

ANOXIC VERSUS OXIC SEDIMENTATION IN THE BANNOCK BASIN AREA, 35,000 YRS B.P. TO PRESENT

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Key-words: Eastern Mediterranean, Anoxic sediments, Oxidic sediments.

Riassunto. Due carote provenienti dall'Area Bannock (Mediterraneo Orientale) sono state studiate e i dati vengono presentati in questo lavoro: una è stata recuperata in una zona di alto e contiene sedimenti pelagici normali mentre l'altra è stata prelevata in una zona depressa ed è caratterizzata da sedimenti scuri depositatisi in un ambiente anossico recente. L'intervallo studiato in dettaglio è compreso tra il tefra Y-5 (età stimata 35.000 anni) e l'interfaccia acqua-sedimento. Le differenze composizionali riscontrate nei sedimenti pelagici normali e in quelli anossici sono dovute a cambiamenti nelle condizioni diagenetiche. Il presente studio geochimico ha messo in evidenza:

- alto carbonio inorganico (TIC), basso carbonio organico, e dissoluzione della silice biogenica nei sedimenti pelagici normali;
- basso carbonio inorganico (TIC), alto carbonio organico, e conservazione della silice biogenica in relazione alle condizioni anossiche e ipersaline esistenti al fondo del bacino e all'alto contenuto di materia organica nei sedimenti anossici.

Il tenore in carbonio organico nei sedimenti anossici del Bacino Bannock è più basso di quello riscontrato nei sapropel, sedimenti che si sono depositi durante brevi periodi di stagnazione in tutto il Mediterraneo Orientale. L'aumento drastico in carbonio organico all'interno dei sedimenti anossici del Bacino Bannock è dovuto alla presenza del sapropel S1; il segnale regionale dell'S1 si è quindi sovrapposto a quello locale legato all'anossia dell'Area Bannock. Inoltre i sedimenti anossici sono più ricchi d'acqua e meno compattati di quelli normali pelagici e di conseguenza la velocità di sedimentazione sembra essere più elevata.

Abstract. Two cores, one raised from a plateau and containing normal pelagic sediments, and one raised from a low, and characterized by dark sediments deposited in an anoxic recent environment in the Bannock Basin area (eastern Mediterranean) were investigated in detail for the interval encompassing Tephra Y-5 (estimated age 35,000 yrs B.P.) and the sediment-water interface (time zero). Compositional differences in the anoxic and oxic sediments seem to be related to changes in the diagenetic conditions and show:

- high inorganic carbon, low organic carbon and selective dissolution of biogenic opal in the normal pelagic sediments.
- low inorganic carbon, high organic carbon and preservation of biogenic opal related to the occurrence of anoxic and hypersaline bottom conditions and to the high content in organic matter in the anoxic sediments.

The organic C content of the anoxic sediments is lower than that of sapropels deposited during short duration episodes of basin-wide anoxia, but a marked increase is recorded at the level of Sapropel S-1, thus showing that the regional signal is superimposed to the

local one. Anoxic sediments are less compacted and more watery than coeval oxic ones, and consequently the sediment accumulation rate is higher.

Introduction.

The Bannock Basin is a depression situated on the southwestern part of the Mediterranean Ridge, North of the Sirte abyssal plain (Camerlenghi & Cita, 1987; Camerlenghi & McCoy, 1990; Fig. 1). It has an area of 22 km² and its shape is elongated in SSW-NNE direction, with a steep eastern wall representing a strike-slip fault. It reaches a maximum depth of 3,520 m with a vertical relief of 800 m. Below 3,200 m the basin is anoxic and brine-filled (Cita et al., 1991).

The geological evolution of the Bannock Basin is influenced by the occurrence of Messinian evaporites at shallow depths below sea floor and conditioned by salt diapirism. The compressive tectonic structures typical of this area of the Mediterranean Ridge are overprinted by local extensional structures, which permit water circulation within the Plio-Quaternary sediments, submarine dissolution of the underlying Messinian salts resulting in large collapse structures.

The Bannock Basin is an enclosed depression with a central bulge and several surrounding smaller basins. The central bulge has been interpreted as a diapiric structure, surrounded by depressions representing collapse features (Camerlenghi & McCoy, 1990). Recent high-resolution seismic investigations (IMERSE group, 1995) along the wedge of the Mediterranean Ridge constrain the processes of dewatering in an accretionary prism dominated by an impermeable cap of Messinian evaporites. According to these data, the decollement occurs at the base of Messinian and pre-Messinian sediments are thus subducted. The Bannock Basin area has thus been interpreted as a subducting seamount the peak of which appears to underlie the central structure.

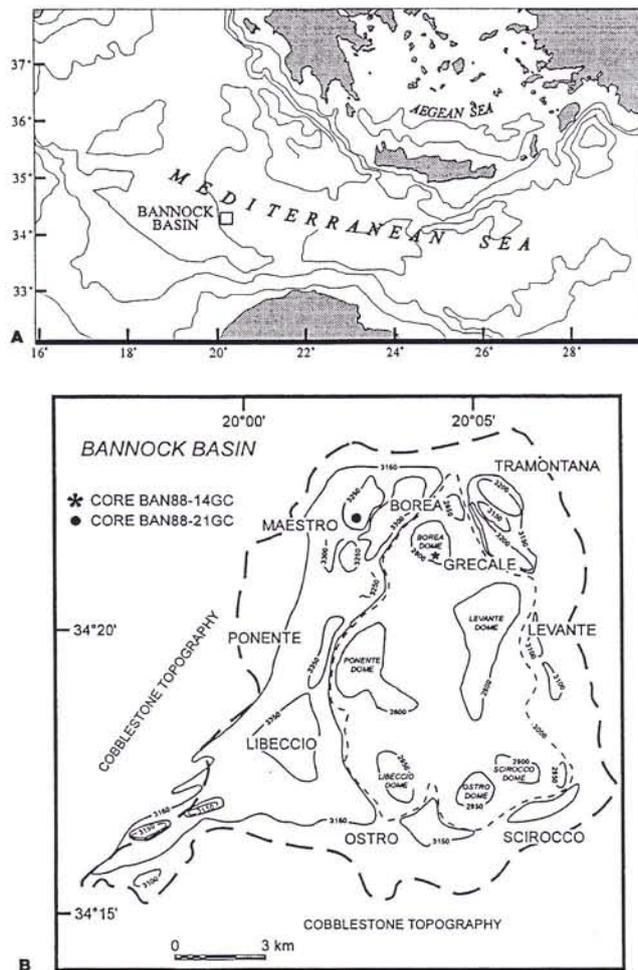


Fig. 1 - A) Location of the Bannock Basin within the Mediterranean Ridge. B) Simplified bathymetric map of the Bannock Area, showing core locations.

