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Recent Sediments of Makirina Cove (Northern Dalmatia, Croatia): Their Origin Viewed Through a Multidisciplinary Approach

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Abstract

Makirina Cove was formed by the Holocene sea-level rise which caused a marine ingression into the depression formed within Albian–Cenomanian dolomites at approximately 4.5 ka B.P. At present, Makirina Cove represents an restricted, stressed, shallow-marine (<2 m) ecosystem characterized by varying seawater temperatures (0–35°C) as well as fluctuating salinities (up to 41‰) affected by seasonally enhanced evaporation, continuous freshwater supply through on-shore and submarine springs associated with the coastal karst area and surface run-off episodes. These environmental conditions have been conducive to high primary production of organic matter resulting in the formation of organic-rich deposits which contain up to 5 wt.% of organic carbon. Up to the present times, 3.5 m of sediments have been deposited indicating a relatively high sedimentation rate estimated at 0.75 m/1.0 ka in the northern central part of the Cove.

The sediments are being deposited mostly as poorly sorted clayey–sandy silts. The distribution and concentration of most of the chemical elements is dependant on the mineralogical composition and granulometric features of the Makirina sediments, which show values more or less similar to those from the Central Adriatic. Accordingly, there is a positive correlation with Al and K concentrations increasing off-shore and with the depth being associated with increasing concentrations of clay minerals within the clay fraction. The same holds true for concentrations of some trace elements, especially Mo and Se which is consistent with the distribution pattern of sulphides.

Selenium is preferentially enriched in authigenic pyrite and it is probably the major source of Se in the Makirina Cove sediments. The concentrations of Ca, Mg and Sr decrease off-shore and they are linked to the composition of the surrounding carbonate rocks. The saturation indices show that the water is supersaturated with respect to carbonates enabling the precipitation of authigenic amorphous or crystalline carbonate phases from the pore water in the upper segment of the sediment column. According to the oxygen isotopic ($\delta^{18}O$) composition, molluscs precipitated their carbonate shells mostly during warmer periods (May to November) at or near isotopic equilibrium with their ambient waters. The carbon isotopic $\delta^{13}C$ composition of mollusc carbonate shells is environmentally affected due to oxidation and decomposition of organic matter as well as influxes of fresh water into the Cove, indicating their formation out of the predicted isotopic equilibrium with atmospheric CO_2. Palynological and organic carbon isotopic ($\delta^{13}C$) composition shows that the sedimentary organic matter (SOM) is 70–90% lipid- and hydrogen-rich and on average 2/3 marine derived (mainly phytoplankton, bacteria and marine macrophytes) and 1/3 terrestrially derived (mainly woody tissue). The variations in composition of SOM have been noted as a function of the distance from the shore. The type and the preservation state of SOM and pyrite as well as the measurements of Eh, pH, total alkalinity, dissolved inorganic carbon (DIC) and the enrichment of redox-sensitive trace elements, indicate oxygen-depleted depositional conditions and that the sediment is highly reductive even in the uppermost segment at the sediment/water interface. According to the results obtained from the applied methods, the features of Makirina sediments strongly reflect the given depositional conditions within this restricted, stressed, shallow-marine environment where these organic-rich sediments originate, and may therefore serve as a calibration standard in further investigations.

1. INTRODUCTION

The markedly indented coastline of both mainland and islands along the Eastern Adriatic has formed numerous bays and coves, mostly representing restricted, shallow marine depositional environments within which Recent (Holocene) sediments accumulate. Some of these sediments have been investigated from a specific viewpoint dealing with a particular problem. A number of papers on Holocene sediments from NE Adriatic sites have been published based on investigation or material of the Göttingen working group (D. Meischner). Accordingly, investigations have been carried out dealing with sedimentology (FÜTTERER, 1969; PAUL, 1970; MEISCHNER, 1972; RANKE, 1974; FÜTTERER & PAUL,

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1976), benthic foraminiferal dynamics (DANIELS 1971; MEISCHNER, 1971; PAUL, 1971) and ostracod assemblages (UFFENORDE, 1971, 1975), pollution problems (STIRN et al., 1974), interstitial water composition (CESCON et al., 1975), heavy metal composition (PAUL & MEISCHNER, 1976), vegetation development (BEUG, 1977), geochemistry and microbiology (GOLUBIĆ et al., 1977), and sea-level changes based on sedimentology, fossil biota and geochemistry (MEISCHNER, 1995). During the last two decades, investigations of Recent sediments have intensified and have also included a number of sites from other regions of the Eastern Adriatic. The study of the Recent sediments of the Krka river estuary has yielded information on heavy metal distribution (PROHIĆ & JURAČIĆ, 1984, 1989; PROHIĆ & KNIEWALD, 1987), organic matter and sediments (JEDNAČAK-BIŠĆAN & JURAČIĆ, 1987), approach to pollution problems (PRAVDIĆ & JURAČIĆ, 1988), suspended matter and sediments (JURAČIĆ & PRAVDIĆ, 1991) and sedimentology (JURAČIĆ & PROHIĆ, 1991). Similarly, the papers dealing with the Raša river estuary Recent sediments have reported on pollution problems (JURAČIĆ et al., 1992), particulates and trace metals (VDOVIĆ & JURAČIĆ, 1993; SONDI et al., 1994) and sedimentology (SONDI et al., 1995; BOGNER et al., 2003). The Recent sediments of Kaštela Bay have been investigated in order to define heavy and trace metal distribution (BOGNER et al., 1998) and in Pirovac Bay selenium distribution (MIKO et al., 1998). The results of the study of the Morinje Bay sediments have included some consideration of kerogen precursor formation processes (KOCH et al., 2000) and pollution problems (KOCH et al., 2002). Recent sediments of the Croatian islands have also been a matter of scientific interest for quite a long time. For example, the study of the Mljet lakes sediments has provided information on sedimentology (SEIBOLD & WIEGERT, 1960; JURAČIĆ et al., 1998; GOVORČIN et al., 2001), vegetation hystory (BEUG, 1961), sea-level, i.e. environmental changes based on diatoms and geochemistry (WUNSAM et al., 1999) and dynamics of benthic foraminiferal assemblages (VANIČEK et al., 2000; ĆOSOVIĆ et al., 2002), whereas from the Vrana lake of Cres island the distribution of trace metals in the surface sediments has been reported (MIKO et al., 2003). In addition, the Recent sediments of Nin lagoon, Karin Bay and Pirovac Bay have been investigated from the balneological point of view being classified as healing mud, i.e. peloids with great potential in medical treatment (MANDIĆ et al., 1969; NOVAK, 1981; OLUIĆ et al., 1984; MIKO et al., submitted).

This overview of selected references and topics concerning the Recent sediments from the Eastern Adriatic sites shows that investigations have been carried out in a particular way depending on the given objectives. Taking into account these known facts, and the general idea that investigations based on a methodologically integrated concept may serve as a basis for solving all implied problems, a working group has been convened at the Institute of Geology, Department of Geology, Zagreb, in order to conceptualise a project for further investigation of the Recent sediments within the research project "Basic Geological Map of the Republic of Croatia, Scale 1:50.000". Consequently, the project "Recent sediments of the coast and the islands of the Republic of Croatia" has been established in order to study the sediments, on the one hand, in all aspects by using the concept of a multidisciplinary approach and, on the other hand, to apply the results obtained from these investigations to a wide range of interests. This means that many types of standards have to be compiled within the calibration of the reference sites which can then be correlated with other sites, and to apply the actualistic principles while studying and interpreting various aspects of recent and fossil sedimentary bodies of similar origin. As all depositional environments are characterised by the complex interaction of biological, physical and chemical processes, any variation may then be interpreted in terms of environmental, i.e. ecological changes which have been caused by natural and/or anthropogenic influences, in Recent sediments and natural influences in fossil sediments. Therefore, the main objectives of this project are to: (1) define the origin of the sediments, especially regarding formation processes, (2) apply the results of the investigation into every potentially interesting field, (3) evaluate the economic value of the sediments, (4) estimate the degree of anthropogenic pollution, and (5) publish the obtained results as far as possible within the frame of the presented investigation objectives.

The investigation of sediments of Makirina Cove, Morinje Bay and Velike Soline has recently been carried out in terms of the concept of a multidisciplinary approach, providing a better insight into the complexity of their origin. The results of this investigation have opened some new perspectives concerning the processes of formation of the sediments within these sensitive depositional environments. Therefore, it is suggested that this multidisciplinary approach may well represent a methodological model for further research work on shallow marine sediments from other sites, both coastal and island, along the Croatian Eastern Adriatic. In this paper we present the results of the investigation of the Makirina Cove sediments with regard to their origin.

2. GEOGRAPHICAL PROPERTIES

The basic geographical property of the SW part of the coastal area of Šibenik, to which Makirina Cove belongs, is the markedly indented coast (Fig. 1). Makirina Cove represents the SW prolongation of Pirovac Bay (Fig. 2) with a N–S extension, approximately 1,250 m in length and 300 m in width. It is surrounded by moderately sloped ground of the Makirina and Gračina hills. Along the shore line, a few periodic, low capacity on-shore springs and low capacity underwater

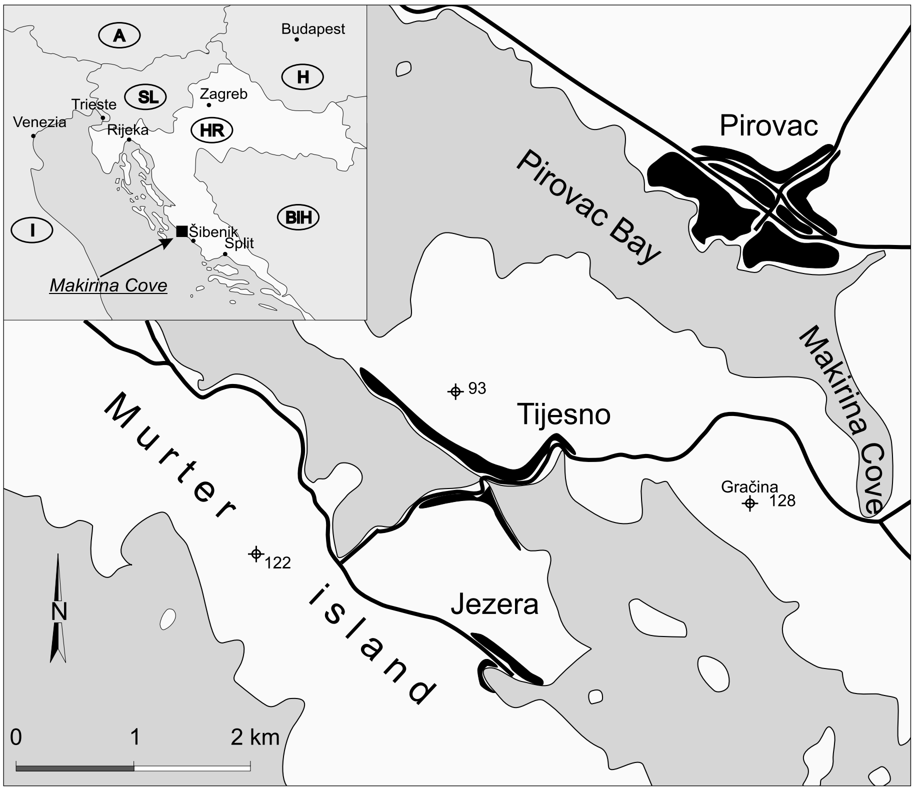

Fig. 1 Index map.

springs occur. The water-wells in the Quaternary deposits contain slightly brackish water. The sea depth of the southern part of the Cove, where a periodical stream flows in, rarely exeeds 0.5 m, gradually increasing towards the NE up to 4.5 m (Fig. 3).

The bottom of the Cove is mainly covered with vegetation, sporadically revealing silty and muddy ground (Fig. 3). Seagrass (*Cymadocea nodosa*), algae (*Codium bursa*), numerous lamellibranchs (*Laevicardium oblongum* and others), gastropods (*Gourmya vulgata* and others), crustaceans and foraminifera, indicate the rather favourable conditions for the development of the floral and faunal communities within this ecosystem.

The climate is typical Mediterranean. The winters are mild, rainy and windy, and the summers are warm and dry with a high insolation rate. According to the number of insolation hours (2572 h/y, measuring station Šibenik), the area of Šibenik belongs to the sunniest parts of the coastal Adriatic. The mean value of annual temperature is 16°C; in January 6–8°C and in June 25–26°C. The sea-water temperature ranges annually from 0–35°C. The salinity is variable, in places due to small capacity submarine springs it is brackish, and reaches values up to 41‰ during the summer. Precipitation has two maximums; the amount during the winter is higher than during the spring. The mean value of the annual precipitation is 840 mm.

The main winds are bura (north-eastern wind, mostly during winter), jugo (south wind) and maestral (landward breeze).

Fig. 2 Makirina Cove.

3. METHODS

3.1. Field work

On the basis of the principles of formation analysis, a geological map 1:10,000 of the region surrounding Makirina Cove was constructed and interpreted.

The sediments of Makirina Cove were investigated by producing profiles which were located perpendicular to the longer axis of the Cove (Fig. 4). The distance between profiles was 24 m in the southern part and 50 m in the northern part.

The distance between the probes was defined with a measuring strip. The topographic map 1:2,500 was

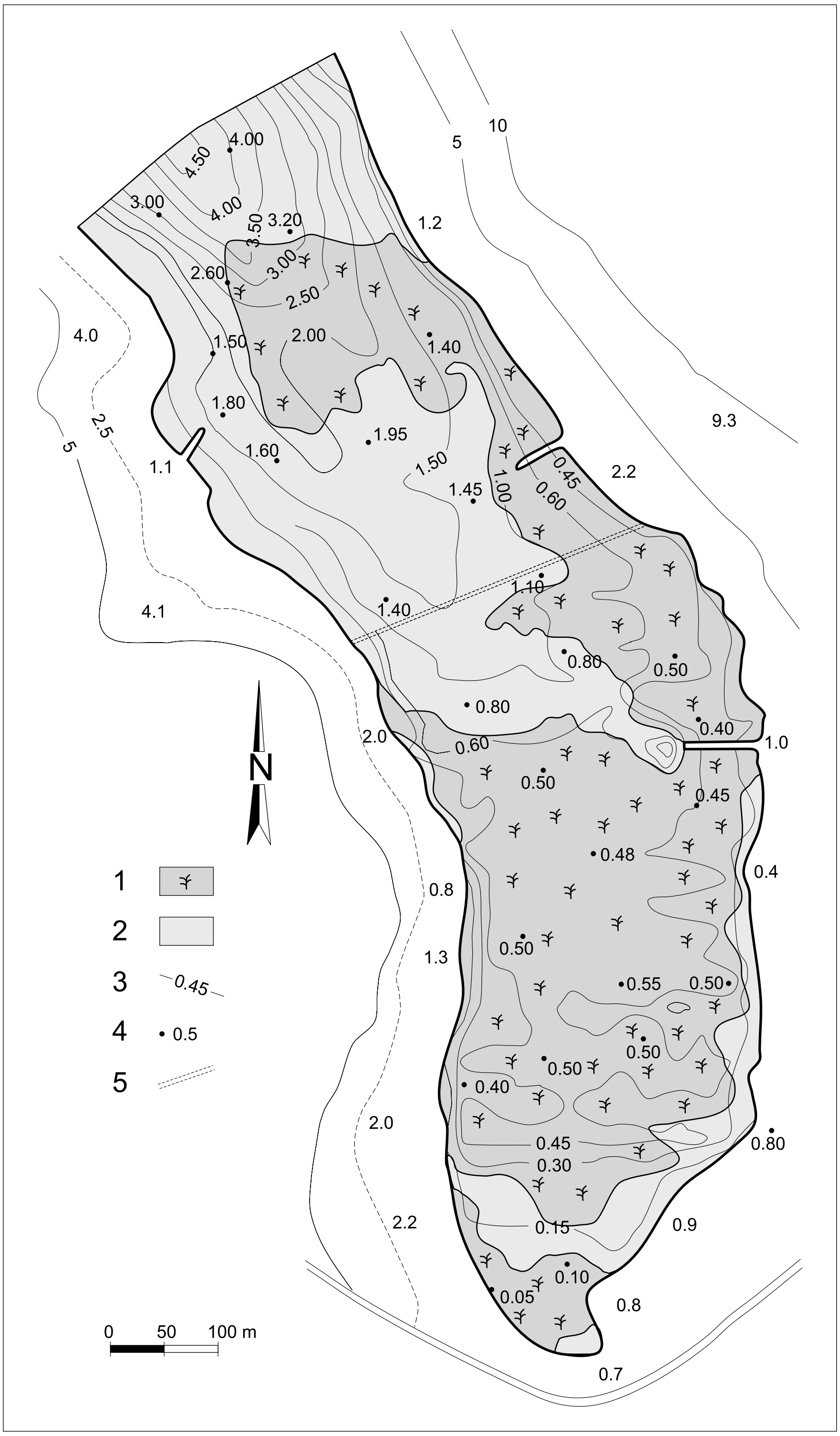

Fig. 3 Sea bed map and sea depths. Legend: 1) the bottom covered with vegetation; 2) sandy–muddy bottom, along the shore gravelly with outcropping rocks; 3) isobath; 4) sea depth; 5) partition wall.

used for the construction of the probe network. Each probe includes a description of the general conditions and measurements (sea depth, sea temperature on top and bottom, bottom features such as: silty, muddy, vegetation cover, etc.) as well as drilling sediments with a spiral borer to enable description of their features (colour, scent, granulometric composition, plasticity, etc.). In this manner, the sediments of the Makirina Cove were investigated with a total of 778 probes. For the purposes of the analytical research, an additional probe network was constructed for core samples (Figs. 4 and 8). The samples were taken with a corer (diameter 5 cm, length 50 cm) from a depth of 1–3 m.

3.2. Analytical methods

3.2.1. Sedimentological analysis

The granulometric composition of the sediments was defined using wet sieving and the laser granulometric method for the <63 μm fraction. Grain size boundary

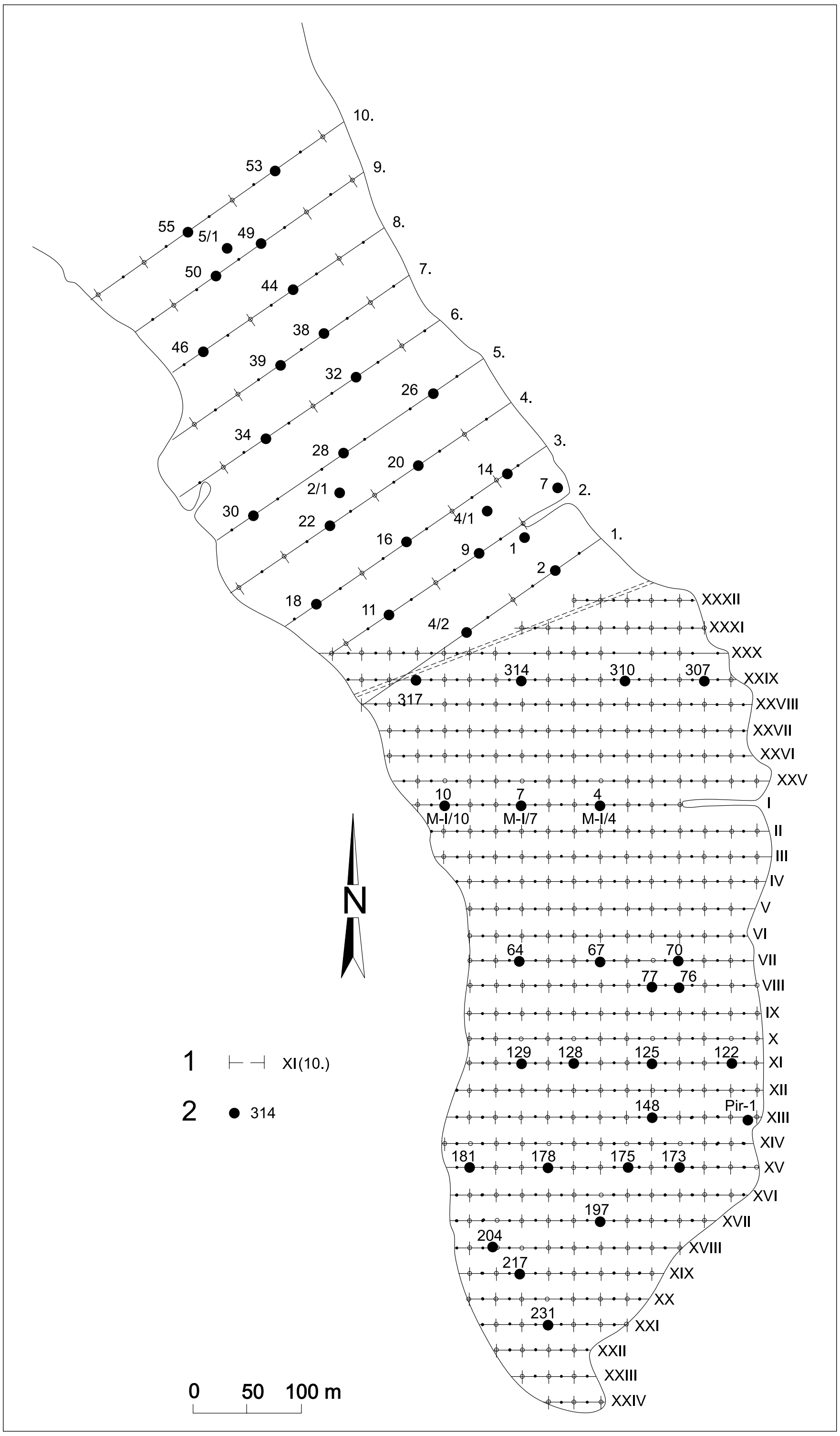

Fig. 4 Probe network. Legend:
1) marked profile line;
2) numbered sample.

values were used according to the standard Wentworth scale. Within the 0.09–0.16 mm fraction, calcite was dissolved with cold 4% HCl. From the remainder, the light and heavy mineral fractions were separated using $CHBr_3$ (s.g. 2.89 g/cm^3). Microscopic slides were made from each part of the fraction. Qualitative and quantitative analysis of the minerals was performed by polarisation microscope.

3.2.2. Geochemical analysis

3.2.2.1. Total content of major, minor and trace elements

Surficial sediment and sediment core samples were taken from 29 sites in the southern part of Makirina Cove (Fig. 5). Sediments were collected with hand-driven plexyglass core samplers (40 cm long and 3.5 cm internal diameter). The sediment samples and cores were air-dried, then split into 5 cm long intervals and stored in

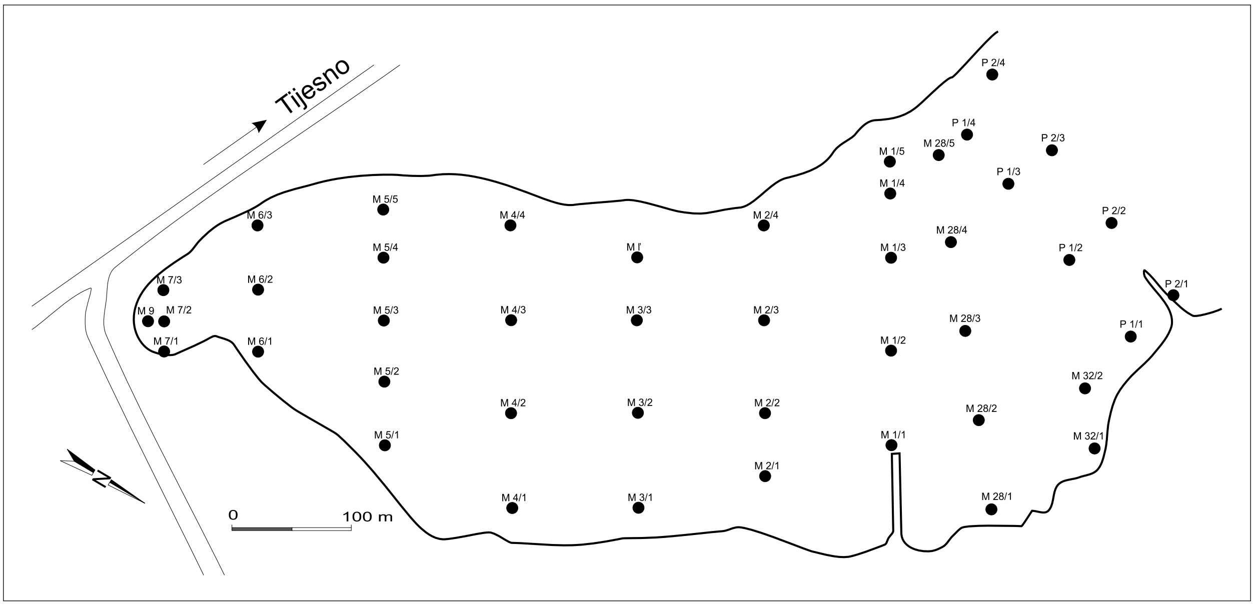

Fig. 5 Sampling points.

clean polyethylene bottles. Only the top 5 cm were used for the purpose of this study. In the laboratory, the dried samples were desegregated and homogenised. Fractions smaller than 1 mm were analysed. Major (Si, Al, Fe, Ca, Mg, Na, K), minor (Mn, Ti, P) and trace elements (Ag, Au, Ba, Be, Bi, Sr, Y, Zr, V, Cu, Pb, Zn, Cd, As, Hg, Ir, Sc, Ta, Ni, Co, Cr, Cs, Hf, Mo, Rb, Sb, Se, Th, U, W, La, Ce, Nd, Sm, Eu, Tb, Yb, and Lu) were determined by ICP, INNA and ICP/MS. Concentrations of Be, Ag, Cd, Bi, Au, Hg, Ir, Ta, and W were generally below the detection limit of the selected method (Be – 2 ppm, Ag – 0.4 ppm, Cd – 0.5 ppm, Bi – 5 ppm, Au – ppb, Hg – 1 ppm, Ir – 5 ppb, Ta – 1 ppm, W – 3 ppm). C and S were analysed separately with a LECO analyser. Analytical blanks were run with the samples, and a marine sediment reference standard MAG–1 (US National Bureau of Standards), as well as our laboratory standards J1 and J2 (surficial sediment from the Northern Adriatic Sea) were used to check the accuracy of the analytical procedure. Geochemical analyses were carried out at the Activation Laboratories, Ontario, Canada. Analytical precision and accuracy were better than ±3% for major elements, ±5% for REE, but between 5 and 9% for minor and remaining trace elements. This was indicated by results of duplicate measurement for 8 samples and the USGS MAG–1 standard.

