

Organic matter and clay minerals in the bottom sediments of Kalloni Bay Lesvos Island, Greece

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ABSTRACT — The total organic matter content in the bottom sediments of Kalloni Bay is 7.40% of dry weight. Average values of 11.6 ppm, 4.90 mg/g and 0.05% have been found for pheophytin, total carbohydrates and lipids, respectively. A positive relationship between montmorillonite - illite ratio, and total organic matter content has been found.

RIASSUNTO — [Materia organica e minerali argillosi nei sedimenti di fondo della Baia di Kalloni, Isola di Lesbo, Grecia] — Il contenuto totale in sostanze organiche dei sedimenti del golfo di Kalloni è 7.40% del peso secco. Il contenuto in feofitini del sedimento secco si è trovato essere 11.6 ppm, dei carboidrati 4.90 mg/g e dei lipidi 0.05%. Si è trovata una relazione positiva tra il contenuto dei sedimenti in montmorillonite e in sostanze organiche.

INTRODUCTION

Organic matter is present in natural waters, in true solution, in colloidal solution, and as suspension of living and dead organisms and as organic detritus. The main producer of organic matter is phytoplankton (diatoms and peridinians). It is well documented that inorganic particles and especially clay minerals adsorb organic substances such as sugars, peptones, amino acids, and others (Khan, 1951; Wilson, 1955; Bader, Hood, and Smith, 1960).

Wangersky (1965) reports that 70% of the naturally occurring particulate matter in the sea is inorganic. According to the same author, inorganic particles are first formed and the organic substances are adsorbed on the inorganic surfaces.

The role of humus — an intricate carbohydrate and protein complex of considerable biochemical stability (Waksman and Renn, 1936) — is very important. It appears that dissolved organic substances react with each other to form humus. Swain (1975) reports that humus can be chemically formed in the following ways: reaction of mineral acids with carbohydrates to form furfurals; condensation of amino acids and peptides with carbohydrates to form melanoids; aldol condensation of amino acids with methy-

glyoxal; oxidation of phenols, quinones, and other aromatic compounds; and opening of lignin rings.

After their formation, humic substances are either adsorbed by clay minerals or formed into insoluble compounds.

The modification of the organic substances continues after deposition. Therefore, the mixed organic matter that accumulates in the sediment probably does not contain any component that has not been modified to some extent. Thus, it is not surprising that humus and other residual organic matter seem to be the most abundant. As it was mentioned before, humic acids and residual organic matter develop from the initial substances as a result of reaction between them. Apparently this process continues after their deposition. In the sediments most of it is in a combined state on the surface of mineral particles, especially clays. A considerable part is in an uncombined state in between the mineral grains. A minor portion (5-10%) is connected with bottom-dwelling animals and bacteria (Oppenheimer, 1960), and an insignificant amount in solution percolates through the sediments.

In addition to humus, other organic substances found in marine sediments include proteins, peptides, amino acids; various carbohydrates (cellulose, sugar,

etc.); pigments (chlorophyll - pheophytin, carotenoids); lipids (fatty acids, hydrocarbons, bitumens); and others.

Factors, such as the size of the basin, depth, hydrologic and hydrodynamic conditions, sediment type, oxygen content, productivity, plankton types, and others, control the quality and quantity of the organic matter in bottom sediments. Diffusion can be an important factor in the balance between insoluble particles kept in place by gravity and the production of dissolved substances that tend to move away from the sediment by diffusion (Vallentyne, 1962).

Generally, oxidative environment and aerobic or anaerobic bacterial action result in the quick degradation and mineralization of the organic matter in the sediments. Skopintsev (1950) has experimentally shown that 70% of the organic matter is mineralized under aerobic conditions.

Moderate oxidation and bacterial action are favorable conditions for the formation of humic acids (Bordovskiy, 1965).

Under reducing conditions, organic substances tend to remain relatively unmodified and the humus content is relatively low.

Nevertheless the characteristics of humus depend on the source organisms (Swain, 1975). Also, the degree of humification increases as the organic concentration in the sediment rises. Due to the higher concentration of organic matter in finer sediments, the degree of humification increases with decreasing grain size. A steady-state equilibrium, where the input balances the output, is more easily achieved in shallow waters.