In the Bannock Area the sediment accumulation rate of the Plio-Quaternary sequence is low, of the order of 2 cm/1,000 yrs (Parisi et al., 1987; Cita et al., 1988; Nolli et al., 1991). The entire thickness of the Plio-Quaternary is about 100-150 m, which permits outcropping of the Messinian salts on the eastern flank of the basin. Leaching of the highly soluble Messinian evaporites (composed of gypsum, halite and K-salts) causes brine formation at the bottom of the Bannock Basin and the development of permanent anoxic conditions, in absence of strong bottom currents. Below a depth of 3,200 m brines have been found with an average salinity of 334‰. (Cita et al., 1985; Corselli & Aghib, 1987; Boldrin & Rabitti, 1990; De Lange et al., 1990).

In the Bannock Area a number of cores have been taken which provide a sedimentary record extending back to the Lower Pliocene. Two cores were raised from the northern part of the basin in 1988: core BAN88-14GC from Borea Dome (water depth 2,790 m) shows a normal pelagic sequence whereas core BAN88-21GC

from the sill separating Borea from Maestro sub-basin (water depth 3,250 m) contains anoxic sediments, after the deposition of the volcanic marker bed Y-5 (of Keller et al., 1978; see also Vezzoli, 1991).

Description of the cores.

Both cores were recovered from the northern part of the basin and are separated by less than two nautical miles.

Core BAN 88-21GC was collected beneath the brine level, at a depth of 3,250 m.

Core BAN88-14GC was collected from the southwestern flank of a dome, at a depth of 2,790 m.

Core BAN88-14GC shows a normal pelagic sequence, with Nanno-ooze and Nanno-marls as major lithologies and tephra and sapropels as minor lithologies.

Core BAN88-21GC contains normal pelagic sediments in its lower part, anoxic sediments in its upper part. The occurrence of Tephra Y-5 at 180 cm from the top of the core, at the base of the anoxic sediments allows to date with a good approximation the onset of anoxia at 35,000 yrs B.P. (Fig. 2). Tephra Y-5 occurs also in core BAN88-14GC, at a depth of 70 cm from the top of the core, so it is possible to closely compare anoxic sedimentation versus normal pelagic sedimentation after deposition of Tephra Y-5 (Fig. 2 and 3).

Core BAN88-14GC contains also Tephra Y-1 and Sapropel S-1, which seemed not to be present within the anoxic sediments of core BAN88-21GC. Indeed, the dark nuances (according to the Munsell colour chart, colours ranging from 2.5Y N5 and 5Y 5/1 gray to 7.5YR N4 dark gray to 5Y 3/2 dark olive gray to 2.5Y N3 very dark gray) of the anoxic sediments obscure eventual minor lithologies (Fig. 3 and 4).

Detailed compositional analyses have been carried out also to point out whether or not these marker beds occur in core BAN88-21GC.

Sediment accumulation rate in core BAN88-14GC is normal for the eastern Mediterranean ranging from 1.16 and 2.66 cm/1,000 yrs (Parisi et al., 1987; Nolli et al., 1991). In the anoxic core sediment accumulation rate is 4.6 cm/1,000 yrs. The latter sediment core is watery and partly disturbed in its upper part (top 45 cm). These data are consistent with data by Nolli et al. (1991) concerning sedimentation rate in the Bannock Basin area. The high sedimentation rate of the anoxic facies seems to be due to the high water content.

The first micropaleontological studies carried out during the cruise BAN-88 indicated that core BAN88-14GC contains only calcareous microfauna, while in core BAN88-21GC siliceous microfauna is also present.

