13. CHERTS FROM RIO GRANDE RISE SEDIMENTS, DEEP SEA DRILLING PROJECT LEG 72, HOLE 516F[1]

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ABSTRACT

Cherts recovered during DSDP Leg 72 from Rio Grande Rise sediments (Site 516) consist of both cristobalite and quartz, and contain ghosts of foraminifers and (more rare) radiolarians. Porcellanite made of disordered cristobalite is found in most old enclosing sediments. Local dissolution of siliceous microfossils during diagenesis is the most likely source of the silica required for the chert formation. As sediment age increases, the proportion of biogenic silica decreases and authigenic silica increases.

INTRODUCTION

Cherts are important as diagenesis stage indicators. One can connect the occurrence of chert with the history of paleocirculation, the evolution of silica accumulation, and other areas of study. Our study adds some detailed knowledge of the mineralogy, chemistry, and structure of cherts that may prove helpful in research dealing with these areas.

METHOD AND DATA BASE

We used optical and electron microscopy, X-ray diffraction, infrared absorption, and chemical analysis to investigate five samples from Hole 516F. Four of these (Samples 516F-4-6, 128–131 cm; 516F-17-1, 68–69 cm; 516F-17,CC; and 516F-18-1, 102–104 cm) are quartz-cristobalitic cherts; one (Sample 516F-80-1, 90–91 cm) is a weakly carbonaceous cristobalitic porcellanite. The age of host sediments ranges from Eocene to Miocene. The following peaks were used for mineral identification on X-ray diffractograms: calcite, 3.03 Å; quartz, 3.33 Å; opal-CT (α-cristobalite, 4.08 to 4.11 Å plus α-trydimite, 4.27 to 4.29 Å); opal-A, halo in area 6–16°2θ; dolomite, 2.903 Å. Biogenic opal-A has a halo in the area of 16–18°2θ (Calvert, 1971); so, in some cases, we can distinguish between biogenic and nonbiogenic opal-A on diffractograms.

The following characteristic bands can be used for the identification of different minerals from infrared spectra: calcite, 1440, 880, and 720 cm^{-1}; opal-CT, 795 to 800 cm^{-1} with weak complication by quartz near 820 cm^{-1}. All spectra show a well-marked band at 1640 cm^{-1} caused by the oscillation of molecular water. The 950 cm^{-1} band is connected with Si-OH group.

VISUAL CHARACTERISTICS

The cherts are greenish gray, yellowish gray, and gray; they are weakly spotted with areas of more-or-less dark color and are very hard (no knife penetration). They have sharp boundaries and conchoidal fracture and do not react with HCl. They form nests and lenses from 1–2 mm to as much as 60 mm in length (Fig. 1). They are enclosed in biomicrite nannoplankton-foraminiferal chalks and chalky limestones. A transition zone of white carbonate–siliceous rock 1–2 mm in width separates the

relatively big chert lenses from the carbonate. Boundaries between cherts and carbonate-siliceous rock are sharp and between the latter and carbonates either sharp or diffuse.

Porcellanite is distinctly different from chert. It resembles white, hard, carbonate-siliceous rock; however, it allows almost no knife penetration, does not show smooth fracture, and reacts weakly with HCl.

One can readily see under the microscope that cherts have been formed by silicification of carbonates. A pelitomorphic matrix consisting of nannoplankton remains and, chiefly, authigenic calcite (micrite) has undergone partial replacement by opal. In some cases, the walls of foraminifers are replaced by microquartz. The chambers of foraminifers are filled with fibrous chalcedony, opal-CT, or authigenic calcite in various degrees, but empty chambers also occur. Opal-A of single spicules has undergone the conversion to opal-CT (α-cristobalite?). Very rare radiolarian skeletons have been calcitized in the cherts and in the transitional zone. This feature is very significant. Sometimes authigenic forms of SiO$_2$, such as opal-CT, chalcedony, or micromozaic quartz, form short veins or elongated small lenses in intergranular spaces. Weak mechanical distension of host rocks may take place under these conditions. The weakly spotted structure of cherts (see macroscopic examination) is due to the conglomerate-like pattern of distribution of the rock areas (1–2 to 25–30 mm^2); each has different ratios of CaCO$_3$ and SiO$_2$.

