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POLYFRAMBOIDAL PYRITE FORMATIONS IN GREEK BEACHES

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Abstract: *The existence of Polyframboidal pyrite formations in blaek sands is discovered for the first time. The phenomenon is observed in the beach of Loutra Eleftheron near Kavala (Grecce). Each Polyframboid spherule, with 0.40 to 0.96 mm diameter, contains many hundreds to some thousands of Framboids with 4.2 to 21.6 μ diameter. In the Framboids the pyrite crystals have a size from 0.5 to 2.0 μ with some exceptions. Except these regular spherical forms, there are also formations with irregular periphery containing recrystallized pyrite which howe ver obviously derives from the crystals of the Framboids. This last form usually appears more limonitized.*

As regards the origin conditions of the above formations the authors accept that the Polyframboid spherules are of recent genesis which takes place in the sea floor mud not far from their present place and in a reducing environment. The presence of many metallic minerals in the black sands, contributes by their weathering to the supplying of the sea with the necessary amount of metal ions for the formation of the Polyframboids. On the contrary, for the irregular forms of recrystallized pyrite they accept that they come from the erosion of sedimentary layers which contain such formations. A confirmation to this, consists the existence of advanced diagenetic phenomena as is the recrystallization of pyrite and the cracks and fractures because of the solidification of the surrounding rock. This view is also supported by the apperance of transportation traces from large distance as are the irregular form and the advanced limonitization.

INTRODUCTION

The term «Framboidal Pyrite» was first given by RUST (1935) during the study of the copper deposit of Cornwall Mine, Missuri, in order to characterize concentrations of microscopic pyrite crystals of special texture. In this texture, minute pyrite crystals are massed together to rounded aggregates, so that finally they give forms like the rasberries.

Formations of this type were also previously known, because they show a great development, in some known pyrite or B.P.G. sulphide deposits as for example in Rammelsberg,W. Germany (RAMDOHR 1975 p. 156). According to VALLENTYNE (1963a), these formations were already known to the investigators of turf peat and narime mud, from the end of the previous century. They are described mineralogically for the first time by DOSS (1912) who considered them as conversions of unstable iron sulphides (melnikovite or hydrotroilite). THIESSEN (1920) has found them in coal deposits. These formations caused a great interest after SCHNEIDERHÖHN (1923) had interpreted similar forms of chalcopyrite, as fossils of micro-organisms (fossil bacteria). According to the above author, the reducing activity of these micro-organisms caused the genesis of many sedimentary copper or B.P.G. sulphide deposits. SCHNEIDERHÖHNS viewpoint was later disputed by SCHOUTEN (1946a, 1946b) and so a scientific argument began among the followers of both views which lasted many years. As regards the term «Framboidal Pyrite», LOVE and AMSTUTZ (1965) notice that it can not cover the great variety of the types and formations in which the aggregates of minute pyrite crystals appear arranged around a common centre. So, they propose the term «cluster» (bunch of grapes) and consider the term «Framboidal» as a particular case of it. The term «Polyframboidal Pyrite» or Polyframboids» was given by LOVE (1971 p. 1038) in order to characterize the spherical compounds which consist of many single Framboidal pyrites or Framboids.

During the last years the «Framboidal» formations are generally studied carefully because of their great significance concerning the origin of the sedimentary ore deposits and the presence of pyrite in a great variety of rocks and in ore deposits. Their discovery in Greek places, and especially in black sands, by the first of the authors causes the writing of the present work, which must not be considered-terminated. Because of the great significance of the «Framboidal Pyrite» formations, the collection of more material and its further study has been planned.

According to the accessible for us bibliography, formations of the «Framboidal Pyrite» type are observed in black sands for the first time. Such formations are also stated in Greece for the first time.

MICROSCOPIC DESCRIPTIONS

During the investigation of black sand samples from diverse beaches of Makedonia and Thrace for the study of their heavy minerals, the existence of formations of the «Framboidal Pyrite» type has been observed in some samples from the area of Loutra Eleftheron near Kavala (PAPADAKIS 1975). These simple spherical aggregates of pyrite crystals are grouped to form greater spheroidal compounts of the Polyframboidal Pyrite type (Fig. 1). The existence of these greater spheroidal compounds has given the possibility of the collection of much material for microscopic study. Thus, from the black sand samples the spheroidal formations were separated and polished sections of them were made for study under the ore microscope. It must be noted that these spheroidal formations of smaller than 1 mm diameter, macroscopically observed resemble the fish eggs while their mixture the roe. Under the stereoscope they show a characteristic luster on their external surface.