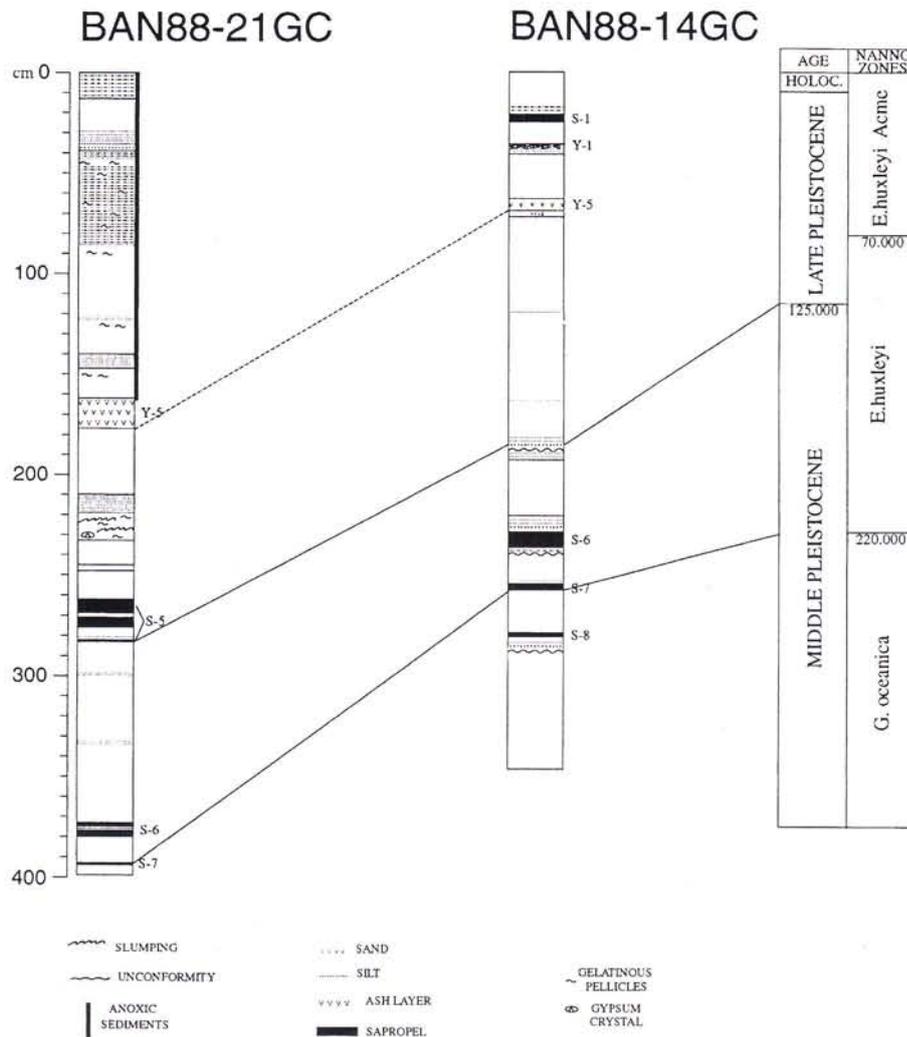


Fig. 2 - Lithological logs of cores BAN88-14GC and BAN88-21GC.

The main objectives of this paper are two:

- firstly to compare normal pelagic versus anoxic sedimentation, considering the variability of the major components;
- secondly to identify the diagenetic conditions affecting the preservation of biogenic silica (siliceous fauna) within the anoxic sediments.

Methods.

Compositional analyses were performed at Woods Hole Oceanographic Institution during a summer student fellowship programme. Samples were taken in both cores with a sampling point every 2,000 yrs.

In core BAN88-14GC (oxic), sediment accumulation rate ranges from 2.66 cm/1,000 yrs (from the top of the core to Tephra Y-1) to 1.16 cm/1,000 yrs (from Tephra Y-1 to Tephra Y-5); consequently sample density is every 5 cm (core top to Y-1) and every 2.3 cm (Y-1 to Y-5). Sapropel S-1 and Tephra Y-1 were not sampled.

In core BAN88-21GC (anoxic), there are no marker beds evident, so the estimated sediment accumula-

tion rate, from the top of the core to Tephra Y-5, is 4.42 cm/1,000 yrs. Samples were taken every 9 cm.

A schematic flow-diagram of the laboratory processing and analyses is shown in Fig. 5. Compositional analyses were performed on unwashed (dried) samples - 19 from core BAN88-14GC (normal pelagic) and 16 from core BAN88-21GC (anoxic) - determining the content in the following major components:

- Total Inorganic Carbon
- Carbonate
- Organic carbon, Hydrogen, Nitrogen
- Biogenic Silica
- Lithogenics
- Combustible
- Non-combustible

Inorganic Carbon levels were determined using a System 140 Inorganic Carbon Analyzer. For the determination of the Total Inorganic Carbon 3 mg of the core samples were acidified converting all forms of inorganic carbon to CO₂. The CO₂ is then purged into the coulometer for measurements.