3.2.2.2. Selenium speciation analysis

The contents of Se in surficial sediments of Makirina Cove were determined by hydride generation inductively coupled plasma atomic emission spectrometry. The surficial sediments (0–20 cm) and shallow core (0–30 cm) sediments were analyzed for Se content by hydride generation ICP atomic emission spectrometry after extraction of sediment Se by three different dissolution techniques: 7 M HNO_3 digestion, aqua regia digestion and the acid mixture HF–HCl–HNO_3. The 7 M HNO_3 digestion could be used for selenium speciation (KULDVERE, 1989; HALL & PELCHAT, 1997).

All reagents were of analytical reagent grade and deionized water was used throughout all dilutions. Standard solutions containing 1000 mg Se^{IV} were obtained from Merck and were also prepared by dissolving SeO_2 (Merck) in water and acidifying with 5 mol L^{-1} HCl. The reducing agent sodium tetrahydroborate (1% solution) was prepared daily by dissolving solid compounds in a 0.1 mol L^{-1} solution of NaOH and filtered (HALL & PELCHAT, 1997).

The use of HNO_3 digestion of stream sediments has found application by some authors (KULDVERE, 1989) for selenium speciation. Namely, this procedure extracts both Se^{IV} and Se^{VI} into solution without reduction of Se^{VI} which is not reactive with sodium tetrahydroborate, and therefore it is possible to determine the quantities of Se^{IV} and total Se (by pre-reduction with 5 M HCl or by aqua regia digestion or by the acid mixture HF–HCl–HNO_3).

3.2.2.3. Pore water geochemistry

Sediment cores were collected manually at site 3 with a plexiglas tube, immediately transferred to the laboratory and cut into 2–4 cm thick sections in a glove bag filled with nitrogen. Redox potential (Eh) was measured immediately after coring by inserting an electrode into the core through 1 cm side openings in the tube, covered with plastic adhesive tape. Pore water was extracted under a pressure of 0.4 MPa through a 0.45 µm membrane filter. The pH and total alkalinity were determined immediately in the glove bag. Subsequent samples were taken for total alkalinity, metal cations, nutrient (NH_4^+, NO_3^-, SO_4^{2-}, S^{2-}, PO_4^{3-}) and $\delta^{13}C$–DIC analyses. An incubation experiment was performed at sites 3 and 5 to determine the *in situ* benthic fluxes of nutrients at the sediment/water interface. Plexiglas chambers with a diameter of 210 mm were inserted about 35 cm deep into the sediment. The height of the water layer in the chambers was about 15 cm, and the height of the water layer above the cover was more than 5 cm even at low tide. The water in the chamber was gently stirred manually a few times per day. Water samples were taken using plastic syringes approximately 5 cm above the bottom at regular time intervals over a period of 10 days. The volume of the sample taken was compensated through a compensation valve. pH, salinity, total alkalinity, δ^{13}C–DIC, and concentrations of the main nutrients, as well as Ca^{2+}, Mg^{2+}, Fe_{tot} and Mn_{tot} were determined; all concentrations were corrected for the compensating dilution. For methane isotopic analysis, sediment from the depth segment 0–15 cm was incubated in the dark as a slurry (sediment+seawater in 1:1 ratio) in diffusion bottles kept upside-down at room temperature. Headspace CH_4 was analysed for δ^{13}C.

The pH of the extracted pore water was measured with a combined pH electrode. Salinity was determined refractometrically (Atago, Japan). Total alkalinity (±2%) was determined by the Gran titration method. The concentration of DIC was calculated from the pH and total alkalinity as described by MILLERO (1995). Nitrate, ammonia, and sulphide concentrations were determined using colorimetric procedures described by GRASSHOFF et al. (1983). Sulphate was determined turbidimetrically (TABATABAI, 1974). The precision of all anion analyses was better than ±2%. Concentrations of Ca^{2+} (±2%), Mg^{2+} (±1%) and Fe_{tot} (±3%) in pore water were measured by flame AAS (Varian AA5). The stable isotopic composition of DIC and CH_4 was determined by mass spectrometry. The water sample for isotopic analysis was injected into an evacuated container with 100% H_3PO_4 and the CO_2 released was analysed using a Europa 20–20 Stable Isotope Analyser with an ANCA TG trace gas separation module. The isotopic composition of CH_4 was determined after oxidation on CuO at 800°C on the same apparatus. The precision of the analysis was better than ±0.2‰. Porosity (φ) was calculated from the weight loss of the sediment dried overnight at 110°C using the relationship:

$$\varphi = (M_w / 1.0) / [(M_s / 2.5) + (M_w / 1.0)],$$

where M_w is the weight loss upon drying, M_s is the weight of dry sediment, and 1.0 and 2.5 are the densities (g/cm^3) of water and sediment, respectively (JOHNSON et al., 1982).

3.2.3. Mineralogy by X-ray powder diffraction

The mineralogy of surficial sediment samples and mollusc shells was determined by X-ray powder diffractometry using a Philips PW 3710 diffractometer and Cu K_α radiation. Powder samples were scanned at the rate of 2° per minute, over the range of 24–60°. The results were stored on a PC computer and analysed with PC–APD diffraction software.

3.2.4. Isotope analyses

3.2.4.1. Biogenic carbonates

Live specimens of *Laevicardium oblongum*, *Nuculana fragilis*, *Monodonta turbinata*, *Columbella rustica* and *Gourmya vulgata* were collected from Makirina Cove, Pirovac Bay and the coastal part of the Murter Sea. Specimens were transported to the laboratory in seawater, immediately rinsed in tap water and killed by freezing at -18°C. The specimens remained frozen until shucked. Shells were scrubbed clean with a plastic scouring pad then air dried, and stored at room temperature until analysed.

Prior to analysis of isotopic composition, powdered samples of the investigated mollusc shells were roasted at 380°C for 1 hour to volatise organic matter. Thereupon the samples were reacted in an acid bath with excess 100% H_3PO_4 at 25°C (McCREA, 1950). CO_2 gas released during acid treatment was cryogenically cleaned and analysed for O and C isotope composition on a Varian–MAT 250 mass spectrometer. The δ^{18}O and δ^{13}C values were normalized by assuming δ^{18}O and δ^{13}C values of -2.44‰ and +2.48‰ for IAEA–CO–1 standard on the VPDB scale. The analytical precision based on multiple analysis of an internal laboratory standard was ±0.01% (1σ) for δ^{18}O and δ^{13}C. The overall analytical replication of the carbonate carbon isotopic data was ±0.1‰.

3.2.4.2. Organic matter (sedimentary organic matter, terrestrial plants, aquatic plants, algae)

Carbon isotopic composition of sedimentary organic matter, terrestrial plants, algae, and aquatic plants were measured in the carbonate-free samples on a Europa 20–20 Stable Isotope Analyser (Europa Scientific Ltd.), with ANCA–NT preparation module for on line combustion of bulk solid samples and chromatographic separation of the gasses. For preparation of total organic carbon, the powdered sediment, terrestrial as well as aquatic plant and algae samples were treated with 3M hydrochloric acid at 50°C to remove the carbonates. Upon cessation of CO_2 evolution, excess acid was removed by repeated washing (three to four times) with double distilled water, until the pH was neutral. After the final decantation of water, the carbonate-free residues, mostly composed of organic matter, were oven-dried at 50°C. Organic carbon isotope ratios were measured in a Europa 20–20 Stable isotope Analyser (as above). Organic carbon isotope values were calibrated using the IAEA–CH–7 standard with a δ^{13}C value of -31.8‰ on the PDB scale. The results are reported in the conventional delta notation as ‰ deviation from the PDB standard. The analytical precision for organic carbon based on multiple analysis of an internal laboratory standard was δ^{13}C ±0.01‰ (1σ). Overall analytical reproducibility of the organic carbon isotopic data was ±0.1‰.

3.2.4.3. Seawater

To define the O and C isotopic composition of ambient seawater and the isotopic composition of ambient seawater DIC, seawater was collected monthly from June 1999 until September 1999. To preserve the water samples and to prevent the possibility of continuing biological activity a few mg of $HgCl_2$ powder was added to each water sample selected for $\delta^{13}C$ analysis. Water samples were stored in a refrigerator until analysed for $\delta^{18}O$ by the procedure outlined in EPSTEIN & MAYEDA (1953) in which $\delta^{18}O$ is measured in CO_2 that has been equilibrated with the water to be analysed at a defined temperature for a number of hours. However, because of the salinity, equilibration was necessary for 48 h at 25°C prior to extracting the CO_2. The "salt correction" equation for ^{18}O was then applied after SOFER & GAT (1975). Stable isotopic analyses were carried out on the Varian MAT–250 mass spectrometer. For $\delta^{13}C$ analyses of DIC the isotopic composition of CO_2 liberated from 5 ml of water after acidification was determined using a Europa 20–20 ANCA–TG mass spectrometer. The results are reported in the conventional delta notation as ‰ deviation from the VSMOW for $\delta^{18}O$ and VPDB standard for $\delta^{13}C$. Overall analytical reproducibility of the isotopic data was better than ±0.15‰ for seawater oxygen, and ±0.1‰ for dissolved inorganic carbon.

3.2.5. Palynofacies

Core-samples were taken approximately 10 cm below the top of the sediments along the transect I (Fig. 4). Samples were dried and 50 g of each was used for palynological processing. The carbonates were dissolved with HCl (10%) and the silicates with HF (40%). Heavy liquid of ZnCl (2.1 kg/l) was used to separate the organic matter from the inorganic components. No further treatment (sieving, oxidation) of the organic residue has been attemped in order to analyse the organic matter as a whole and to avoid alteration of organic matter preservation due to processing. Palynological slides were made always using the same amount of organic residue of each sample and glycerin gelatin as the mounting medium.

Microscopic examination of the palynodebris was carried out in both transmitted and incident blue light.

Qualitative analysis of the palynological organic matter (POM) was conducted using the diagnostic criteria of palynomorphs and palynodebris. Microscopic examination in incident blue light was applied to identify hydrogen-rich and lipid-rich structured, structureless and amorphous organic matter, and to assess their relative fluorescence intensity.

Quantitative analysis is based on both the relative estimation of structureless and amorphous organic matter, and calculated absolute frequencies of both land and marine derived structured categories per palynological slide.

4. RESULTS AND DISCUSSION

4.1. Geological setting of Makirina Cove

4.1.1. Lithostratigraphy

The geological map (Fig. 6) shows that Makirina Cove is mostly surrounded by Cretaceous carbonate successions. The area of Ivinj Draga is covered with a relatively thin layer of Quaternary clastic deposits. According to the lithological features and microfossil assemblages, the following informal lithostratigraphic units may be discerned: A) *Ivinj dolomites*; B) *Makirina limestones and dolomites*; C) *Kamena "rudist limestones"*, and D) *Ivinj Draga deluvial deposits.*

A) *Ivinj dolomites* (Albian–Cenomanian) – extend over the Ivinj Draga area, southern slopes of Makirina and the northern slopes of the Kamena hills. Towards the NW, the Unit dips beneath the sea in Pirovac Bay. The SW contact with Unit C is reversed, whereas towards the NE it passes continuously into Unit B. Unit A consists of medium grained late-diagenetic dolosparites and dolomicrosparites with relics of primary micrites. They are mostly exposed as well-bedded layers between 10–50 cm thick, sporadically as laminated variations. The shore of Makirina Cove is built up of diagenetic dolomitic breccia (Fig. 6 – geological column; for more information on diagenetic breccia in contemporaneous deposits see VLAHOVIĆ et al., 2002). Within the succession of Unit A, lenses and intercalations of dolomitic micrites, dolosparites, dolomicrosparites and dolomitic breccia occur. Rare occurrences of partly recrystallized fossiliferous micrites were also identified. The thickness of the Unit A is 250 m.

The dolomitisation processes have destroyed the fossil content, thus the stratigraphic position of Unit A is approximate according to similar successions in Dalmatia and the overlying Unit B.

B) *Makirina limestones and dolomites* (Cenomanian–Turonian) – Unit B conformably overlies Unit A on the northern slopes of the Makirina and Čelo hills (Fig. 6). It is characterized by the vertical alteration and interfingering of limestones and dolomites. Limestones are well-bedded (in layers 10–30 cm thick) and substantially recrystallized. They have been identified as micrites, biomicrites and biopelmicrudites. Thin layered limestones (5–15 cm thick) occur along the boundary with Unit A and throughout the Unit as intercalations and lenses. Crystallinic peletoid biomicrudites were sporadically found. The dolomites belong to the group of late diagenetic dolosparites with a varying percentage of dolomite and limestone relics indicating the degree of dolomitisation.

The limestones of Unit B contain specifically indeterminable rudists (*Radiolites sp.*) and lamellibranchs (*Chondrodonta* sp.). The microfossil assemblage contains numerous benthic foraminifera (e.g. *Chrysalidina gradata*, *Broeckina* (*P.*) *balcanica*), *Aeolisaccus kotori*

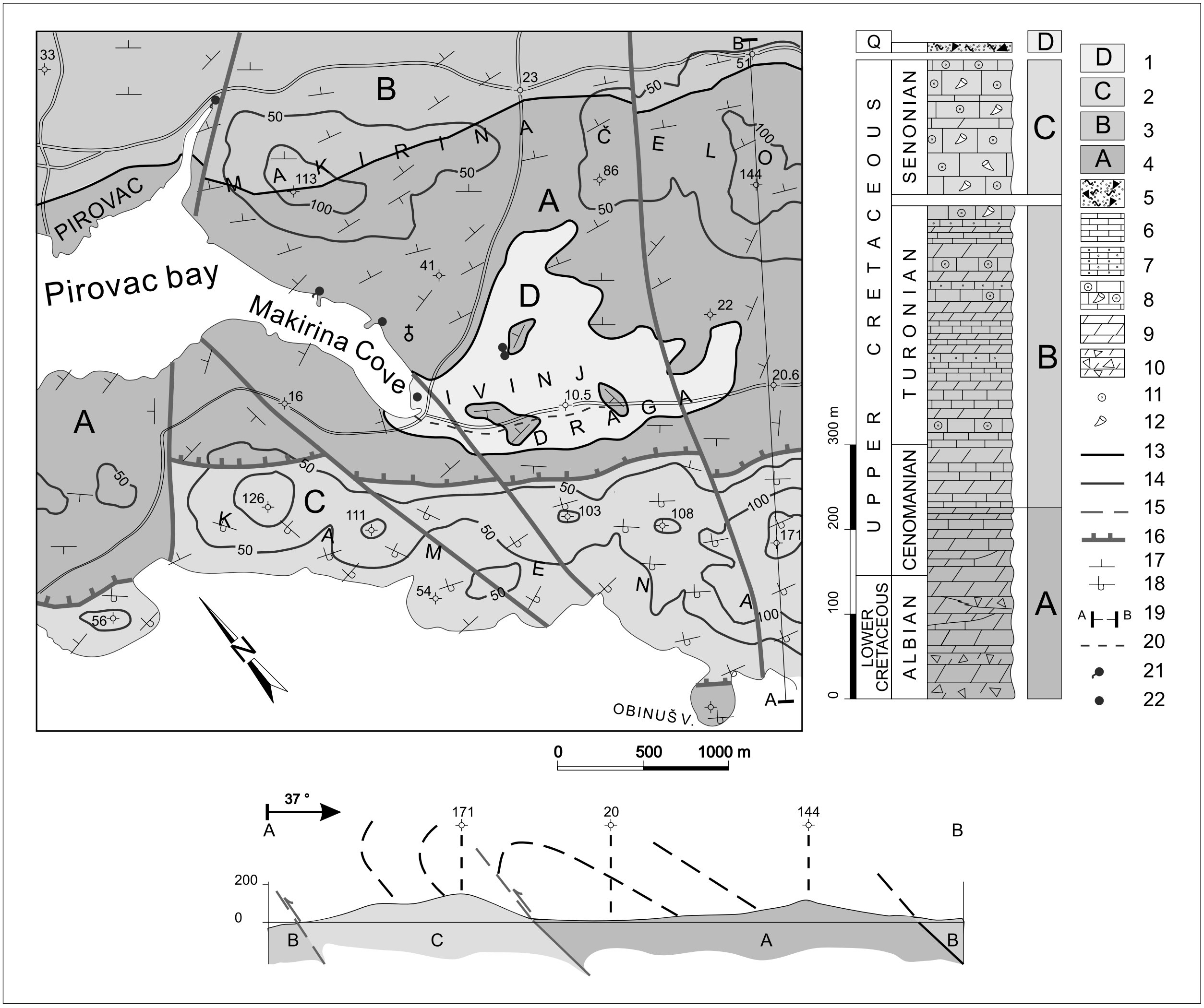

Fig. 6 Geological map, geological column, geological profile, lithostratigraphic units and lithology. Legend: 1) *Deluvial deposits Ivinj Draga*; 2) *Kamena "rudist limestones"*; 3) *Makirina limestones and dolomites*; 4) *Ivinj dolomites*; 5) clastic sediments; 6) bedded limestones; 7) detrital limestones; 8) bioclastic limestones); 9) dolomite; 10) dolomitic breccia; 11) microfauna; 12) rudists; 13) conformable boundary; 14) isohypse; 15) fault; 16) reverse fault; 17) strike and dip of bed; 18) overturned bed; 19) profile line A–B; 20) periodic surface waterway; 21) submarine spring; 22) well.

and *Thaumatoporella parvovesiculifera*. Most of Unit B was deposited in quiet, periodically lagoonal settings, whereas the grainy (crystallinic) limestones are related to shallow marine, agitated environments. The thickness of Unit B is 350 m.

C) *Kamena "rudist limestones"* (Early Senonian) – Unit C continuously succeeds Unit B on the SW part of Kamena hill (Fig. 6). Unit C is represented by well-bedded, strongly karstified and partly or completely recrystallized bioclastic limestones. The thickness of the layers is 20–150 cm. The limestones were mostly identified as varieties of biosparites and biomicrites. Sporadically, intercalations of dolomitic limestones occur.

The limestones of Unit C contain a rich fossil assemblage consisting mainly of rudists and numerous benthic foraminifera (including *Pseudocyclammina sphaeroidea*, *Scandonea samnitica* and *Murgella lata*). They were deposited in quiet to agitated, shallow marine settings.

D) *Ivinj Draga deluvial deposits* (Quaternary) – These deposits originated due to erosion of older sediments of the area surrounding Ivinj Draga (Fig. 6). Unit D consists of silty clay mixed with gravel.

4.1.2. Tectonics

The structure and orientation of the area under consideration corresponds to the structure of the region of northern Dalmatia, characterized by folds with "Dinaric" vergences (NW–SE). The folds are mostly elongated, often overturned. The faults are longitudinal, mostly reverse. These structures were formed during the Pyrenean tectonic phase, and they are disturbed by Neotectonic movements resulting in transversal and diagonal, vertical faults of N–S and NE–SW extension.

In the wider area of Makirina Cove, the most striking structure is the overturned and tectonized Ivinj anticline, the core of which is built up of Unit A. The NE part of this structure is represented by Unit B. The SW part of this structure is isoclinally folded and disturbed with longitudinal reverse faults (Fig. 6 – profile A–B). Along these reverse faults, Unit A has been tangentially moved onto the Unit C and the latter one (peninsula Obinuš V.) onto the Unit B. The structure is disturbed with vertical faults.

4.2. The sediments of Makirina Cove

Recent sediments of Makirina Cove are being accumulated on a Albian–Cenomanian dolomite basement 1200 m in length and 280–300 m in width. The gradual increase of sediment thickness (0–>3 m) from the coast towards the central part of the Cove, especially along the longer axis, gives an appearance of the sediment body in a form of an elongated lense (Fig. 7). The beginning of the transgression into the Cove of Makirina is related to global sea-level rise, rather than epirogenetic movements. In this case, we have defined the entrance of Pirovac Bay into Makirina Cove at 4.5 m isobath (Fig. 4). On the basis of the sea depth, sediment thickness and the estimation of the sea-level rise during the Holocene for the area of north Dalmatia (ŠEGOTA, 1982; ŠEGOTA & FILIPČIĆ, 1991), it is concluded that 4600 y B.P. the sea level was 6.6 m lower than at present. Therefore, the 6.6 m isobath of that period was within Pirovac Bay, meaning that Makirina was part of the land, being inundated later. The considerations on sea-level rise of Makirina Cove are in accordance with other sites of the Adriatic Sea as reported from Istria (MEISCHNER, 1995), Gargano subaqueous delta (CATTANEO et al., 2003), lakes of Mljet island (WUNSAM et al., 1999) and along the Eastern Adriatic encountering several submerged speleothems (SURIĆ et al., 2005).

It is noteworthy to quote a historical fact considering the sea-level rise of Makirina Cove. At the end of the 13th century (1295), a salt-work of the Šibenik diocese existed in the southern part of the Cove. The top of the partition-wall of the Cove (Fig. 3) is at present some 30 cm below the sea level, and it was certainly a functional part of a Middle Ages salt-work. Within the space of the salt-work of that period, the sea level is at present 0.10 m (near shore) to 0.30 m (partition-wall) higher, and the thickness of the sediments is 0.75 m. According to these data, in the last 700 years the sea level has risen approximately 1 m, and during that period some 0.75 m of sediments have been deposited.

4.2.1. Sedimentological features of Makirina Cove sediments

The colour of the sediments varies from gray, grayish brown, dark gray to black. The predominant colour is dark gray. Over the whole surface down to 0.5 m depth the sediments are mostly black. Along the shore to 0.5 m depth the sediments occur in a liquid state. Otherwise, they contain 56–61% moisture and their plasticity is rather pronounced. In the NE, deeper part of the Cove, the sediments gradually pass into clayey, sporadically sandy–gravelly layer with fine faunal debris. In different horizons of the sedimentary column, metre-sized lumachele lenses built up of mollusc shells (Fig. 8) sporadically occur.

The granulometric composition shows that most of the sediments in the Cove are represented by poorly sorted (So>2.0) clayey–sand and sandy silt (Table 1). Along the shore and on the bottom, various debris, gravel and clay occur. Towards Pirovac Bay, the sediments consist of sandy silt mixed with gravel and clay (Fig. 8, profile 10).