In thin section, the porcellanite differs from the above-described cherts by the absence of any forms of chalcedony or quartz, by generally weaker silicification, and by the presence of dolomite. Dolomite and opal-CT are found both in the matrix and in foraminiferal chambers.

These features of chemical and mineral composition of the siliceous rocks are corroborated and complemented by data of other analyses.

CHEMICAL ANALYSES

According to results of chemical analyses (Table 1), the samples from Hole 516F consist of SiO$_2$ (60–76%),
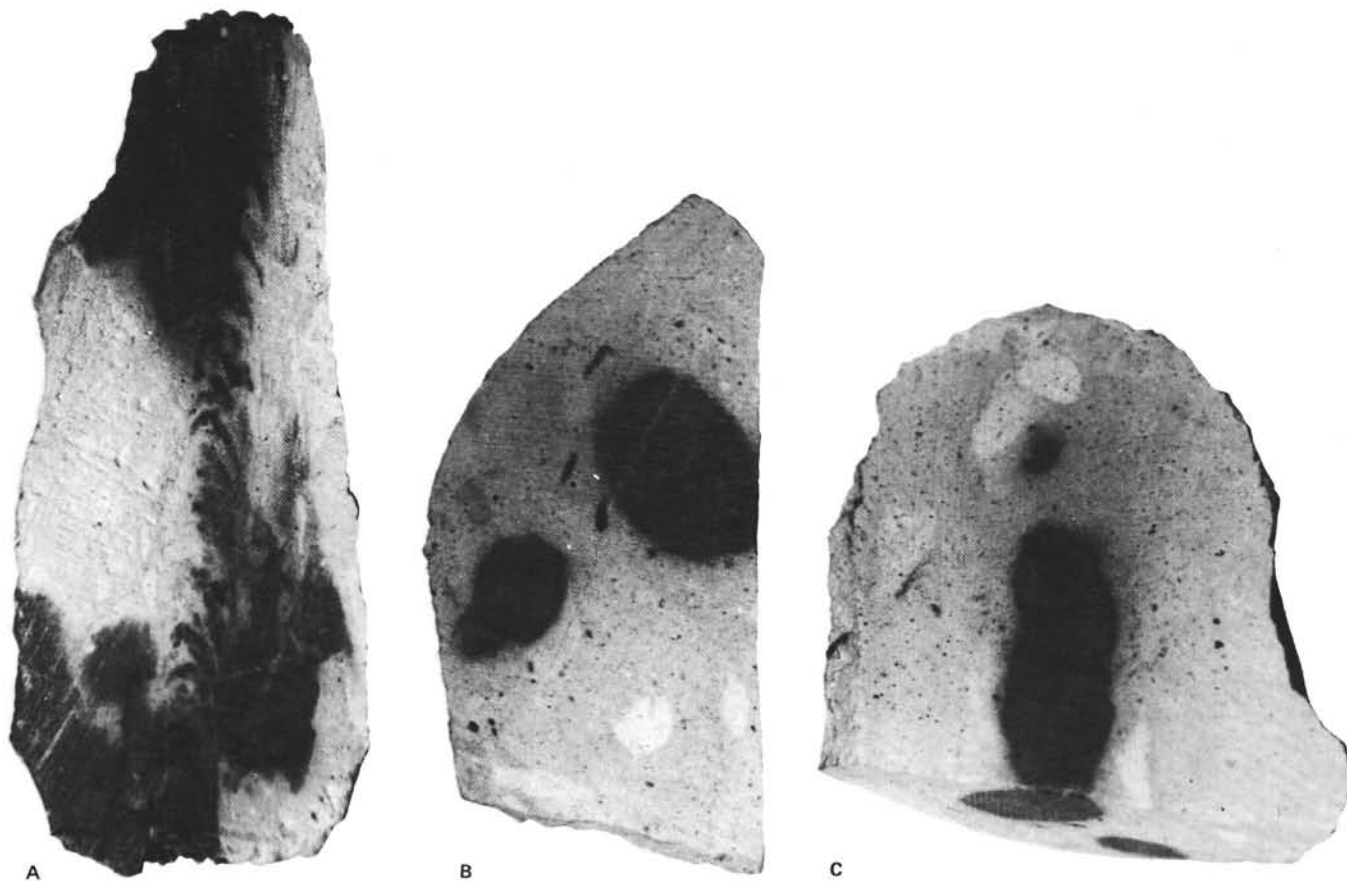
Figure 1. Cherts (black) in carbonate deposits (light). Magnifications are final magnifications. A, Sample 516F-17-1, 68–69 cm, magnification 2×; B, Sample 516F-17,CC, magnification 1.3×; C, Sample 516F-4-6, 128–131 cm, magnification 1.3×.