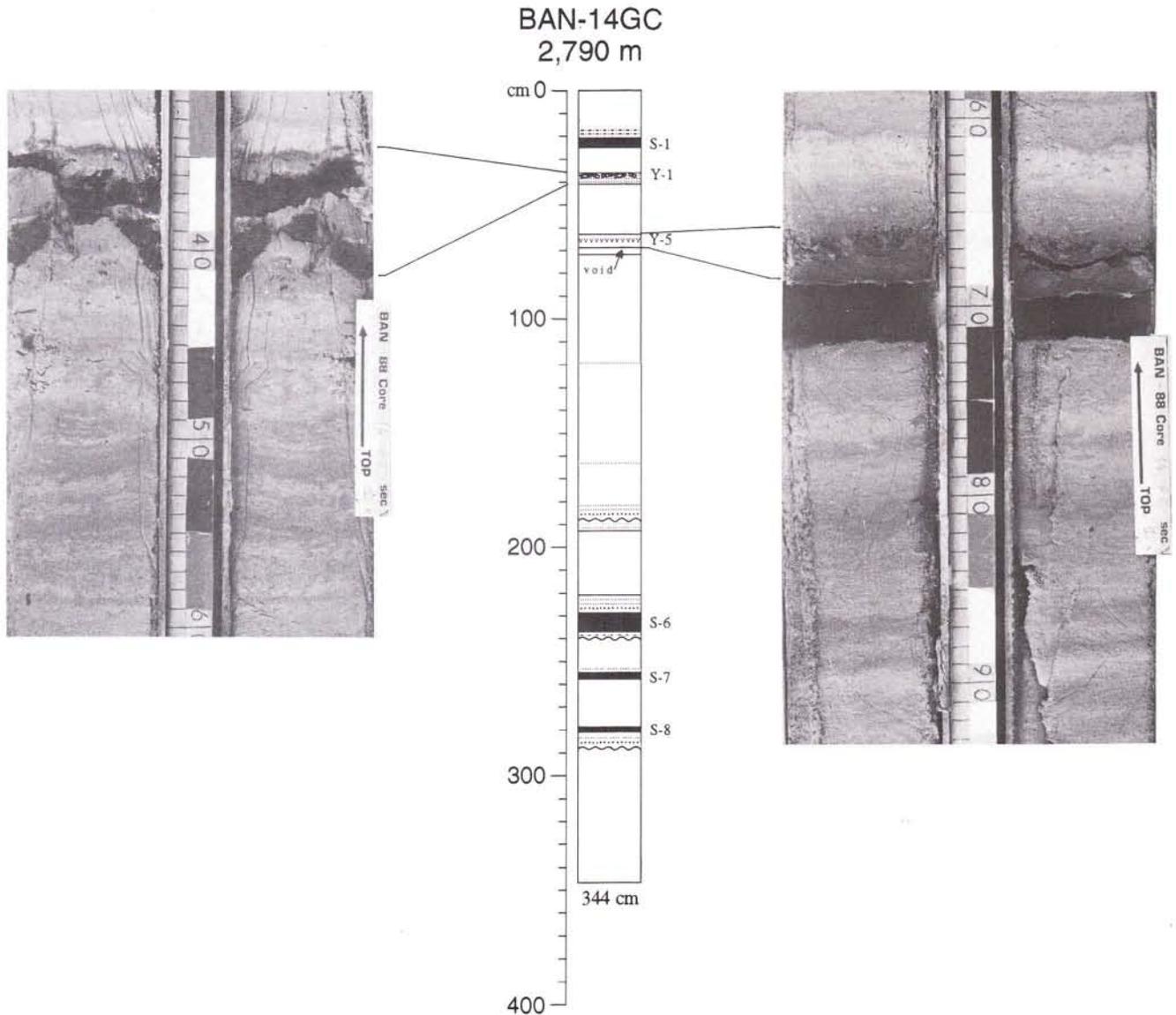


Fig. 3 - Lithological log of core BAN88-14GC and close-ups from section 1 (left) showing Tephra Y-1 and (right) showing pelagic sedimentation and Tephra Y-5.

For the determination of the carbonate content the dried sample was immersed in 10% acetic acid and ultrasonically dispersed. After 24 hours at room temperature the sample was filtered, rinsed with distilled water, dried and re-weighed. The carbonate content was computed from the weight loss considering the dry weight difference before and after decalcification by acetic acid.

All core samples were analyzed for CHN (Carbon, Hydrogen, Nitrogen) contents: samples were first acidified to remove carbonate and then washed, dried and ground into a fine powder. The organic carbon contents were then determined by analyzing about 10 mg of the decalcified sample using a Hewlett-Packard CHN analyzer.

The biogenic silica contents were obtained from about 10 mg of the decalcified sample material using a method modified after Eggiman et al. (1980) who found that sediments with a biogenic silica/clay ratio larger

than 1.0 can be analyzed by a single leach with 2M Na_2CO_3 solution without correction for silica that also had been leached from the clays. Determination of the reactive silicate depends on the production of a silicomolybdate complex forming between silica, leached by the Na_2CO_3 into solution, and ammonium-molybdate which was then added. A reducing solution containing methanol and oxalic acid was then added, which reduced the silicomolybdate complex to give a blue reduction compound. The absorbance of this compound was measured with a spectrophotometer to yield a ppm value of biogenic silica in the sample.

The lithogenic contents were determined indirectly. About 10 mg of decalcified sample were combusted at 500°C in a muffle furnace to remove the organic material. From the weight of the ash the non-combustible component was determined. The lithogenic component

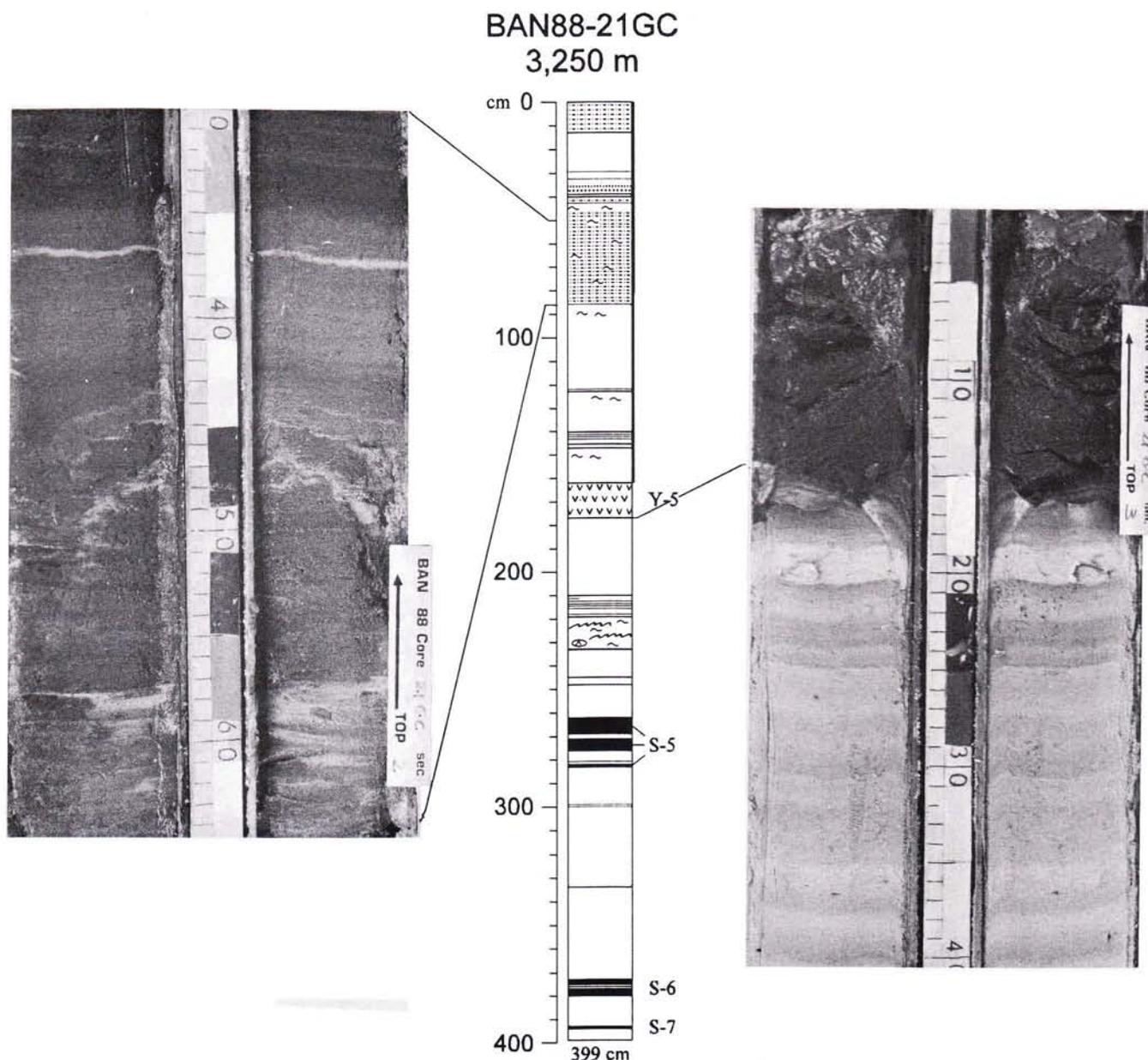


Fig. 4 - Lithological log of core BAN88-21GC and close-ups from section 2 (left) showing anoxic sediments and section 3 (right) showing Tephra Y-5 and pelagic sedimentation.

was then computed by subtracting the biogenic silica component from the non-combustible component, under the assumption that the non-combustible component was a sum of biogenic silica and terrigenous detritus (mostly clay, quartz, feldspar and volcanic shards).