In general, the sediments are characterized by silt fraction (mean value 51%), sand fraction (predominantly fine-grained sandy subfraction, mean value 31%) and clay fraction (mean value 14%). The content of the gravel fraction is very low, and it only occurs in some samples as fragments of mollusc shells. The mean value of the grains of all samples is 0.04 mm. The sorting coefficient, which was estimated by use of the quartile method, shows a very low degree of sorting.

Granulometric analysis of the upper 10 cm of the sediments revealed that sandy silts prevail, which pass towards the shore into gravelly–sandy silt. The mean values of the fractions are: silt 58%, sand 27%, clay 8% and gravel 7%. While the fractions of silt, sand and clay are relatively constant, the fraction of gravel reaches values up to 22% along the shore (VREČA et al., 1999).

In the mineral composition of the sediments, non-carbonate minerals (mean value 61%) predominate over carbonate minerals (mean value 39%) down to 35 cm depth (Table 2).

Within the group of non-carbonate minerals, clay minerals prevail (36%), followed by quartz (22%), halite (3%), pyrite and marcasite (2%). The association of minerals is dominated by muscovite, and followed by illite and other clay minerals with a common illite/montmorillonite type of structure (mean value 27%) (Table 2). The content of clay minerals with a common chlorite/montmorillonite type of structure is low. The abundance of clay minerals is highest in the central part of the Cove, decreasing towards the shore. Their abundance increases with the depth. The content of quartz is higher towards the shore, whereas in the central part of the Cove it is considerably lower. The amount of halite and travertine decreases towards the shore. The highest concentrations of authigenic pyrite and marcasite occur in the central part of the Cove, decreasing towards the shore. Within an anaerobic environment with sulphate reduction, the released sulphur from pore waters enables the formation of authigenic sulphides (APPELO & POSTMA, 1994). This process is encouraged by sulphate reducing microorganisms.

Among the carbonate minerals, dolomite and amorphous calcite predominate (mean value 30%). The remainder (9%) consists of travertine and authigenic minerals, i.e. crystallized calcite and aragonite. Their origin is, linked to saturation of pore waters in the sediments: saturation indices SI > O are favourable for formation of calcite and aragonite. The content of dolomite

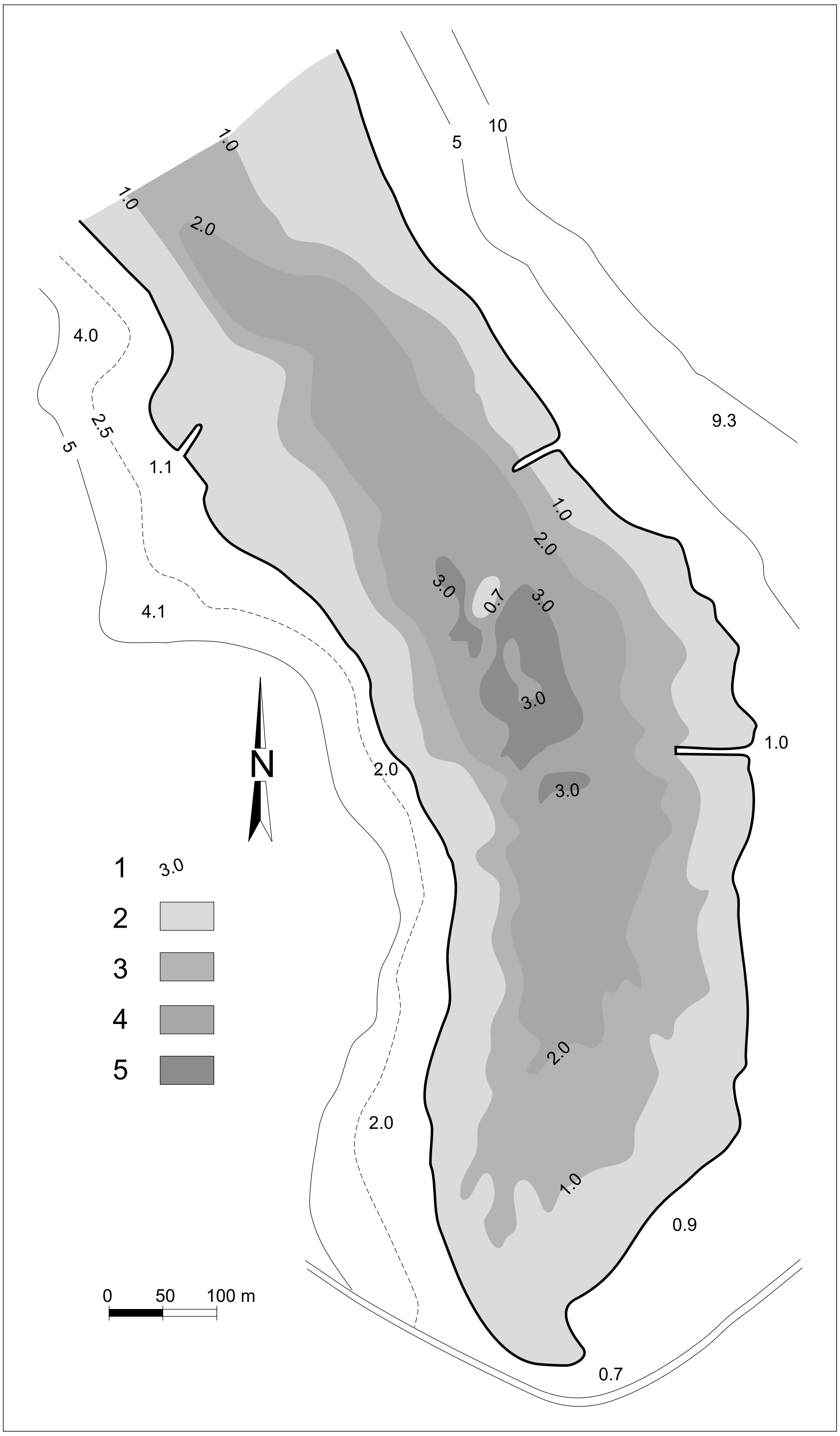

Fig. 7 Isopach map. Legend: 1) isopachs of sediments thickness; 2) thickness of sediments of 0.0–1.0 m; 3) thickness of sediments of 1.0–2.0 m; 4) thickness of sediments of 2.0–3.0 m; 5) thickness of sediments more than 3.0 m.

and calcite near the shore is considerably higher (54%) compared to gradually decreasing values towards the central part of the Cove. The same trend is related to depth. The highest concentration of aragonite is in the central part of the Cove, gradually decreasing towards the shore (VREČA et al., 1999).

The sediments were dried at 107°C, revealing 16–21% of organic and 79–86% of inorganic matter. Dilute HCl dissolved 32–47% of inorganic matter of which 33–50% represents the insoluble residue. Within the 0.09–0.16 mm fraction of insoluble residue, the composition of the light and heavy mineral fraction was identified (Table 3).

The light mineral fraction contains quartz, feldspars and rare fragments of chert and quartzite. Quartz predominates with 63% (mean value). The grains are mostly semi-rounded of an irregular shape. The feldspars occur regularly in all samples (mean value 32%). The grains of feldspars are mostly semi-rounded and allotriomorphic, but weakly rounded, hypidiomorphic grains

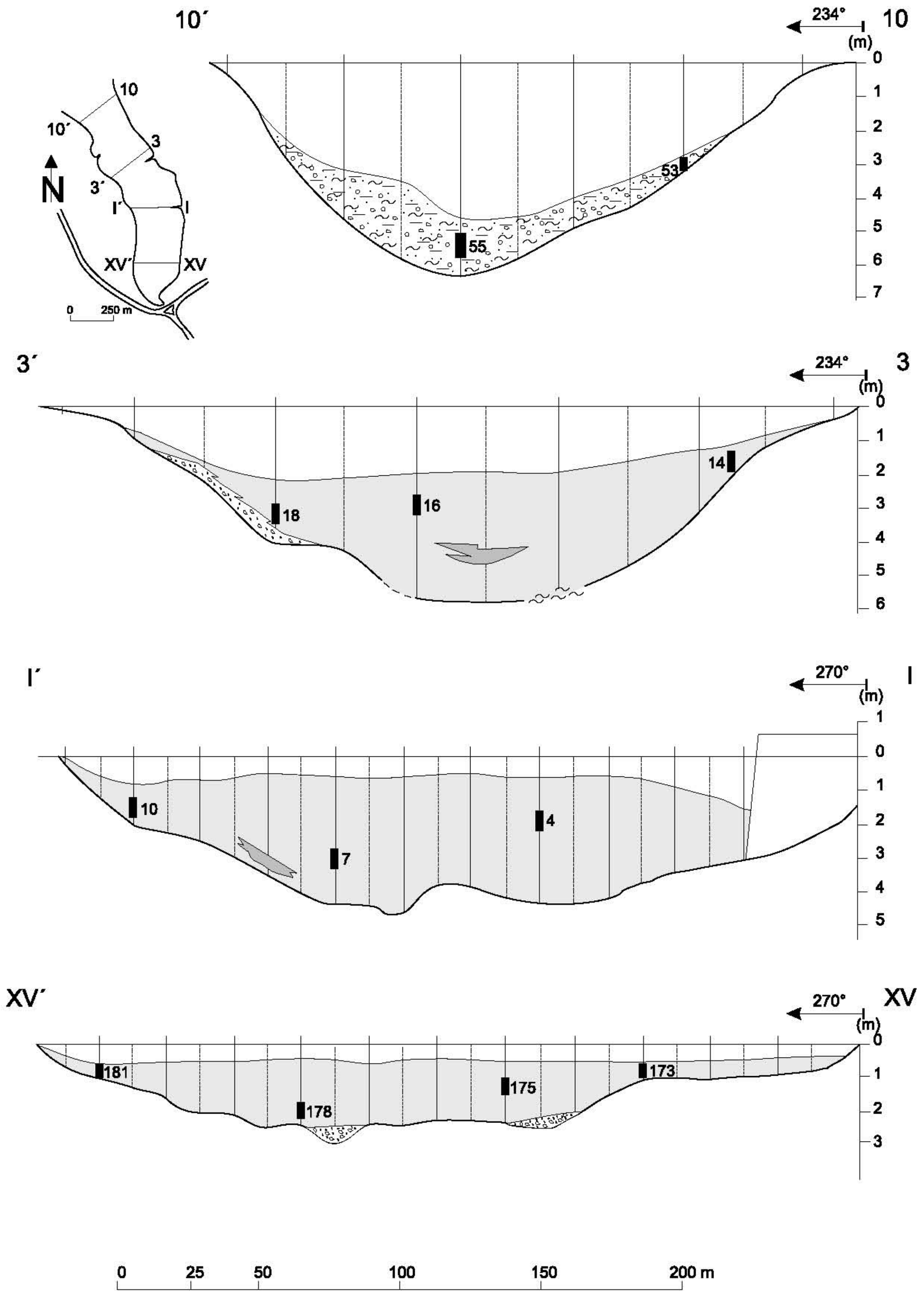

Fig. 8 Geological profiles. Legend: 1) clayey–sandy silt; 2) clay; 3) silt; 4) sand; 5) gravel; 6) lumachelle, lamellibranchs, gastropods; 7) probes with measurements of sediment thickness; 8) probes with measurements of sediment thickness and description of sediments; 9) sample.

Sample	Gravel	Sand	Silt	Clay	Sediment	Granulometric parametres	
		%				Md	So
1/2	3	27	55	15	clayey–sandy silt	0.03	3.0
2/7	7	43	50	-	sandy silt	0.07	2.2
2/9	-	11	59	30	clayey–sandy silt	0.01	5.3
2/11	-	18	57	25	clayey–sandy silt	0.02	5.1
3/14	-	-	62	38	clayey silt	0.01	2.9
3/16	-	13	65	22	clayey–sandy silt	0.01	3.6
3/18	4	28	63	5	sandy silt	0.10	4.0
4/18A	-	70	30	-	silty sand	0.08	1.5
4/22	3	27	59	11	clayey–sandy silt	0.03	3.5
5/28	-	40	51	9	sandy silt	0.05	2.4
6/32	5	20	60	15	clayey–sandy silt	0.03	2.9
6/34	6	35	47	12	clayey–sandy silt	0.04	3.0
7/38	17	33	42	8	gravely–sandy silt	0.06	6.9
7/39	4	41	45	10	sandy silt	0.05	3.7
8/44	7	30	52	11	clayey–sandy silt	0.05	3.5
8/46	3	32	52	13	clayey–sandy silt	0.04	3.3
9/50	6	27	52	15	clayey–sandy silt	0.03	4.2
10/53	8	40	41	11	clayey–sandy silt	0.06	3.3
10/55	7	50	31	12	clayey–silty sand	0.09	4.6

Table 1 Granulometric composition of the sediment.

Sample cm	Depth %	M/I+Rx %	KLO+Rx2 %	qua. %	hal. %	arag. %	cal. %	D+K %	trav. %	pyr., marc.
M3/3-A	0-5	27	18	10	6	2	5	27	3	2
M3/3-B	5-10	30	7	15	8	4	7	25	-	3
M3/3-C	10-15	23	8	16	6	3	10	29	3	3
M3/3-D	15-20	27	12	11	6	3	3	37	-	2
M3/3-E	20-25	35	9	14	6	4	3	25	1	3
M5/3-A	0-5	23	6	21	-	2	5	42	-	1
M5/3-B	5-10	21	6	21	-	2	6	42	-	2
M5/3-C	10-15	27	6	25	-	3	6	31	-	2
M5/3-D	15-20	27	3	23	-	3	5	35	2	3
M5/3-E	20-25	24	6	21	4	3	4	32	3	3
M5/3-F	25-30	30	9	24	4	2	4	19	4	2
M5/3-G	30-35	44	14	19	6	-	3	10	4	2
M7/2-A	0-5	12	3	11	6	-	13	54	-	1
M7/2-B	5-10	27	14	21	-	-	15	21	-	2
M7/2-C	10-15	17	8	23	-	-	8	44	-	1
M7/2-D	15-20	17	11	22	-	2	9	38	-	1
M7/2-E	20-25	34	8	30	-	-	5	21	-	1
M7/2-F	25-30	34	16	24	-	-	11	14	-	1

Table 2 Mineral composition of the sediments from the probes M3/3, M5/3 i 7/2. Legend: M/I+Rx1 – muscovite/illite + clay minerals with a common illite/montmorillonite type of structure; KLO+Rx2 – chlorite + clay minerals with a common chlorite/montmorillonite type of structure; qua. – quartz; hal. – halite; arag. – aragonite; cal. – calcite; D+K – dolomite + amorphous calcite; trav. – travertine; pyr. – pyrite; marc. – marcasite.

also occur. Plagioclase is frequent, whereas K-feldspars are subordinate.

The content of the heavy mineral fraction is approximately the same in all samples and varies between 3–15%: opâque minerals are estimated at 30% (mean value), whereas transculent heavy minerals at 70%.

Garnet is the most frequent transculent heavy mineral (mean value 30.4%). The grains are irregular,

Sample	L. m.f. (100%)				H. m.f.	H. m.f. (100%)		Translucent minerals (100%)										
	q	f	r	v.g.	%	op	translc.	ep	am	py	g	cr	t	zr	ru	ti	ap	gl
1/2	61	34	5	-	3	28	72	15	25	24	28	1	1	3	1	1	1	2
2/7	65	32	3	-	3	36	64	9	22	20	30	-	1	11	1	1	1	1
2/11	68	24	8	-	3	35	65	8	26	16	36	1	-	10	2	-	1	1
3/14	69	27	4	+	8	28	72	12	20	20	34	-	1	9	1	1	2	1
3/16	65	31	4	+	7	30	70	11	21	23	32	1	1	8	1	1	1	1
4/18a	62	33	5	-	15	25	75	8	30	26	27	1	1	8	2	-	1	1
5/26	60	37	3	+	4	28	72	7	31	14	35	-	1	9	1	-	2	1
5/30	67	29	4	+	7	37	63	9	25	26	28	1	1	6	2	1	1	1
7/39	55	36	9	-	6	25	75	12	23	18	29	1	1	9	-	2	5	1
8/44	59	35	6	+	7	27	73	11	21	20	31	2	2	8	-	2	4	1
8/46	58	35	7	+	7	24	76	14	23	16	30	-	2	8	1	1	5	2
10/55	64	31	5	-	5	42	58	8	28	27	25	1	-	6	3	1	1	1

Table 3 Mineral composition of the light and heavy mineral fractions of the insoluble residue. Legend: L. m.f. – light mineral fraction; q – quartz; f – feldspar; r – rock particles; v.g. – volcanic glass; H. m.f. **–** heavy mineral fraction; op – opâque minerals; translc. min. - translucent minerals; ep – epidote; am – amphibole; py – pyroxene; g – garnet; ti – titanite; cr – chromspinel; t – tourmaline; zr – zircon; ru – rutile; ap – apatite; gl – glaucophane.

weakly rounded and often broken. Sometimes, they are semi-rounded, idiomorphic and “fresh” in appearance. Colourless and brown garnets are most frequent, but rosy variations were also identified (Plate I, Figs. 9, 10, 13 and 16).

The amphibole group of minerals accounts for 24.5% (mean value). The grains mostly appear as broken, semi-angular prismatic forms (Plate I, Fig. 7). Although glaucophane is represented in very low concentrations, its presence in all samples is characteristic (Plate I, Figs. 5 and 6). Pyroxene concentrations within the transculent heavy mineral fraction are estimated at 20.8% (mean value). The grains are semiangular to angular, prismatic in shape, often irregularly broken (Plate I, Fig. 8). Epidote and zoisite are present in all samples. Zircon represents 8% (mean value) of the fraction. The grains are variably shaped, ranging from angular to rounded forms (Plate I, Figs. 11, 15, 17 and 18).

The composition of the light and heavy mineral fractions indicate that their source is related to metamorphic rocks and also to extrusive rocks due to the influence of explosive volcanic eruptions. The morphometric features of the resistant minerals show that some have been transported for long distances and resedimented in several cycles.

One of the problems related to the origin of the sediments of Makirina Cove is the interpretation of the source and the transportation mechanism of the light and heavy mineral fractions which are represented in a relatively high concentration. It has already been documented that the Cretaceous successions of the area surrounding Makirina do not contain light and heavy mineral fractions. On the other hand, a similar mineralogical assemblage has been identified in Dalmatia in Eocene flysch and Quaternary deposits (ŠPARICA et al., 1995). However, the closest exposures of Eocene flysch are situated some 6 km NE of Makirina and they are physically separated from Makirina by the NW–SE extension of the structures. The same holds true for the Quaternary deposits, though located in the vicinity of Makirina. The mineralogical assemblage contains grains of different specific weights, indicating the absence of separation of the grains during the transport. This implies that the wind probably played a subordinate role in their transportation, but also the absence of selective settlement within the depositional area according to their hydrodynamic features. Nevertheless, it is clear that most of the light and heavy mineral fractions originated through erosion of Eocene flysch deposits. Some influence of most probably Holocene explosive volcanic activity is exemplified by the presence of volcanic glass characteristically absent in Eocene flysch deposits.

4.2.2. Selenium speciation in sediments

Since no marine sediments with certified contents of selenium were available, analysis of the geologic reference soil material GXR–2 (USGS) was performed. The certified Se content of this material (GLADNEY & BURNS, 1984) is 0.57±0.17 mg kg^{-1} and the following results were obtained: 0.35 mg kg^{-1} Se by 7 mol HNO_3 digestion, 0.47 mg kg^{-1} Se by hot aqua regia digestion and 0.51 mg kg^{-1} Se by closed microwave HF–HCl–HNO_3 digestion. The results of selenium analysis by all three digestions in the marine sediments from Makirina Cove are presented in Table 4.

The amount of selenium extracted with 7 mol HNO_3 was the lowest as expected, and is approximately 50% of the selenium obtained by closed microwave HF–HCl–HNO_3 digestion, ranging from 0.19 to

Sample	P1	P2	P3	P4	P5	1	2	3	4	5	6	7	8
7 mol HNO_3	0.30	0.30	0.31	0.27	0.30	0.19	0.27	0.24	0.19	0.24	0.26	0.20	0.29
aqua regia	0.34	0.34	0.35	0.34	0.36	0.35	0.29	0.32	0.28	0.28	0.32	0.28	nd
HF–HCl–HNO_3	0.76	0.56	0.56	0.46	0.58	nd	0.46	0.46	0.47	0.48	0.51	0.42	0.46

Table 4 Results for Se (mg/kg) in sediment core samples (P) and in surface samples (M) by 7 mol HNO_3 digestion, hot aqua regia and closed microwave HF–HCl–HNO_3 digestion.

0.31 mg kg^{-1}. The hot aqua regia digestion gave only slightly higher amounts of selenium in the range from 0.27 to 0.35 mg kg^{-1}. The closed microwave HF–HCl–HNO_3 digestion gave approximately 40% higher Se contents than the hot aqua regia digestion, ranging from 0.42 to 0.76 mg kg^{-1} (MIKO et al., 1998). Selenium bioavailability from sediments is a longstanding impediment to determining Se effects in ecosystems, since it is an essential trace element, which is toxic if present in excessive concentrations. In natural systems, it exists as selenate (SeO_4^{2-}), selenite (SeO_3^{2-}), and organic and inorganic forms of selenide (Se^{2-}) (CUTTER & BRULAND, 1984). Selenium is preferentially enriched in authigenic pyrite (MERCONE et al., 1999) and this is probably the major source of Se in the Makarina Cove sediments. The aim of the various acid extractions was to evaluate the Se bioavailability of the sediments. Some experimental and field observations showed significant Se uptake via ingestion implying that particulate organo-Se in diatoms exposed to selenite was assimilated with >80% efficiency by a variety of bivalves (WANG et al., 1996), and that elemental Se precipitated in sediments by microbial dissimilatory reduction was less bioavailable. The bioavailability of Se in Makirina Cove sediments based on the concentration difference of Se extracted with 7 mol HNO_3 and total Se (HF–HCl–HNO_3) implies a range of 40–60%. Sulphate-reducing bacteria are capable of reducing selenate to selenide (ZEHR & OREMLAND, 1987). The importance of the oxic-boundary in organic-rich sediments for Se mobility has been stressed by MERCONE et al. (1999) and CRUSIUS & THOMSON (2003), who found that the effect was similar to the reduction mechanisms that cause enrichment of V and U from bottom waters to anoxic sediments.

4.2.3. Geochemical characteristics of the surficial sediment

The results of the geochemical characterisation of the 29 surficial sediment samples with mean, minimum and maximum values are given in Table 5. The regional distribution of major, minor and trace elements in the Makirina Cove as indicated by the total analyses of surficial sediments are shown in Plates II–V.

Geochemical data indicate that the concentrations of the majority of trace elements are similar to those reported for argillaceous sediments and shales. Some of them, including Ni, Co, As, Cr, Zn, Sc, and V also exhibit similar values to the surficial sediments from the Central Adriatic (VREČA et al., 1999), while the concentrations of others (Ba, Mo, Cu, Pb, Th, U, La and Zr) are higher. The distribution of major elements and their relative abundances are attributed to the mineralogical compositions of sediments. Elevated SiO_2 contents imply the presence of relatively high percentages of quartz in the sediments. Al_2O_3 and K_2O concentrations suggest the clay minerals to be the most important factor controlling the distribution of Al and K. K_2O contents may also reflect a close association with the feldspars. CaO, Sr and, to some extent, MgO concentrations usually follow the carbonate content (calcite, aragonite and dolomite). Na_2O contents are probably due to the presence of feldspars and salt and are somewhat modified by the influence of the fresh water inflow through small sources along the coast.

Iron is principally associated with the silt–clay fraction and shows a similar distribution pattern to K and Al. Occurrences of iron sulphides in small cores indicate reducing conditions. This is also evident from H_2S development during the summer. The relatively high organic content (from 2.93 to 7.17%) of the sediment most probably suggests that the iron sulphides are the product of the oxidation of organic matter by microbial mediated sulphate reduction (STUMM & MORGAN, 1996).

Trace metal distribution is also roughly controlled by the mineralogical composition of the sediment, although post-depositional processes may have modified the initial trace element content at the time of sedimentation. Our results showed that the surficial sediment of the Makirina Cove is relatively unaffected by pollution. Anthropogenic contamination was observed in the southern part of the Cove in the vicinity of the road Kapela–Tisno. The elevated concentrations of Cu, Pb, Zn and Ni in this relatively very limited area could be attributed to the traffic circulation and agricultural activity. Higher concentrations of Cu along the eastern coast of the Cove also reflect the anthropogenic component of Cu. The elevated values of this element extend away from the coast where there are fresh water inputs of Cu to the marine environment, due to the agricultural activities in this area.