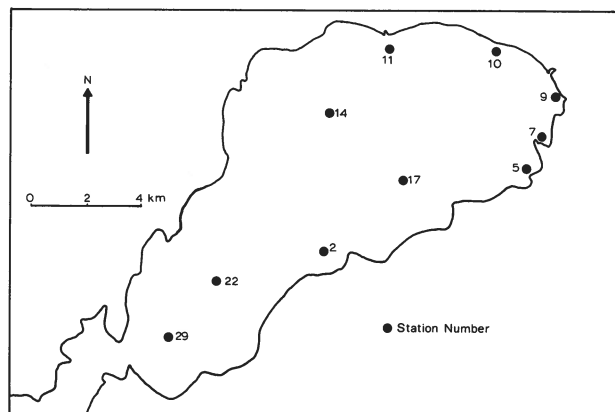
According to Parsons and Seki (1970), in shallow waters most of the organic carbon is concentrated in the sediments, while in ocean water most of it is present as soluble organic carbon.

From the phytoplankton - which is the main producer of organic matter - only a small number of cells die a natural death and start sinking to the bottom. Most diatoms and dinoflagellates are intensively consumed by zooplankton and filter-feeders before they die.

Trask (1932) estimated that 2% of phytoplankton produced reaches the sea floor in the shallows, as against 0.02% in the open sea. Uspenskiy (1956), quoted by Moore (1969), believes that less than 1% of the primary production of organic matter escapes decomposition and precipitates.

LABORATORY PROCEDURES AND RESULTS

Surface sediment samples were collected from 10 stations, put into small plastic jars, and frozen until they were measured (Text-fig. 1).



Text-fig. 1 - Sampling stations in Kalloni Bay (organic matter analysis).

The following laboratory procedures have been followed:

1. Ignition Loss: Approximately 1 gram of dried at 110°C, shell-free sediment was weighed and it was put for 2 hours into an oven at 550°C. The sample was then left to cool at room temperature, and then it was weighed again.

2. Pigments: Five ml of 90% acetone were added to 2 grams of wet sample. The sample was extracted in the dark for 24 hours and the pigment content was measured by absorption spectrophotometry (Bausch and Lomb Spectronic 20). The sediment chlorophyll degradation product (SCDP) was calculated by the formula:

$$\text{SCDP} = \frac{(\text{absorbance at } 6650\text{\AA}) \times (\text{volume of solvent})}{\text{dry weight of sample}}$$

Then the SCDP was multiplied by 21.5 in order to determine the ppm concentration of pheophytin (Swain, Paulsen, and Ting, 1964).

3. Total Carbohydrates: A 2-3 gram aliquot of the wet sample was extracted with 30 ml of 50% H₂SO₄ for 24 hours. It was often stirred during the first 12 hours. The determination of the concentration of the total carbohydrates was made by means of the phenol-sulfuric acid method (Dubois, Gilles, Hamilton, Rebers, and Smith, 1956).

4. Lipids: An aliquot of 7-10 grams from the wet sample was put in a 20 ml test tube. Then 15 ml of 4:1 benzene-methanol solution was added and the samples were extracted for 4 hours in an ultrasonic tank. After that the samples were centrifuged in order to separate the two facies (benzene and lipids; and methanol, water, and pigments). The benzene-lipid fraction was pipetted and placed in a preweighed beaker, air dried, and weighed.

Table 1 presents the results of analysis for the different organic compounds, and Table 2 presents the pH and moisture content in each station.

Station	Ignition Loss (%)	Pheophytin (ppm)	Total Carbohydrates (mg/g)	Lipids (%)
2	6.90	13	1.76	0.87
5	6.90	7	5.33	0.06
7	7.74	7	5.66	0.05
9	42.78	10	102.25	0.09
10	5.25	10	3.87	0.04
11	6.93	13	4.56	0.04
14	6.36	11	5.71	0.04
17	8.32	17	8.62	0.04
22	9.01	9	6.77	0.05
29	9.16	12	2.57	0.06
Average	7.40*	11.6	4.90*	0.05**

* Station 9 not included

** Station 2 not included

Tab. 1 - Organic matter and individual components in the Kalloni Bay sediments (based on dry weight).

