in the abundance of kaolinite (± chlorite) is noticed from 50 to about 5% with increasing depth within the finest fractions (Fig. 2). The depth interval over which a loss in kaolinite appears, coincides with the depth interval over which there is a gain in illite from 10 to about 80% in the illite/smectite phase (Fig. 3), as well as with that over which the formation of some discrete illite occurs, increasing with depth from 15 to about 40% (Fig.

4). Discrete illite, characterized as mica in the >2μm fractions, is present in all samples. The 1M plus $1M_d$ illite polymorphs predominate in the examined samples.

The interstratification between illite and smectite according to REYNOLDS & HOWER (1970) standards, is ordered of the allevardite type I/S, because the percentage of smectite layers is less than 35%.

According to HOWER et al (1976) the mineralogical and chemical variations during the different stages of diagenesis can be expressed by the general reaction:

$$\text{smectite} + Al^{+3} + K^{+} = \text{illite} + Si^{+4}$$

They suggested that the source of Al and K is from K-feldspar and some mica which decompose with increasing depth. The Si that is lost from the tetrahedral layers of the clays probably forms quartz.

No detectable progressive gain or loss of feldspar and micas is noticed with increasing depth. The mineralogical evidence indicates strongly that the smectite to illite conversion proceeds by the metasomatic or pore water introduction of K in the studied area. The most probable source of Al might be the decomposition of kaolinite, the abundance of which decreases systematically with depth.

Consequently, we can assume that the mineralogy of the Nestos delta Miocene sedinents has been affected by burial diagenesis. The main diagenetic change is the conversion of mixed-layer illite/smectite of high expandability to an illite/smectite of low expandability. The extent of this conversion is proportional to the depth of burial.

The average clay minerals composition of the analysed samples of both wells is:

Kaolinite (± Chlorite)	= 21%
Discrete illite	= 28%
Mixed-layer illite/smectite	= 51%

These percentages coincide almost completely with those of worldwide distributed silt-and claystones of Miocene (WEAVER, 1967).

EVALUATION OF NESTOS DELTA SEDIMENTS POTENTIAL FOR HYDROCARBON PRODUCTION

Recent argillaceous sediments are relatively enriched in kaolinite and mixed-layer clays with a high proportion of expandable layers, while Pre-Mesozoic sediments are depleted in these phases, but enriched in illite and chlorite (WEAVER, 1967).

The clay minerals in sandstones are more apt to alteration after deposition than the clays in other rock types. These alterations can take place immediately after deposition or at any time after burial (WEAVER, 1962).

Young sediments usually contain more smectite and mixed-layer illite/smectite than rocks of any other age (WEAVER, 1959).

Smectite contains more interlayer water than any other non-expanded clay mineral. Also, a greater pressure is required to squeeze this interlayer water from between the unit layers (MIELENZ et al., 1955). Water is presumably necessary to remove hydrocarbons from shales and mudrocks to sanstones. The expulsion of hydrocarbons from fine grained rocks is influenced by several factors, as are the type of the clay minerals of the source rocks, the degree of diagenesis, the depth and time.

To evaluate the diagenesis stage of the Nestos Delta sediments and their potential for hydrocarbon generation, data which have been derived from this work were combined with those of WEAVER (1961), BURST (1969), PERRY & HOWER (1970) and FOSCOLOS & KODAMA (1974). Results are presented in Table 3 and are summarized as follows:

a. Expandable clays are present all over the studied depth interval (1780-3550m). However, the percentage of smectite layers in mixed-layer illite/smectite decreases with depth.
b. No 2M illite polymorph has been detected. The 1M & $1M_d$ illite polymorphs predominate.
c. The crystallinity index is ‹14mm and the sharpness ratio ›1.2. A small increase with depth is noticed in crystallinity index.
d. Kaolinite is present all over the examined depth interval decreasing with depth.
e. No significant decrease of micas and feldspars with increasing depth is noticed.

On the basis of all the above data it is confirmed that the sediments of the examined depth interval (1780-3550m) have undergone low-grade diagenesis.

BURST (1969) has shown that, during the transformation of smectite to illite, a dehydration process takes place which is strongly correlated with the production of hydrocarbons. The transformation occurs at temperatures not greater than 150° C and is accompanied by production of large amounts of water (PERRY & HOWER, 1972). PRICE (1973) has shown that deeply burried water at 150° C could transfer large amounts of hydrocarbons. Since the average geothermal gradient for both wells has been estimated as 2.5° C/100 m, the temperature range under which all the examined sediments have been submitted can be considered Iow (65° to 109° C). Therefore, the dehydration of mixed-layer clays is low. If there were any hydrocarbons they might be attached on clay mineral surfaces.