The geographical distribution of trace elements also reflects the differences in redox conditions in the Cove. Elevated values of certain trace elements such as V, Zn, Cu, Ni, Pb, As, Cs, Br, Mo, Sb, Sc, Rb, Th and V in

Element	SiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	TiO_2
Units	%	%	%	%	%	%	%	%	%	%
Mean	34.75	8.21	2.47	1.7	0.04	6.01	15.22	2.17	1.48	0.49
Minimum	22.19	3.99	0.01	0.94	0.02	3.31	5.96	0.53	0.80	0.31
Maximum	48.52	14.79	4.30	3.24	0.12	8.19	24.26	3.59	2.59	0.77

Element	P_2O_5	Ba	Sr	Y	Zr	V	Cu	Pb	Zn	Ag
Units	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Mean	0.07	162.44	329.73	22.31	176.00	75.93	32.13	25.09	51.44	
Minimum	0.04	97.00	102.00	16.00	111.00	37.00	12.00	13.00	25.00	<0.40
Maximum	0.33	335.00	578.00	33.00	261.00	133.00	68.00	42.00	87.00	0.50

Element	Ni	Cd	Au	As	Br	Co	Cr	Cs	Hf	Mo
Units	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Mean	31.42			13.00	123.33	11.31	112.87	5.24	5.75	
Minimum	15.00	<0.50	<5	5.00	18.00	6.00	74.00	1.50	3.50	<5
Maximum	61.00	0.60	19.00	26.00	410.00	21.00	170.00	12.00	8.70	47.00

Element	Rb	Sb	Sc	Ta	Th	U	W	La	Ce	Nd
Units	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Mean	78.13	0.95	8.76		10.34	4.43		37.94	79.40	35.76
Minimum	30.00	0.40	4.80	<1	5.80	-0.50	<3	24.30	51.00	18.00
Maximum	198.00	4.20	17.00	3.00	20.00	11.00	5.00	58.70	126.00	50.00

Element	Sm	Eu	Tb	Yb	Lu
Units	ppm	ppm	ppm	ppm	ppm
Mean	5.96	1.28	-0.11	2.24	0.36
Minimum	4.00	0.80	-0.50	1.20	0.20
Maximum	9.60	2.30	1.80	3.80	0.59

Table 5 Mean, minimum and maximum concentrations of chemical elements in surficial sediment from Makirina Cove.

the northern part of the Cove most probably reflect their close association with clay mineralogy, (high Al_2O_3 and K_2O content) and more reducing conditions (high FeO content). The more characteristic feature of this area is highly elevated concentration of Mo (up to 47 ppm). Although these may be attributed to the use of phosphate fertilisers, they still remain a puzzle. However, Mo is also best known for its enrichment in anoxic or organic-rich sediments. Within a given anoxic environment, Mo tends to be enriched in the centres or most H_2S-rich portion of the area (CRUSIUS et al., 1996).

4.2.4. Organic-matter isotope geochemistry

The $\delta^{13}C$ of terrestrial plants (Plate VI) in the area surrounding Pirovac Bay and Makirina Cove revealed values mostly in the range between -23.34 to -30.48‰ (Table 6, Fig. 9). The only exception is *Camphorosoma monospeliacea* with $\delta^{13}C$ in the range from -12.04 to -13.22‰. *Codium bursa*, which is a very common alga in the Cove, showed $\delta^{13}C$ values ranging from -17.14 to -17.88‰. In contrast, the seagrass *Cymadocea nodosa*, which also covers the greater part of the bottom in the Cove, is considerably enriched in ^{13}C, exhibiting $\delta^{13}C$ values between -7.36 and -8.24‰.

The $\delta^{13}C$ composition of marine plankton and benthic animals as well as macrofauna was not directly measured. However, the $\delta^{13}C$ of marine plankton and most of the marine organisms in the bay seems to exhibit similar values as were measured for plankton and other marine organisms in the North-Western Adriatic, i.e. -21.8 to -22.9‰ (VREČA, 1998).

Mass-spectrometric analyses of organic carbon in surficial sediment in Makirina Cove (Table 7, Fig. 10) revealed high values (between -13.10 to -19.87‰) in the central and northern part of the Cove and somewhat lower values (between -17.32 to -24.89‰) in the southern and coastal part affected by allochthonous input. The relative contribution of marine and terrestrial organic matter to sediment may be evaluated from $\delta^{13}C$ measurement if the isotopic composition of the two end members are known and are different. Due to the considerable variability of carbon isotopic composition in marine derived organic carbon end members ($\delta^{13}C$ values between -7.36 and -22.9‰) such calculation is rather limited. Nevertheless, the geographical distribution of $\delta^{13}C$ values in organic carbon (Fig. 11) clearly indicates the prevailing influence of terrestrial organic matter in the southern, as well as in the coastal part of

Plant	Stem	Leaf	Flower	Other*
Agropyron pungens	-28.82		-27.98	
Artemisia coerulescens	-24.72	-28.75	-23.42	
Arthrocnemum fruticosum	-27.19	-27.85		
Arthrocnemum glaucum	-24.50			
Arthrocnemum glaucum	-27.78		-26.91	
Arundo donax		-27.39		
Avena barbata	-28.39	-28.46	-26.78	
Camphorosma monspeliaca	-12.04			-13.22
Carex	-25.83		-26.91	
Centaurium erythraea	-27.79	-30.35	-26.58	
Clematis flammula	-25.75	-24.18	-26.89	
Crithmum maritimum	-27.77	-28.57		
Dactylis hispanica	-26.57	-28.11	-27.62	
Dancus carota	-28.02	-30.04	-27.14	
Halimione portulacoides	-24.52	-23.76	-24.37	
Halimione portulacoides	-25.50	-28.44	-25.11	
Helichrysum italicum	-27.39	-29.80	-28.96	
Helichrysum italicum	-27.39	-29.80	-28.96	
Helichrysum italicum			-28.67	
Helichrysum italicum		-28.33	-26.79	
Hypericum perforatum subsp. *veronense*	-26.26	-23.75	-28.24	
Inula chrithmoides	-25.12	-24.26	-24.59	
Inula crithmoides	-23.39	-25.63		
Inula spiraeifolia		-30.68	-29.70	
Inula viscosa	-25.15	-27.15	-23.05	
Juncus acutus	-28.97	-29.79		
Juncus maritimus	-27.44			-26.00
Juniperus oxycedrus		-25.97	-26.79	
Lagurus ovatus	-29.26		-28.76	
Lavandula angustifolia	-27.58	-27.75	-25.92	
Limonium serotinum	-25.44	-26.83	-25.16	
Limonium serotinum	-24.59		-24.69	
Linum tenuifolium		-24.96	-25.56	
Melica ciliata		-26.67	-25.39	
Myrtus communis		-28.00		
Olea europaea	-24.47	-24.90	-29.34	-25.57
Olea europaea			-27.71	
Pinus halepensis	-29.41	-26.95		24.46
Pistacia lenticus	-24.55	-26.41	-23.97	
Puccinelia palustris	-28.02	-26.95		
Reichardia picroides	-26.66		-25.52	
Scabiosa maritima	-25.96	-27.90	-26.81	
Scabiosa triandra	-25.71	-28.39	-27.35	
Schoenus nigricans	-28.16			-27.24
Spartium junceum	-24.35	-24.55	-23.72	
Spartium junceum			-26.06	-25.92
Suaeda maritima	-24.64	-25.02		
Codium bursa	-17.77	-17.88	-17.14	
Seagrass (*Cymadocea nodosa*)	-9.15			
Seagrass (*Cymadocea nodosa*)	-8.24	-7.36	-7.38	

Table 6 Carbon isotope composition of terrestrial and aquatic plants from Makirina Cove and Pirovac Bay. Legend: * seed, pollen, root

the Cove, and marine derived organic compounds in the northern and central part of the Cove.

Variations in the carbon isotopic composition of sedimentary organic matter in surficial sediment thus have been noted as a function of the distance from the shore. Changes in $\delta^{13}C$ values in sediment cores may be related to a varying influx of terrestrial carbon and/or diagenetic effects. Because diagenetic processes in sediments result only in minor differences between the source and the residual carbon, the decrease in ^{13}C content at -25 cm towards shore line undoubtedly reflects a dilution of endogenous marine organic compounds by an increased contribution of terrestrial organic debris in the past, when the sea level was to some extent lower.

The relative contribution of marine and terrestrial organic matter to sediments was evaluated from $\delta^{13}C$ of the two end members with known and significantly different carbon isotope composition, using the mixing

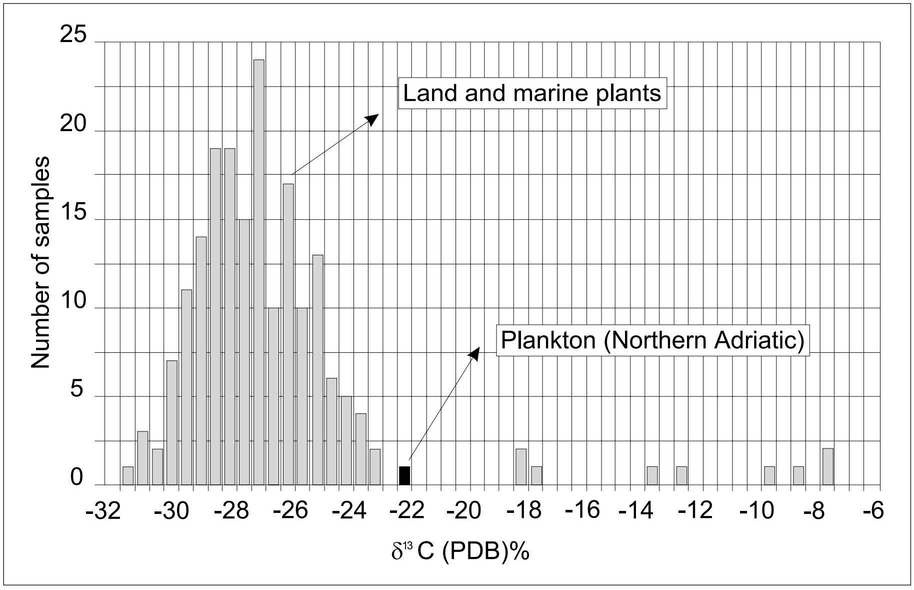

Fig. 9 Carbon isotope composition of land and marine plants from Makirina Cove and Pirovac Bay.

equation proposed by CALDER & PARKER (1968). For $\delta^{13}C$ values of terrigenous (C_t) and marine (C_m) organic matter in the equation:

$$\delta^{13}C = F_m\,\delta^{13}C_m + Ft\,\delta^{13}C_t\text{, and}$$

$$F_m + F_t = 1$$

The percentage of terrigenous (F_t) and marine (F_m) organic matter in surficial sedimentary organic matter was determined. For $\delta^{13}C_t$ the mean value for terrestrial plants (-26.44‰) was used, while for $\delta^{13}C_m$ a value of -12.68‰ was taken. This value considers the influence of aquatic plants, especially *Cymadocea nodosa* and *Codium bursa*, on the isotopic composition of marine organic matter. The percentage of terrigenous organic matter in sedimentary organic matter is relatively high in the southern coastal part of Makirina Cove (40–60%). In the central part of the Cove the influence of marine inorganic matter is dominant, and the percentage of terrigenous organic matter input is less than 40%.

4.2.5. Biogenic carbonate isotope geochemistry

The isotopic composition and the mineralogy of the molluscs (Plate VII) are shown in Table 8 together with the associated isotopic composition of the ambient seawater and $\delta^{13}C$ DIC values. As can be seen, there is significant isotopic variation between different shells of the same species, at the same site. However, isotopic variations between shells of the same species at different sample sites are even greater (Table 8, Fig. 12).

The cross plot of mollusc $\delta^{18}O$ and $\delta^{13}C$ (Fig. 12) indicates a relatively narrow range of $\delta^{18}O$ values (from +1.05‰ to +2.53‰) and a wide range of $\delta^{13}C$ values (from -3.26‰ to +2.92‰). The data are roughly separated into two groups, primarily on the basis of $\delta^{13}C$

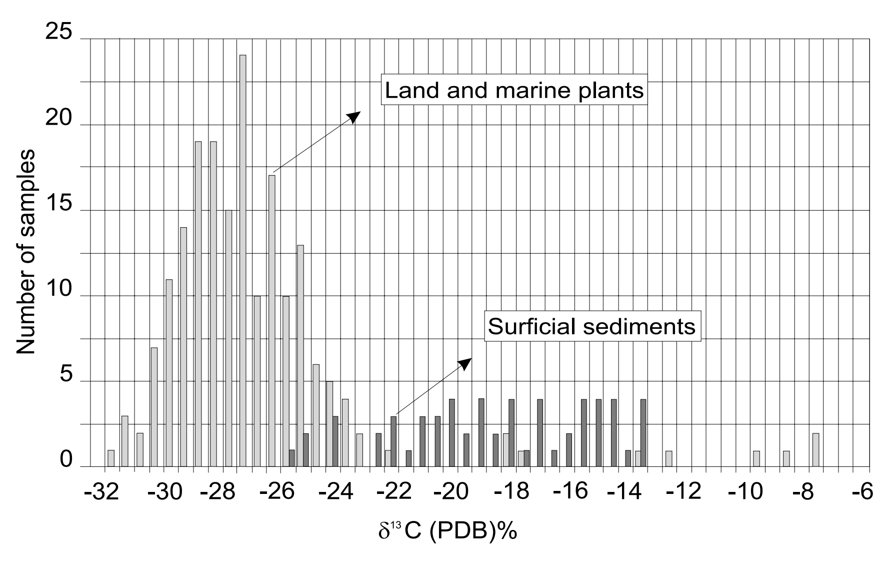

Fig. 10 Isotopic composition of organic carbon in surficial sediment from Makirina Cove.

Profile	Samp. No.	Depth interval (cm)	δ^{13}C (PDB) ‰	Profile	Samp. No.	Depth interval (cm)	δ^{13} (PDB) ‰
M1	M1/1–A	0–5	-19.18	M4	M4/3–A	0–5	-16.65
M1	M1/1–E	20–25	-19.91	M4	M4/3–E	20–25	-18.06
M1	M1/2–A	0–5	-13.19	M4	M4/4–A	0–5	-16.77
M1	M1/2–D	20–25	-14.79	M4	M4/4–E	20–25	-19.87
M1	M1/3–A	0–5	-15.40	M5	M5/1–A	0–5	-18.04
M1	M1/3–D	20–25	-13.10	M5	M5/1–D	20–25	-20.54
M1	M1/4–A	0–5	-14.39	M5	M5/2–A	0–5	-17.57
M1	M1/4–E	20–25	-15.98	M5	M5/2–G	20–25	-20.42
M1	M1/5–A	0–5	-13.19	M5	M5/3–A	0–5	-17.32
M1	M1/5–D	20–25	-13.10	M5	M5/3–G	20–25	-22.41
M2	M2/1–A	0–5	-16.29	M5	M5/4–A	0–5	-18.62
M2	M2/1–E	20–25	-16.91	M5	M5/4–F	20–25	-22.29
M2	M2/2–A	0–5	-14.85	M5	M5/5–A	0–5	-18.72
M2	M2/2–D	20–25	-14.11	M5	M5/5–E	20–25	-19.84
M2	M2/3–A	0–5	-17.76	M6	M6/1–A	0–5	-20.28
M2	M2/3–D	20–25	-14.09	M6	M6/1–F	20–25	-20.84
M2	M2/4–A	0–5	-15.89	M6	M6/2–A	0–5	-21.58
M2	M2/4–D	20–25	-14.10	M6	M6/2–F	20–25	-21.95
M3	M3/1–A	0–5	-17.86	M6	M6/3–A	0–5	-21.21
M3	M3/1–E	20–25	-19.18	M6	M6/3–E	20–25	-20.66
M3	M3/2–A	0–5	-15.03	M7	M7/1–E	20–25	-23.99
M3	M3/2–E	20–25	-14.64	M7	M7/2–A	0–5	-19.95
M3	M3/3–A	0–5	-15.26	M7	M7/2–F	20–25	-24.64
M3	M3/3–E	20–25	-15.31	M7	M7/3–A	0–5	-20.01
M3	M3/4–A	0–5	-13.77	M7	M7/3–F	20–25	-23.57
M3	M3/4–D	20–25	-14.83	M8	M8–A	0–5	-24.57
M4	M4/1–A	0–5	-17.76	M8	M8–D	20–25	-25.33
M4	M4/1–E	20–25	-18.51	M9	M9–A	0–5	-21.75
M4	M4/2–A	0–5	-16.63	M9	M9–D	20–25	-23.55
M4	M4/2–E	20–25	-18.94				

Table 7 Isotope composition of organic carbon in surficial sediment from Makirina Cove.

values, with one group having δ^{13}C values of <-0.04‰ and the other with values of >0.35‰. The group with lower δ^{13}C values represents molluscs from Makirina Cove characterized by a shallow marine water environment with intense evaporation and decomposition of sedimentary organic matter.

The group with higher δ^{13}C values represents molluscs from Pirovac Bay and the coastal part of the Murter Sea. We must point out that the water of Makirina Cove is enriched with heavy oxygen and light carbon isotopes with respect to the water from Pirovac Bay and the Murter Sea (Table 8). However, the water from Pirovac Bay also contains a variable amount of light oxygen and carbon isotopes due to the influence of fresh water from Lake Vrana through an artificial canal, as well as through numerous submarine sources in the immediate vicinity of the coast in the bay. However, it is only slightly depleted with heavy oxygen and light carbon with respect to the normal seawater of the Murter Sea.

The specimens of the gastropod *Gourmia vulgata* from Makirina Cove yielded a range of δ^{18}O from +1.47‰ to +1.20‰ and of δ^{13}C from -1.2 to -0.79‰. A larger scatter of isotopic compositions was found in *Gourmya vulgata* shells from Pirovac Bay (δ^{18}O from +1.05‰ to +1.69‰; δ^{13}C from +0.71‰ to +1.98‰) and the coastal part of the Murter Sea (δ^{18}O from +1.11‰ to +1.82‰; δ^{13}C from +1.39‰ to +2.92‰). Similar low δ^{18}O in the range between +1.24‰ and +1.53‰ and δ^{13}C in the range between -2.40‰ and -2.34‰ were exhibited by shells of the gastropod *Monodonta turbinata* collected in Makirina Cove. These values are considerably lower than in shells of the same species from the coastal part of the Murter Sea. Their δ^{18}O and δ^{13}C values are up to 1.0‰ and 3.97‰ higher relative to those of *Monodonta turbinata* from Makirina Cove. Mussel shells of *Nuculana fragilis* and *Levicardium oblongum* from Makirina Cove are also considerably enriched in the light carbon isotope and show slightly lower δ^{18}O values relative to mollusc shells from Pirovac Bay or the Murter Sea.

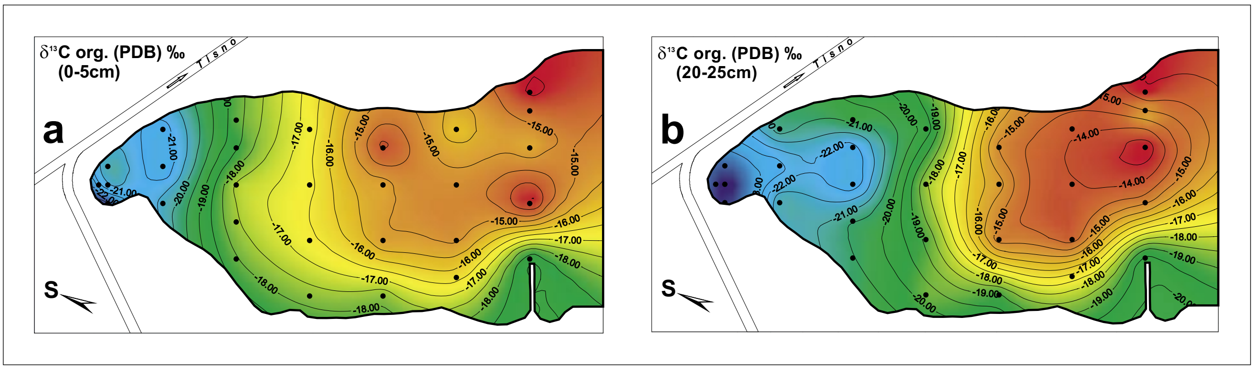

Fig. 11 Organic carbon isotopic composition of recent sediment from Makirina Cove.

Variations in the oxygen and carbon isotopic composition of the shells analysed most probably indicate that these molluscs store valuable information about the ambient water isotopic composition of oxygen and carbon, as well as temperature and salinity. In general, molluscs are believed to exert only a minimal vital effect over their isotopic composition (JONES, 1985), and thus their isotopic values are representative of environmental water conditions.

This study indicates that the oxygen isotope composition of the mollusc shells investigated reflects formation in or near equilibrium with their ambient waters. Any variations in the isotopic signatures thus indicate variable environmental conditions and temperature changes. The calculated equilibrium temperatures for mollusc shell aragonite and calcite from the investigated locations give reasonable temperature determinations, which are consistent with those measured from

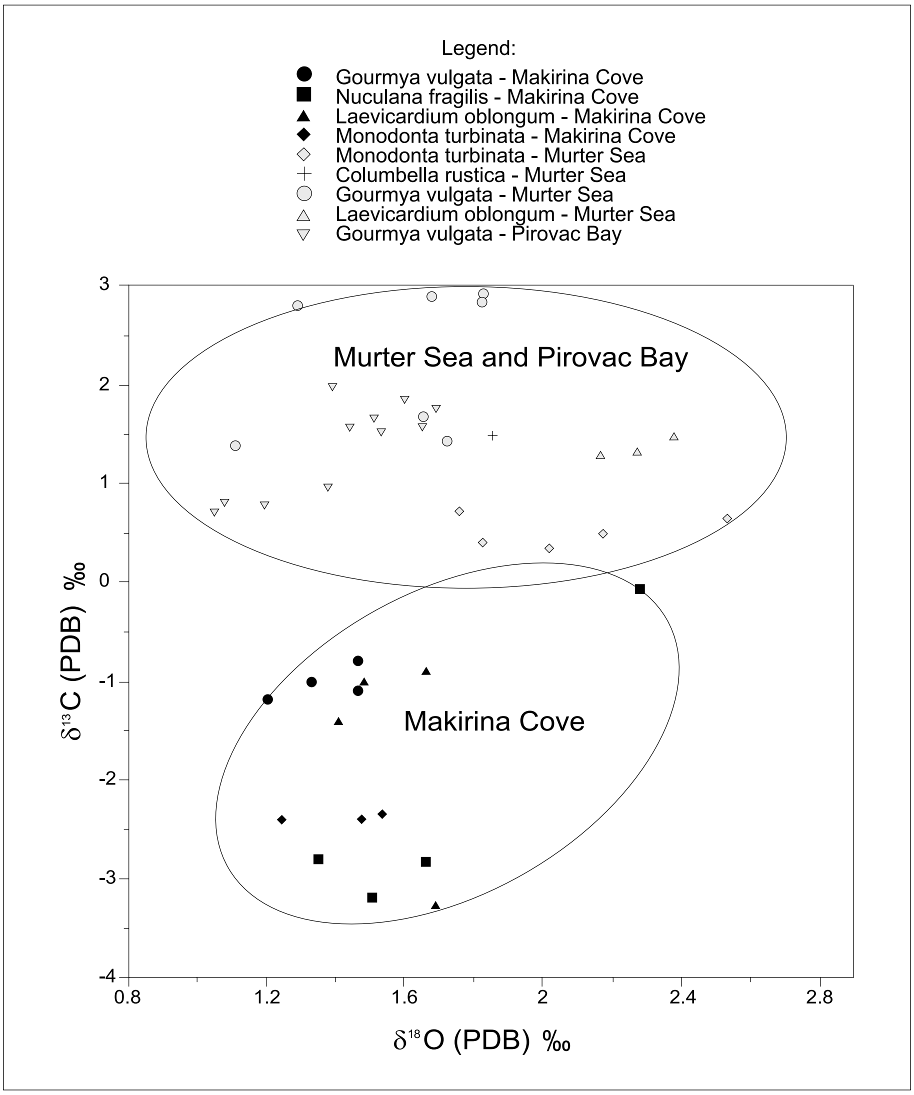

Fig. 12 Oxygen and carbon–oxygen isotope composition of mollusc shells from Makirina Cove, Murter Sea and Pirovac Bay.