Smear slides were made for each sample (35) in order to determine the amount of biogenic/non-biogenic particles, using fresh sample.

Composition of sediment samples from cores BAN88-14GC and BAN88-21GC.

Data concerning the compositional analysis of the core samples are shown in Tab. 1. According to the

smear slides data, the matrix of core BAN88-14GC (normal pelagic) is composed mostly by biogenic carbonate (mainly coccoliths and planktonic foraminifera), with an average content up to 90%. No siliceous fauna is present.

The matrix of core BAN88-21GC (anoxic) is also composed mostly by biogenic carbonate (with an average content up to 50%) but siliceous fauna (radiolarians and diatoms) is preserved (with an average content up to 30%).

No significant downcore changes are evident in both cores.

The composition of the sediment samples from core BAN88-14GC is drastically different from that

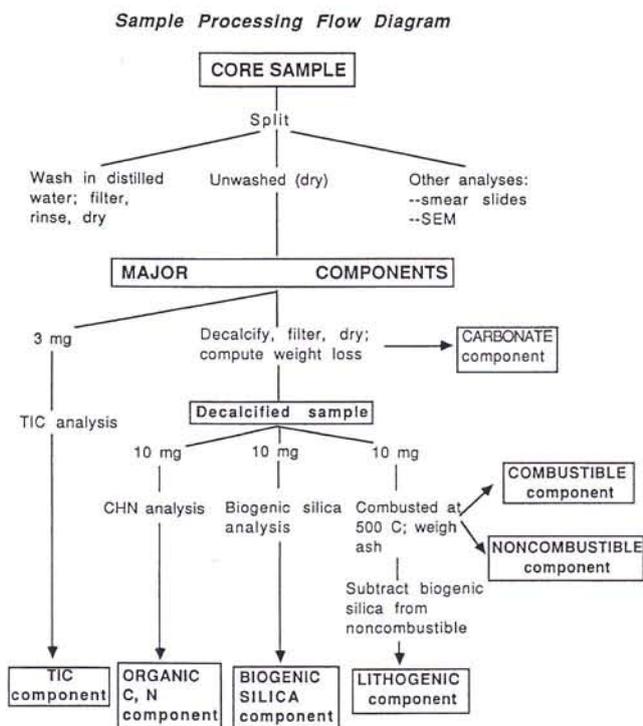


Fig. 5 - Schematic flow-diagram of the laboratory processing and analysis of the Bannock sediment samples.

Core	Depth cm	TIC	CaCo ₃	C	H	N	Opal	Litho
BAN88-14GC	5.00	6.086	50.696	0.359	0.293	0.037	0.333	2.804
	10.00	6.981	58.148	0.242	0.263	0.028	0.460	1.976
	15.00	2.931	24.414	0.318	0.358	0.031	0.447	4.135
	20.00	6.476	53.947	0.232	0.216	0.025	0.506	2.897
	25.00	5.043	42.012	0.236	0.321	0.151	0.629	3.063
	30.00	6.071	50.570	0.133	0.291	0.039	0.397	2.113
	35.00	2.597	21.629	0.139	0.456	0.013	0.014	2.195
	37.30	5.857	48.785	0.062	0.267	0.062	0.456	1.312
	39.60	6.130	51.063	0.271	0.242	0.034	0.583	7.309
	41.90	6.750	56.223	0.083	0.185	0.033	0.562	1.656
	44.20	6.258	52.128	0.387	0.235	0.040	0.552	1.270
	46.50	5.957	49.622	0.047	0.195	0.066	0.501	0.684
	48.80	4.911	40.906	0.157	0.370	0.030	0.596	1.440
	51.10	5.532	46.078	--	--	--	0.346	19.068
	53.40	3.737	31.130	0.150	0.286	0.042	0.549	7.138
	55.70	6.566	54.698	0.057	0.203	0.054	0.344	0.212
58.00	4.004	33.353	0.139	0.395	0.021	0.543	2.999	
60.30	2.937	24.463	0.040	0.398	0.115	0.177	2.751	
63.00	0.308	2.568	0.092	0.510	0.234	1.300	19.870	
BAN88-21GC	28.00	5.502	45.831	0.359	0.090	0.028	0.249	0.759
	37.00	5.174	43.100	0.186	0.049	0.036	0.216	0.367
	50.50	1.703	14.188	0.890	0.277	0.084	1.741	2.084
	59.50	2.800	23.321	--	--	--	4.660	2.007
	82.00	1.620	13.495	2.015	0.399	0.154	6.353	1.884
	90.00	1.331	11.087	2.156	0.366	0.185	7.203	2.456
	99.00	2.032	16.929	1.010	0.262	0.146	7.269	3.505
	108.00	2.378	19.807	0.614	0.232	0.040	2.602	2.053
	117.00	1.824	15.192	0.543	0.318	0.113	2.840	2.854
	126.00	0.928	7.727	0.458	0.206	0.037	3.188	1.004
	135.00	2.714	22.610	0.634	0.321	0.048	2.217	1.322
	144.00	1.940	16.164	0.734	0.238	0.083	2.866	--
	153.00	1.968	16.397	0.970	0.389	0.056	4.088	2.895
	162.00	2.336	19.462	0.794	0.380	0.147	3.100	2.101
	166.00	3.079	25.652	0.834	0.538	0.070	2.625	0.300
	175.00	0.043	0.354	0.048	0.171	0.048	2.631	5.318

Tab. 1 - Compositional analysis of core samples from cores BAN88-14GC and BAN88-21GC.

from core BAN88-21GC (Fig. 6 and 7). The normal pelagic sediments contain from 21.63% to 58.15% of carbonate, the anoxic sediments show values from 11.9% to 45.83%. The average content in carbonate for the nor-

mal pelagic core is up to 45%, for the anoxic core is 20%. The sharp decrease at the bottom of both cores is related to the occurrence of Tephra Y-5 (Fig. 6).