Fig. 1. A Polyframboidal pyrite spherule in a black sand sample. Polished section, 75 X.

Under the microscope their sections show about a uniform image. Every Polyframboidal Pyrite compound consists of many hundreds to some thousands of Framboidal Pyrite spherules as results after calculations. The characteristic spericity of the Polyframboids is remarkable. In almost all the studied sections their perimeter is slightly different from the ideal circular shape (Fig, 1. 2). But in the simple

Fig. 2. A Polyframboidal pyrite spherule with nearly ideal circular shape. Polished section, 145 X.

Framboids, which constitute the Polyframboids, considerable divergences from the spherical shape appear (Fig. 3,4).

The diameter of the Framboids varies between 4.2 and 21.6 μ while that of the Polyframboid compounds between 400 and 960 (0.4-0.96 mm). For comparison we mention that LOVE and AMSTUTZ (1969) observred diameters of Framboids from 5 to 25 μ in a Permian andesite in Plotz of Germany and LOVE (1974) diameters of Polyframboids from 35 to 900 μ in sedimentary rocks (Silurian greywackes) of north Wales.

In order to measure the dimensions of the individual pyrite crystals, which constitute the Framboid spherules we used photographical magnifications of them. So, we avoided measurement errors using a micrometer scale under the microscope, because of the very small dimensions of the pyrite crystals. The results of the measurements on the two black sand samples with number 11 and 12 from Loutra Eleftheron, Kavala are given in table I. There were measured 260 and 498 crystals respectively.

On the base of the data of table 1 the two histogrammes of Fig. 5 have been made.

Fig. 3. Framboids with very different shapes (pyrite crystals are white) Polished section. Oil immersion, 1500 X.

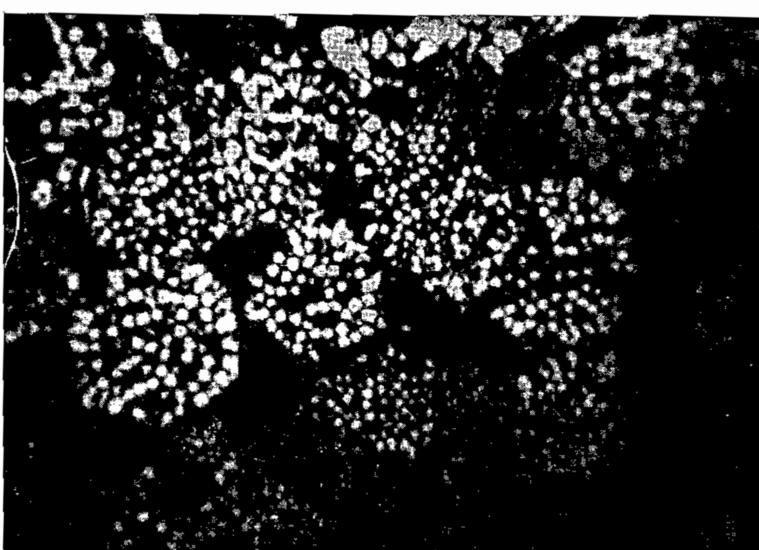

Fig. 4. Framboids of pyrite crystals (white) with very different shapes. Polished section. Oil immersion, 1500 X.