Table 1. Chemical composition of cherts and porcellanites from Hole 516F.

	Core-section (interval in cm)				
	4-6, 128-131	17-1, 68-69	17,CC	18-1, 102-104	80-1, 90-91
SiO_2	74.20	76.30	75.50	66.85	60.00
TiO_2	0.04	0.06	0.06	0.04	0.02
Al_2O_3	1.15	1.84	1.75	1.24	0.50
Fe_2O_3	0.30	0.65	0.39	0.36	0.77
MnO	0.01	0.01	0.01	0.01	0.04
MgO	0.87	1.20		1.00	1.50
CaO	9.00	6.36	7.18	13.05	16.00
Na_2O	0.73	0.79	0.26	0.85	1.33
K_2O	0.20	0.27	0.26	0.19	0.05
Loss of ignition	13.50	13.50	14.90	16.60	20.90
Total	100.00	100.98	100.31	100.19	101.11
CO_2	7.07	5.00	5.64	10.25	12.57

Note: Analyses of CO_2 and loss of ignition were made by the weight method by N. P. Tolmacheva and T. G. Kuzmina. Other analyses were made by X-ray fluorescence by T. G. Kuzmina. A blank indicates that the sample was not investigated for that compound.

$CaCO_3$ (11–29%), H_2O (6–9%), and some aluminosilicate admixture (2–4%).

SCANNING ELECTRON MICROSCOPE OBSERVATIONS

Under scanning electron microscope, differences in the character of the contact between porous chalk and that of the dense "molten" chert are apparent. Skeletal remains of foraminifers and nannofossils point to the relict organogenic nature of cherts. Well-developed lepispheres of opal-CT occupy the chambers of planktonic foraminifers and intergrain spaces (Fig. 2), and the succession of authigenic mineral formation in porcellanite is calcite–opal-CT–dolomite. This succession is fully analogous to the vertical zonation of authigenic minerals (from the top downwards) in the carbonate section of Rio Grande Rise sediments. Sometimes well-formed crystals of zeolite (clinoptilolite?) can be found in porcellanite.

X-RAY AND INFRARED ABSORPTION ANALYSES

X-ray diffractograms (Fig. 3) and infrared absorption spectra (Fig. 4) show that opal-CT, quartz, calcite, and authigenic opal-CT are the principal minerals of cherts. Opal-CT, calcite, and, in minor quantities, dolomite and opal-A, but not quartz, were found in the porcellanite.

Variations of the calcite/opal-CT ratio on diffractograms and infrared spectra correspond to the variations recorded in the chemical analyses (Table 1). Aluminosilicate minerals are not reflected in this instance because of their negligible content.