Sample No.	Mollusc shells	Mineralogy	$\delta^{18}O$ (PDB) ‰	$\delta^{13}C$ (PDB) ‰	$\delta^{18}O$ (SMOW) ‰
M-10	*Gourmya vulgata*	calcite	+1.46	-1.09	+32.42
M-11	*Gourmya vulgata*	calcite	+1.20	-1.20	+32.15
M-12	*Gourmya vulgata*	calcite	+1.33	-1.01	+32.28
M-9	*Gourmya vulgata*	calcite	+1.47	-0.79	+32.42
M-2	*Nuculana fragilis*	calcite	+1.51	-3.19	+32.46
M-13	*Nuculana fragilis*	calcite	+1.35	-2.80	+32.30
M-14	*Nuculana fragilis*	calcite	+1.66	-2.83	+32.62
M-6	*Nuculana fragilis*	calcite	+2.29	-0.04	+33.27
M-3	*Laevicardium oblongum*	calcite	+1.66	-0.89	+32.62
M-4	*Laevicardium oblongum*	calcite	+1.48	-0.99	+32.44
M-5	*Laevicardium oblongum*	calcite	+1.69	-3.26	+32.65
M-16	*Laevicardium oblongum*	calcite	+1.41	-1.40	+32.36
M-7	*Monodonta turbinata*	calcite/aragonite	+1.47	-2.39	+32.43
M-8	*Monodonta turbinata*	calcite/aragonite	+1.53	-2.34	+32.49
M-15	*Monodonta turbinata*	calcite/aragonite	+1.24	-2.40	+32.19
MU-1	*Monodonta turbinata*	calcite/aragonite	+2.02	+0.35	+32.99
MU-2	*Monodonta turbinata*	calcite/aragonite	+2.53	+0.65	+33.52
MU-3	*Monodonta turbinata*	calcite/aragonite	+1.76	+0.73	+32.72
MU-12	*Monodonta turbinata*	calcite/aragonite	+1.82	+0.41	+32.79
MU-13	*Monodonta turbinata*	calcite/aragonite	+2.17	+0.50	+33.15
MU-4	*Columbella rustica*	calcite	+1.85	+1.49	+32.82
MU-5	*Gourmya vulgata*	calcite	+1.65	+1.68	+32.61
MU-6	*Gourmya vulgata*	calcite	+1.11	+1.39	+32.05
MU-7	*Gourmya vulgata*	calcite	+1.72	+1.44	+32.69
MU-8	*Gourmya vulgata*	calcite	+1.82	+2.85	+32.79
MU-9	*Gourmya vulgata*	calcite	+1.29	+2.80	+32.24
MU-10	*Gourmya vulgata*	calcite	+1.68	+2.90	+32.64
MU-11	*Gourmya vulgata*	calcite	+1.82	+2.92	+32.79
MU-14	*Laevicardium oblongum*	calcite	+2.16	+1.30	+33.14
MU-15	*Laevicardium oblongum*	calcite	+2.27	+1.33	+33.25
MU-16	*Laevicardium oblongum*	calcite	+2.38	+1.49	+33.36
PZ-1	*Gourmya vulgata*	calcite	+1.38	+0.96	+32.33
PZ-2	*Gourmya vulgata*	calcite	+1.69	+1.76	+32.65
PZ-3	*Gourmya vulgata*	calcite	+1.53	+1.52	+32.49
PZ-4	*Gourmya vulgata*	calcite	+1.65	+1.57	+32.61
PZ-5	*Gourmya vulgata*	calcite	+1.44	+1.57	+32.39
PZ-6	*Gourmya vulgata*	calcite	+1.51	+1.66	+32.47
PZ-7	*Gourmya vulgata*	calcite	+1.39	+1.98	+32.34
PZ-8	*Gourmya vulgata*	calcite	+1.60	+1.85	+32.56
PZ-9	*Gourmya vulgata*	calcite	+1.08	+0.81	+32.02
PZ-10	*Gourmya vulgata*	calcite	+1.19	+0.78	+32.14
PZ-11	*Gourmya vulgata*	calcite	+1.05	+0.71	+31.99

seawater	$\delta^{18}O_{water}$ (May)	$\delta^{18}O_{water}$ (August)	$\delta^{13}C_{DIC}$ (May)	$\delta^{13}C_{DIC}$ (August)
Makirina Cove	+1.0‰	+2.56‰	-2.31‰	-4.38‰
Murter Sea	+1.0‰	+0.65‰	-0.5‰	-1.0‰
Pirovac Bay	+1.0‰	+0.5‰	-0.5‰	-1.1‰

Table 8 Oxygen and carbon isotope values and mineralogy of mollusc shells and isotope composition of seawater from Makirina Cove (M), Murter Sea (MU), and Pirovac Bay (PZ).

May to November. These molluscs thus seem to precipitate their carbonate skeleton mostly during the warmer period.

Furthermore, it can be seen that environmental factors affect the carbon isotope composition of mollusc shells. The variations in carbon isotope composition of dissolved inorganic carbon due to oxidation and decomposition of organic matter in Makirina Cove, as well as the influxes of fresh water into Pirovac Bay seems to be the most important factors. Furthermore, we can also conclude that the $\delta^{13}C$ values of shell carbonates are out

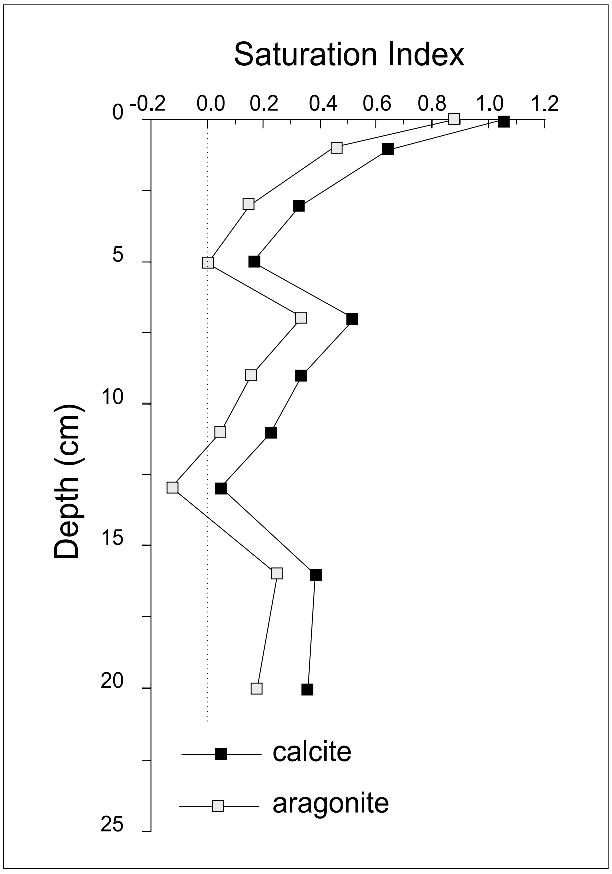

Fig. 13 Saturation indices (SI) of calcite and aragonite in the pore water at site M 1/3.

of the predicted isotopic equilibrium with atmospheric CO_2.

4.2.6. Carbonate saturation state in the pore water

To check the saturation state of calcite and aragonite in the pore water, the saturation indices (SI) were calculated using the PHREEQUE program package (PARKHURST et al., 1980), with equilibrium constants adapted for seawater conditions. The calculated saturation indices in pore water, together with the supernatant in the benthic chambers, (using the values of the solubility products of calcite and aragonite), show that the water was clearly supersaturated with respect to both carbonates (Fig. 13). So, the precipitation of authigenic amorphous or crystalline carbonate phases from the pore water in the upper 20 cm of the sediment column was thermodynamically possible.

4.2.7. Benthic fluxes

In situ benthic fluxes were estimated from linear regressions of solute concentrations vs. time (Table 9), and then compared to those calculated from depth profiles of the solute distribution in the pore water. Positive fluxes represent an efflux of the solute from the sediment, whereas negative fluxes represent an influx from the supernatant into the interstitial solution.

Anoxic conditions in the sediments strongly influenced the speciation and benthic fluxes of nitrogen and sulphur, as well as iron. The high benthic flux of dissolved inorganic carbon at both sampling sites is easily explained by decomposition of sedimentary organic matter followed by a decrease in $\delta^{13}C$ of released DIC which is typical of the increasing influence of organic-derived dissolved carbon (McNICHOL et al., 1991). The carbon isotopic composition of the DIC flux was calculated after LANSDOWN et al. (1992) and BOEHME et al. (1996) as:

$$\delta^{13}C_{J-DIC}=\frac{\Sigma\delta^{13}C_{DIC,t_2}[DIC]_{t_2}-\delta^{13}C_{DIC,t_1}[DIC]_{t_1}}{\Sigma[DIC]_{t_2}-[DIC]_{t_1}}$$

where $\delta^{13}C_{DIC,\,t}$ and $[DIC]_t$ are the isotopic composition and concentration of dissolved inorganic carbon at the two time periods, respectively. $\delta^{13}C_{J\text{-}DIC}$ was found to be -6.7±2.1‰ at site 3 and -8.2±1.6‰ at site 5. $\delta^{13}C$ of the sedimentary organic matter, which is assumed to be the predominant source of DIC, has been determined to be -15‰ and -16.5‰, respectively at the same sites. Carbonate dissolution cannot be considered as a significant source of DIC, since the pore water is supersaturated with respect to both calcite and aragonite. Methanogenesis is therefore a potential source of ^{13}C-enriched DIC producing isotopically light methane, as concluded from the positive correlation between DIC

	***In situ* benthic flux [mmol m^{-2}day^{-1}]**		**Calculated diffusive flux [mmol m^{-2}day^{-1}]**
Solute	**Site 5 0–120 h**	**Site3 0–240 h**	**Site 3**
Mn_{tot}	0.20	0.08	–
Fe_{tot}	-0.16	0.04	–
NH^{4+}	-1.87	-2.03–0.92	-0.58
NO^{3-}	-0.40	-0.15–0.62	-0.28
DIC	18.50	12.67	9.81
PO_4^{3-}	-0.004	0.002	0.002
SO_4^{2-}	-33.5	-22.21	–

Table 9 *In situ* benthic fluxes at sampling sites M 1/3 and M 1/5 during a 120 and 240-hour incubation experiment, respectively; at site 3, the NH_4^+ and NO_3^- fluxes were calculated separately for periods from 0–70 h and from 70–240 h.

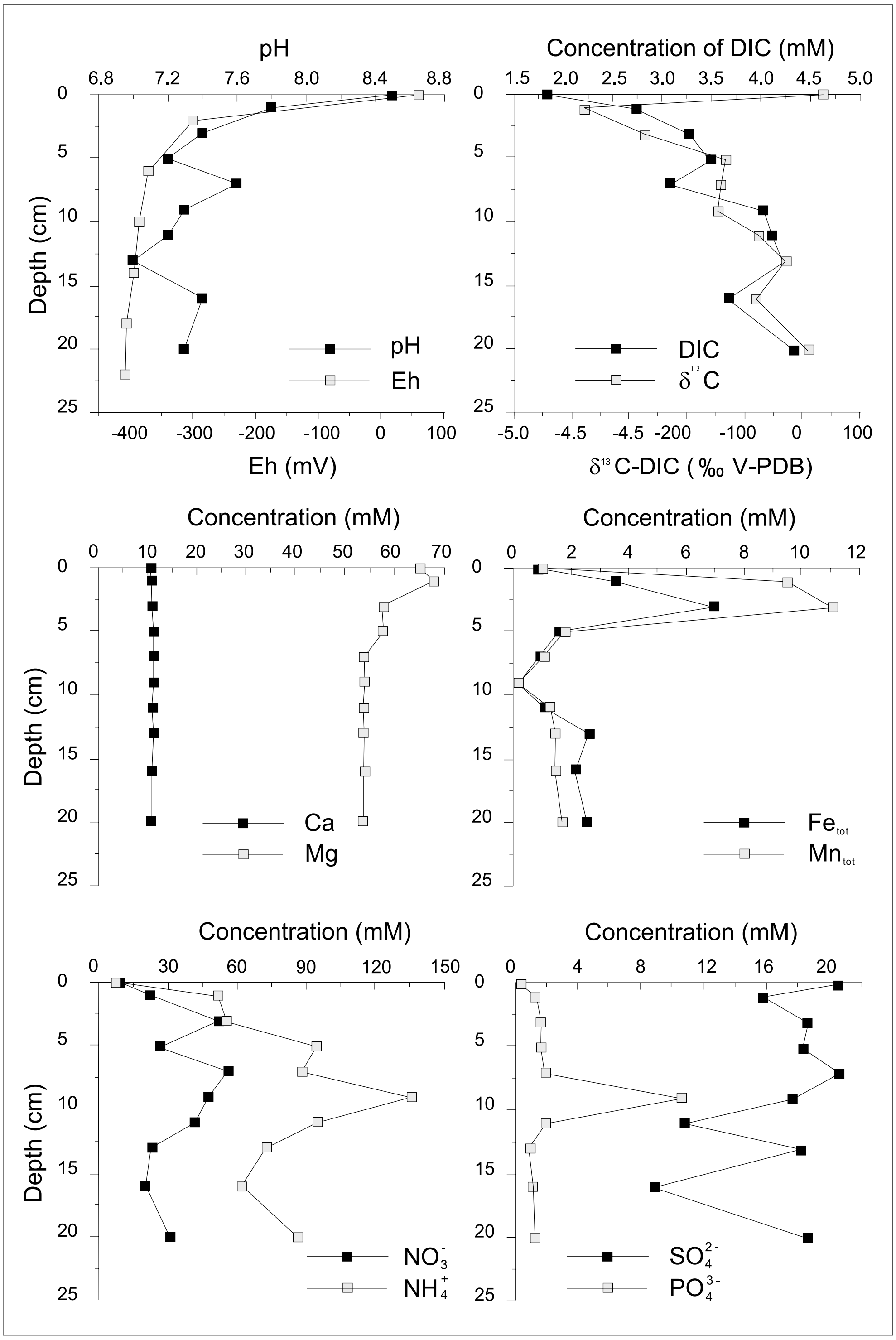

Fig. 14 pH and solute concentration vs. depth profiles in the pore water at sampling point M 1/3.

concentration and its δ^{13}C value (LANSDOWN et al., 1992). As it was found in the incubation experiment, methane formation indeed took place in the sediment, producing CH_4 with δ^{13}C about -53‰, i.e. a typical value for partially oxidised marine methane (OREMLAND et al., 1987).

4.2.8. Solute distribution in pore water

Eh, pH and solute concentrations vs. depth profiles in the pore water at sampling point 3 are presented in Fig. 14. The decreasing pH, as well as increasing total alkalinity and DIC concentration with depth, is attributed to the processes accompanying the decomposition of sedimentary organic matter. Eh measurement showed that, in spite of the presence of benthic organisms, the sediment was highly reductive even in the uppermost segment, (e.g. below -300 mV 2 cm below the sediment/water interface). The concentration profiles of solutes in the pore water were described using a one-dimensional model adapted to porous sediments, in the form of the general diagenetic equation by BERNER (1980), where advection was taken to be unimportant relative to diffusion over the entire depth interval, and enhanced transport due to irrigation was also not included. If the sediment solute distribution is controlled by one-dimensional vertical transport and reaction processes, the diffusive flux of a constituent across the sediment/water interface, J_{diff}, is independent of transport (ALLER, 1980), and can be calculated from Fick's first law. Diffusive fluxes calculated from the concentration profiles of dissolved constituents in pore water at site 3 are represented in Table 1. These results are in quite good agreement but nevertheless somewhat lower than fluxes measured *in situ*, although an underestimation of calculated fluxes is regularly reported compared to measured ones (BERELSON et al., 1990; McNICHOL et al., 1991). This is attributed to the topography effect caused by an underestimation of the actual sediment surface area when performing one-dimensional calculations of the fluxes modelled (ČERMELJ et al., 1997).

4.2.9. Palynofacies analysis

The objectives of the palynofacies analysis were (1) identification of the biological origin of POM, i.e. palynomorph and palynodebris categories and their classification according to their primary facies distribution, (2) estimation of quantitative distribution of the recognized categories, (3) evaluation of the ratios between different categories, and (4) interpretation of the depositional environment.

4.2.9.1. Biological origin and classification of Palynological Organic Matter (POM)

According to their primary facies distribution, the POM has been classified into land derived (I) and marine derived (II) palynomorphs and palynodebris groups of categories. To each category, comments on biological origin, shape, relative preservation of the structure, framboidal pyrite inclusions (FPI) and relative fluorescence intensity (FI) have been added.

I. Land derived palynomorphs and palynodebris

A. Black particles; oxidized woody tissue, mostly angular in shape, no fluorescence.

B. Brown to yellow particles; woody tissue (skeleton and vascular tissue and vegetal cell wall tissue of higher plants), semi-angular to rounded shape, low to medium preserved structure, low to moderate FI (Plate IX, Figs. 1–4).

C. Cuticular tissue; leaf remains, semi-angular to angular shape, low to medium preserved structure, often with FPIs, medium to high FI (Plate VIII, Fig. 1).

D. Spores; pterydophytes, low to medium preservation, medium to FI.

E. Pollen; gymnosperms and angiosperms, low to medium preservation, often with FPIs, high FI (Plate VIII, Fig. 2).

F. Land derived structureless organic matter; various land plant tissue, morphology ranges from membranous, filamentous, homogenous, often pseudoamorphous, partly with FPIs, low to high FI, in this category small homogenous globulae of cellular secretions of leaf-parenchyma and resins/waxes with high FI are also included (Plate VIII, Figs. 8 and 9; Plate IX, Figs. 1–4).

II. Marine derived palynomorphs and palynodebris

A. Organic walled dinoflagellate cysts; phytoplankton, low to medium preservation, often with FPIs, high FI (Plate VIII, Fig. 3).

B. Tintinnid chitinous loricae; zooplankton, medium to well preserved, often with FPIs, no fluorescence (Plate VIII, Fig. 5).

C. Foraminiferal test linings; chitinous inner walls of benthic foraminifera, medium to well preserved, often with FPIs, no fluorescence (Plate VIII, Fig. 4).

D. Chitinous skeletons; planktonic crustaceans, moderately preserved, often with FPIs, no fluorescence (Plate VIII, Fig. 6).

E. Scolecodonts, chitinous teeth of annelids, benthic, medium to well preserved, no fluorescence (Plate VIII, Fig. 7).

F. Marine macrophyta (seagrass, seaweeds); well preserved, some irregular structure, membranous, filamentous, fibrous, transculent, high FI (Plate VIII, Figs. 8 and 9; Plate IX, Figs. 1–4),

G. Marine derived amorphous organic matter (AOM); various marine organisms, derived mostly from phytoplankton, various bacteria, marine macrophyta and faecal pellets, morphology ranges from disseminated, granular, aggregated granular (heterogenous–liptodetrinitic), spongy (homogenous–liptinic), with FPIs, moderate to high FI (Plate VIII, Figs. 8 and 9; Plate IX, Figs. 1–4).

4.2.9.2. Quantitative distribution of the categories of POM

The overall palynological composition indicates that the analysed samples contain about 32% land derived (I) and 68% marine derived (II) organic matter (Table 10). The palynomorphs constitute about 1.4% of sedimentary organic matter (SOM). Zooplanktonic palynomorphs are most abundant (41.5%), followed by foraminiferal test linings (21.6%), pollen, predominantly coniferalean bisaccate type (21.5%), organic walled dinoflagellate cysts (7.7%) and spores (7.7%) (Table 11).

The ratio I/II (land derived/marine derived) may be regarded as an indicator of the proximo–distal position of the sediments related to shore line (TYSON, 1995). The values of this ratio (Table 12) increase along the transect landwards indicating higher input of terrestrial organic matter near shore.

The ratio phytoplankton/zooplankton (IIA/IIB, D) may reflect changes in the composition of primary

Samples	M I/4 (%TPOM)	M I/7 (%TPOM)	M I/10 (%TPOM)
IA	0.4	0.7	5.7
IB	6.7	7.2	18.0
IC	0.3	0.2	0.2
ID	0.1	0.1	0.1
IE	0.3	0.4	0.2
IF	20.0	20.0	15.0
IIA	0.1	0.1	0.1
IIB	0.1	0.1	0.1
IIC	0.3	0.4	0.2
IID	0.4	0.5	0.2
IIE	0.1	0.1	0.1
IIF	1.2	0.2	0.1
IIG	70.0	70.0	60.0
Σ%	**100.0**	**100.0**	**100.0**

Table 10 Quantitative distribution of the categories of POM (% of total POM).

Samples	M I/4 (%TP)	M I/7 (%TP)	M I/10 (%TP)
ID	7.2	5.9	10.0
IE	21.3	23.4	20.0
IIA	7.2	5.9	10.0
IIB	7.2	5.9	10.0
IIC	21.4	23.5	20.0
IID	28.5	29.5	20.0
IIE	7.2	5.9	10.0
Σ%	**100.0**	**100.0**	**100.0**

Table 11 Quantitative distribution of palynomorphs (% of total palynomorphs).

Samples	M I/4	M I/7	M I/10
I / II	0.39	0.41	0.64
IIA / IIB, D	0.20	0.16	0.33
IIA / IID	0.25	0.20	0.50
IB-E, IIA-F / IF, IIG	0.11	0.11	0.25
IA, IIB-E / IB-F, IIA, F,G	0.014	0.018	0.067
IA / IB	0.06	0.10	0.31

Table 12 Ratios of the categories of POM.

bioproduction, which is controlled through many variable ecological factors (VILIČIĆ, 1989; VILIČIĆ et al., 1998). It has to be emphasized that this ratio and its interpretation is closely related to the varying preservation potential of organic matter within different environments. The values of this ratio (Table 12) are variable along the transect, which may indicate some variations in primary production.

The ratio dinosporin cysts/chitinous exoskeletons of crustaceans (IIA/IID) is a ratio of relatively high resistant/low resistant components of organic matter. From a chemical point of view, chitin (polysaccharides) represent relatively low resistant components with a relatively low preservation potential. However, their preservation potential may vary within different environmental conditions, and is closely related to the processes of degradation; in Recent sediments, chitinoclastic bacteria are responsible for most chitin breakdown that occurs in the upper aerobic zone, a marked slowdown or cessation of bacterial activity may occur in anoxic conditions and, under conditions of high productivity and high sedimentation rate, the preservation potential of chitinous remains in surficial sediments may become considerably enhanced (VAN WAVEREN & VISSCHER, 1994). Chitinous material is moderately preserved in the Makirina sediments, indicating very low activity of chitinoclastic bacteria. This ratio may potentially be high and may still contain preserved chitinous material. Therefore, higher near shore values of the ratio may suggest some variations in primary production as the environmental conditions were conducive to preservation of chitinous material. The values of this ratio (Table 12) are low and variable along the transect.

The ratio structured/amorphous (IB–E, IIA–F/ IF, IIG) reflects the pattern and the relative degree of organic matter degradation and preservation of sedimentary organic matter (SOM), which is closely related to a complex interaction of several factors before, during and after its deposition; primary bioproduction, preservation potential of organic matter, sinking rate, sedimentation rate, oxic–anoxic relationships within the depositional environment, proximo–distal position to source of terrestrial organic matter and granulometry of the sediments are the most important ones. In order to emphasize the relative degree of organic matter degradation, the category IF is treated as “amorphous”, although it is mostly structureless, thus not really amorphous. This is because bacterial degradation of some primary structured organic matter results in secondary structureless organic matter. Unaltered SOM consists of structured organic matter, structureless organic matter and amorphous organic matter (AOM), and with the exception of chitin and lignin, all other constituents of SOM are more or less hydrogen-rich and lipid-rich, thus exhibiting fluorescence properties under excitation of UV or blue light.

It has been demonstrated that the preservation of palynomorphs is possible in environments where the aerobic and anaerobic processes are short and/or weak enough during sedimentation and diagenesis (ORR & GAINES, 1973; HART, 1986). Consequently, SOM is well preserved within conditions which mostly comprise dysoxic and/or environments with high sedimentation rate, where the palynological record would reveal preserved primary structure of SOM and its primary fluorescence properties. However, depending on the type, intensity and duration of bacterial degradation within different aquatic depositional environments, SOM may convert partly or completely, according to the preservation potential of each component, into organic matter with various morphological and fluorescence properties. So, in depositional sets with dysoxic conditions and/or high sedimentation rate, the ratio structured/amorphous is mostly dependant on quantity of primary AOM which is well preserved due to favourable conditions. In contrast, this ratio is, in oxic and anoxic environments, mostly dependant on degradation, resulting in varying qualities of organic matter as compared to unaltered material.