The concentration of organic carbon in core BAN88-14GC is very low (0.3%). In core BAN88-21GC anoxic sediments have an average content up to 1.2%, but consistently lower than sapropels (>2%) (Fig. 8a): these sediments correspond to "sapropelitic muds" (Kidd et al., 1978).

The occurrence of Sapropel S-1 in core BAN88-21GC (Fig. 7) is geochemically marked, at a depth of 80 cm, by an increase in organic carbon up to 2% and a decrease in carbonate down to 20%. These values are in agreement with the composition of sapropels according to Kidd et al. (1978).

The ratio organic carbon/inorganic carbon for the anoxic sediments of core BAN88-21GC has always values ranging between that for normal pelagic sediments (BAN88-14GC) and sapropels (Fig. 8a).

The average N content for the normal pelagic sediments is 0.05%, for the anoxic sediments is 0.1% (Fig. 6 and 7); considering the ratio organic carbon/nitrogen the anoxic sediments have always values higher than normal pelagic sediments, which are depleted in N, and lower than sapropels (Fig. 8b).

Biogenic opal is 0.5% in the sediment samples from the normal pelagic core (BAN88-14GC) in contrast to 20% in the anoxic sediments from core BAN88-21GC (Fig. 6 and 7); a sharp increase up to 30% at cm 80 corresponds to sapropel time (org C > 2, see Fig. 7).

Discussion.

Anoxic basins are well-known in marine environments as in the Black Sea, Orca Basin, in the Red Sea, and also in the eastern Mediterranean. A comparison is difficult, due to the different geological setting and sedimentary evolution affecting the Eastern Mediterranean anoxic basins and in particular the Bannock Basin area.

The eastern Mediterranean has shown - in general - low primary production. The biogenic fluxes change over the annual cycle has been documented in the anoxic basins of the eastern Mediterranean in a recent study (Ziveri et al., 1995). According to the study, the biogenic fluxes contain mostly flora consisting of coccolithophores, calcareous dinoflagellates, diatoms, silicoflagellates, and fauna comprising foraminifera and radiolaria.

The peculiar geological setting of the Bannock Basin controls the evolution of the recent persistent anoxic conditions occurring at the basin floor. Sedimentation in the Bannock Basin is controlled by the deep-seated high density brines derived from the submarine dissolution of Messinian evaporites. Anoxic sediments consist

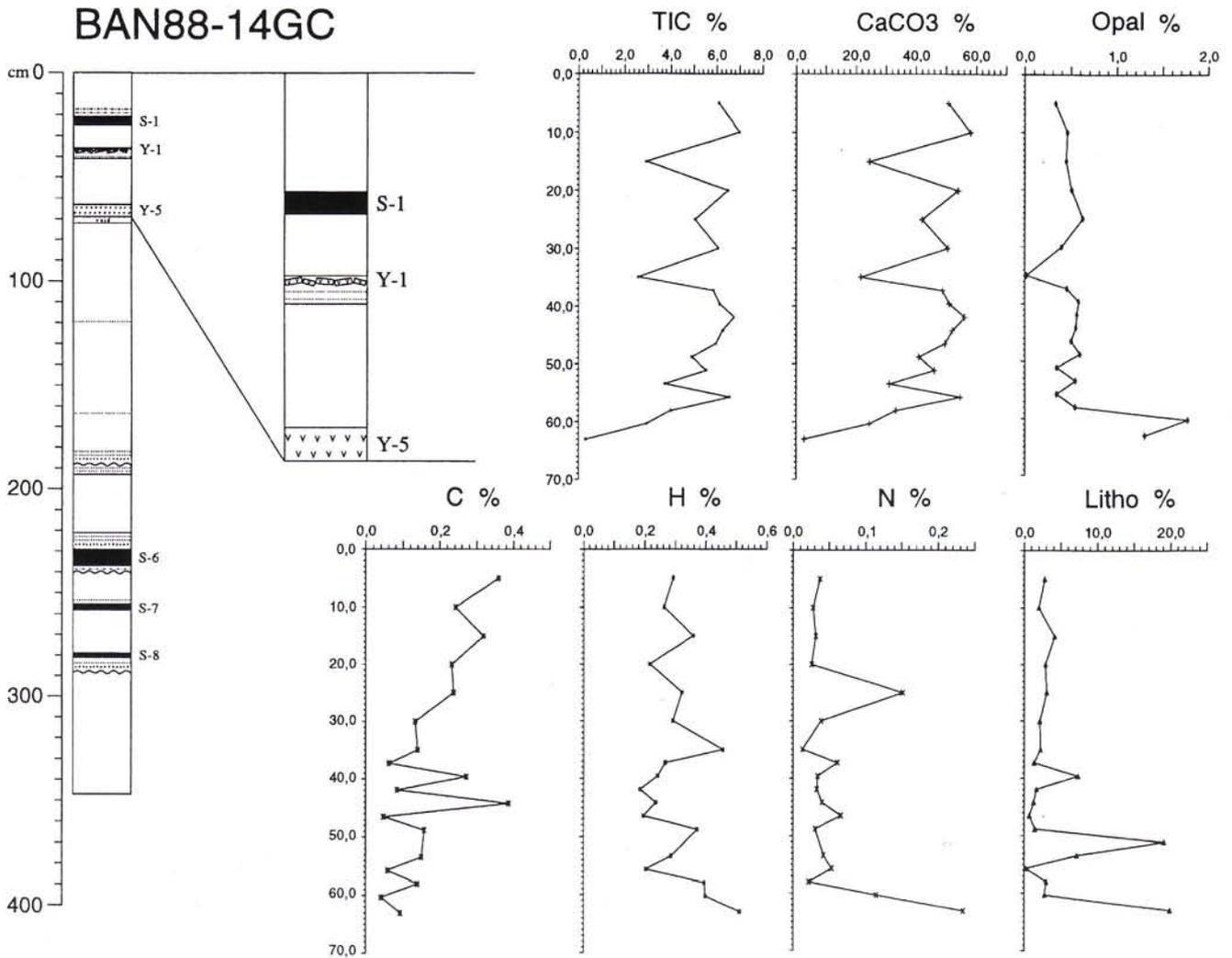


Fig. 6 - Lithological log of core BAN88-14GC and concentration vs. depth profiles (TIC=Total Inorganic Carbon, Carbonate, Biogenic Opal, Organic Carbon, Hydrogen, Nitrogen, and Lithogenics).