Consequently, the existence of traces of gaseous and liquid hydrocarbons in the examined area may be due to:

a. The limited presence of fine clastic sediments, which are considered source rocks fot the formation of hydrocarbons.

b. The migration of these products from the pelitic source rocks to adjacent psammitic reservoir rocks (i.e. trough of Prinos, fig. 1), because of the intense tectonic activity at this area during Neogene and Quaternary.

Figures

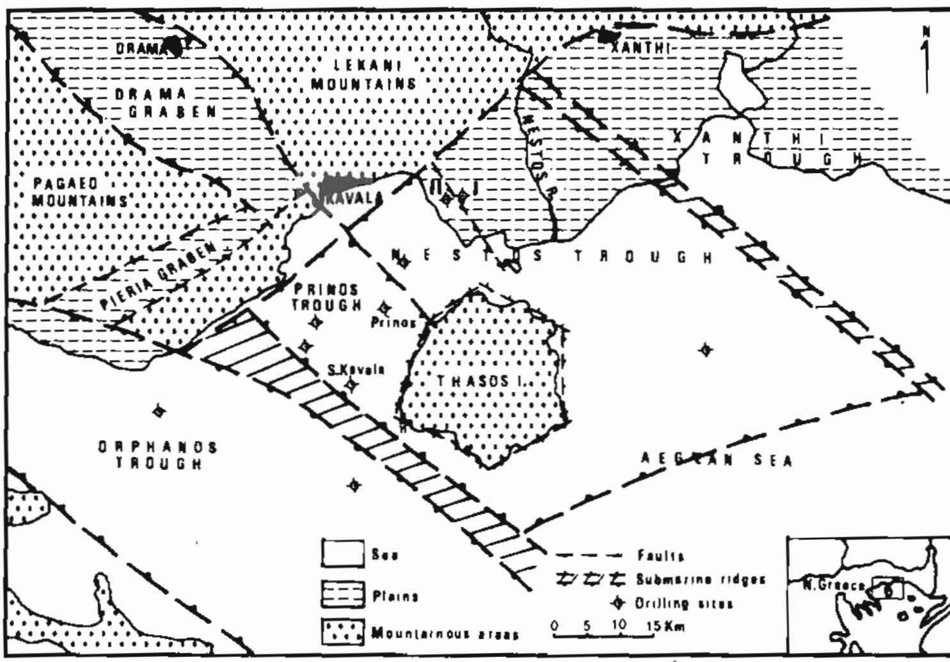

Fig. 1. Tectonic sketch map of the studied area.

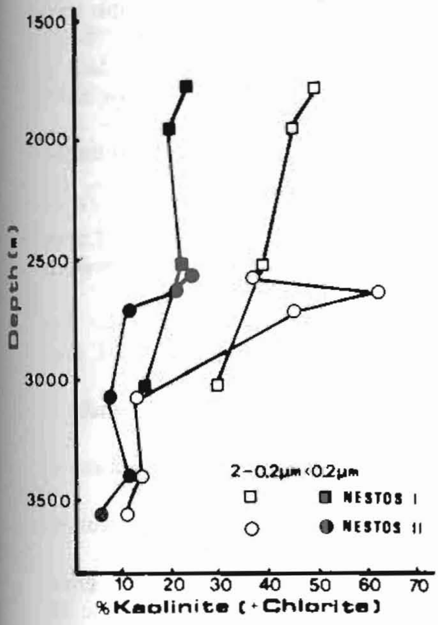

Fig. 2.

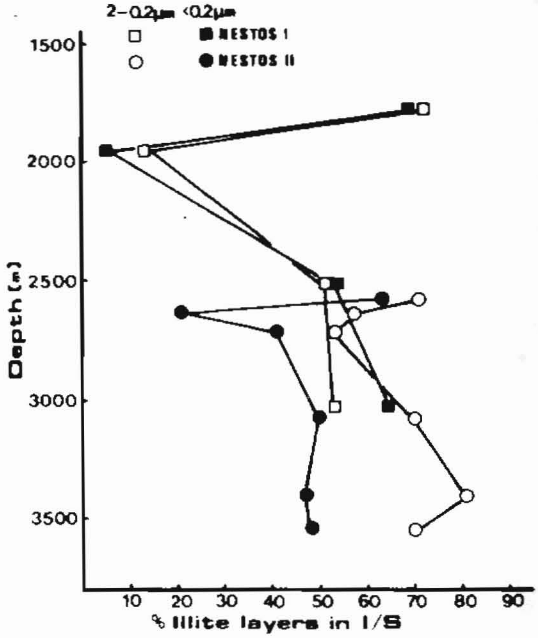

Fig. 3.