The available materials allow us to consider opal-CT as the main form of authigenic SiO_2 in the Hole 516F
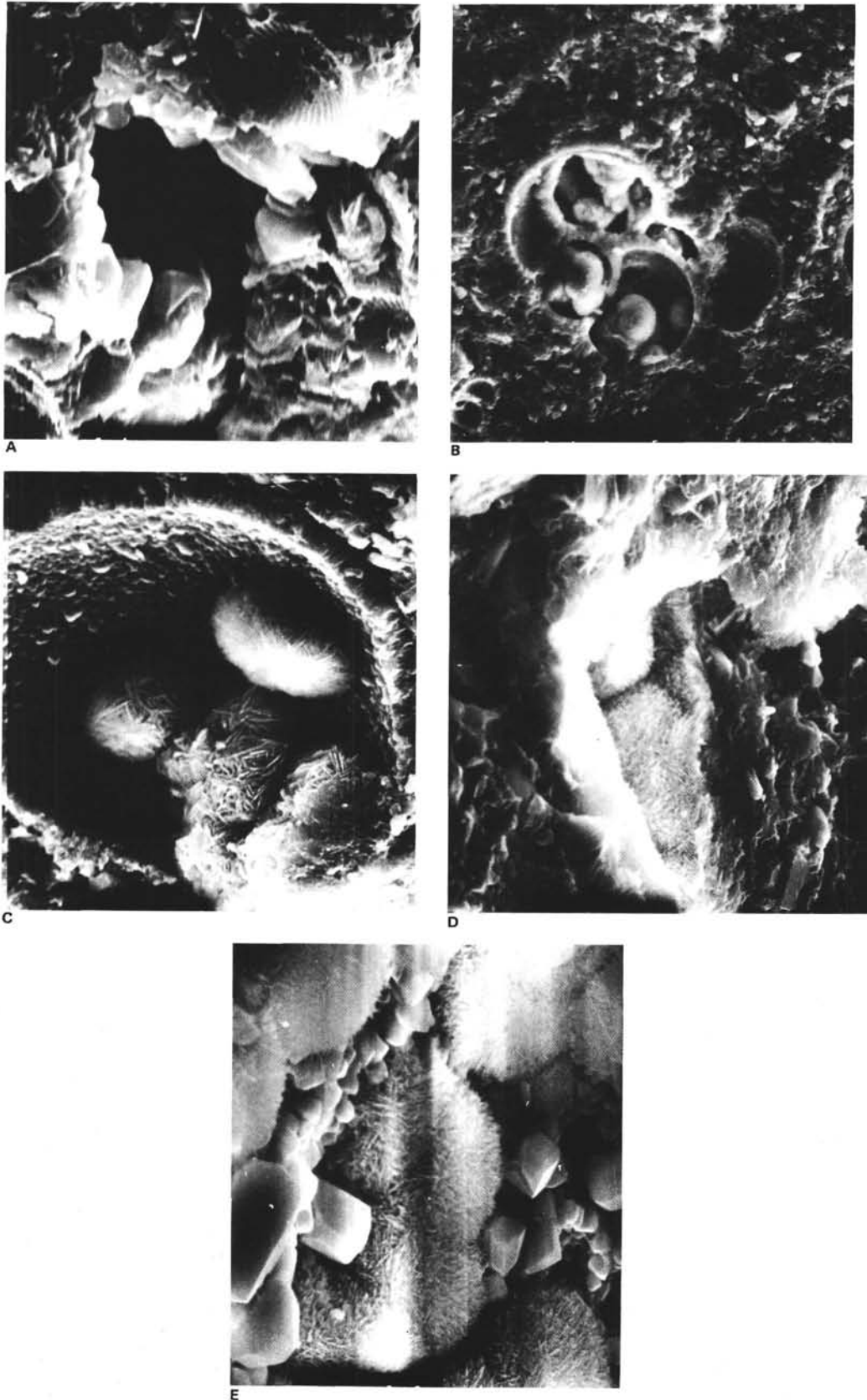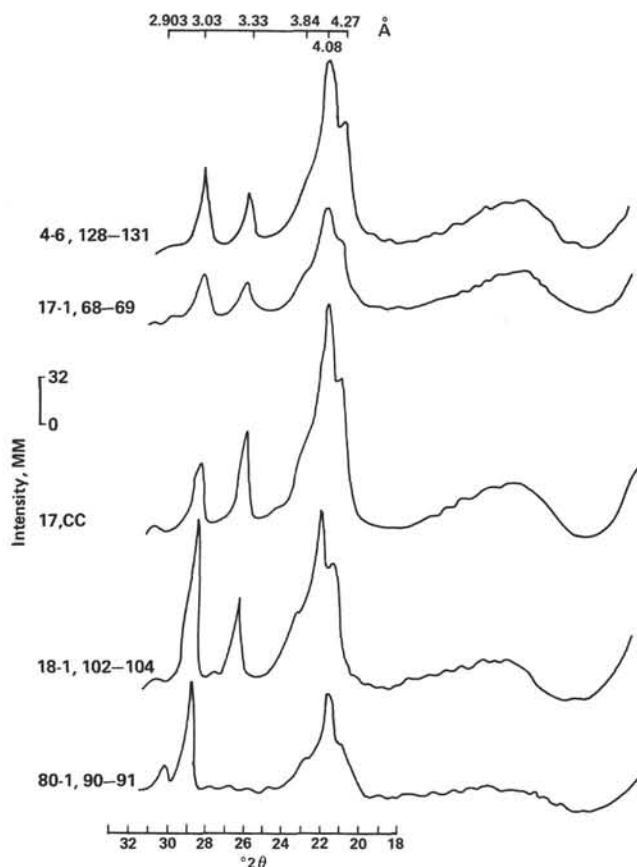
Figure 2. Cherts under scanning electron microscope. Magnifications are final magnifications. A, crystals of authigenic calcite and coccoliths in Sample 516F-4-6, 128–131 cm, magnification 4200×; B, lepispheres of opal-CT in chambers of planktonic foraminifers; Sample 516F-4-6, 128–131 cm, magnification 850×; C, same as B, 2250×; D, filling of intergrain space with joined lepispheres of opal-CT, Sample 516F-80-1, 90–91 cm, magnification 1400×; E, crystals of authigenic dolomite in the porcellanite, Sample 516F-80-1, 90–91 cm, magnification 2800×.