Station	Classification	Depth (meters)	pH	Moisture* (%)
2	shM	11.0	7.70	66
5	shsM	7.0	7.50	70
7	(sh) M	5.0	7.30	70
9	shsM	6.0	7.50	68
10	M	5.5	7.10	51
11	M	4.0	7.05	54
14	shM	9.0	7.15	58
17	shM	12.0	7.30	71
22	(sh) M	18.0	7.50	69
29	(sh) sM	20.0	7.70	65
Average		10.0	7.40	64

* dried at 110°C

Tab. 2 - Depth, pH, and moisture content of the Kalloni Bay recent sediments (classification included).

A. TOTAL ORGANIC MATTER AND PIGMENTS

Orr, Emery, and Grady (1958) suggested that chlorophyll decomposition is perhaps best indicated by expressing the pheophytin content in terms of total

organic matter, rather than total dry sediment. On the other hand, if pheophytin content is expressed in terms of dry sediment, it gives a good indication of the production and dilution of chlorophyll. Consequently a comparison of the two sets of values in different areas should give an idea of the importance of production and dilution versus decomposition.

Sedimentation of inorganic particles can affect the dilution and decomposition rate in opposing ways. A higher sedimentation rate will dilute the organic material, but on the other hand, because of faster burial, it will slow the decomposition rate. The opposite will happen in the case of lower sedimentation rate.

In Kalloni Bay both pheophytin content in dry sediment and in organic matter are relatively low compared to other areas (see Tab. 3). The pheophytin content in the organic matter in Kalloni Bay is almost 10 times less than in the shallow sediments of the California shelf. The total organic matter and the pheophytin content in dry sediment is 15 and 2 times more, respectively, in Kalloni Bay. These facts suggest that production is higher, dilution is lower, and the degree of decomposition is higher in Kalloni Bay.

On the other hand, the organic matter content in Kalloni Bay and Tomales Bay is almost the same. In Tomales Bay, pheophytin content in dry sediment is 6 fold more and in organic matter is 4.5 times more. Swain *et al.* (1964) give supporting evidence that Tomales Bay has a highly oxidizing environment. Thus, the above results suggest that the possibility for such an environment is stronger in Kalloni Bay.

Another interesting aspect of the pheophytin content of the organic matter is that it permits a comparison between the available amount of chlorophyll and the fraction that has precipitated. Table 4 shows the possible sources and the amount of chlorophyll that each contains.

If we take an average of 8.4% for all marine plants, the amount of chlorophyll that is preserved in the organic matter of the sediments is about 0.2%.

Sample Group	Depth (meters)	No. of samples	Total Organic Matter (%)	Pheophytin ppm, based on:		Author
				dry sediment	organic matter	
Kalloni Bay, Greece	10 (4 - 20)	9	7.40 (5.25 - 9.16)	11.7 (7 - 17)	157 (23 - 204)	Tassos
Tomales Bay, California	5	1	10.00	68	680	Swain <i>et al.</i>
Mainland and Island Shelf	12.5 (2 - 18)	10	0.48* (0.19 - 0.95)	5.8 (2.1 - 11.1)	1370 (540 - 3300)	Orr <i>et al.</i>

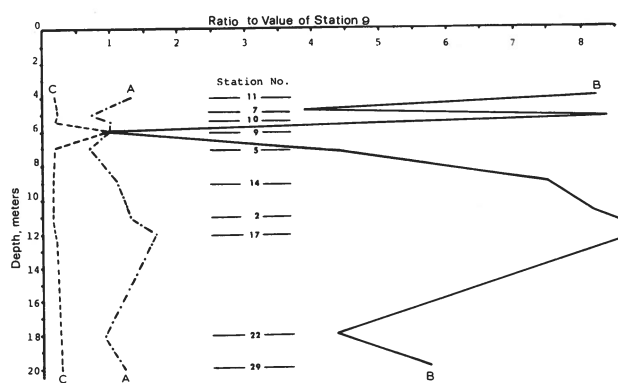
* Total organic matter was calculated after multiplying the nitrogen content of dry sediment by 17 (Orr *et al.*, 1958).

Tab. 3 - Averages and ranges for depth, total organic matter, and pheophytin in shallow water sediments.