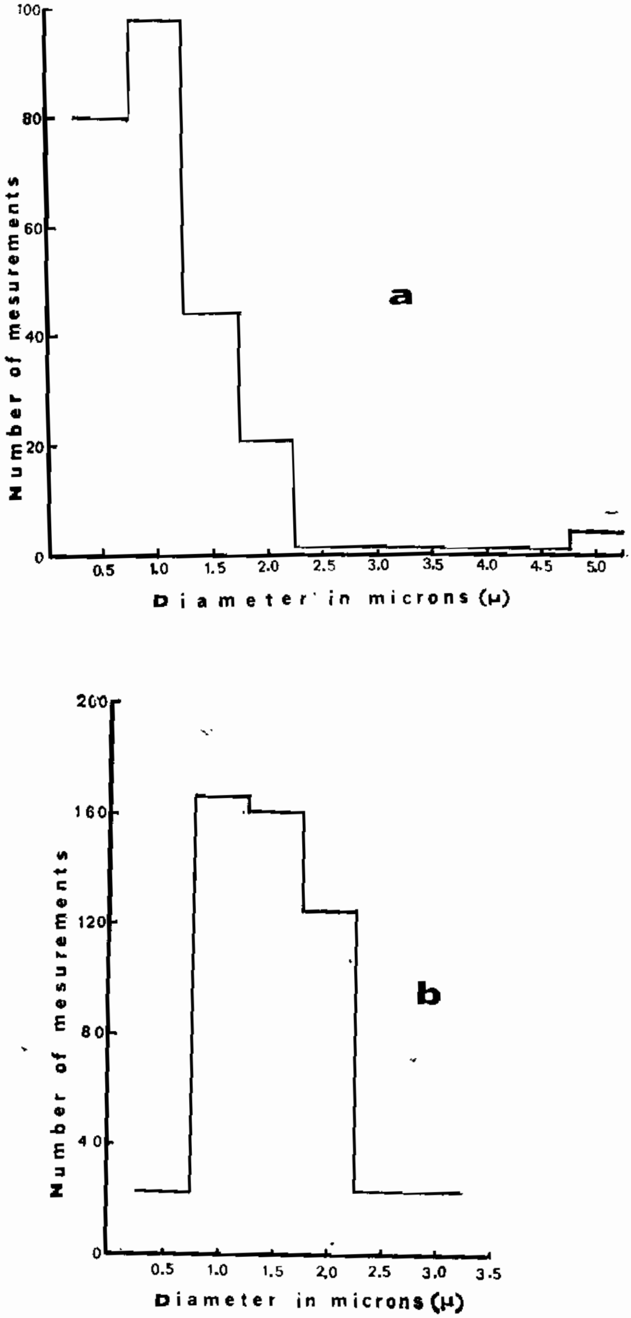

Fig. 5. Size distribution of pyrite crystals in Framboids of black sand samples from Loutra Eleftheron, Kavala (a number 11, b number 12).

From the comparison of these diagrams with those given by LOVE and AMSTUTZ (1969) for the pyrite crystals of the Framboids of Plotz andesite, results that we generally found a smaller size which reaches the half of the latters. But this probably is due to the advance recrystallization of pyrite in the Plotz Framboids.

TABLE I

Size distibution of pyrite crystals in Framboids

Black sand sample 11		Black sand sample 12	
Diameter in μ.	Number of measurements	Diameter in μ.	Number of measurements
1	80	0.5	23
1	98	1	166
1.5	44	1.5	161
2	21	2	125
3	1	3	23
4	1		
5	4		
6	1		
7	3		
8	1		
9	3		
10	1		
11	3		
12	—		
13	1		
14	1		
15	1		
16	—		
17	1		
18	1		
	260		498

Except the above described speroidal Polyframboids, sometimes very different forms appear. They have an elliptical or irregular shape (Fig. 6, 7) and consist of distinctly recrystallized pyrite crystals (Fig. 8) which originate from initial Framboids or Polyframboids. Because of the recrystallization the size of the pyrite crystals is greater than the regular rising up to 50 μ. These more rare irregular bodiess show, except the recrystallization, and other phenomena of advanced diagenesis as for example cracks beçause of the solidification of the sediment. They also show traces of transportation from greater distances as it is the irregular shape and the more intense limonitization of them.