of non-bioturbated muds, dark in colour, rich in organic gelatinous pellicles and containing large gypsum crystals (Erba, 1991). The sediment accumulation rate in the deeper part of the Bannock Basin area ranges from 4 to 10 cm/1,000 yrs (Montagnana & Sala, 1993) higher than that related to the normal pelagic sedimentation in the eastern Mediterranean (1-2 cm/1,000 yrs) (Parisi et al., 1987). According to Ziveri et al. (1995) the total biogenic fluxes are always higher in the trap positioned in the anoxic brines probably due to reworked biogenic material sliding from the slopes of the basin. This suggests that the mechanism of the particle transport throughout the stratified water column to the basin floor is controlled by the interface between normal seawater/brines (Ziveri et al., 1995). The high density of the hypersaline brines slows down the suspended particles but inhibits compaction of the sedimented materials on the basin floor. The bottom sediments, due to the high porewater content, are therefore only slightly compacted, soft and

watery. The local biogeochemical environments existing at the bottom of the basin inhibits consumption of organic matter; the related high content in organic C of the anoxic sediments ranges from 0.5 to 1.5% and is always higher than that of the normal pelagic but lower than sapropels (>2%). In the anoxic sediments siliceous fauna is always abundant and preserved: a positive correlation between biogenic opal and organic carbon content (Fig. 9) may suggest that the anoxic and hypersaline conditions inhibit dissolution of opal within the anoxic sediments. Preservation of biogenic opal and low consumption of organic matter may also contribute to a higher sediment accumulation rate, as observed in the anoxic basins of the Bannock Area.

Geochemical data of core BAN88-21GC shows at cm 80 a sharp decrease in carbonate content and a sharp increase in organic C. This suggests that the regional signal related to Sapropel S-1, a climatically-induced basin-wide anoxia, recorded throughout the eastern Medi-

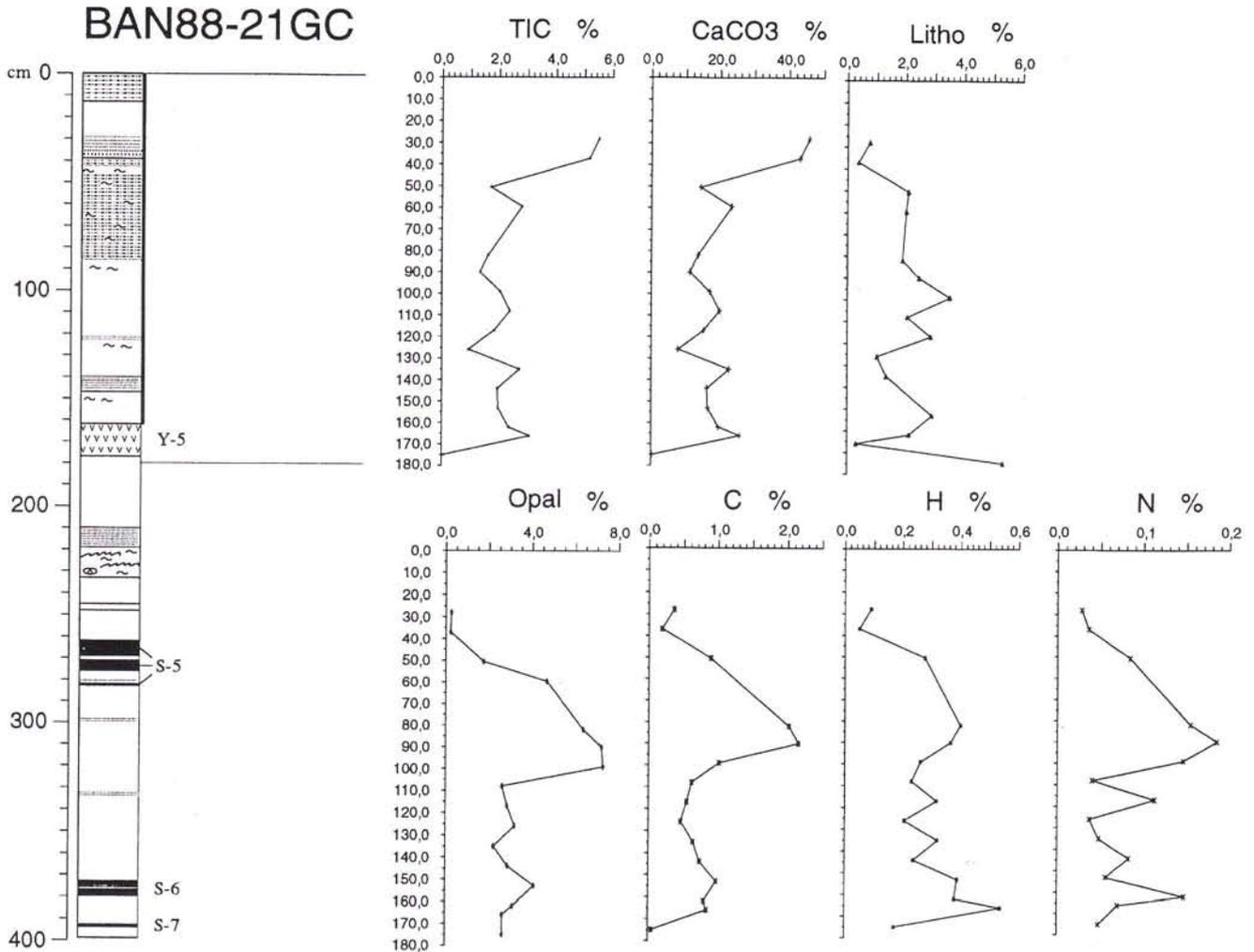


Fig. 7 - Lithological log of core BAN88-14GC and concentration vs. depth profiles (TIC=Total Inorganic Carbon, Carbonate, Biogenic Opal, Organic Carbon, Hydrogen, Nitrogen, and Lithogenics).