Plant Type	Chlorophyll Content (%)	Author
Algae	3.3 (0.05 - 25)	Swain <i>et al.</i>
<i>Zostera</i>	15.8 (6.6 - 28.6)	Swain <i>et al.</i>
Phytoplankton	6 (2 - 10)	Orr <i>et al.</i>
Average of all marine plants	8.4	
Land Plants	0.8	Willstätter and Stoll

Tab. 4 - Averages and ranges of chlorophyll content of marine plants, phytoplankton, and land plants (based on ash-free, dry weight).

To compare the factors that control the distribution of pheophytin in the recent sediments of Kalloni Bay, the values of each station were first divided by the values for Station 9 (see Text-fig. 2). Station 9 was selected for two reasons: it has the lowest pheophytin content in organic matter and the highest total organic matter content in the dry sediment (see Tab. 5). The ratios of pheophytin content in organic matter and in dry sediment reach a maximum of 9 and 1.7, respectively, at Station 17. The ratios of organic matter reach a minimum of 0.12 at Station 10.



Text-fig. 2 - Station averages for contents of pheophytin in dry sediment (A), pheophytin in organic matter (B), and of total organic matter in dry sediment (C). Ratios to value of Station 9.

The high value of total organic matter at Station 9 can be explained by the organic material, especially wood fiber and plant fragments, that is supplied into the area by the adjacent stream. The low pheophytin content in the organic matter, at the same station, probably is the combined result of intensive oxidation and relatively low primary production.

In order to avoid the effect of the extreme values at Station 9, all three values (total organic matter, pheophytin in dry sediment, and in organic matter)

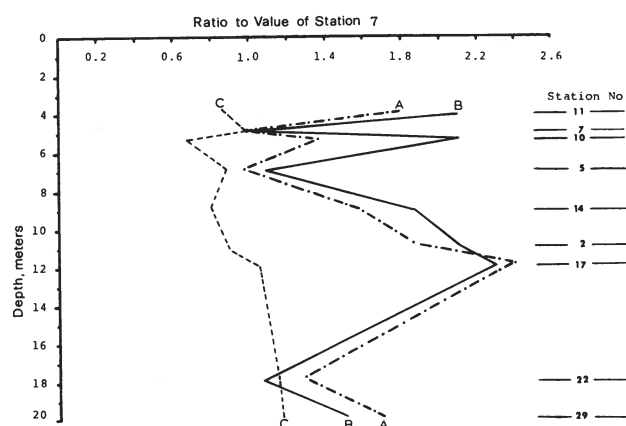
at each station have been divided by the values of Station 7 (see Text-fig. 3).

Station	Depth (meters)	Total Organic Matter (% dry sediment)	Pheophytin ppm in dry sed.	Pheophytin ppm in organic matter
2	11	6.90	13	188
5	7	6.90	7	101
7	5	7.74	7	90
9	6	42.78	10	23
10	5.5	5.25	10	190
11	4	6.93	13	188
14	9	6.36	11	173
17	12	8.32	17	204
22	18	9.01	9	100
29	20	9.16	12	131

Tab. 5 - Depth, total organic matter, and pheophytin content in dry sediment and in organic matter in the recent sediments of Kalloni Bay.

The first interesting observation from this graph (Text-fig. 3) is that the percentage of organic matter (curve C) does not seem to affect either curve A or B. Only in Stations 2 and 4, a relatively good correspondence between curves A, B, and C appears to exist. In Stations 5, 10, 7, and 11 there is an opposite effect, while Stations 29, 22, and 17 have a relatively constant organic matter content, but the ratios in curves A and B fluctuate.

Also, it can be seen that for depths greater than 12 m, curve A lies to right of curve B, thus suggesting that the effect of dilution. This observation,



Text-fig. 3 - Station averages for contents of pheophytin in dry sediment (A), pheophytin in organic matter (B), and of total organic matter in dry sediment (C). Ratios to value of Station 7.

combined with the relatively uniform concentration of organic matter, suggests that a greater decomposition rate is responsible for the decline of pheophytin content in dry sediment and organic matter to a depth

of 18 m. Below that depth there is an increase in pheophytin concentration due to the reducing environment and the resulting better preservation.

For depths shallower than 12 m, curve A lies to the left of curve B, indicating a greater effect of dilution and production.

Finally from Table 6, it can be seen that proteins, humus, and insoluble organic residue account for almost 90% of the organic matter composition. It can also be seen that the content of these substances tends to rise with depth.