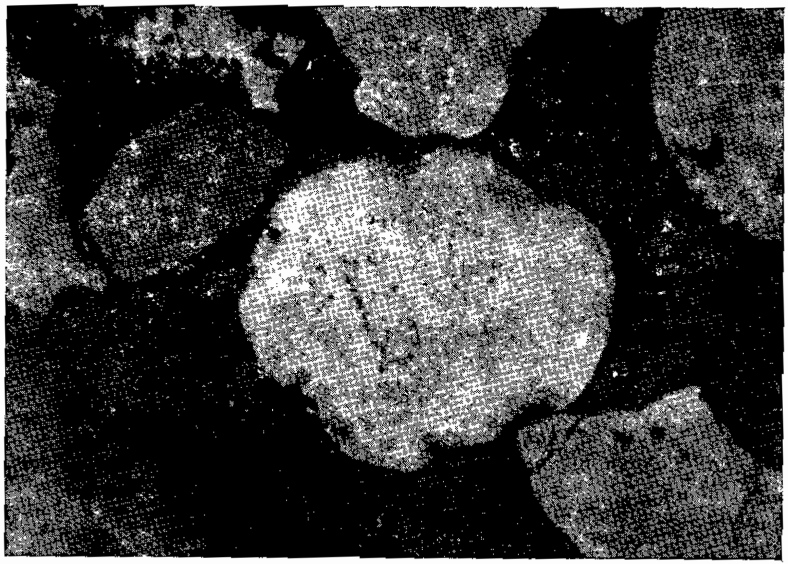

Fig. 6. A Polyframboid of pyrite with very irregular shape. Polished seetion, 75 X.

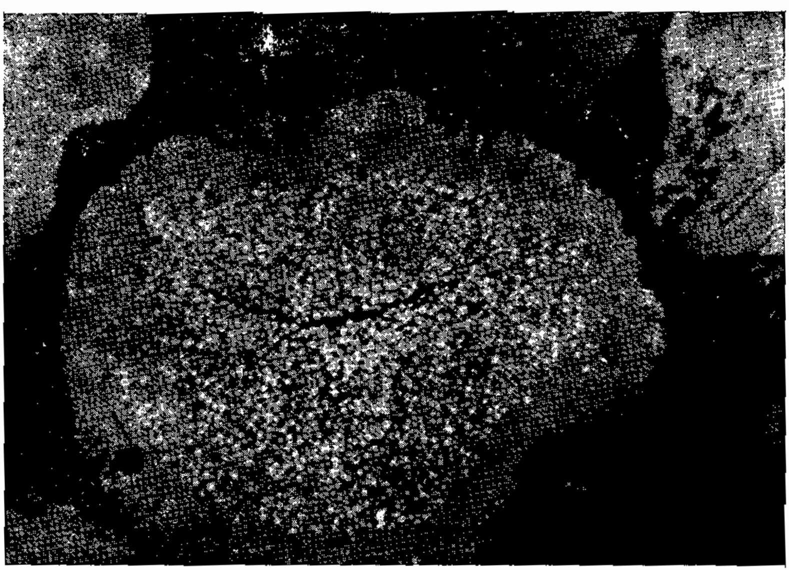

Fig. 7. A Polyframboid of pyrite with very irregular shape and with reerystallized pyrite crystals (white). Polished section, 145 X.

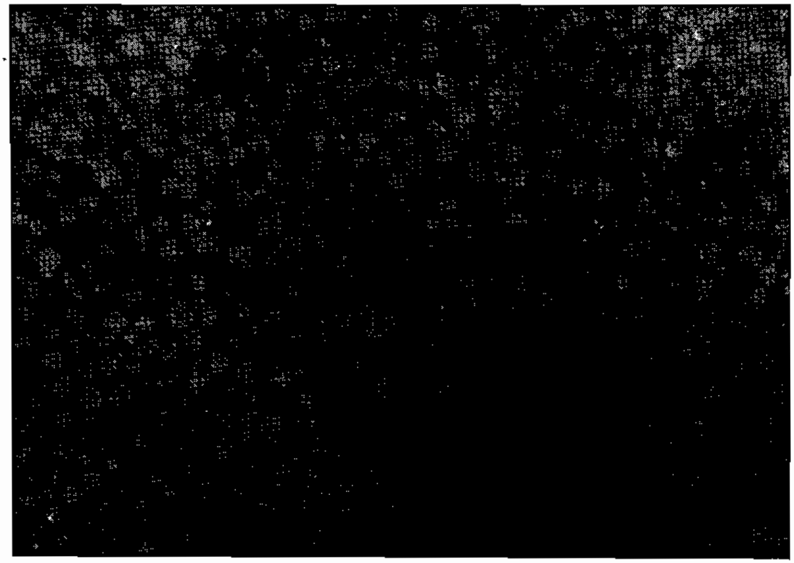

Fig. 8. The same as in Fig. 7 under high magnification. Oil immersion, 750 X.