terranean is superimposed to the local one -related to the episodic and persistent geologically-induced anoxia (Cita et al., 1991). The occurrence of Sapropel S-1 within the anoxic sediments of the Bannock Basin has been previously discussed by Olausson (1991) considering the carbon and oxygen isotope composition of *Globigerina bulloides* and *Globigerinoides ruber* from two cores of the Bannock Basin: one containing a normal pelagic sequence recovered from a topographic high (BAN84-08GC), and one consisting of anoxic sediments deposited beneath the brines (BAN84-02PC). Sapropel S-1 is geochemically marked within the anoxic sediments of core BAN84-02PC -at cm 130- by a slight decrease in carbon and oxygen isotope composition as recorded in normal pelagic sequences from nearby areas (Parisi, 1987). On the same cores studied by Olausson, Tomadin and Landuzzi (1991) carried out a detailed clay mineral investigations which showed that the clay mineralogy reflects the different sedimentation environments. The anoxic sediments showed an important decrease in

smectite crystallinity whereas well-organized smectite and a higher amount of kaolinite characterize the normal pelagic sediments. Moreover, the correlation of the clay-dependent climatic curve obtained by Tomadin and Landuzzi (1991) and the oxygen isotope curve obtained by Olausson (1991) has shown a good correspondence for warm and cold oscillations registered from the Middle-Pleistocene and Holocene.

Concluding remarks.

The anoxic versus normal pelagic sedimentation in the Bannock Basin shows that:

1) preservation of siliceous fauna and the related high content in biogenic opal seems to be by the high level in organic C in the anoxic sediments of core BAN88-21GC; on the other hand, it seems that siliceous fauna is completely dissolved in core BAN88-14GC: the low concentration of biogenic opal in the

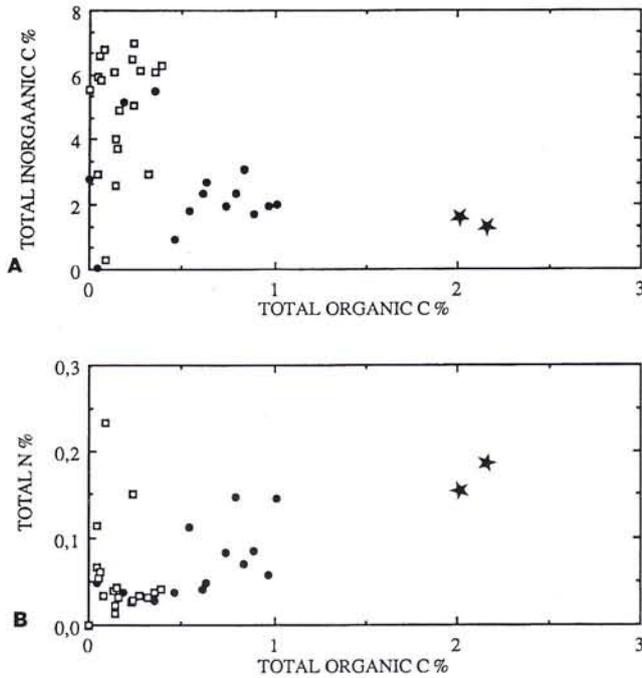


Fig. 8 - A) Ratio Inorganic Carbon/Organic Carbon in normal pelagic sediments from core BAN88-14GC (whites), anoxic sediments from core BAN88-21GC (black dots) and sapropels (black stars). B) Ratio Nitrogen/Organic Carbon in normal pelagic sediments from core BAN88-14GC (whites), anoxic sediments from core BAN88-21GC (black dots) and sapropels (black stars).

normal pelagic sediments is thus apparently caused by selective solution of the sedimented material.

2) The occurrence of Sapropel S-1 within the anoxic sediments of core BAN88-21GC at a depth of 80 cm is geochemically marked by an increase in organic carbon

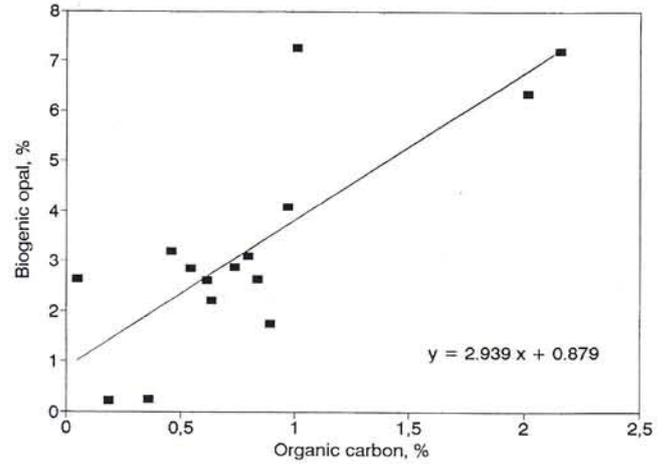


Fig. 9 - Relationship between organic carbon and biogenic opal in the anoxic sediments from core BAN88-21GC.

up to 2%, and a decrease in carbonate down to 20%. These values are in agreement with the composition of sapropels according to Kidd et al. (1978, see Fig. 7 and 8a). The anoxic sediments from the Bannock Basin have always values corresponding to those of "sapropelitic muds".

Acknowledgements.

This study would not be possible without dedicated support by Prof. M. B. Cita. I am therefore gratefully to her valuable suggestions and criticism to this research. I also thank Dr. S. Honjo who provided laboratory facilities at WHOI during my summer fellowship programme. The paper was critically reviewed by G. de Lange and L. Tomadin to whom I owe my sincere gratitude.

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Received February 5, 1996; accepted May 21, 1996