Station	Percent content based on total organic matter			
	Pigments	Lipids	Total Carbohydrates	Protein & insoluble residue (calc.)
2	0.019	12.60	2.55	84.83
5	0.010	0.87	7.73	91.39
7	0.009	0.65	7.31	92.03
9	0.002	0.21	23.90	75.88
10	0.019	0.76	7.37	91.85
11	0.019	0.58	6.58	92.82
14	0.017	0.63	8.98	90.37
17	0.020	0.48	10.36	89.14
22	0.010	0.55	7.51	91.93
29	0.013	0.66	2.81	96.52
Average	0.015*	0.60**	6.80*	89.68

* Station 9 not included

** Station 2 not included

Tab. 6 - Pigment, lipid, and total carbohydrate content based on total organic matter in Kalloni Bay sediments (for depth and total organic matter see Tab. 5).

B. TOTAL CARBOHYDRATES

The total carbohydrate content of the recent Kalloni Bay sediments is considerably higher than those in Broadkill Marsh and Delaware Bay (see Tab. 7). On the other hand, the content is lower than in the recent sediments of the Gulf of California at 1210 fathoms depth.

Source material, degree and rate of oxidation, depth, and turbulence are among the factors that control the observed differences.

In the case of Broadkill Marsh and Delaware Bay, the depth is almost the same as in Kalloni Bay. On the other hand due to the low oxidation rates, the reducing environment, and the high hydrostatic pressures that result from deep Gulf waters, sugars are better preserved in the Gulf of California (Swain and Bratt, 1971). According to them, low-energy, reducing conditions and high hydrographic pressures inhibit microbial action.

It appears that dramatic differences in the degree of oxidation can not fully explain the high carbohydrate concentration in Kalloni Bay, as compared to the two shallow marine environments of Delaware.

Location	Depth (meters)	Total Carbohydrates (mg/gr)	Author
Kalloni Bay, Lesvos, Greece	10 (4 - 20)	4.90 (1.76 - 8.62)*	Tassos
Delaware Bay, Delaware	6	1.67 (0.40 - 7.98)	Swain and Bratt
Broadkill Marsh, Delaware	—	0.47 (0.03 - 2.96)	» »
Gulf of California, California	2213	12.22 (7.40 - 25.40)	» »

* an extreme value of 102.25 is not included.

Tab. 7 - Comparison of the total carbohydrate values (average and range) from four different sampling locations.

Probable differences in the source material could very well be the decisive factor responsible for the higher values in Kalloni Bay. Peridinians contain almost four times more carbohydrates than diatoms or copepods (see Bordovskiy, 1965). Nevertheless, the possibility of differences in oxidation rates can not be excluded.

The extremely high value of 102 mg/gr in Station 9 is most likely related to the plant material brought in by the stream that flows into the adjacent area. Also, low concentrations of terrigenous minerals allow the organic matter to cover the surface of the sediments. It is also possible that some of the dead plant material brought in by the streams enriches the rest of the bay area.

C. LIPIDS

The average lipid content of the recent Kalloni Bay sediments (see Tab. 1) is comparable with that in Delaware Bay (see Swain, 1972). Lipids include bitumens, fatty acids, waxes, and some organic pigments (Swain, 1970).

It should be noted that both the yield and the composition of lipids are affected by the different solvents and extraction methods. The ultrasonic method that was used in this study produces rather conservative results.

Another factor that has to be considered in explaining the lipid content is its composition. Clarke and Mazur (1941) have experimentally shown that when a bitumen extract from planktonic diatoms was kept under aerobic conditions for 6 months the amount of bitumen and of the combined fatty acids had been halved, the amount of uncombined fatty acids had been reduced to less than a third, but the hydrocarbons were practically unaffected. Lipids are among the more resistant to microbiological oxidation, but prolonged suspension (caused by frequent mixing) and oxidizing water environment could result in a degradation of some of the lipid constituents.