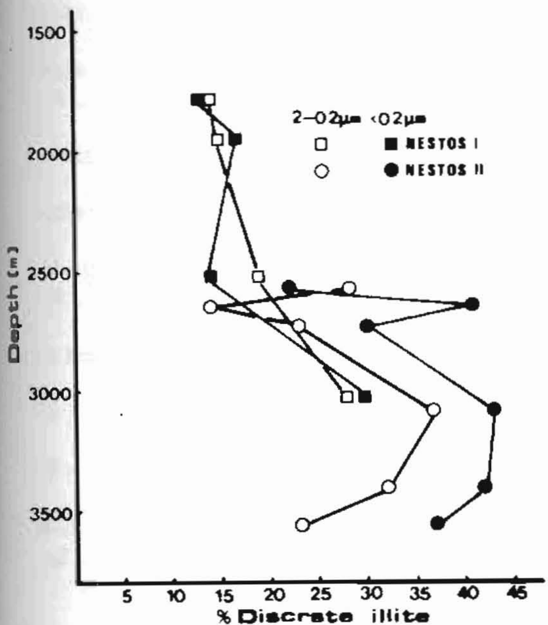

Fig. 4.

List of Figures

REFERENCES

BURST, J.F. (1969): Diagenesis of Gulf Coast clayey sediments and its possible relationship to petroleum migration. - *Am. Assoc. Petrol. Geol. Bull., 53, 73-93.*

DUNYOER DE SEGONZAC, G. (1964): Les argiles du Cretace superieur dans le bassin de Doula (Cameroun). Problemes de diagenese. - *Bull. Serv. Carte Geol. Als. Lorr., 17, 287-310.*

DUNYOER DE SEGONZAC, G. (1970): The trnasformation of clay minerals during diagenesis and lower grade metamorphism. A review. - *Sedimentol., 15, 287-396.*

FOSCOLOS, A.E. & KODAMA, H. (1974): Diagenesis of clay minerals from Lower Cretaceous shales of north eastern British Columbia. - *Clays & Clay Minerals, 22, 319-335.*

HOWER, J., ESLINGER, E.V., HOWER, M.E. & PERRY, E.A. (1976): The mechanism of burial metamorphism of argilaceous sediments. I. - Geol. Soc. Am. Bull., 87, 725-737.

JACKSON, M.L. (1974): Soil chemical analysis. Advanced course. 2nd ed. Madison, Wisconsin. Publ. by the author.

JOHNS, W.D., GRIM, R.E. & BRADLEY, W.F. (1954): Quantitative estimation of clay minerals by diffraction methods. - J. Sed. Petrol., 24, 242-251.

KUBLER, B. (1966): La cristallinite d' illite et les zones tout a fait superieur du metamorphisme. In Coll. sur les Etages Tect. a la Baconn., 105-122.

MAXWELL, D.T. & HOWER, J. (1967): High-grade diagenesis and low-grade metamorphism of illite in the Precambrian Belt series. - *Am. Mineral., 52, 843-857.*

MIELENZ, R.C., SHIELTZ, N.C. & KING, M.E. (1955): Effect of exchangeable cation on X-ray diffraction patterns and thermal behaviour of a montmorillonite clay. *-Natl. Acad. Sci, Natl. Res. Counc., Publ. 395, 146-173.*

OBERLIN, A. & FREULON, J.M. (1958): Mineralogical study of some paleozoic clays of Tassili N'Ajjer and Fezzan. - *Bull. Soc. Franc. Mineral. Crist., 81, 186-189.*

PERRY, E. & HOWER, J. (1970): Burial diagenesis in Gulf Coast pelitic sediments. *-Clays & Clay Minerals, 18, 165-177.*

PERRY, E. & HOWER, J. (1972): Late stage dehydration in deeply buried pelitic sediments. - *Am. Assoc. Petr. Geol. Bull., 56, 2013-2021.*

POWERS, M.C. (1967): Fluid release mechanisms in compacting marine mudrocks and their importance in oil exploration. - *Am. Assoc. Petrol. Geol. Bull., 51, 1240-1253.*

PRICE, L.C. (1973): Solubility of hydrocarbons and petroleum in water as applied to primary migration of petroleum. - *PhD thesis, Univ. Calif. Rivers.*

PUBLIC PETROLEUM CORP. GREECE, (1977-79): Geologic initial reports of Nestos I & II, Kavala (in Greek).