Experiments have shown that plant tissue may convert into structureless, semi-amorphous organic matter under oxic conditions (MASRAN & POCOCK, 1981). However, this type of organic matter does not exhibit fluorescence properties. Even very resistant lipid-rich components, both land (cuticles) and marine (dinocysts) derived, loose their fluorescence features and often their primary structure. Non-fluorescent chitinous organic matter is degraded in oxic environments and it often appears as amorphous. In general terms, the palynological record of oxic environments does not contain fluorescent structureless organic matter or fluorescent AOM, although a high sedimentation rate may be conducive to preservation of some primary fluorescent AOM which is otherwise degraded into non-fluorescent AOM revealing features of an land plant origin. This is important to differentiate, because “humic” AOM is also produced in large amounts by the biodegradation of planktonic or microbial mat organic matter (TYSON, 1995). On the other hand, palynofacies of anoxic environments are dominated by fluorescent organic matter, represented by varying amounts of structured, structureless and amorphous organic matter which is dependant on the overall environmental conditions and preservation potential. The biological praecursors, i.e. the source of fluorescent organic matter are hydrogen-rich, i.e. lipid-rich components, both land derived (cellulose, poorly lignified tissue, suberine, suberified tissue, cuticle, leaf parenchyma secretions, resins, waxes, spores, pollen) and marine derived (algae, phyto-, zooplankton, lipids of various organisms including a variety of bacteria as well as poorly lignified vascular and non-vascular tissue of marine macrophytes). Lipid-rich constituents are resistant to anaerobic bacterial degradation, whereas others, for example primary structured woody tissue (*s.l.*), are, under the same conditions, converted into structureless organic matter showing fluorescence features. Fluorescent AOM may be regarded as a product of the decomposition of algae, phyto-, zooplankton and bacteria with a contribution of bacterially altered land plant tissue (STACH et al., 1982; TISSOT & WELTE, 1984; ROBERT, 1988; TYSON, 1995; BATTEN, 1996). However, typical AOM, as the term should be used, consists of primary AOM of organic aggregates derived from phytoplankton blooms, and particulate organic matter of sea water as well as algal and zooplankton extracellular exudates. The same holds true for algal mats formed by cyanobacteria (“blue-green algae”) and thiobacteria (sulphur bacteria), because the preservation potential of their structured sheets is very low and they are rapidly degraded. Palynological examination of modern deposits with cyanobacterial mats has shown that all but the surficial layers contain only AOM (TYSON, 1995). AOM is also derived from other sources. Part of AOM is represented by the faecal remains of zooplankton feeding on phytoplankton and other organic material (HABIB & MILLER, 1989). In some organic-rich sediments, faecal pellets compose a significant part of AOM (ROBBINS et al., 1996). Due to degradation and fragmentation during and after deposition, faecal remains often occur as numerous small aggregates. In this case, palynofacies containing abundant AOM, bisaccate pollen, dinoflagellate cysts and acritarchs may infer the presence of faecal pellets (HABIB et al., 1994). Fluorescent faecal pellets are considered to be of zooplanktonic origin, and were probably deposited in anoxic environments, whereas non-fluorescent ones indicate a benthic origin and oxic environments (ROBBINS et al., 1996). Finally, sediments of some shallow water environments may contain abundant AOM derived from marine macrophytes. Due to the fact that they are easily degraded, they appear in modern sediments mostly as amorphous aggregates (TYSON, 1995).

Sediments of anoxic depositional sets yield various amounts of fluorescent AOM and fluorescent structureless organic matter depending on primary production, proximo–distal position and the amount of terrestrial organic matter input. Fine-grained sediments of distal, basinal, anoxic environments contain entirely typical AOM which is ultimately derived from phytoplankton and bacteria (LEWAN, 1986; RAYNAUD et al., 1989; TYSON, 1995; BATTEN, 1996). Fine-grained sediments of proximal, shallow marine, anoxic environments contain typical AOM in lower concentrations, due to the proximity to the source of terrestrial organic matter, but also a certain amount of land and marine derived structureless organic matter, (partly primary structureless, partly derived from microbially altered organic matter). Nevertheless, sediments of all anoxic environments are usually dominated by typical AOM. Expressed as percentages, high values of typical AOM with high fluorescence intensity are indicators of reducing, i.e. at least temporarily dysoxic to anoxic environments with high preservation of autochthonous planktonic organic matter or benthic microbial mat organic matter (TYSON, 1995). Within the sediments of the central part of Makirina Cove, approximately 70% of typical AOM has been estimated, decreasing landwards along the transect to 60% due to the increased input of terrestrial organic matter (Table 10).

Low values of the ratio structured/amorphous (Table 12) slightly increase landwards along the transect and they suggest a relatively high degree of degradation and preservation of organic matter resulting in accumulation of fluorescent AOM and fluorescent structureless organic matter as indicators of oxygen-depleted conditions.

The ratio non-fluorescent/fluorescent organic matter (IIB–E/IB–F, IIA, IIF, IIG) is herein evaluated as an indicator of the organic matter organic matter preservation, i.e. as a relative indicator of oxidation processes which may have affected primary fluorescent organic matter before, during and after deposition. Any oxidation of fluorescence categories would result in a certain loss of fluorescence intensity or lack of fluorescent properties. The most labile of them is the finely divided and spongy fraction of fluorescent AOM. The lack of fluorescence of this fraction mainly indicates partial oxidation before or during final deposition (TYSON, 1995). This type of AOM has not been identified within the analysed sediments. However, AOM of near shore samples needed 3 minutes of excitation in blue light before reaching the same fluorescence intensity and colour spectrum as exhibited by other samples almost immediately after the beginning of excitation. This may indicate very weak and/or very short oxidation probably after deposition (activity of benthic organisms), because oxidation before or during the deposition would have resulted in a stronger reduction, if not completely, of fluorescence intensity. An important indicator that oxidation processes before, during and after deposition have left little signature on organic matter of Makirina sediments is the fact that all but primary non-fluorescent organic matter (lignin and chitin) consists of fluorescent organic matter. Very low values of this ratio slightly increase landwards indicating a high degree of preservation of organic matter and protection against secondary oxidation.

The ratio IA/IB indicates the degradation pattern. Unaltered woody tissue reveals fluorescence properties and once they become settled in the sediment, may suffer various alterations depending on the oxic–anoxic relationships of different environmental conditions. Oxidation processes remove fluorescent components and convert organic matter either into non-fluorescent AOM or dark to black organic clasts. Anaerobic bacterial degradation converts woody tissue into structureless organic matter with some fluorescence properties. In general, black organic clasts (IA) suggest biodegradation under oxic conditions, i.e. various wet but not saturated environments, where rooting and fungal activity took place (BATTEN, 1996), whereas brown-yellow, structureless organic clasts (IB) suggest bacterial degradation under anoxic conditions (TYSON, 1995). The higher the ratio, the more oxic conditions prevail and, vice versa, the lower the ratio, the more anoxic conditions prevail. The palynological record of environments with a strong terrigenous input of black organic clasts may exhibit a relatively high IA/IB ratio even if anoxic conditions prevail in environments where these organic clasts are finally deposited. Therefore, this ratio should be evaluated together with the ratios of structured/amorphous and non-fluorescent/fluorescent organic matter. The values of this ratio slightly increase landwards along the transect suggesting anoxic degradation pattern of organic matter.

4.2.9.4. Depositional environment

According to the palynological composition of both type and amount of organic matter, the Recent sediments of Makirina Cove may be characterized as organic-rich deposits. This is consistent with the organic carbon values representing up to 5 wt.% of the total sediment (LOJEN et al., 1999). The high amount of organic matter, of which 2/3 is marine derived, suggests that the Makirina sediments originate within an environment with high primary bioproduction and conditions which are conducive to its preservation. An important indicator of primary bioproduction is the quantity of phytoplankton which enables determination of the trophic level of marine ecosystems. The development of phytoplankton populations is controlled through a combination of ecological factors (supply and concentration of nutrients, thermohaline relationships, and light) where hydrography, influenced by specific karst-hydrology, plays an important role (VILIČIĆ et al., 1998; CARIĆ et al., 1999; BURIĆ et al., 1999). Studies of recent phytoplankton along the Croatian coast have shown that ecosystems similar to Makirina Cove are moderately eutrophic (VILIČIĆ, 1989; VILIČIĆ et al., 1998).The palynological record of the Makirina sediments shows a relatively high proportion of typical marine AOM which is in general terms derived from phytoplankton and bacteria. Very low abundances of dinosporin cysts, i.e. low values of the ratio phytoplankton/zooplankton, can be explained in terms of the ecological conditions where the motile stage of dinoflagellate communities prevailed and the production of their cysts is reduced (TYLER et al., 1982; TYSON, 1987, 1995). This means that dinoflagellates must have contributed more biomass than is actually recorded in the palynological composition. A similar palynological relationship has also been recorded in Recent sediments of the restricted, shallow marine (<2.5m) environment of Morinje bay (20 km SE from Makirina Cove), where the phytoplankton quantity of the sea water column indicates a moderately eutrophic ecosystem (KOCH et al., 2002; BAČANI et al., 2004). In addition, stressed, shallow marine eutrophic environments are characterized by populations of small, opportunistic foraminiferal species (HALLOCK, 1988), which is consistent with the palynological record of the Makirina sediments which contain small-sized foraminiferal test linings. Studies of the area under consideration have indicated sea-level rise during the Holocene and up to the present (ŠEGOTA, 1982; FILIPČIĆ, 1992), which is also considered to be a factor that influences primary bioproduction: the formation of marine, organic-rich sediments often coincides with transgression (TYSON, 1987, 1989, 1995; TYSON &

FUNNELL, 1987; TRIBOVILLARD & GORIN, 1991; STEFFEN & GORIN, 1993; BATTEN, 1996).

The organic matter of Makirina sediments is characterized by abundant inclusions of framboidal pyrite indicating reducing conditions and a supply of reactive iron. Pyrite is typically most abundant in anoxic environments and occurs together with AOM (STACH et al., 1982; TISSOT & WELTE, 1984; ROBERT, 1988; TYSON, 1995, BATTEN, 1996). However, in anoxic environments with a low supply of iron, the formation of pyrite is rather limited (BERNER, 1981; ALLISON, 1990). As most of the iron is detrital in origin, within anoxic environments with a low iron supply, such as carbonate facies, pyrite formation is limited and the sulphur is incorporated into organic molecules (TISSOT & WELTE, 1984; MOLDOWAN et al., 1992; JERINIĆ et al., 1994; TYSON, 1995). Therefore, the content of pyrite is often positively correlated with both siliciclastics and the relative percentage of terrestrial organic matter (TYSON, 1995) which is the case in the Makirina sediments. However, due to the carbonate sorroundings of Makirina Cove, the source of iron and the mechanism of its supply is at present insufficiently understood.

In spite of obvious benthic activity within the shallow marine environment of Makirina Cove, oxidation processes which might have affected organic matter before, during and after the final deposition had no or very little impact on its preservation state. Most of the organic matter of Makirina sediments consists of fluorescent material and a relatively high portion of AOM, indicating a high degree of preservation which is possible only under oxygen-depleted conditions. Therefore, it is suggested that the anoxic/oxic conditions are delineated at or very near the sediment/water interface. This may find support in terms of the presence of cyanobacteria which are widely distributed in shallow environments with fluctuating salinities where they may flourish at salinities of 40–250‰ (TYSON, 1995). As the salinity in Makirina Cove varies during the summer period between 40–41‰ (LOJEN et al., 2000), the cyanobacteria may have formed mat structures which reduce the vertical permeability of the sediment, helping to retain the saline anoxic pore waters. These conditions encourage the preservation of the lipoid fraction which is refractory to anaerobic bacteria (TYSON, 1995). The high preservation degree of AOM also reflects the stable environmental conditions of Makirina Cove, preventing lateral flushing of depositional pore waters and the introduction of aerobic bacteria (TYSON, 1995). In general terms, the oxygen depleted conditions and accompanying marine transgression in restricted environments mostly control the preservation of AOM (TYSON, 1995; BATTEN, 1996). In addition, the burial rate and preservation of organic matter is positively correlated with sedimentation rate (BETTS & HOLLAND, 1991; TYSON, 1995), which is in Makirina Cove estimated at 0.75 m/1000 y in the central part of the Cove.

5. CONCLUSION

On the basis of the multidisciplinary investigation of the Recent sediments from Makirina Cove, the following conclusions regarding their origin may be outlined:

(1) The Albian–Cenomanian dolomite basement of the Makirina depression was inundated by the sea approximately 4500 y B.P. due to the Holocene sea-level rise. The morphological features of the surrounding land and the geometry of the depositional basin, as well as the balanced relationship between the ongoing Holocene sea-level rise and the sedimentation rate, enabled formation of a restricted, shallow marine (<2 m) environment which persists up to the present time. Makirina Cove represents a stressed environment with seawater temperatures varying during the year from 0–35°C and fluctuating salinities reaching values up to 41‰ caused by seasonally enhanced evaporation, a continuous freshwater supply through low capacity submarine springs associated with the coastal karst area and surface runoff episodes. These environmental conditions have been conducive to high primary production of organic matter resulting in the formation of overall organic-rich deposits which contain up to 5 wt.% of organic carbon. During approximately 4500 years, up to 3.5 m of sediments were deposited, indicating a relatively high sedimentation rate estimated at 0.75 m/1000 y in the northern central part of the Cove.

(2) The Recent sediments are composed of weakly sorted clayey–sandy silts. Of the non-carbonate minerals, clays predominate over quartz, and lesser amounts of halite, pyrite and marcasite are present. The carbonate minerals are represented by dolomite and amorphous calcite which are more abundant than authigenic calcite and aragonite. The content of clay minerals, halite, pyrite, marcasite and aragonite is highest in the central part of the Cove decreasing towards the shore, whereas quartz, dolomite and calcite are inversely distributed. The mineralogical composition of the relatively high concentrations of light and heavy mineral fractions indicates reworking from Eocene flysch deposits, which remains puzzling because the surroundings of Makirina Cove are built-up of Cretaceous carbonate rocks lacking these fractions. The morphometric features of the resistant minerals show that some of them have been transported for long distances and resedimented in several cycles.

(3) The majority of trace elements are similar to those reported for argillaceous sediments and shales. Some of them show values similar to those of the surficial sediments from the Central Adriatic, while others are higher. Nevertheless, most of chemical elements (Fe, Na, Ti, P, As, Ba, Br, Ce, Co, Cs, Cu, Eu, La, Lu, Nd, Ni, Pb, Sc, Sm, Th, U, V, Y, Yb, Zn) of the surfical sediment from Makirina are associat-

ed with clay minerals within the clay fraction. Their increasing concentrations have been found to correlate with distance to shore and with depth. Some of the major elements, such as iron, are principally associated with the silt–clay fraction and show similar distributions to K and Al. The occurrence of iron sulphide suggests that they are a product of the oxidation of organic matter by microbial mediated sulphate reduction. The presence of Ca, Mg and Sr is associated with the carbonate content of the surroundings with increasing values towards the shore. Sediments of the central northern part of the Cove are characterised by elevated concentrations of some trace elements (V, Zn, Cu, Ni, Pb, As, Cs, Br, Sb, Sc, Rb, Th), especially Mo and Se, indicating reducing conditions, which is consistent with the same distributional pattern of sulphides. Selenium is preferentially enriched in authigenic pyrite, and it is probably the major source of Se in the Makirina Cove sediments.

(4) The organic carbon isotopic ($\delta^{13}C$) composition of the sedimentary organic matter shows that the surficial sediments of the southern coastal parts of the Cove contain 40–60% terrigenous organic matter, whereas in the central northern part less than 40%. The variations in the carbon isotopic composition have been noted as a function of the distance from the shore.

(5) The oxygen isotopic ($\delta^{18}O$) composition of the mollusc shells reflects formation at or near equilibrium with their ambient waters. The molluscs precipitated their carbonate shells mostly during warmer periods (May to November). Environmental factors affected the carbon isotopic composition of mollusc shells. Variations in carbon isotopic composition are caused by dissolved inorganic carbon due to oxidation and decomposition of organic matter as well as by influxes of fresh water into the Bay. It is concluded that the $\delta^{13}C$ values of shell carbonates are out of the predicted isotopic equilibrium with atmospheric CO_2.

(6) The saturation indices show that the water was clearly supersaturated with respect to carbonates, meaning that the precipitation of authigenic amorphous or crystalline carbonates phases was thermodynamically possible from the pore water in the upper 20 cm of the sediment column.

(7) Anoxic conditions in the sediments strongly influenced the speciation and benthic fluxes of nitrogen and sulphur, as well as iron. The high benthic flux of DIC is explained by decomposition of sedimentary organic matter followed by a decrease in $\delta^{13}C$ of released DIC, which is typical of the increasing influence of organic-derived dissolved carbon. As carbonate dissolution cannot be considered as a significant source of DIC, since the pore water is supersaturated with respect to both calcite and aragonite, methanogenesis is a potential source of ^{13}C-enriched DIC producing isotopically light methane. It has been found that methane formation took place in the sediment, producing CH_4 typical for partially oxidized marine methane.

(8) The decreasing pH, as well as increasing total alkalinity and DIC concentration with depth is attributed to processes accompanying decomposition of the sedimentary organic matter. Eh measurement showed that, in spite of the presence of benthic organisms, the sediment was highly reductive even in the uppermost segment, 2 cm below the sediment/water interface.

(9) Palynological analysis shows that most of the organic matter (70–90%) consists of hydrogen-rich and lipid-rich amorphous and structureless material with framboidal pyrite inclusions, indicating accumulation and bacterial decomposition of both marine and land derived organic matter under oxygen-depleted conditions. The sediments of the central part of the Cove contain 70% marine derived organic matter, decreasing to a level of 60% near the shore. A relatively high portion of typical marine AOM, which is derived from phytoplankton, bacteria and marine macrophyta, suggests at least moderately eutrophic conditions of the Makirina ecosystem. The combination of nutrient supply through continuous transgression, submarine springs and seasonal run-off episodes enhanced the primary bioproduction. According to the quality and quantity of organic matter, most of the primary biomass, although microbially altered, is well preserved under conditions of oxygen deficiency, accompanying marine transgression and a relatively high sedimentation rate.

According to the results obtained from the applied methods, the features of Makirina sediments strongly reflect the given depositional conditions within this restricted, stressed, shallow-marine environment, where these organic-rich sediments originate, and may therefore serve as a calibration standard in further investigations.

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Revised manuscript accepted April 15, 2005.

PLATE I

Mineralogical composition of the 0.09–0.16 mm fraction of the insoluble residue of the Makirina Cove sediments

1 Pyrite, 160x, N-. Agglomeration of authigenic pyrite.

2 Chert, 160x, N+. Particles of chert rock.

3 Feldspar, 160x, N+. Hypidiomorphic and semirounded quartz grain.

4 Quartz, 160x, N+. Asymmetric and semiangular quartz grain.

5, 6 Glaucophane, 170x, N-. Fig. 5) vibration direction of blue pleochroism; Fig. 6) vibration direction of violet pleochroism.

7 Amphibole, 170x, N-. Crumbled, semiangular amphibole with green pleochroism.

8 Pyroxene, 160x, N-. Prismatic green pyroxene, angular, may also be volcanic in origin.

9 Garnet, 160x, N-. Brownish garnet, semiangular, asymmetric in shape.

10 Garnet, 160x, N-. Pale-pinky garnet of an asymmetric shape.

11 Zircon, 160x, N-. Rounded to very well rounded zircon grain.

12 Tourmaline, 160x, N-. Semirounded tourmaline.

13 Zircon, 160x, N-. Rounded zircon grain.

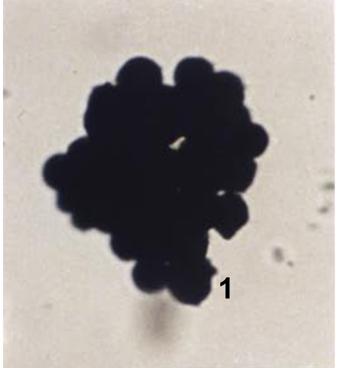
14 Garnet, 160x, N-. A colourless grain of garnet, angular and asymmetric in shape.

15 Zircon, 160x, N-. These features of a zircon grain indicate a volcanic origin.

16 Garnet, 160x, N-. A colourless garnet, semiangular and asymmetric in shape.

17 Zircon, 160x, N-. Idiomorphic, angular to semirounded crystal of zircon.

18 Zircon, 500x, N-. Zircon is prismatically elongated, crumbled, completely angular, idiomorphic with volatile inclusions and a thin tube inclusion which indicates a volcanic origin.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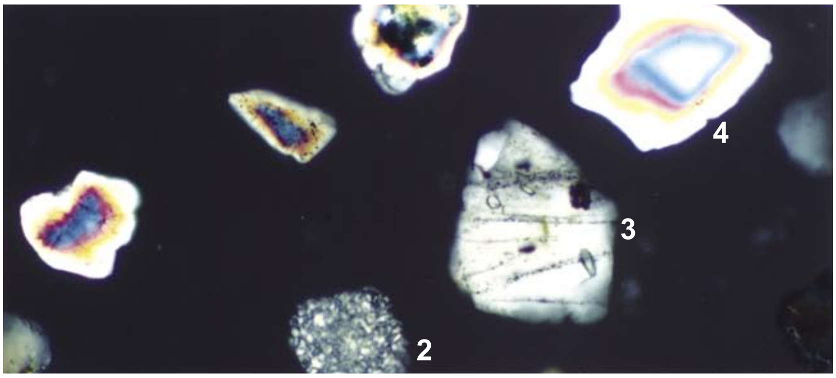
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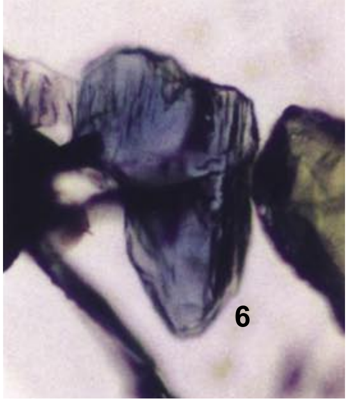
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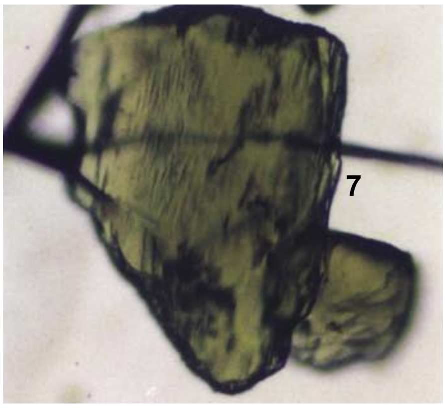
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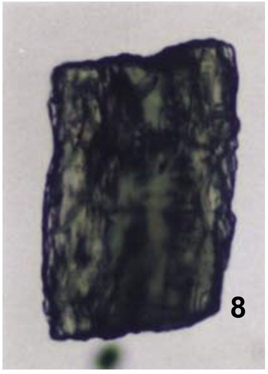
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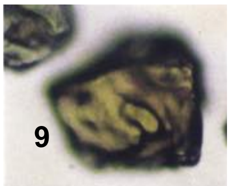
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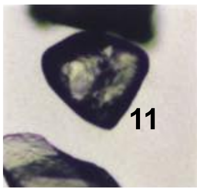
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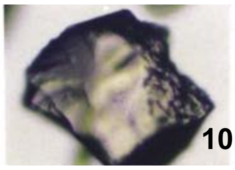
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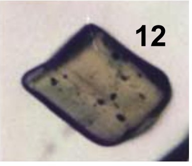
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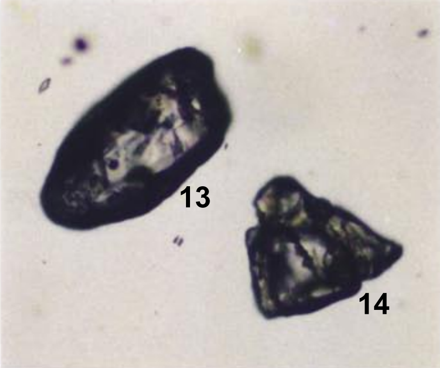
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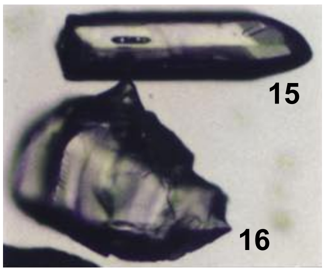
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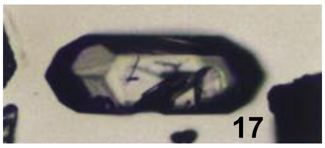
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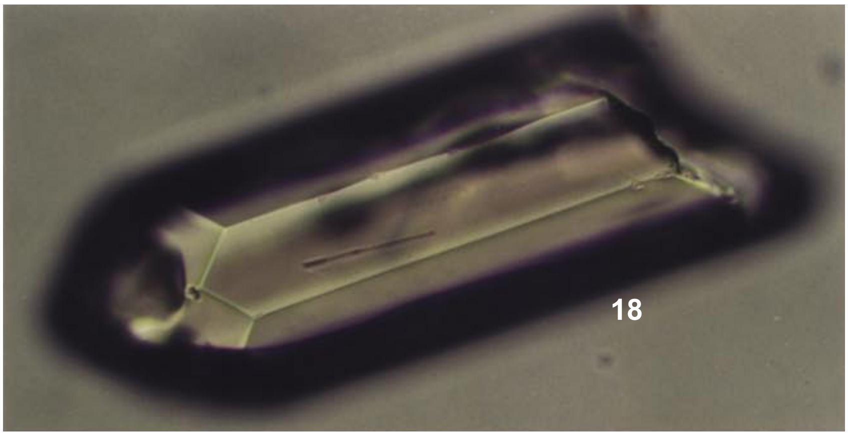
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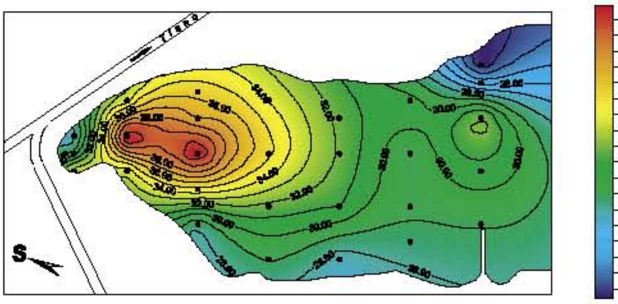
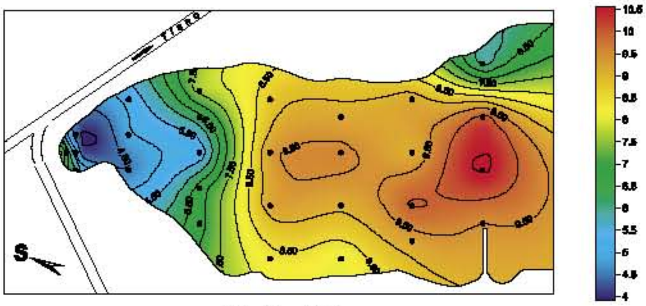
PLATE II