DISCUSSION AND CONCLUSIONS

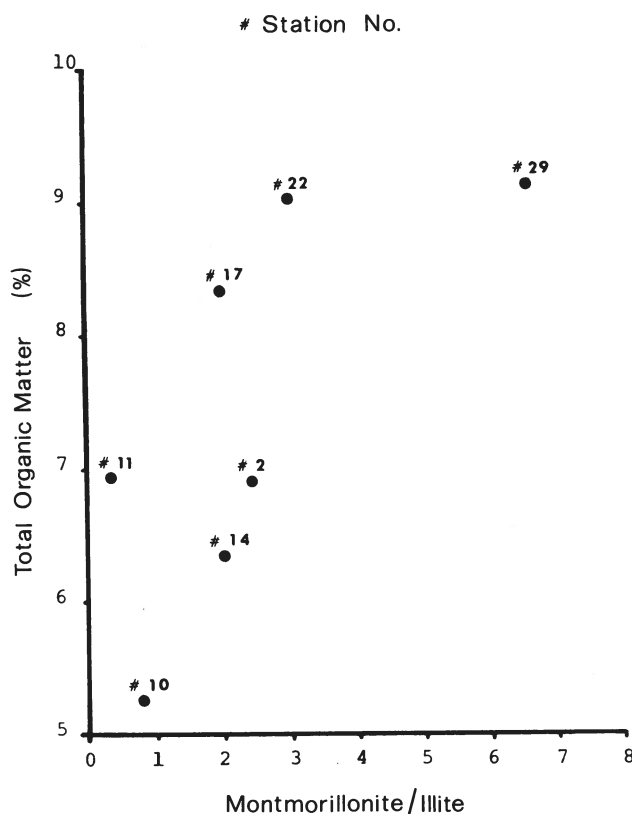
The recent sediments of Kalloni Bay are mostly composed of shelly mud, and their polymodal character suggests different transporting mechanisms. Apparently the surrounding volcanic assemblage is the ultimate source of sediment, while currents keep the entrance to the bay open by washing away the fine grains. Angular quartz and feldspar are the main minerals of the sand and silt-sized material. Montmorillonite is the major clay mineral, with illite, kaolinite, and minor amounts of chlorite also present.

The presence of montmorillonite, resulting from the volcanic nature of the source area, as the primary clay mineral, is believed to be responsible for the large amount of organic matter that is preserved in the bay sediments. Among the clay minerals, the montmorillonite group has the most lyophilic properties (Worral, 1968). Lyophilic colloids are very stable, adsorb the dispersion medium, and have high viscosity. Montmorillonite has been found to adsorb fatty acids, polysaccharides, amines, and proteins (Jordan, 1949; Talibudeen, 1955; Worral, 1968). The formation of colloids is assisted by the small size of montmorillonite (less than 1 micron). Brownian movement of suspended clay facilitates collision with the various solvent molecules. This will be particularly true during the summer because of the appreciable increase in temperature and subsequent increase in particle motion.

Text-fig. 4 shows a general relationship between the montmorillonite-illite ratio and the total organic matter in the recent sediments of Kalloni Bay.

The high productivity of the bay combined with the abundance of montmorillonite and the relatively reducing environment of the bay sediments result in high organic matter content of the bottom samples. The abundance of aggregates in the recent Kalloni Bay sediments suggests that flocculation of the organo-mineral compounds plays a very important role in the precipitation of organic matter.

Carbohydrates seem to be higher than average in these sediments which may reflect rather high concentration of sugars in the source material. The surface of a montmorillonite particle, combined with relatively high oxygen content and large bacterial concentrations, could facilitate the reactions leading to the formation of humic acids. The amount of protein and insoluble organic residue increases with depth. Also an increase in pH of the bottom sediments was observed in areas deeper than 12 meters (pH of 7.50, versus 7.30 for shallower water). While direct oxygen data is lacking, it is believed that most of the bay water is well oxygenated due to intense wind action.



Text-fig. 4 - Relationship between montmorillonite-illite ratio, and total organic matter content in the recent sediments of Kalloni Bay.

The low transparency of the bay is most likely related to the abundance of suspended clays and plankton. Whitehouse, Jeffrey, and Debbrecht (1960) reported that the average settling velocities at 26°C for montmorillonite, illite, and kaolinite are 1.8, 15.8, and 11.8 meters per day, respectively.

It should be mentioned that possibly a small part of the ignition loss might represent water that was trapped in the montmorillonite mineral. Worral (1968) reports that while the absorbed water by kaolin-type clays can be removed by heating to 105°C, montmorillonite requires a temperature of 250°C.

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