REYNOLDS, R.C. & HOWER, J. (1970): The nature of interlayering in mixed-layer illite/montmorillonites. - *Clays & Clay Minerals, 18, 25-36.*

SCHULTZ, L.G. (1964): Quantitative interpretation of mineralogical composition from X-ray and chemical data for the Pierre Shale. - *U.S. Geol. Surv. Sp. Paper, 391-C.*

TSIRAMBIDES, A.E. (1983): Granulometric, mineralogical and oxygen isotope study of Neogene sediments of Nestos delta. - *Phd thesis, Univ. of Thessaloniki, Greece (in Greek).*
WEAVER, C.E. (1959): The clay petrology of sediments. - *Clays & Clay Minerals, Proc. 6th Natl. Conf., 154-187.*
WEAVER, C.E. (1961): Minerals of the Quachita structural belt and adjacent foreland in the Quachita System. - *Bureau Econ. Geol. Austin, 147-160.*
WEAVER, C.E. (1967): The significance of clay minerals in sediments. - *Fundam. Asp. Petrol. Geoch. Elsevier, N. York, 37-76.*
WEAVER, C.E. & BECK, K.C. (1971): Clay water diagenesis during burial: How mud becomes gneiss. - *Geol. Soc. Am. Spec. Paper, 134, 96p.*

Table 1. Depth and particle size distribution of the analysed core samples.

Depth (m)	Sample	COI	>20	Grain size (μm) 20-5	5-2	2-0.2	<0.2
1781	I-1	7	63	10	7	8	5
1945	I-2	11	51	12	9	11	6
2517	I-3	6	50	17	11	11	5
3025	I-4	2	74	11	5	6	2
2568	II-1	13	64	10	6	5	2
2635	II-2	5	85	4	3	2	1
2713	II-3	6	82	6	3	2	1
2714	II-3'	5	77	8	4	5	1
3077	II-4	12	73	7	4	3	1
3080	II-5	8	83	2	3	3	1
3400	II-6	10	76	5	3	5	1
3545	II-7	2	88	3	2	4	1

COI = Carbonates + Organics + Iron oxides

Sample	Particle size (μm)	Q	Or	Pl	cl	K+Ch	I	I/S
I-1	20-5	41	9	17	33			
1781m	5-2	35	7	7	51			
	2-0.2	tr			100	50	14	36(10)*
	<0.2				100	23	13	64(20)
I-2	20-5	43	10	15	32			
1945m	5-2	42	9	9	40			
	2-0.2	tr			100	45	15	40(35)
	<0.2				100	20	17	63(60)
I-3	20-5	46	7	14	33			
2517m	5-2	32	6	9	53			
	2-0.2				100	39	19	42(20)
	<0.2				100	22	14	64(30)
I-4	20-5	25	7	18	50			
3025m	5-2	19	tr	12	69			
	2-0.2				100	29	28	43(20)
	<0.2				100	14	30	56(20)
II-1	20-5	35	7	17	41			
2568m	5-2	33	6	11	60			
	2-0.2				100	37	28	35(10)
	<0.2				100	24	22	54(20)
II-2	20-5	25	21	29	25			
2635m	5-2	19	13	20	48			
	2-0.2		tr	tr	100	63	14	23(10)
	<0.2				100	21	41	38(30)
II-3	20-5	22	7	23	48			
2713m	5-2	17	6	12	65			
	2-0.2				100	68	11	21(10)
	<0.2				100	10	49	41(35)
II-3′	20-5	22	6	22	50			
2714m	5-2	16	7	13	64			
	2-0.2				100	45	23	32(15)
	<0.2				100	11	30	59(35)
II-4	20-5	28		18	54			
3077m	5-2	18		11	71			
	2-0.2				100	13	37	50(15)
	<0.2				100	7	43	50(25)
II-5	20-5	28	15	22	35			
3080m	5-2	23	15	20	42			
	2-0.2		tr	tr	100	4	34	62(10)
	<0.2				100		41	59(25)
II-6	20-5	38		6	56			
3400m	5-2	35		6	59			
	2-0.2	tr			100	14	32	54(10)
	<0.2				100	11	42	47(25)
II-7	20-5	38	18	31	13			
3545m	5-2	26	18	28	28			
	2-0.2			tr	100	11	23	66(20)
	<0.2				100	5	37	58(30)

Q=quartz, Or=orthoclase, Pl=plagioclase, cl=total clays, K=kaolinite, Ch=chlorite, I=illite, I/S=mixed-layer illite/smectite.
* : smectite layers in I/S.