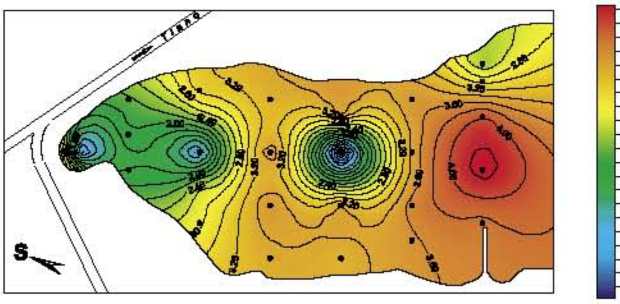
Distribution of SiO_2, Al_2O_3, Fe_2O_3, FeO, MnO, MgO, CaO, Na_2O, K_2O and TiO_2 in the surficial sediments of Makirina Cove



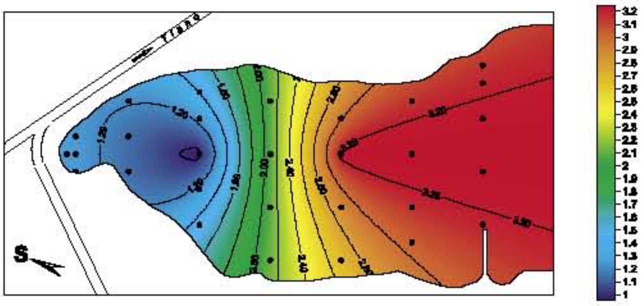
SiO_2 (%)



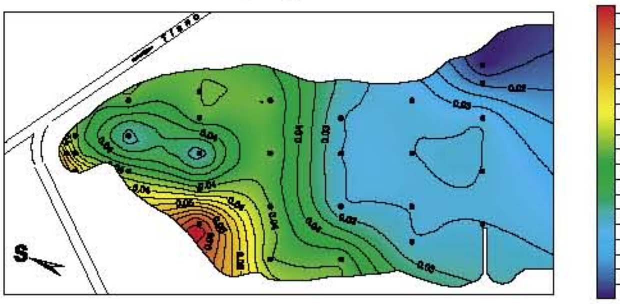
Al_2O_3 (%)



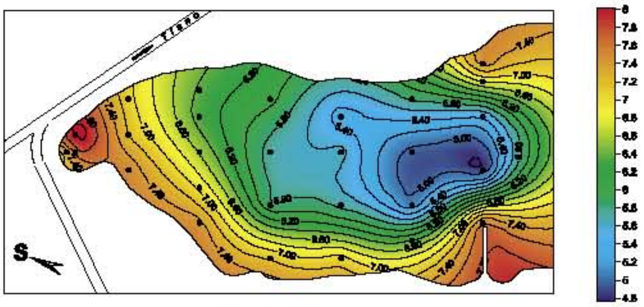
Fe_2O_3 (%)



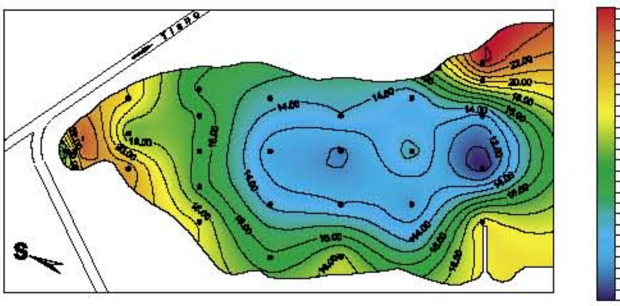
FeO (%)



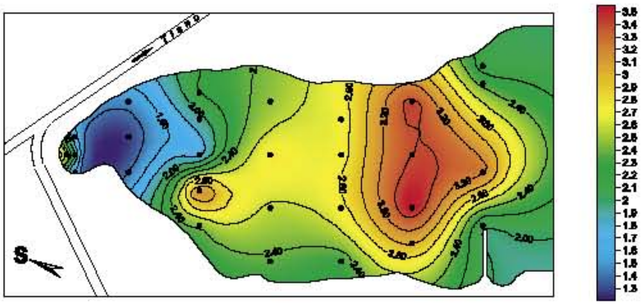
MnO (%)



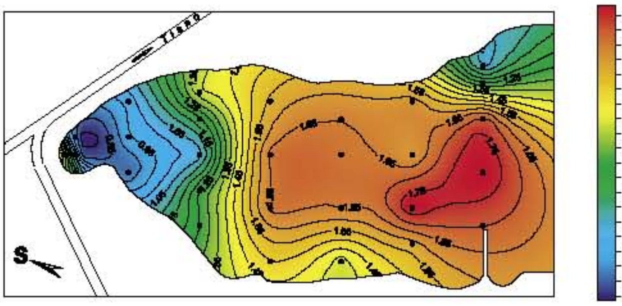
MgO (%)



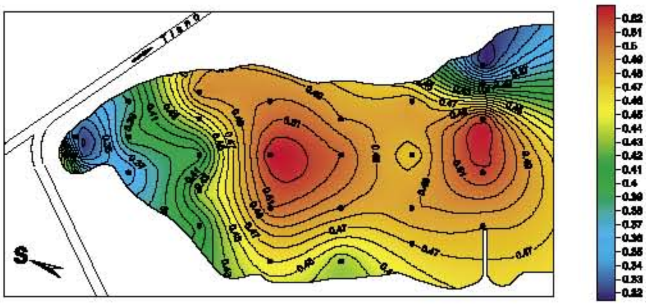
CaO (%)



Na_2O (%)



K_2O (%)

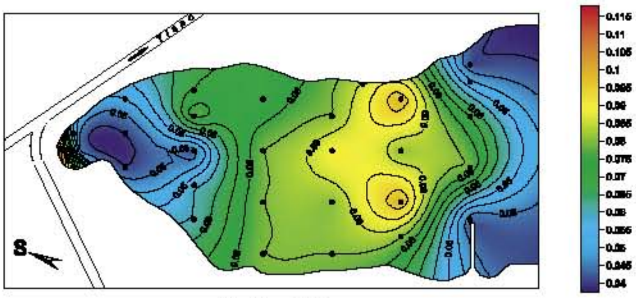


TiO_2 (%)

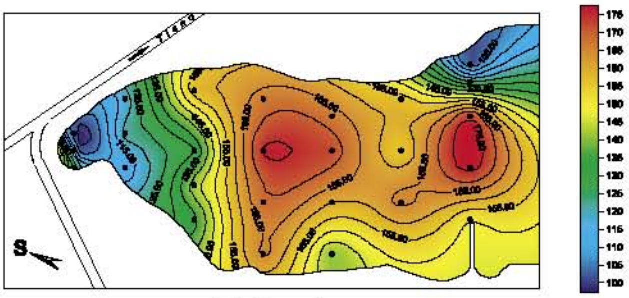
PLATE III

Distribution of P_2O_5, Ba, Sr, Y, Zr, V, Cu, Pb, Zn and Ni in the surficial sediments of Makirina Cove

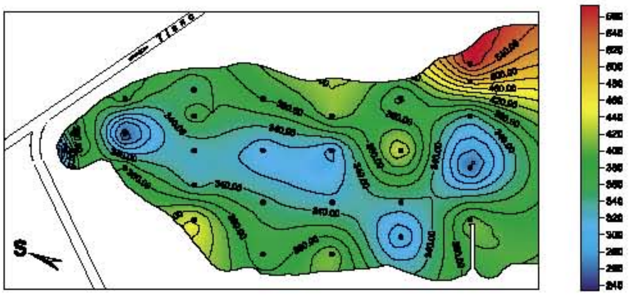
PLATE III



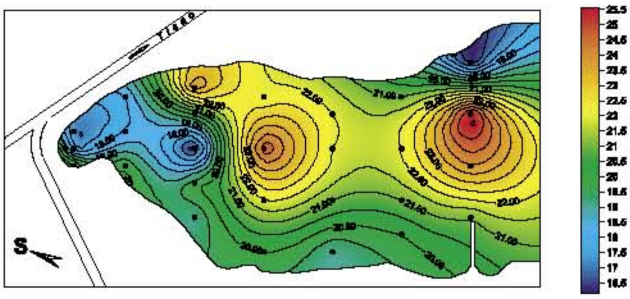
P_2O_5 (%)



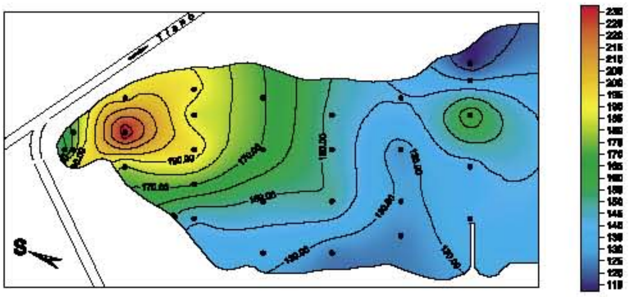
Ba (ppm)



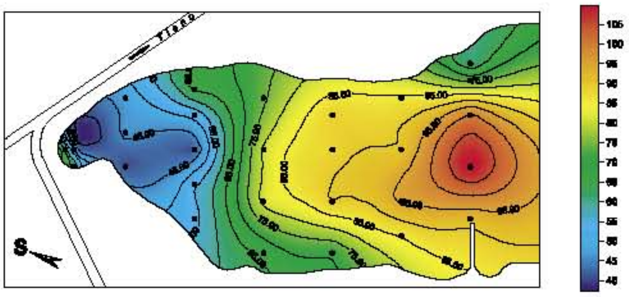
Sr (ppm)



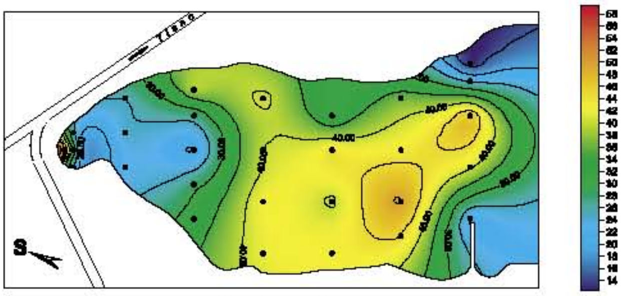
Y (ppm)



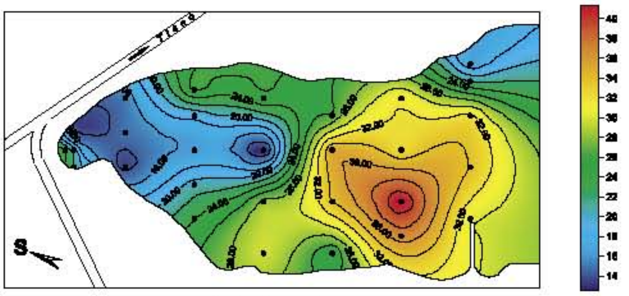
Zr (ppm)



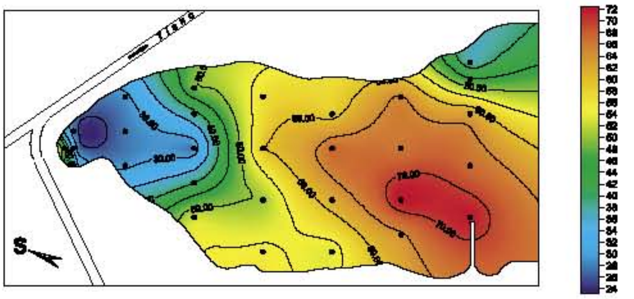
V (ppm)



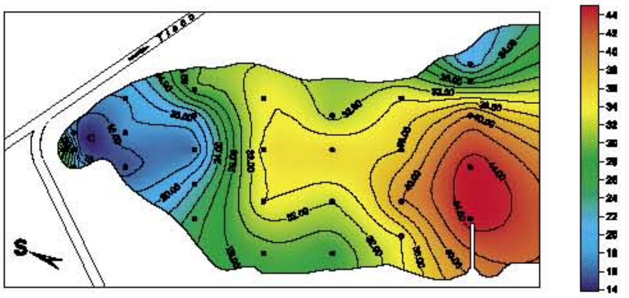
Cu (ppm)



Pb (ppm)



Zn (ppm)

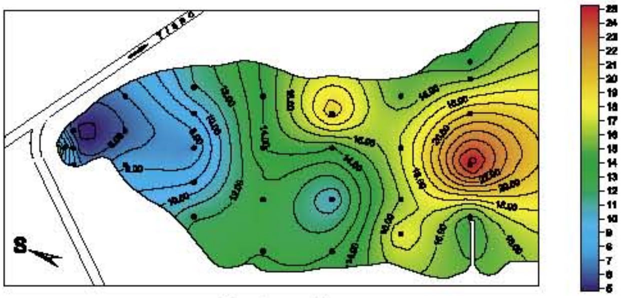


Ni (ppm)

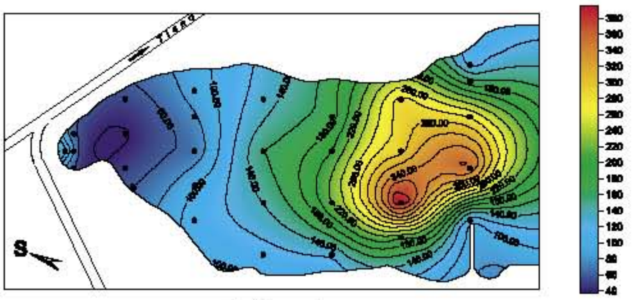
PLATE IV

Distribution of As, Br, Cs, Hf, Mo, Rb, Sb, Sc, Th and U in the surficial sediments of Makirina Cove

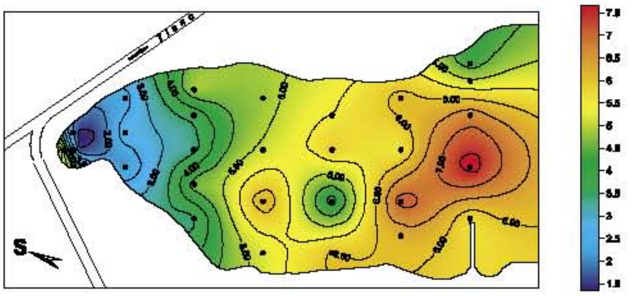
PLATE IV



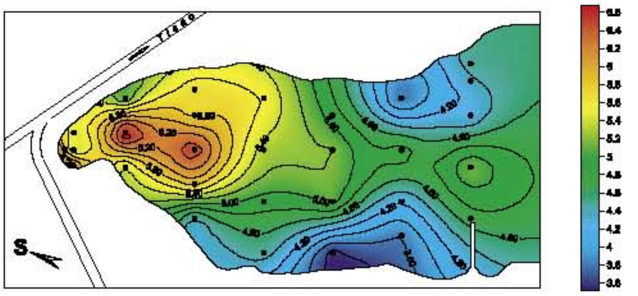
As (ppm)



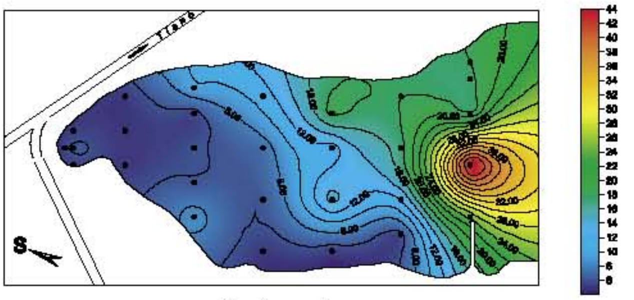
Br (ppm)



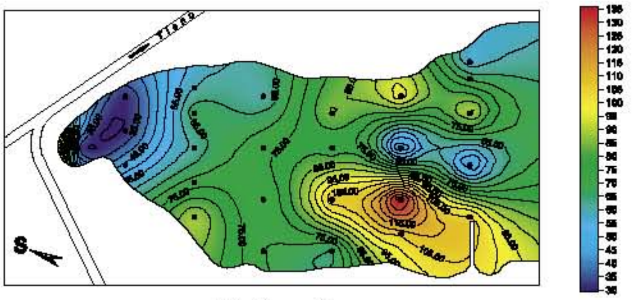
Cs (ppm)



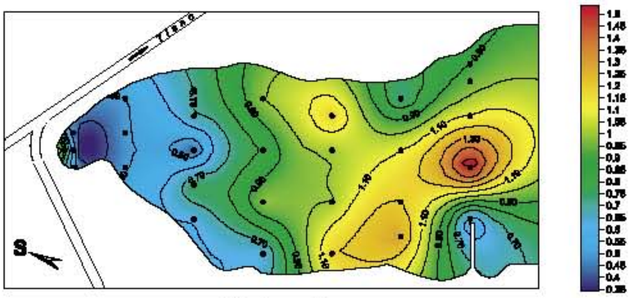
Hf (ppm)



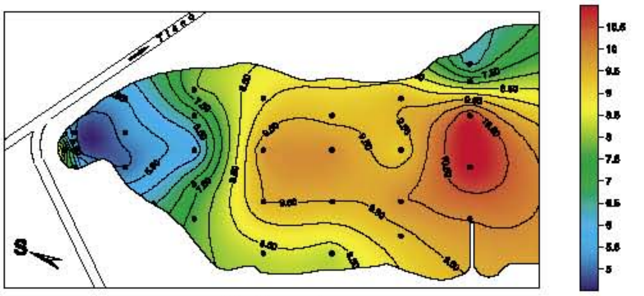
Mo (ppm)



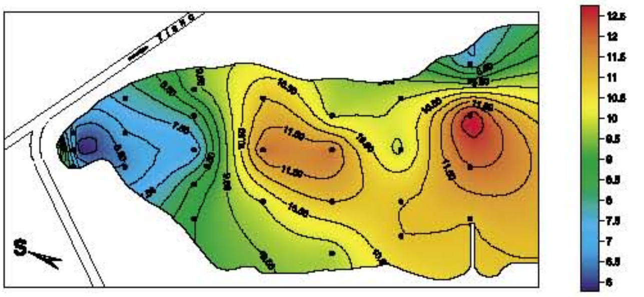
Rb (ppm)



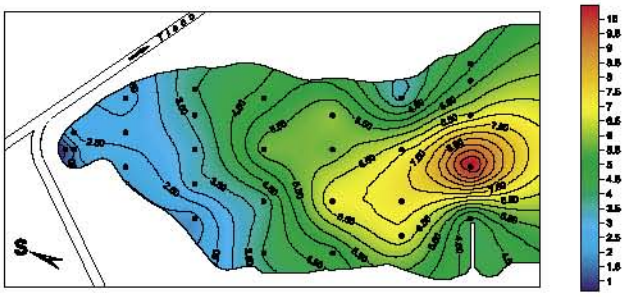
Sb (ppm)



Sc (ppm)



Th (ppm)

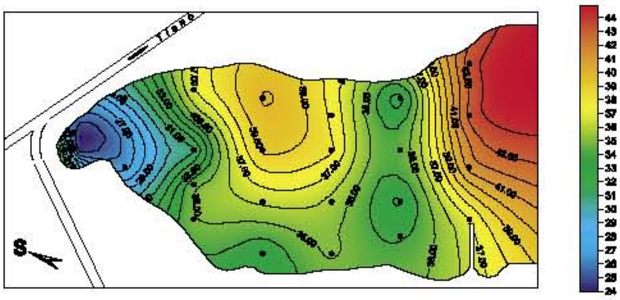


U (ppm)

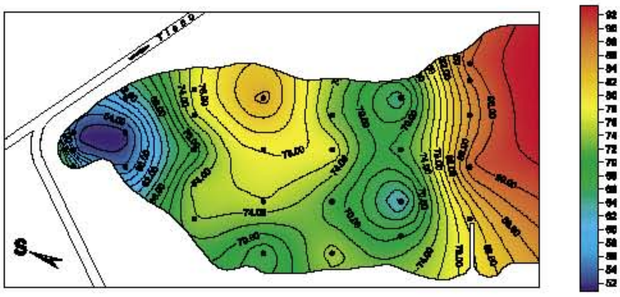
PLATE V

Distribution of La, Ce, Nd, Sm, Eu, Yb, Lu, S and C in the surficial sediments of Makirina Cove

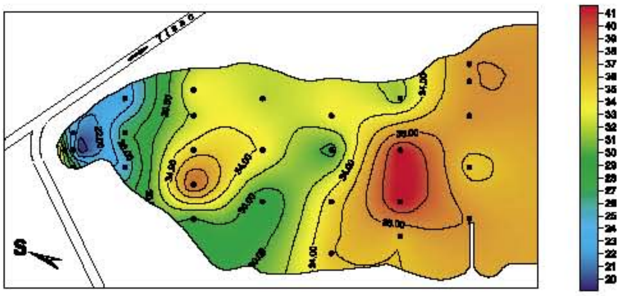
PLATE V



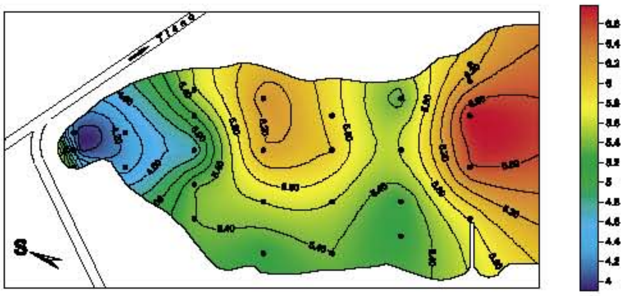
La (ppm)