Figure 3. X-ray diffractograms of Hole 516F cherts (CuKα radiation).

Figure 4. Infrared absorption spectra of Hole 516F cherts.

samples. Peak heights measured from the X-ray diffractograms (Fig. 3) reveal some trends in the relationships between the authigenic silica minerals (Table 2).

The cherts from upper Oligocene deposits within the sub-bottom range of 322–332 m have a strongly variable mineral composition. If, however, average values are taken, the decrease of opal-A and opal-A/opal-CT ratio with increasing age and sub-bottom depth can be considered well proven.

Much less certain is the trend of an increased ratio of quartz/opal-CT in the upper Oligocene cherts compared to the lower Miocene cherts. Many more samples are required for firmer conclusions about the mineralogy of SiO_2. The cause of the absence of quartz in the oldest and most deeply buried sample of porcellanite remains unknown.

The isotopic composition of carbonates from cherts indicates that complete isotopic exchange between biogenic carbonates and interstitial waters took place (Ta-
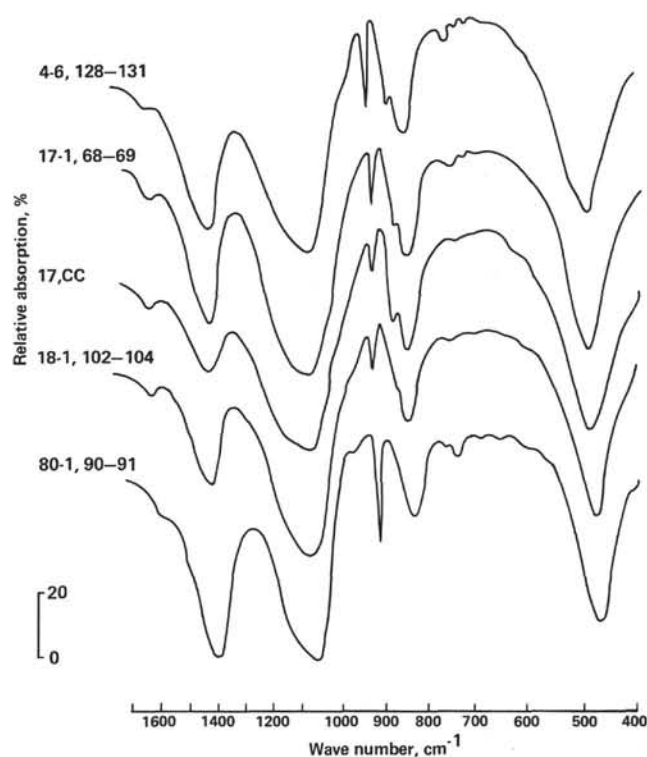
ble 3). The diagenetic carbonates were deposited under conditions of isotopic equilibrium with interstitial water. Isotope indicators of biogenic carbonates have been obliterated in the course of postsedimentation processes.