Table 2. Semiquantitative mineralogical results. NESTOS I & II.

Diagenetic stage	Hydrocarbons	Crystallinity index (mm)		Sharpness ratio		Illite in I/S (%)		Kaolinite (%)		Depth (m)		Temperature (2.5°C/100m)	
		I	II	I	II	I	II	I	II	I	II	I	II
early	traces	7	9	1.8	1.6	72	71	50	37	1781	2568	65	84
		9	11	3.2	1.7	13	57	45	63	1945	2635	69	86
		11	13	2.3	1.5	52	52	39	68	2517	2713	83	88
		11	14	2.4	1.6	53	53	29	45	3025	2714	96	88
			12		1.5		70		13		3077		97
			14		1.4		84		4		3080		97
			10		1.2		81		14		3400		105
			12		1.5		70		11		3545		109

Table 3. *Correlation between crustallinity index, sharpness ratio, % illite in I/S, % kaolinite, burial depth and temperature for assessing the degree of diagenesis and hydrocarbon generating potential of Nestos delta sediments.*

ΠΕΡΙΛΗΨΗ

ΔΙΑΓΕΝΕΣΗ ΚΑΙ ΠΙΘΑΝΗ ΓΕΝΕΣΗ ΠΕΤΡΕΛΑΙΟΥ ΤΩΝ ΜΕΙΟΚΑΙΝΙΚΩΝ ΙΖΗΜΑΤΩΝ ΑΠΟ ΤΟ ΔΕΛΤΑ ΤΟΥ ΝΕΣΤΟΥ

Από
Α. ΤΣΙΡΑΜΠΙΔΗ και Κ. ΣΟΛΔΑΤΟ
Τομέας Ορυκτολογίας - Πετρολογίας - Κοιταμασματολογίας Α.Π.Θ.

Γίνεται λεπτομερής ορυκτολογική μελέτη Μειοκαινικών αργιλικών ιζημάτων που πάρθηκαν από πυρήνες χερσαίων γεωτρήσεων στο δέλτα του Νέστου με σκοπό να υπολογιστεί ο βαθμός διαγένεσης των ιζημάτων καί η πιθανή γένεση πετρελαίου αυτών.

Αναλύθηκαν τέσσερα κλάσματα προερχόμενα από βάθη 1780 μέχρι 3550 μέτρων από δύο γεωτρήσεις. Παρατηρούνται μερικές ορυκτολογικές μεταβολές με το βάθος. Η πιο διαδομένη μικτή φάση ιλλίτη/σμεκτίτη τροποποιείται με αύξηση των φύλλων ιλλίτη από 10 σε 80%. Στο ίδιο διάστημα βάθους ο καθαρός ιλλίτης αυξάνει από 15 σε 40%, ενώ ο καολινίτης (± λίγος χλωρίτης) μειώνεται από 50 σε 5%. Οι πολυμορφίες 1M και $1M_d$ του ιλλίτη επικρατούν.

Το στάδιο διαγένεσης μπορεί να χαρακτηριστεί σαν πρώιμο. Οι θερμοκρασίες στις οποίες έχουν υποβληθεί όλα τα εξεταζόμενα ιζήματα είναι χαμηλές (65-109°C). Επομένως, η αφυδάτωση των μικτών αργιλικών ορυκτών τους είναι χαμηλή. Το μικρό περιεχόμενο των ιζημάτων του δέλτα του Νέστου σε υδρογονάνθρακες οφείλεται στην περιορισμένη παρουσία λεπτομερών κλαστικών ιζημάτων και στη μετακίνηση του πετρελαίου σε γειτονικά πετρώματα, εξαιτίας της έντονης τεκτονικής δραστηριότητας στην περιοχή κατά τη διάρκεια του Νεογενούς και του Τεταρτογενούς.

Τα χειρόγραφα κατατέθηκαν στις 4.2.86