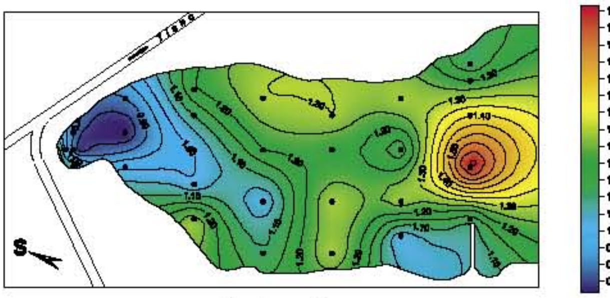
Ce (ppm)



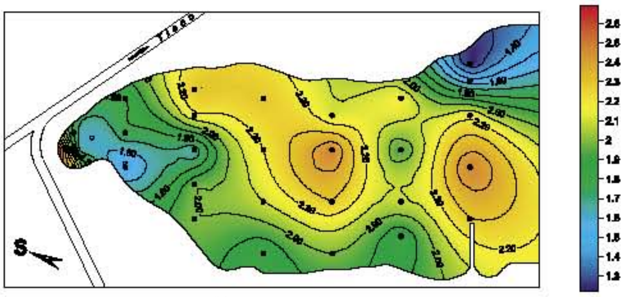
Nd (ppm)



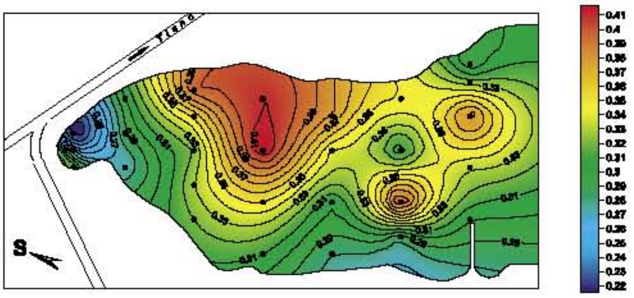
Sm (ppm)



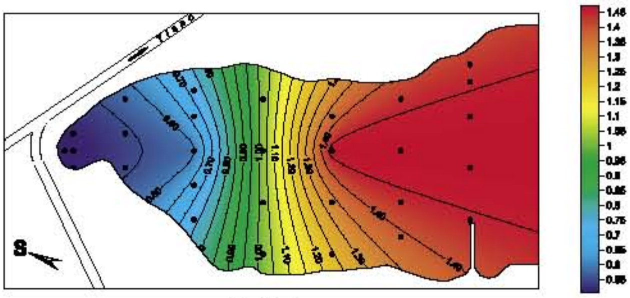
Eu (ppm)



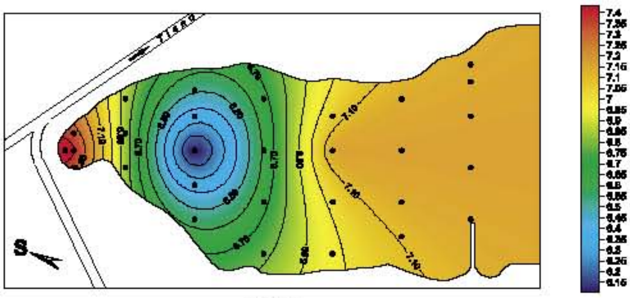
Yb (ppm)



Lu (ppm)



S (%)



C (%)

PLATE VI

The most characteristic plants in the area of Makirina and Pirovac Bay

1	*Arundo donax*
2	*Schoenus nigricans*
3	*Juncus maritimus*
4	*Arthrocnemum glaucum*
5	*Limonium serotinum*
6	*Juncus acutus*
7	*Helicrysum italicum*
8	*Codium bursa*

PLATE VI

1

2

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4

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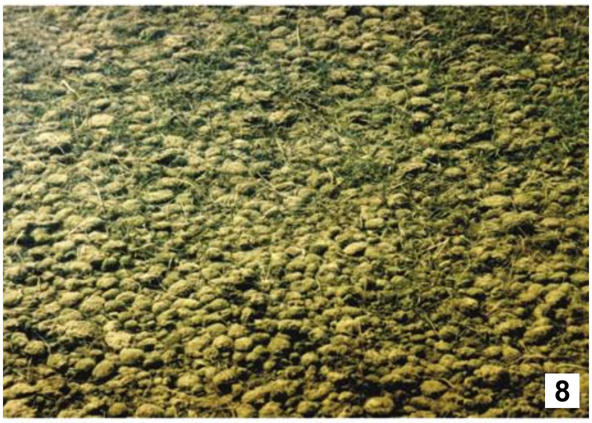

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PLATE VII

Some of the most characteristic molluscs of Makirina Cove

1 *Laevicardium oblongum*

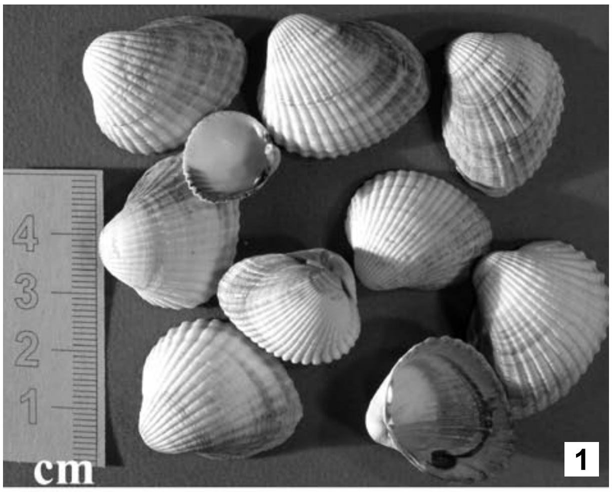
2 *Nuculana fragilis*

3, 4 *Gourmya vulgata*

5 *Monodonta turbinata*

6 Coralline algal crusts around different mollusc shells.

PLATE VII



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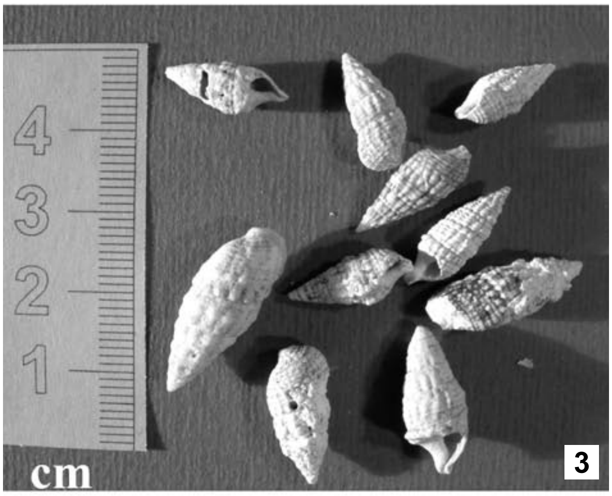

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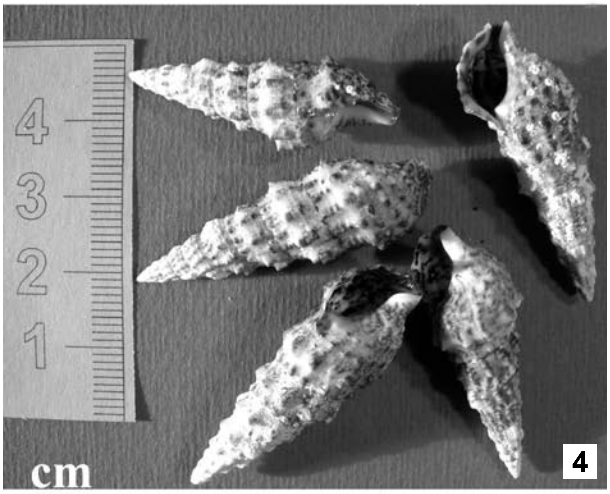

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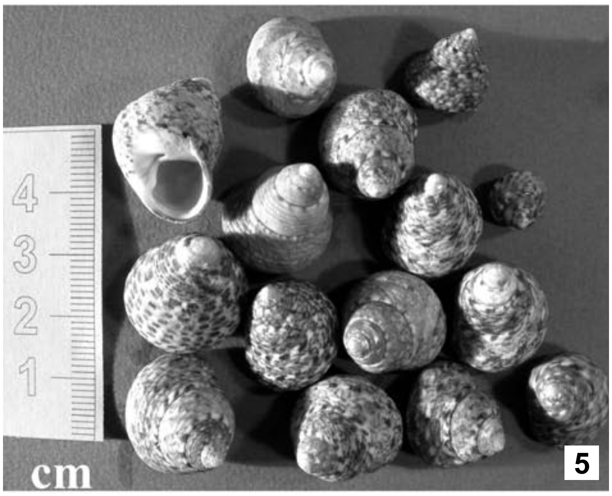

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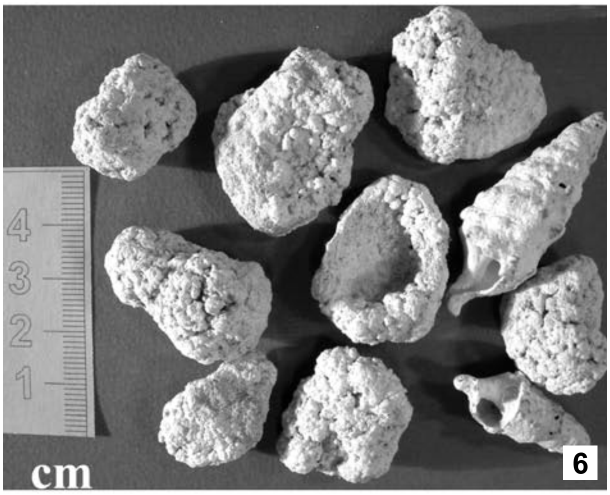

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PLATE VIII

1 Cuticular tissue with framboidal pyrite inclusions (FPI).

2 Pollen (bisaccate, Conifer) with FPIs.

3 Organic walled dinoflagellate cyst (*Spiniferites* type) with FPIs.

4 Foraminiferal test lining with FPIs.

5 Tintinnid chitinous lorica with FPIs.

6 Crustacean chitinous skeleton with FPIs.

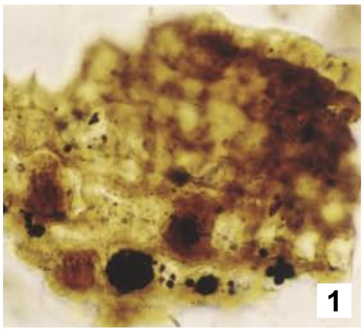
7 Scolecodont and granular to spongy amorphous organic matter (AOM) with FPIs.

8 Disseminated, granular to spongy AOM with FPIs, fragments of faecal pellets, fibrous to membranous strucureless organic matter, algal tissue and small globules of waxes/resins; transmitted white light.

9 *Idem*; incident blue light (note fluorescence).

1–9 Sample M–I/4; 1, 4–9 – 400X; 2, 3 – 800X.

PLATE VIII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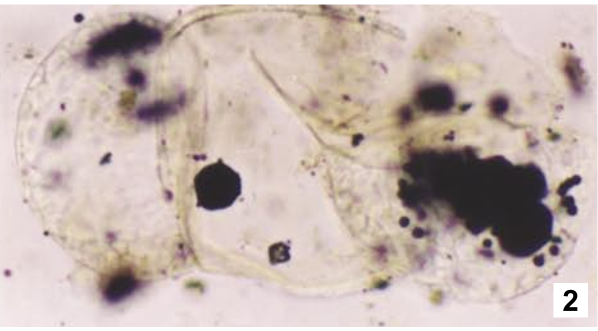
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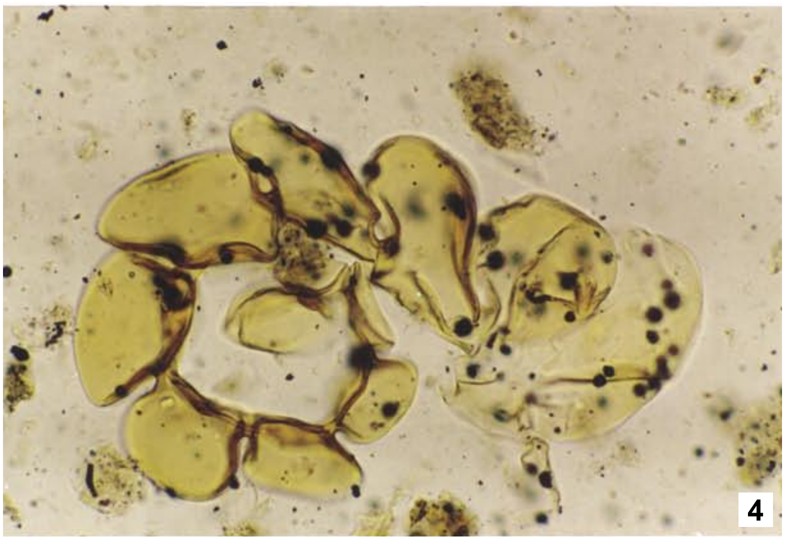
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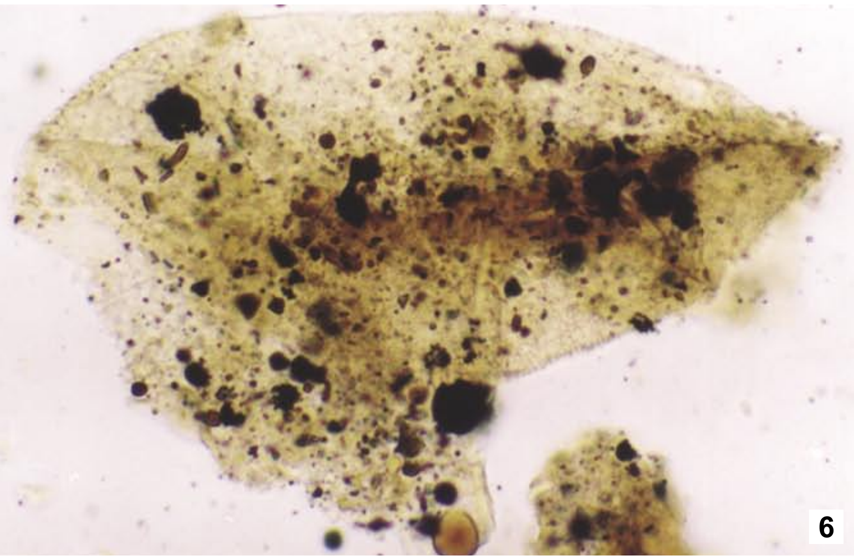
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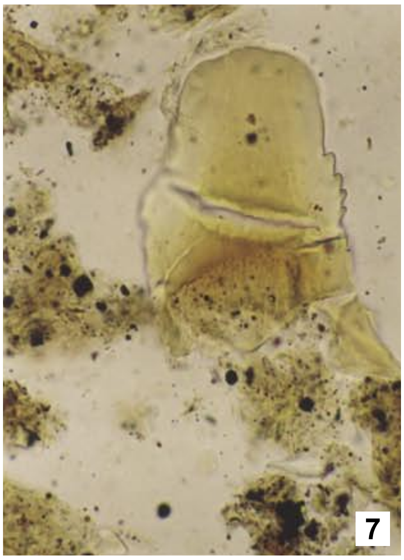
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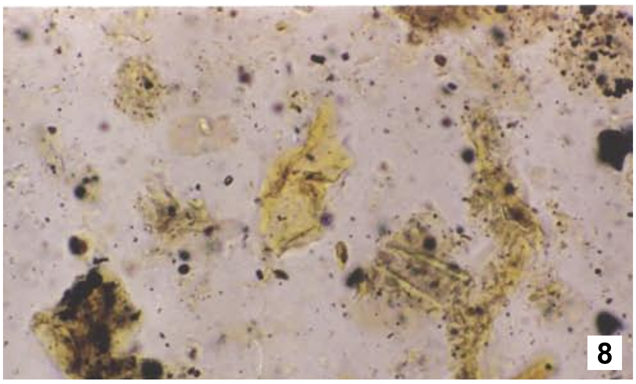
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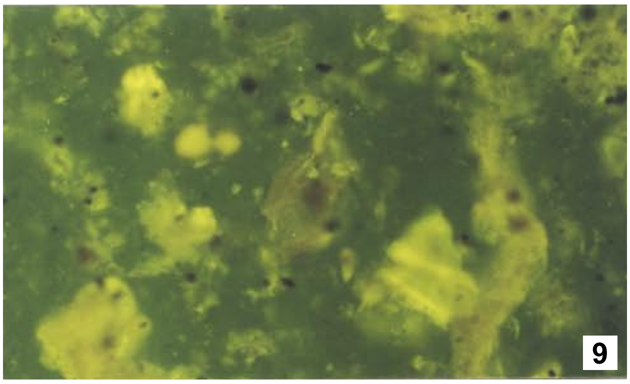
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PLATE IX

1 Disseminated, granular, aggregated granular to spongy AOM with FPIs, fragments of faecal pellets, membranous, fibrous to filamentous structureless organic matter, ligno-cellulosic tissue, algal tissue and small globules of waxes/resins; transmitted white light.

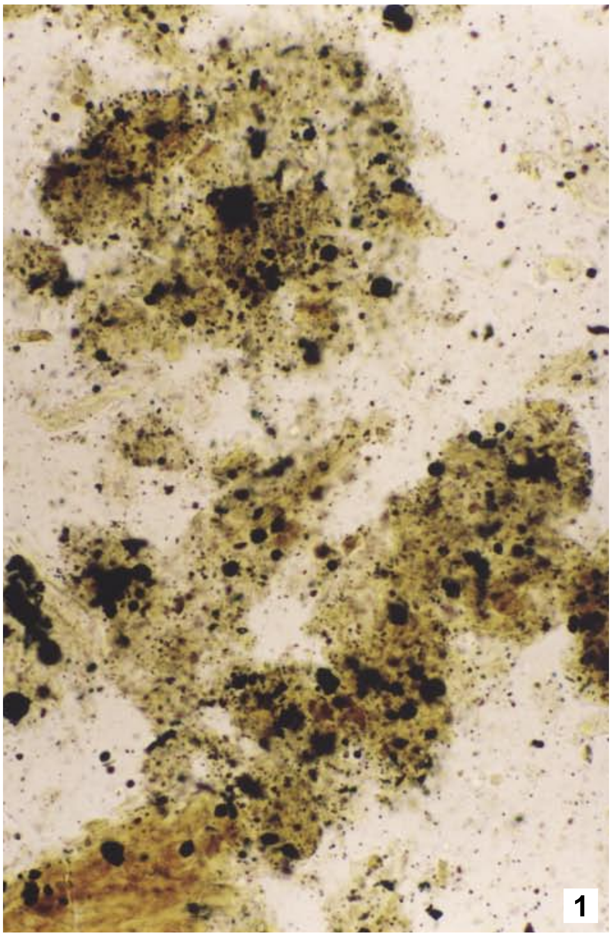
2 *Idem*; incident blue light (note fluorescence).

3 Granular to spongy AOM with FPIs and ligno-cellulosic tissue; transmitted white light.

4 *Idem*; incident blue light (note fluorescence).

1, 2: Sample M–I/4; 3, 4: Sample M–I/10; 1–4 – 400X.

PLATE IX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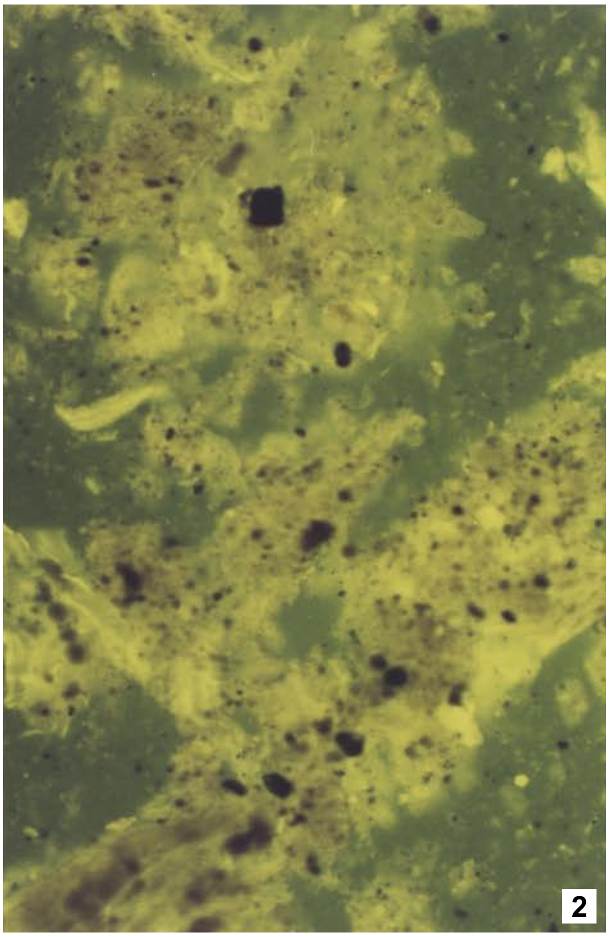
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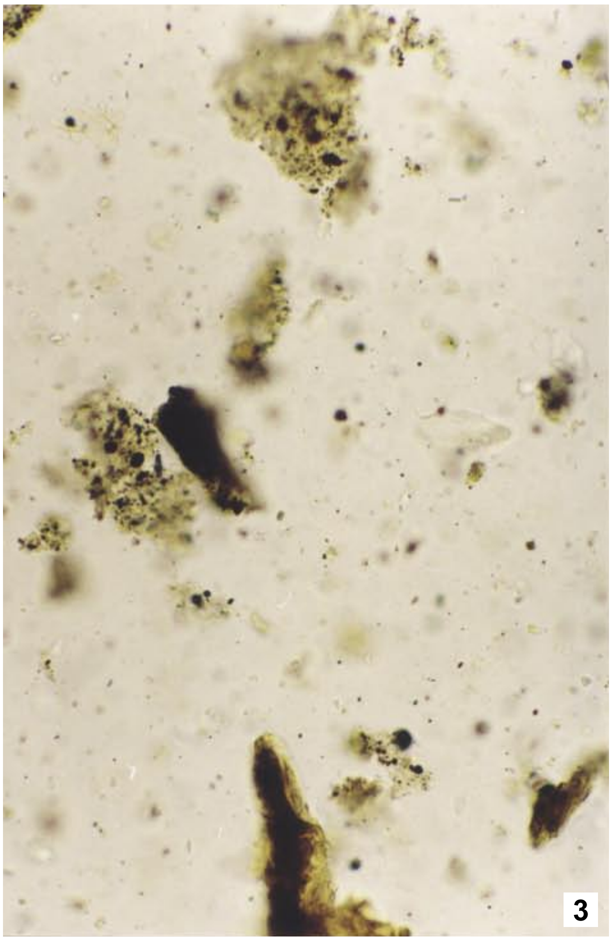
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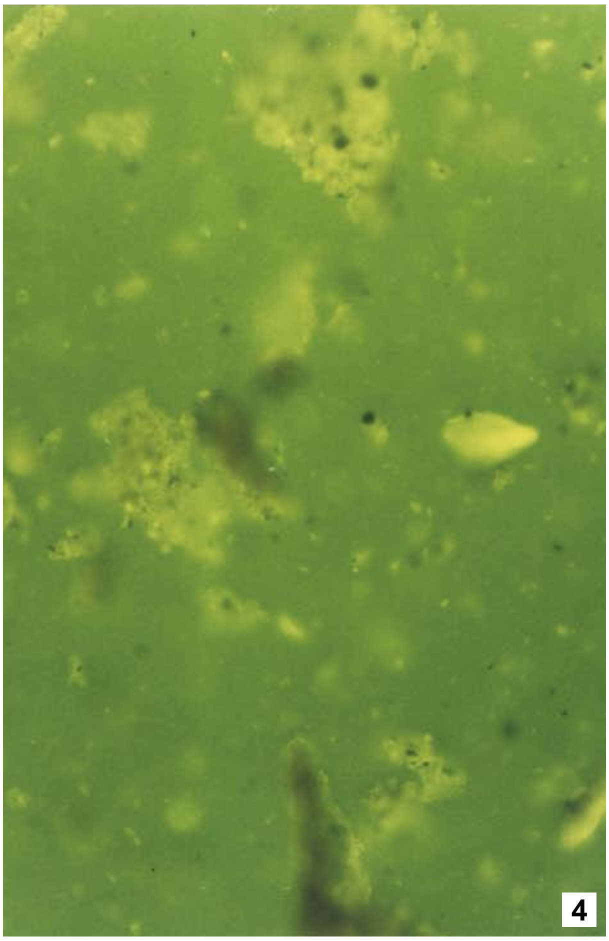
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