DISCUSSION

At present most authors consider biogenic SiO_2 as the main source for chert formation. We have already mentioned the occurrence, though rare, of radiolarian skeletal remains replaced with calcite and noted recrystallized sponge spicules both in the transitional zone around cherts and within them. Siliceous remains (2–5%) occur in the lower Miocene of Hole 516F but were absent in older sediments.

Table 4 summarizes the data on the correlation of stratigraphic levels of enrichment with biogenic and authigenic SiO_2 in the southwestern Atlantic sediment cover. As shown in Table 4, in the samples from Southwestern Atlantic one can readily see the downward displacement of both the upper and the lower boundaries of the age of sediments containing cherts compared to the age range of sediment enrichment with biogenic silica.

Table 2. Ratios of main peak heights of SiO_2 minerals on diffractograms of cherts from Hole 516F.

No.	Core-section (interval in cm)	Age	Depth (m)	Opal-A (mm) (halo 6–16° 2θ)	Opal-CT (mm) (4.08– 4.11 Å)	Quartz (mm) (3.33 Å)	Ratio opal-A/ opal-CT	Ratio quartz/ opal-CT
1	4-6, 128–131	early Miocene	206	30	113	31	0.27	0.27
2	17-1, 68–69	late Oligocene	322	28	67	22	0.42	0.33
3	17,CC	late Oligocene	324	33	411	59	0.08	0.14
4	18-1, 102–104	late Oligocene	332	25	107	51	0.23	0.48
5	Average for #'s 2, 3, 4	late Oligocene	326	29	195	44	0.24	0.32
6	80-1, 90–91	early-middle Eocene	878	11	63	0	0.18	0

Table 3. Isotopes of carbon and oxygen in chert carbonates from Hole 516F samples.

Core-section (interval in cm)	$\delta^{13}C$ ‰ PDB	$\delta^{18}O$ ‰ standard mean ocean water
4-6, 128–131	−1.1	+34.6
17,CC	−2.3	+33.3
18-1, 102–104	−3.2	+34.5
80-1, 90–91	−1.2	+32.0

Table 4. Stratigraphic levels of enrichment of the southwestern Atlantic sediment cover with SiO_2 of different genesis.

Morphologic feature	Hole	Enrichment of sediments with biogenic SiO_2	Authigenic SiO_2 in sediments
Rio Grande Rise	22	late Oligocene–early Miocene	middle Eocene, late Oligocene
	357	late Oligocene–early Miocene	Santonian, early Paleocene–early Eocene
	516F	Absent	middle Eocene, late Oligocene, early Miocene
São Paulo Plateau	356	early–middle Eocene	early Eocene
	355	middle Eocene	No
Brazil Basin	515	late Oligocene–middle Miocene	?
Argentine Basin	358	late Oligocene–early Miocene; late Miocene–Pleistocene	middle Eocene–middle Oligocene; middle Miocene
Falkland Rise	513	late Oligocene–Pleistocene	early Oligocene

Note: ? indicates lack of information concerning SiO_2 in that hole.

Similar analysis (with mapping) for the Pacific sediment cover (Levitan and Bogdanov, 1980) has shown that chert formation in Cenozoic deposits is restricted to areas with high absolute masses of biogenic silica. This trend was not established for Mesozoic deposits.

Finally, the comparison of evolution of the biogenic silica accumulation in the World Ocean (Levitan and Bogdanov, 1980) on one hand with the ratio frequency of cherts/age (Levitan, 1980) on the other, reveals an inverse trend and age displacement of biogenic and authigenic silica accumulations.

In conclusion, the local and regional features of biogenic and authigenic SiO_2 ratios at Hole 516F and in the southwestern Atlantic sediment cover reflect the general principles valid for the whole of the ocean.

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