ORIGIN CONDITIONS

As it was already mentioned in the introduction, the first estimation of SCHNEIDERHOEHN)(1923) that the formations of the «Framboidal Pyrite» type present remains of micro-organisms (sulphur ba-
boidal Pyrite» type present remains of micro-organisms (sulphur ba-
cteria) which caused the ore mineralization found SCHOUTEN (1946a, 1946b) opposite. LOVE (1957) found organic matter accompaning the Framboids and later on (LOVE 1957, 1962) he identified some forms of Framboidal Pyrite which appeared in bitoumenous shales as microfossils (Pyritosphaera 20-35 μ diameter and Pyritella 20-55 μ diameter). After the newer systematic investigations of LOVE (1964) and VALLENTYNE (1963a, 1963b) it was found that there is no evidence that the Framboidal formations represent fossils of micro-organisms or have a direct biogenic origin. KAPLAN EMERY and RITTENBERG (1963) and BERNER) (1964a, 1964b, 1964c) consider sure that the source of the contained in recent sediments pyrite (where the Framboidal forms are abundant) is in the reaction between sulphides yielded from bacterial reduction of sulphades and iron originally brought in as detridal iron bearing minerals. So, an indirect biogenic origin is accept. But this conversion is not simple. It goes first through

an initial iron sulphide form, which is amorphe in X-ray diffraction, or constitutes a colloidal state (probably this form is similar whith kansite). According to BERNER (1964a, 1964c) the conversion of this mineral form into pyrite is completed by the bacterially produced elemental sulphur. LOVE's observations, as it is mentiomed by LOVE and AMSTUTZ (1965 p 302), indicate the existence of primary black sulphide spherules which can be infered by observing smears on the sediments. Later on, these smears change to brown and in these brown smears some red spherules are observed in a matrix which probably is limonite with another less perfectly defined material. All these formations are accompanied by pyrite spherules and single pyrite cry stals.

From the above results that the problem of the origin of the Framboidal and Polyframboidal pyrite formations is not completely eluci dated yet.

As regards the spherical ordering of the pyrite crystals in the Framboids DOSS (1912) and RUST (1935) have attributed it to the initial colloidal state of the material. This view is also accepted by LOVE and AMSTUTZ (1965). PAPONEN (1966) accepts that this texture is due to the reaction between the iron hydroxide which is contained in the drops of colloidal humus, and the hydrogen sulphide of water. AMSTUTZ, ZIMMERMANN and LOVE (1974) also accept a colloidal origin for the Framboids of the stratiform copper deposit at Cornwall Missuri.

Especially, as regards the origin conditions of the Framboids and Polyframboids of the Greek black sands, we can state the followings. The Polyframboid spherules always appears single, without any intergrowth or assemblage with other petrological or metallic material. On the other hand, they don't show any traces of diagenetic influence as for example compression due to the solidification of the rock, as LOVE (1974) states for similar formations in consolidated sediments. This excludes the case that the Polyframboids constitute residues of a sulphide deposit or generally a sedimentary layer rich in Polyframboids from which they arrived in the black sands by erosion and transportation, as it happens with the other componets of the black sands (PAPADAKIS 1975). The Polyframboid spherules also show a complete lack of transportation traces such as fractures and detachment of pieces from them e.t.c. This shows that either they were formed in their present place i.e., in the black sands, something which is impossible, or they have been transported from a small distance. On the other hand, the low degree of limonitization of the pyrite in the Polyframboids shows a relatively short stay in their present place, which place, as we know, is an oxidizing environment.

From the above observations results that for the single Polyframmboid spherules we must accept a recent formation. We consider that this formation is completed in the mud of the sea floor in a relatively small depth under a reducing enviroment, according to the LOVE and ASTUTZ (1965) model. The weathering of the metallic minerals of the black sands on the sea floor contributes to the supplying of the environment with the proper amount of metallic ions, mainly iron ions, for the formation of the pyrite. Newer disturbances of the sea floor due to the intense waving, whose the action arrives up to the area of formation of the Framboids, causes their removal and redeposition on the beach by the waves, according to the known way of the black sands formation (rejection of all the mineralogical componets of the sea floor on the beach by the wave action and return of only the light componets back to the sea)..

A greater difficulty appears in the interpretation of the irregular (not spherical) Polyframboidal pyrite compounds with clear recrystallization phenomena of the pyrite as well as greater limonitization of it. The shape of the grains denote a trasportation from a greater distance while the recrystallization phenomena an advanced diagenetic stage. Consequently, it is not about contemporary and adjacent formations. They probably derived from the erosion of sedimentary rocks which contain such formations as it is known for example for the Belgian Ardennes (LOVE and VANGUESTAINE 1976). In this case, their coexistence with the usual spheroidal Polyframboids is only symptomatic.

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ΠΕΡΙΛΗΨΗ

ΣΧΗΜΑΤΙΣΜΟΙ ΣΙΔΗΡΟΠΥΡΙΤΟΥ ΥΠΟ ΜΟΡΦΗΝ POLYFRAMBOIDAL PYRITE ΕΙΣ ΕΛΛΗΝΙΚΑΣ ΑΚΤΑΣ

Ὑπὸ

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Διὰ πρώτην φορὰν ἀνακαλύπτεται ἡ ὕπαρξις σχηματισμῶν Polyframboidal Pyrite ἐντὸς μαύρων ἄμμων. Τὸ φαινόμενον παρατηρεῖται εἰς τὰς ἀκτὰς τῶν Λουτρῶν 'Ελευθερῶν Καβάλας ('Ελλάς). Τὰ σφαιρίδια τῶν Polyframboids, διαμέτρου 0,4-0,96 χιλιοστά, περιέχουν ἕκαστον ἀρκετὰς ἑκατοντάδας ἕως μερικὰς χιλιάδας Framboids διαμέτρου 4,2-21,6 μικρῶν. 'Εντὸς τῶν Framboids οἱ κρύσταλλοι τοῦ σιδηροπυρίτου ἔχουν διαστάσειςἀπὸ 0,5 ἕως 2 μικρά, μέ τινας ἐξαιρέσεις. 'Εκτὸς αὐτῶν τῶν κανονικῶν σφαιρικῶν μορφῶν ὑπάρχουν καὶ σχηματισμοὶ ἀκανονίστου περιμέτρου μὲ περιεχόμενον ἀνακρυσταλλωθέντα σιδηροπυρίτην ὁ ὁποῖος ὅμως σαφῶς προέρχεται ἐκτῶν κρυστάλλων τῶν Framboids. 'Η τελευταία μορφὴ ἐμφανίζεται συνήθως περισσότερον λειμωνιτιωμένη.

Διὰ τὰς συνθήκας γενέσεως τῶν ὡς ἄνω σχηματισμῶν οἱ συγγραφεῖς παραδέχονται ὅτι τὰ σφαιρίδια τῶν Polyframboids εἶναι προσφάτου γενέσεως ἡ ὁποία συντελεῖται ἐντὸς τῆς ἰλύος τοῦ πυθμένος τῆς θαλάσσης ὄχι μακρὰν τῆς σημερινῆς των θέσεων καὶ εἰς ἀναγωγικὸν περιβάλλον. 'Η παρουσία πολλῶν μεταλλικῶν ὀρυκτῶν τῶν μαύρων ἄμμων συντελεῖ διὰ τῆς ἀποσαθρώσεώς των εἰς τὴν τροφοδότησιν τῆς θαλάσσης διὰ τῆς ἀναγκαίας ποσότητος ἰόντων μετάλλων πρὸς σχηματισμὸν τῶν Polyframboids. 'Αντιθέτως διὰ τὰς ἀκανονίστους μορφὰς ἀνακρυσταλλωθέντος σιδηροπυρίτου δέχονται ὅτι προέρχονται ἐκ διαβρωθέντων ἰζηματογενῶν στρωμάτων περιεχόντων τοιούτους σχηματισμούς. 'Επιβεβαίωσιν αὐτοῦ ἀποτελεῖ τὸ γεγονὸς τῆς παρουσίας φαινομένων προχωρημένης διαγενέσεως, ὡς ἡ ἀνακρυστάλλωσις τοῦ σιδηροπυρίτου καὶ ρωγμῶν καὶ θρυμματιστῶν λόγω στερεοποιήσεως τοῦ περιβάλλοντος πετρώματος. 'Η ἐμφάνισις ἰχνῶν μεταφορᾶς ἐκ μεγάλης ἀποστάσεως ὡς εἶναι τὸ ἀκανόνιστον σχῆμα καὶ ἡ προχωρημένη λειμωνιτίωσις ἐνισχύει αὐτὴν τὴν ἄποψιν.